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ECCE-6 Book of Abstracts - Volume 1

Edited by

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Preface

This two-volumes ECCE-6 book of abstracts contains the final camera ready abstracts of most of the papers presented at the conference. Each volume contains approximately 1150 pages with close to 500 abstracts per volume. In addition, a proceedings of the ECCE-6 in a CD-ROM (containing all submitted abstracts in their final version, the full manuscripts submitted by a large percentage of authors, the technical program, the author-program index and many more) has been prepared for distribution to all participants of ECCE-6.

ECCE-6 is the sixth in the series of congresses on chemical engineering launched by the EFCE in 1997 in Firenze, the venue for ECCE-1. Since 1997, ECCE has been organized in France (Montpellier, 1999), Germany (Nurnberg, 2001) and Spain (Granada, 2003). In 2005, the ECCE-5 was combined with the World Congress of Chemical Engineering in Glasgow. The objective of this biennial congress is to provide engineers, scientists, researchers, technologists, students and others a platform to present their latest results, to interchange ideas, to make new contacts, to establish new collaborations, and many more. The conference addresses the full spectrum of chemical engineering practice, including current trends and future needs.

Volume 1 includes the abstracts from themes 1, 3, 4, 6, special sessions 1-3, the EPIC-I symposium, the special workshop on education, and the symposiums on Chemical Product Design & Engineering (CPD&E) and Environmental Protection and Sustainability (EP&S). Volume 2 contains the abstracts from themes 2, 5 and the LMC Congress (ECCE-1 Symposium on Innovations in Food Technology). Out of a total of 1224 abstracts that were initially selected from more than 2000 submissions, about 500 will be presented in 12 parallel oral sessions while an equal number will be presented as posters in 4 plenary sessions, one on each day.

We would like to thank the members of the international scientific committee for their reviews, their advice during the selection process and the preparation of the technical program. We would like to thank all authors for submitting their abstracts. Also, we would like to thank the supporting group at the Department of Chemical Engineering for their help in getting these books ready for the printer. Special thanks in this respect goes to Mrs Eva Mikkelsen for the administrative/secretarial support, to Dr. Loic d'Anterroches for the electronic transfer of necessary data, and the student helpers for various jobs related to getting the abstracts ready for the book. The following PhD-students (Kavitha, Merlin, Piotr, Bena-Marie, Leila, Elisa) and MSc-students (Christine, Reaz, Shafique) deserve special thanks. Also, we would like to acknowledge the help from Wonderful Copenhagen organization with respect to the selection of the background picture ("Nyhavn" by Morten Jerichau) on the front and back covers of the book volumes.

We hope that these books of abstracts will serve as a valuable record of reference of the contributions made at ECCE-6.

Rafiqul Gani & Kim Dam-Johansen   September 2007

Chemical Engineering Department,
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ECCE-6 International Scientific Committee (ISC)

Co-chairs: Rafiqul Gani (DK), Kim-Dam-Johansen (DK), Ryszard Pohorecki (PL)

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Theme	Theme Title	Coordinators
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2	Advancing the chemical engineering fundamentals	O Hassager (DK), J Drahos (CZ)
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4	Systematic methods and tools for managing the complexity	E N Pistikopoulos (UK), B Braunschweig (F)
5	Integration of life sciences & engineering	J Villadsen (DK), F Muller (UK)
6	Educating chemical engineers for coming challenges	M Molzahn (DE)

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S4	EPIC-1: 1st European Process Intensification Conference	A. Stankiewicz (NL) A Gorak (DE)
S5	Innovations in Food Technology	A Friis (DK)
S6	The Future of European Chemical Engineering Education in a Globalized World	M Molzahn (DE)
S7	Environmental Protection & Sustainability	B Kawalec-Pietrenko (PL)
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Editorial Notes

Inclusion of abstracts

The conditions for inclusion of an abstract in the ECCE-6 books of abstracts have been the following:

- acceptance of the abstract in the technical program
- use of the supplied abstract template for the ECCE-6 book of abstracts
- not exceeding the 2-page limit as well as remaining within the specified page margins, etc.
- submission (uploading) of the final camera ready abstract document on time

Therefore, some authors may not find their abstracts included in these books. This does not effect their inclusion in the technical program and/or the form of presentation.

Guide to abstract-author search

Because of the large number of abstracts, we have divided the book of abstracts into two volumes. Also, because of the very large number of authors involved (more than 3000 and not all of them registered in the database of authors), it has not been possible for us to link the author-index to the corresponding page numbers. Instead, we have linked the author-index to the session numbers and organized the abstracts according to the session numbers. In order to quickly and efficiently find the abstract of your interest, you may find the following guidelines useful:

1. To find a paper on a specific topic

Locate the theme and then the topic under the theme and then the session under the topic. The locations of these are indexed with page numbers (see the tables in the table of contents pages). Go to the corresponding page. On this page, a list of the abstracts corresponding to this session is given together with an indication of which abstracts have been included. The abstracts marked with "yes" can be found in the pages following the table, ordered as they appear on the table.

Alternatively, find the session number where the paper of your interest is to be presented. Go the corresponding page for the session and then find if the abstract of your interest is included. If yes, find the abstract within the pages corresponding to this session.

2. To find an author and his/her papers

In this case, the author-index linked to the session numbers (provided at the end of the book) can be useful. Note that this author index is in terms of session numbers and not page numbers. Also, only those authors who had signed-in to

the database are indexed. So , it is possible that authors listed in the technical program may not be found in this author-index.

Locate the surname of the author and the corresponding session number. Go to the contents page and find the page number where the session table is given. Find the abstract in the pages following the session table.

Table of Contents – Volume 1

Abstracts-index according to themes

Abstract-index according to session topics

For the list of abstracts under each topic, go the corresponding page of the topic.

Session T0-Plenary: Plenary Lectures

Abstract Number	Paper Title & Authors	Included
4177	Chemical Engineering – An answer to mankind's challenges A Noack	Yes
4178	Chemical Engineering – Whatever Next J Perkins	Yes
4177	Chemical Engineering and the impact on white biotechnology P falholt	Yes
4179	Chemical Processing by Self Assembly : Lets take it seriously M Tirrell	Yes

Session T0-Plenary

Chemical Engineering – An answer to mankind's challenges

Achim Noack

Managing Director, Bayer Technology Services GmbH, Leverkusen, Germany

Abstract

The plenary talk will cover topics such as smartly engineered processes, tailor made materials, integrated products, biomass conversion, plant made pharmaceuticals and many more (Editorial note).

Achim Noack

Chemical Engineering - Whatever Next

John Perkins

Vice-President and Dean of Engineering and Physical Sciences, The University of Manchester, Manchester, United Kingdom

Abstract

The arts of chemical technology have a very long history, but the modern profession and discipline of chemical engineering developed during the 19th , and particularly in the 20th, centuries to support the emergence of a large-scale chemical industry around the world. From its beginnings the profession has successfully established its relevance to a wide range of industries where processing is a common theme. This has been achieved by the profession recognising the unique core strengths of chemical engineers, and their applicability to a broad spectrum of industrial and societal issues.

The last quarter of the 20th century saw the initiation of a new period of questioning about the future of the profession, in the light of developments in relevant industries. A personal view of the current position of chemical engineering, and some thoughts on the future challenges, particularly in education and research and development, will be presented in this plenary lecture.

John Perkins

Chemical Engineering and the impact on White Biotechnology

Per Falholt

Chief Scientific Officer, Novozymes A/S, Krogshoejvej 36, Bagsvaerd, 2880, Denmark

Abstract

White Biotechnology has gotten increased impact in the society over the last 4 decades. In the last decade a very huge interest has emerged with White Biotechnology really getting a major role in terms of moving the society forward towards a more sustainable future in terms of supplying a number of basic raw materials. The importance of Chemical Engineering disciplines in order to make Biotechnology competitive will be described as well as the progression on fast upscaling methods.

Going forward linking the lab to full scale application and full scale production is going to be one of the crucial challenges in which continued development in the Chemical Engineering competencies.

A large number of challenges with regards to even cheaper production methods and equipment are going to move Biotechnology to the next level and it is expected that these will be developed over the next decade.

Per Falholt

Chemical Processing by Self Assembly: Lets Take it Seriously

Matthew Tirrell

Richard A. Auhll Professor and Dean College of Engineering, University of California, Santa Barbara, Harold Frank Hall Room 1030, Santa Barbara, CA 93106, USA

Abstract

Self-assembly is a route to processing of chemical products that relies on information content built into the process precursors. A challenge for engineers is to develop the practical routes to technologically important self-assembly processes. Self-assembly occurs frequently in biology but translating that bio-inspiration to controllable chemical processing presents many interesting problems. The complexity built into self-assembled products is at the level of supermolecular structure. Complexity, in the sense of development of emergent properties of an assembly that cannot readily be envisioned from the constituents, can arise spontaneously during self-assembly and often does, especially in biological systems. We are only beginning to develop sufficiently sophisticated synthetic assemblers to mimic biology in this way. Other routes to self-organization may also be of interest for nanotechnology. Prospects for success and current efforts in biomaterials, porous materials, molecular electronics and other areas will be discussed.

M Tirrell

Session T1-K: Theme-1 Keynote Lectures[*]

Abstract Number	Paper Title & Authors	Included
4085	CO2 from Capture to Storage Pierre Le Thiez	Yes
4157	Harnessing methane emissions from coal mining Krzysztof Warmuzinski	Yes
4158	Autothermal Reforming - development of state of the art syngas technology for advanced fuel production Martin Østberg, Thomas S Christensen, Kim Aasberg-Petersen, Martin S Skjøth-Rasmussen, Olav Holm-Christensen, Jens H Bak-Hansen	Yes

* To be presented in different keynote sessions (see the technical program for details)

CO2 – From capture to storage

Pierre Le Thiez

IFP, CCS project manager, France

1. Summary

The risks associated with climate change have been the subject of much debate in recent years. Today, most experts think that these risks are real and directly linked to the emission of greenhouse gases, especially CO2. Recent decades have witnessed a large rise in CO2 emissions, thereby increasing the concentration of CO2 in the atmosphere. Scenarios established by the IPCC (Intergovernemental Panel for Climate Change) show that the CO2 content could rise from a current value of about 360 ppm to a value that, unless preventive measures are taken, could exceed 1000 ppm by the end of the century.

Among the options for mitigating the risks of climate change due to greenhouse gas emissions, CO2 capture, transport and geological storage (CCS) appears as one of the most promising options, specially applicable to large CO2 emitters like thermal power stations, steal and cement industries.

The major challenges which have to be addressed are:

- to store huge amounts of CO2

- to reduce the costs, mainly for capture

- to ensure the long-term safety of the geological storage

This paper will describe and analyze the main issues - both technical and non technical - involved for achieving a large deployment of the technologies of capture, transport and storage which are required.

Examples of ongoing large R&D effort will also be given, like the CASTOR project which aims at a significant technology development for the separation of CO2 from low pressure and diluted flue gases. Planned medium and large-scale demos of power production with CCS will also be briefly discussed, showing the strong wish from the

industry, the research community and the public bodies to accelerate the development and the validation of technologies for achieving a strong cut in CO2 emissions.

Harnessing methane emissions from coal mining

Krzysztof Warmuzinski

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1. Summary

Methane emissions associated with coal-mine ventilation pose a tremendous environmental problem and lead to inadvertent loss of a valuable energy source. The proportion of methane released through underground ventilation is as high as 70 per cent of all the coal-related emissions. Additionally, the CH_4 Global Warming Potential is 21 (for a timescale of 100 years), compared with 1 for carbon dioxide. If the heat of combustion of the methane could be usefully employed, this would bring a twofold benefit of avoiding both CH_4 release and CO_2 emission from the production and use of the fuel thereby displaced. The projects carried out in the Institute of Chemical Engineering, Polish Academy of Sciences explored three major routes for utilizing ventilation air methane (VAM): (1) using VAM as combustion air in conventional boilers, (2) oxidizing VAM in reverse flow reactors (either catalytic or non-catalytic) to produce heat, (3) enriching VAM (via pressure swing adsorption or membrane separation) to concentration levels suitable for use in gas turbines or reciprocating engines. The investigations have now been focused upon homogeneous combustion of VAM in reverse flow reactors.

Keywords: ventilation air methane, reverse flow reactor, pressure swing adsorption, membrane separation

2. Extended Abstract

Large quantities of methane are exhausted into the atmosphere with coal-mine ventilation air with very low CH_4 content (0.1 to 1 vol. %). The global emissions of methane from this source are estimated at, roughly, 15 Mt/year [1]. Apart from the environmental impact, this leads to considerable energy losses, as methane is a fuel in its own right. In the studies carried out in the Institute of Chemical Engineering, Polish Academy of Sciences, three principal routes for utilizing ventilation air methane were explored: using VAM as combustion air in conventional boilers, oxidizing VAM in reverse flow reactors (either catalytic or homogeneous) to produce heat, and enriching VAM (via pressure swing adsorption or membrane separation) to concentration levels suitable for use in gas turbines or reciprocating engines.

2.1. VAM as Combustion Air

The use of VAM as combustion air in existing conventional boilers was analysed in terms of four principal parameters: net profit resulting from a decreased fuel consumption, concentration of CH_4 in VAM, the distance between the source and the boiler, and VAM flow rate. It is found that the use of VAM can still generated some profit for transportation distances as long as 4-5 kilometres [2].

2.2. Oxidation of VAM in reverse flow reactors

Both catalytic (CFRR) and homogeneous (TFRR) reverse flow reactors were investigated. Simulations and experimental studies reveal [3] that CFRRs are characterized by relatively high operating temperatures which may lead to a rapid deactivation of the catalyst. Therefore, non-catalytic oxidation in TFRRs was studied in more detail. The studies clearly demonstrate than TFRRs can become an attractive alternative to CFRRs, provided reasonable values of the operating parameters and a suitable mode of heat withdrawal [4] are selected.

2.3. Preconcentration of VAM

A rise in methane content in the feed may considerably increase the efficiency of heat production in either CFRRs or TFRR. Therefore, total annual costs were evaluated for the enrichment of mine ventilation air in methane using pressure swing adsorption or membrane separation. A wide range of the operating parameters (including CH_4 concentration in the feed gas, flow rates, enrichment degree, adsorption pressure and permeate pressure) was analysed. It is revealed that the cost of the membrane separation is of the same order of magnitude that of the PSA process. However, the structure of the costs is altogether different, with a much larger share of the capital cost and a much lower proportion of the operating cost in the case of membrane permeation. Finally, the profit resulting from an increased heat production in a catalytic flow reversal reactor is found to only partly offset the cost of the enrichment.

Acknowledgements

References

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2. Warmuzinski, K., Gosiewski K., Tanczyk, M. and Jaschik, M., (2003) *Energy Policy*, 6, 407-422 (in Polish).
3. Gosiewski, K., Matros Y., Warmuzinski, K., Jaschik, M. and Tanczyk, M, (2006) *Proceedings of USPC-5 (Osaka), 85-86.*
4. Gosiewski, K. and Warmuzinski, K., (2007) *Chemical Engineering Science*, **62**, 2679-2689.

Autothermal Reforming - development of state of the art syngas technology for advanced fuel production

Martin Østberg, Thomas S. Christensen, Kim Aasberg-Petersen, Martin Skov Skjøth-Rasmussen, Olav Holm-Christensen and Jens Henrik Bak-Hansen

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

1. Summary

Haldor Topsøe is today leading within technology for synthesis gas production using autothermal reforming. This technology is one of the preferred for GTL units producing synthetic fuels or methanol. The basis for the present technology is the Topsoe-SBA process developed in the 1950'es. This presentation focuses on the development work that has lead to the present state-of-the-art autothermal reforming technology.

2. Extended Abstract

The basis for Haldor Topsøe's present autothermal technology, which latest have been demonstrated in the Oryx GTL plant in Qatar, has been the Topsoe-SBA process developed in the 1950's for production of town gas and ammonia. Today we differentiate between several types of Autothermal reformers. In the secondary air-blown reformers used for ammonia production units, process gas from a tubular reformer is mixed with air or enriched air to introduce nitrogen for the ammonia synthesis and oxygen for further conversion of the remaining hydrocarbons in the process gas. In the oxygen-fired autothermal reformers used for synthesis gas production e.g. in large gas to liquids units producing synthetic fuels or methanol, the feed gas is natural gas and steam at low steam to carbon ratios. This feed gas is typically preformed to allow for higher preheat temperatures before it is mixed with oxygen in the turbulent-diffusion burner being a core element of the autothermal reformer technology. This presentation will focus on the oxygen-fired autothermal reformer not the secondary reformer technology used for ammonia production.

The challenges to mature the Topsoe-SBA technology from units mainly producing hydrogen to modern ATR reactors producing synthesis gas with high concentrations of carbon monoxide and hydrogen have been numerous. A non complete list is given below:

- The development of the CTS™ burner for ATR expanding significantly the lifetime of the burner.
- Control of the substoichiometric combustion ensuring a stable central flame core with soot-free operation under very fuel-rich conditions and at low steam to carbon ratios.

- Update of reactor design having a refractory lined reactor with high temperature resistant materials enabling operation at the elevated temperatures in the combustion chamber and the catalytic bed.
- Development of catalyst to resist the high temperature and to maintain low pressure drops for extended operating time.
- Development of waste heat boilers that effectively cools the very aggressive synthesis gas.
- Process optimisation to develop a cost effective process layout both regarding to investment and operation cost.
- Scaling of the technology mainly from pilot scale (100 Nhm^3/h natural gas feed) to industrial scale (up to 200,000 Nm^3/h natural gas feed).

These challenges have been met using laboratory and pilot plant experiments, using various models including CFD, FEM, process calculations, detailed catalytic reactor models and detailed chemical kinetic modelling.
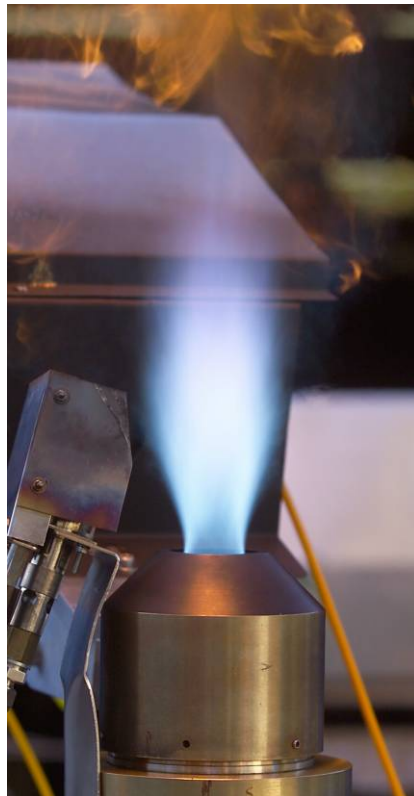
Figure 1: CTS™-burner firing natural gas and oxygen at an atmospheric test. Flames for the remaining fuel burning with air are seen in top of the figure.

Keywords: autothermal reforming, synthesis gas, GTL, methanol production

Session T1-1: Modelling of Ionic Liquids

Abstract Number	Paper Title & Authors	Included
673	Modeling of ionic liquid binary and ternary mixture phase equilibria at low and high pressure with the tPC-PSAFT I Economou, E K Karakatsani, M C Kroon, C J Peters, G-J Witkamp	Yes
1493	Equations of state for electrolyte solutions K Thomsen, Y Lin	Yes
2221	Liquid phase behaviour in the binary system 1-ethyl-3-methylimidazolium ethylsulfate + alkane (n-heptane, methylcyclohexane, toluene) M Bendova, Z Wagner	Yes
3094	Liquid-liquid equilibria of water + ionic liquids M G Freire, R. L Gardas, P J Carvalho, L M N B F Santos, I M Marrucho, J A P Coutinho	Yes

Modeling of ionic liquid binary and ternary mixture phase equilibria at low and high pressure with the tPC-PSAFT

I.G. Economou[a,b], E.K. Karakatsani[a], M.C. Kroon[c,d], C.J. Peters[c], G.-J. Witkamp[d]

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1. Summary

The truncated Perturbed Chain-Polar Statistical Associating Fluid Theory (tPC-PSAFT) is applied for the correlation of low and high pressure phase equilibria of ionic liquids with carbon dioxide, water and other gases and solvents over a wide temperature range. A binary interaction parameter is fitted to experimental data. Good agreement between experiment and theory is obtained in all cases.

Keywords: ionic liquids, phase equilibria, PC-SAFT

2. Results and Discussion

Ionic Liquids (ILs) have unique physical properties compared to traditional solvents and in recent years have emerged as suitable alternatives for the development of efficient and environment friendly chemical processes. Accurate knowledge of thermodynamic properties and phase equilibria of IL mixtures with organic solvents, water, carbon dioxide and other widely used compounds is a definite prerequisite in order that such mixtures are considered in an industrial process. Experimental measurements as well as accurate thermodynamic models can be used in this respect.

In this work, a molecular thermodynamic model based on tPC-PSAFT is developed for the prediction / correlation of IL binary and ternary mixtures. tPC-PSAFT accounts explicitly for size and shape differences between unlike molecules and also for different intermolecular forces, including van der Waals forces, polar forces (due to permanent dipoles and quadrupoles) and hydrogen bonding forces between like

(self-association) and unlike (cross-association) molecules [Karakatsani *et al.* 2005]. As a result, tPC-PSAFT can be used reliably for thermodynamic and phase equilibria calculations over a wide temperature and pressure range. Here, the model is used to correlate high pressure phase equilibria data for IL – CO_2 and IL – H_2O mixtures as well as ternary IL mixtures measured in Delft. In addition, literature phase equilibria data for various IL mixtures are considered. Representative results for binary mixtures with CO_2 are shown in Figure 1.

In the current theoretical framework, IL molecules are considered as molecular species with high dipole moment and no ion dissociation is considered [Maaike *et al.* 2006]. The protocol for model parameter estimation for ILs is developed based on well justified theoretical considerations. The absence of vapor pressure data for ILs calls for an alternative way for parameter estimation compared to what is used for other non-polymer compounds [Karakatsani *et al.* 2007]. Binary interaction parameters are fitted to experimental data and used with non further adjustment to predict ternary mixture phase equilibria. For most of the mixtures examined, the agreement between experimental data and model correlation / prediction is very good. In some cases as for example in aqueous mixtures, deviations are observed that require further attention and possible refinement and extension of the model.
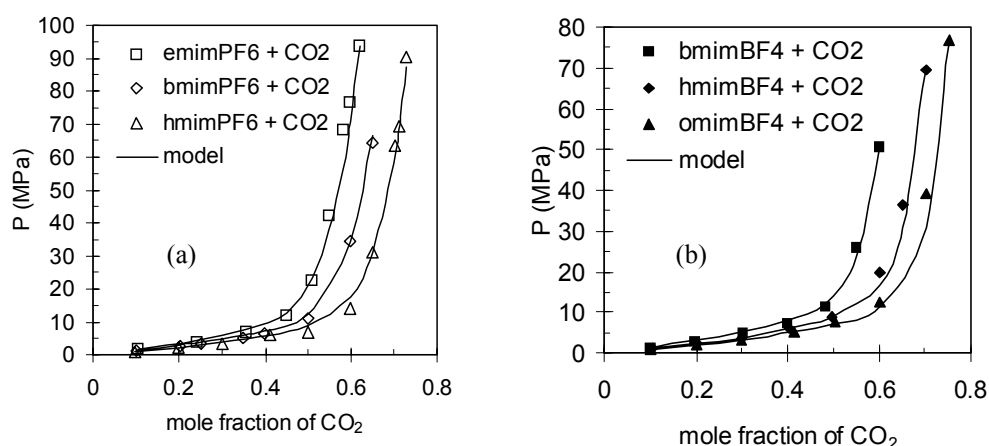
Figure 1: Experimental data and tPC-PSAFT correlation for the bubble-point pressure of (a) $[emim^+][PF_6^-]$ + CO_2, $[bmim^+][PF_6^-]$ + CO_2 and $[hmim^+][PF_6^-]$ + CO_2 mixtures at 333.15 K and (b) $[bmim^+][BF_4^-]$ + CO_2, $[hmim^+][BF_4^-]$ + CO_2 and $[omim^+][BF_4^-]$ + CO_2 mixtures at 333.15 K..

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Karakatsani, E.K., Economou, I.G., Kroon, M.C., Peters, C.J. and Witkamp, G.-J. (2007) *J. Phys. Chem. B,* in press.
Kroon, M.C., Karakatsani, E.K., Economou, I.G., Witkamp, G.-J. and Peters, C.J. (2006) *J. Phys. Chem. B,* 110, 9262 – 9269.

Equations of State for Electrolyte Solutions

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1. Summary

In this presentation, four different equations of state for electrolytes are presented. A comparison of the equations of state is presented. The models were compared by determining ion specific model parameters for a test system consisting of the aqueous Na^+, Ca^{++}, H^+, Cl^-, $SO4^{--}$, OH^- system.

Keywords: electrolyte solutions, equation of state, mean spherical approximation.

2. Extended Abstract

The properties of solutions containing electrolytes have usually been described by activity coefficient models. While significant results have been achieved using such models, they are far from perfect. Activity coefficient models do in general not have pressure dependency and can't be used for calculating the density of electrolyte solutions. Activity coefficient models are most accurate for binary and ternary solutions, but the accuracy usually decreases with an increasing number of components.

It is important to know the pressure dependency of the properties of electrolyte solutions in applications relating to the oil industry and the production of geothermal energy. The density of electrolyte solutions is an important property for process simulation. Industrial processes with natural brines typically contain many components, and a good accuracy in calculating the phase behavior of such solutions is therefore required.

In order to improve the thermodynamic modeling of electrolyte solutions we have examined the use of some equations of state for solutions containing electrolytes. Equations of state relate pressure, volume and temperature of a solution to each other. Flexible mixing rules for equations of state enable these to describe mixture properties from pure component properties. It is possible that some of the shortcomings of activity coefficient models for electrolyte solutions can be alleviated by introducing equations of state adapted for electrolyte solutions.

In this work we have examined different combinations of traditional equations of state and terms that take the long range electrostatic interactions of electrolyte solutions into account. The equations of state used for short range interactions are the Soave-Redlich-Kwong and the Peng-Robinson equations of state with or without a Wertheim association term. For the long range interactions we have used two different versions of the Mean Spherical Approximation term, a simplified Debye-Hückel term, and a Born term.

Ion specific interactions were determined for a multi component test system of ions in water. The pure component parameters for cubic equations of state are usually calculated from their critical state properties. For ions such critical state properties do not exist, the corresponding parameters were therefore considered as adjustable parameters and fitted to experimental data for electrolyte solutions. Two cubic equation of state parameters and an ion size parameter used in the Mean Spherical Approximation term and in the Born term were fitted.

The temperature dependence of the parameters offered another problem. A temperature dependence similar to the one used for the equation of state parameters of traditional components did not work well for ions and had to be modified.

Reference

Yi Lin, Kaj Thomsen and Jean-Charles de Hemptinne, (2007) *AIChE Journal*, 53(4) 989-1005.

Liquid phase behaviour in the binary system 1-ethyl-3-methylimidazolium ethylsulfate + alkane (n-heptane, methylcyclohexane, toluene)

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1. Summary

Liquid-liquid equilibrium in three binary systems containing an ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate and alkanes was studied. Two experimental methods were used to obtain experimental data; the volumetric and the analytical method. The data were subsequently described by the modified Flory-Huggins equation and the molecular-thermodynamic lattice model proposed by Qin and Prausnitz using the gnostic regression to optimize model parameters.

Keywords: liquid-liquid equilibrium, ionic liquids, thermodynamic models, gnostic regression

2. Extended Abstract

Ionic liquids as possible greener and more efficient solvent alternatives to volatile organic compounds have been studied extensively over more than a decade now. The large number of combinations of cations and anions provide a tunability to required applications that makes them utilisable as e.g. lubricants, entrainers in extractive distillation, and due to their practically zero vapour pressure solvents also at low to vacuum pressures.

In the present contribution, liquid-liquid equilibrium in three binary systems 1-ethyl-3-methylimidazolium (abbr. $[emim][C_2H_5SO_4]$) + alkane is investigated. $[emim][C_2H_5SO_4]$ is a cheap ionic liquid available on ton scale that could be used e.g. to extract aromatics from naphtha cracker feeds. Therefore, liquid-liquid equilibria in systems with three C7 alkanes – an aliphatic, a cyclic and an aromatic one – were measured to compare the mutual solubility of the individual hydrocarbons and the ionic liquid.

Two experimental methods are available in our laboratory: the volumetric and the direct analytical methods. Tie lines were obtained in previous work [1] using a volumetric apparatus built in our laboratory [2]. The experiment consists of

measuring the volumes of the equilibrium phases; the equilibrium compositions are then obtained using simple mass balance formulas:

$$x_1^{(1)} = \frac{n_{1,I}V_{2,II} - n_{1,II}V_{2,I}}{V_{2,II}\left(n_{1,I} + n_{2,I}\right) - V_{2,I}\left(n_{1,II} + n_{2,II}\right)} \tag{1}$$

$$x_1^{(2)} = \frac{n_{1,II}V_{1,I} - n_{1,I}V_{1,II}}{V_{1,I}\left(n_{1,II} + n_{2,II}\right) - V_{1,II}\left(n_{1,I} + n_{2,I}\right)} \tag{2}$$

where $x_i^{(k)}$ is the mole fraction of the i-th component in the k-th phase, $V_{k,I}$ and $V_{k,II}$ is the volume of the k-th phase in the first and second set of measurements respectively, and $n_{i,I}$ and $n_{i,II}$ is the chemical amount of the i-th component in the first set and second set of measurements respectively.

To check the data, the direct analytical method was used. To measure the solubility of the ionic liquid in the studied alkanes, samples of the organic phase were analyzed by a suitable analytical method. As the imidazolium-based ionic liquids absorb UV rays, UV/Vis spectrophotometry was used to determine the contents of [emim][$C_2H_5SO_4$].

The data acquired in this work were also compared with those by Meindersma et al. [3].

To describe the experimental data and to correlate them with literature values the modified Flory-Huggins equation proposed by de Sousa and Rebelo [4] and the molecular-thermodynamic lattice model proposed by Qin and Prausnitz [5] were used. The choice of these models primarily designed for mixtures of polymers is based on findings that ionic liquids show to some extent polymer-like behaviour [6, 7] and also on previous successful use of the modified Flory-Huggins equation in descriptions of thermodynamic properties of mixtures of ionic liquids [2, 8, 9]. Optimization of model parameters was carried out by means of a regression of both our and literature data along a gnostic influence function [2].

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Liquid-Liquid Equilibria of Water + Ionic Liquids

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1. Summary

Ionic liquids (ILs) have garnered increased attention recently due to their potential as "green" replacements for common volatile solvents used in reactions and separations, and their miscibility with water is an important factor for their industrial applications. Therefore in this work, the mutual solubilities between water and several ILs were measured and the COSMO-RS predictive capacity was evaluated.

Keywords: ionic liquids; water; mutual solubilities, green chemistry, COSMO-RS.

2. Extended Abstract

ILs belong to the class of molten salts and commonly consist on the assembly of large organic cations and inorganic or organic anions of smaller size and more asymmetrical shape. These factors tend to reduce the lattice energy of the crystalline structure of the salt and hence to lower their melting point and thus they generally remain liquid at or near room temperature. Besides, unlike molecular liquids, the ionic nature of these liquids results in an unique combination of particular properties namely their high thermal stability, large liquidus range, high ionic conductivity, negligible vapour pressure, non-flammability and a highly solvating capacity, for organic, inorganic and organometallic compounds, determining the high potential of this liquids to be exploited as "green solvents" [1,2].

Among the several applications foreseeable for ionic liquids in the chemical industry, such as solvents in organic synthesis, as homogeneous and biphasic transfer catalysts and in electrochemistry, there has been considerable interest in the potential of ILs for separation processes as extraction media where, among others, ILs have shown to be promising in the liquid-liquid extraction of organics from water [3]. Nevertheless, for the extraction of organic products from chemical reactions that proceed in aqueous media and for liquid-liquid extractions from aqueous phases, ionic liquids with lower solubility in water are preferred. Although they cannot contribute to air pollution due

to their negligible vapour pressure, they do have in fact a significant solubility in water and, as a result, this is the most likely medium through which ILs will enter the environment. Moreover, the loss of ILs into the aqueous phase may be an important factor in estimating the cost of the ionic liquid used and the cost of water treatments. Furthermore, it was already shown that the presence of water in the ionic liquid phase can dramatically affect their physical properties [1].

In this work we address the mutual solubilities between several imidazolium, pyridinium, pyrrolidinium and piperidinium-based ionic liquids and water in the temperature range from (288.15 to 318.15) K and at p=0.1 MPa. The water content in the IL-rich phase was analyzed by Karl Fischer titration and the IL in the water-rich phase was measured by UV-vis spectroscopy.

One of the ILs intrinsic attribute is the potential of tuning their physical and chemical properties by varying different features of the ionic liquid including the alkyl chain length and number of alkyl groups of the cation and the anion identity, and therefore the impact of that fine-tuning in the mutual solubilities was evaluated with the purpose of picture their use as "designer solvents".

The predictive capability of COSMO-RS [4], a predictive model based on unimolecular quantum chemistry calculations, was also evaluated on the description of the liquid-liquid equilibria of water and the ILs binary mixtures as shown in the example depicted in Figure 1.
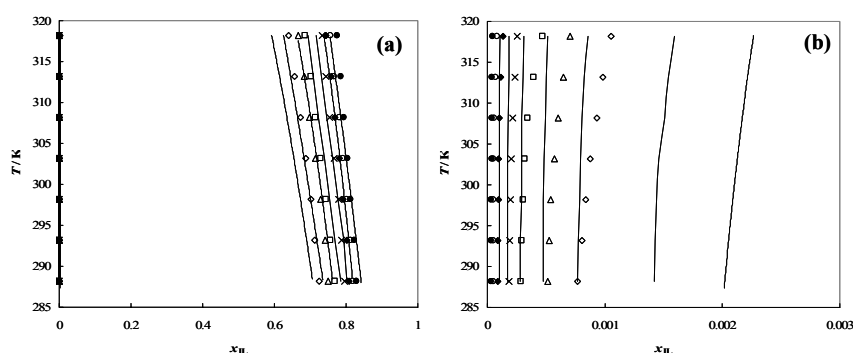
Figure 1: Liquid-liquid entire phase diagram for water and ILs (a) and in the water-rich phase (b): ◊, [C_2mim][Tf_2N]; Δ, [C_3mim][Tf_2N]; □, [C_4mim][Tf_2N]; ×, [C_5mim][Tf_2N]; ♦, [C_6mim][Tf_2N]; ○, [C_7mim][Tf_2N]; ●, [C_8mim][Tf_2N]. The single symbols and the solid lines represent respectively the experimental data and COSMO-RS predictions.

The COSMO-RS proved to describe qualitatively well the experimental mutual solubilities tendency along with the ILs structural modifications and can be very helpful in the scanning of the ILs growing set in order to find suitable candidates for a certain task or to design new ILs for specific applications.

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Session T1-2: Green Organic Synthesis Routes

Abstract Number	Paper Title & Authors	Included
743	Utilization of Lignin for the production of chemicals T Voitl, P R von Rohr	Yes
1130	Investigation of response surface optimization of benzoin synthesis N Yildiz	No
1694	Free radical polymerization in ionic liquids - Explanation of the solvent influence G Schmidt-Naake	No
1822	Highly selective, high-speed hydrolysis-free O-acylation induced with subcritical water micro-reaction system in the absence of catalyst M Sato, K Matsushima, H Kawanami, T Yokoyama, Y Ikushima	Yes
3087	SILP aatalysis – An innovative concept for benign continuous, solvent-free processes using Ionic liquids A Riisager, R Fehrmann, M haumann, P Wasserscheid	Yes
3776	Computer-aided solvent selection for increased reaction rate M Folic, C S Adjiman, E N Pistikopoulos	Yes

Utilization of Lignin for the Production of Chemicals

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1. Summary

We have investigated the various possibilities of producing phenolic compounds of industrial interest from technical lignins. The stability of desired products from the decomposition of lignin was first investigated under different reaction conditions. We then carried out the depolymerization of three commercially available lignins from three different suppliers. Thus the alkaline oxidation and the catalytic hydrogenation of the various lignins following some of the reaction conditions described elsewhere in the literature were investigated. The yield of lignin-derived monomeric products obtained was very low (< 4 wt%) for every experiment, suggesting that the depolymerization reaction conditions as described in the literature, are not fully adequate to transform technical lignins into monomeric species. Based on this experience, we propose and show a new method for the conversion of lignin to high-value products, which is capable of overcoming many well-known difficulties.

Keywords: lignin, alkaline, oxidation, stability, vanillin

2. Extended Abstract

2.1. Stability measurements

The targeted compounds (Figure 1) were completely stable at 200 °C in various solvents (e.g. water, dioxane/water, ethanol) in the presence of either air or nitrogen and in the presence of redox catalysts (e.g. $CuSO_4$, $Fe_2(SO_4)_3$).
Experiments were carried out to determine the stability end-points of the different targeted compounds in water. An increase in T to 300 °C resulted in the formation of unwanted products. These products formed were identified as dealkylated species from the targeted compounds. Thus, a 6.2 % of dealkylated species were identified when performing the reaction in N_2 and 7.4 % when the reaction was carried out in the presence of air. Also, condensation products were observed, although in small quantities (1.0 % and 2.2 % in N_2 and air respectively).
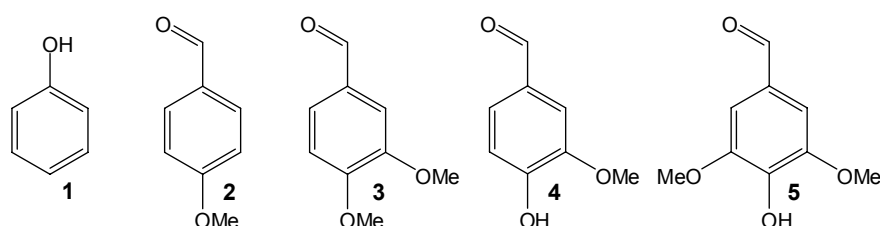
Fig 1. Targeted chemical compounds of industrial interest from the decomposition of commercially available lignins (phenol **1**, p-anisaldehyde **2**, veratraldehyde **3**, vanillin **4**, syringaldehyde **5**).

2.2. Alkaline oxidations

Three different types of commercially available lignins were used in our investigation, Granit (from agricultural plants), STFI (softwood) and Aldrich (spruce). Table 1 shows results from the alkaline oxidations of these lignins according to standard procedures.

Lignin	Precipitates (g)	Products in extracted organic phase (g)	Products identified by GC/MS (mg)	Products in aqueous phase (g)
Aldrich	2.1	1.25	160	
Granit	2.1	1.4	200	5.1
STFI	2.2	1.4	260	

Table 1: Distribution of compounds from the alkaline oxidation of 10g lignin.

The conversion of lignin, calculated from the weight of starting material and precipitates, typically reached values up to 80 %. About 1-2 g of the lignin was converted to products soluble in the organic phase. Out of these 1.4 g of ether-soluble products in the case of STFI lignin oxidation, only 260 mg of components (mainly: vanillin 145 mg, vanillic acid 73 mg and acetovanillone 12mg) were identified by GC/MS. This corresponds to a yield of about 3 wt% based on the dry lignin. In general, most of the reaction products remained in the aqueous phase (approx. 50 wt%). HPLC/MS analysis of the aqueous phase suggested that the products formed were mainly dimeric and trimeric species. The amount of CO_2 produced was approximately 4.6 g. Therefore, the yield of desired products that could be obtained from technical lignins under alkaline oxidation reaction conditions remained below the values reported in the literature (of about 15 wt%). These relatively high yields of monomeric species reported in the literature however, were obtained using steam-explosion hardwood lignin [1] and precipitated hardwood lignin [2].
We are currently investigating novel approaches, including the use of highly selective oxidation catalysts. First experiments, which will be shown in the oral presentation, resulted in a substantial improvement of the yield of monomers in comparison to alkaline oxidations.

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Highly Selective, High-Speed and Hydrolysis-Free O-acylation induced with subcritical water micro-reaction system in the absence of catalyst.

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1. Summary

Highly selective, high-speed and hydrolysis-free O-acylation of alcohols and phenols was developed with subcritical water micro-reaction system in the absence of catalyst. This system nicely demonstrates the potential benefits resulting from the combination of subH$_2$O properties and microprocess in advanced progress of O-acylation

Keywords: non-catalytic, hydrolysis-free, acylation , anhydride, subcritical water

2. Extended Abstract

The acylation of alcohols and phenols by carboxylic anhydride to esters is a fundamental chemical transformation for the production of a large variety of important intermediates and fine chemical products (Green and Wuts).
Catalytic methods for this reaction are being investigated intensively to replace non-stoichiometric acylation processes that generate large amounts of carboxylic acid and solvent waste (Corma and García). Lewis acid shows very promising catalytic properties and found to provide effective activity but those catalysts are expensive, suffered high acidity for acid-sensitive alcohols (Yamamoto). Moreover, the major general limitations of the catalytic approach relate to rapid catalyst deactivation by deposition of char or coke on catalyst surface, which is troublesome and costly for regeneration and re-use of catalyst (van Santen and Niemantsverdriet). In addition to that, a large amounts of organic solvents and long reaction times for depletion was needed for batchwise solution-phase processes (Orita *et al.*).
    In this situation, we have developed a high-speed, highly selective and hydrolysis-free acylation of various monohydroxy compounds such as primary and secondary alcohols and phenols by anhydride even in the absence of catalyst with the

furnace
in vacuum thermometer sheath
flow cell
1) microreactor
   or
2) in situ IR flow cell
heated coil tube
thermometer
TI
Syringe pump
H₂O
Syringe pump for washing
H₂O or solvent
Back pressure regulator
effluent including products
substrate (alcohol-acetic anhydride mixture)
Zn-Se windows
inlet tube for substrate
tube for effluent
washing tee
cooling flange
furnace

Scheme 1

$$R\text{-}CO\text{-}O\text{-}CO\text{-}R + R_1OH \xrightarrow[\mu\text{-subH}_2O]{\text{no cat.}} R\text{-}CO\text{-}OR_1$$

Scheme2

1.1equiv. Ac₂O
no cat. μ-subH₂O
2.2equiv. Ac₂O

Figure 1 A schematic diagram of μ-subH₂O system

use of a flow-type of subcritical water μ–reaction (μ-subH₂O) system (Figure 1), in which the desired ester products are obtained in excellent yields >93% and quantitative selectivities at temperatures of 200 to 250°C and at constant pressure of 5MPa (Scheme 1 and Table 1). Tertiary alcohols can be successfully transformed into the corresponding esters by using a large excess amount of anhydride at lower temperatures below 200°C. By controlling the equivalent molar acetic anhydride to alcohols, moreover, the μ-subH₂O system makes possible to regioselectively acylate any hydroxyl groups of various dihydroxy compounds (Scheme 2).

substrate	acid anhydride eq.	T °C	P MPa	τ sec	conv. %	sel. %	yield %
(geraniol structure) OH	Ac₂O (1.1)	200	5	9.9	98.8	100	98.8
(bicyclic alcohol) OH	Ac₂O (1.1)	225	5	9.9	99.0	100	99.0
α-tocopherol	Ac₂O (1.1) /AcOH (1)	250	5	9.9	99.0	100	99.0

Table 1 Typical O-acylation for primary, secondary alcohol and phenol derivatives

This system nicely demonstrates the potential benefits resulting from the combination of subH₂O properties and microprocess in advanced progress of O-acylation. Finally, it seems worth noting that this approach induced by μ-subH₂O system is environmentally benign process that is applied in commercial industrial acylation, thus making this approach of general interest for "green" organic synthesis.

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SILP Catalysis – An Innovative Concept for Benign Continuous, Solvent-free Processes using Ionic liquids

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1. Summary

Supported ionic liquid phase (SILP) materials comprising a *non-volatile*, ionic liquid catalyst phase are new heterogeneous-type catalysts with selectivity and efficiency like homogeneous catalysts highly applicable for use in homogeneous catalysed reactions in continuous, gas-phase design using fixed-bed technology. Here the facile use of Rh-complex based SILP catalysts is demonstrated for industrially important processes: C_3-C_5 alkene hydroformylation and methanol carbonylation. Furthermore, SILP catalysis in reaction series is exemplified for processing of technical Raffinate-II (C_4 mixture) by a hydroformylation-isomerization sequence.

Keywords: catalysis, green chemical processes, ionic liquids, reaction engineering, supported ionic liquid phase (SILP) catalysts

2. Extended Abstract

In recent years, non-volatile room-temperature ionic liquids (mixed organic-inorganic salts) have proven to be very versatile solvents for organic synthesis and for immobilizing of homogeneous catalysts in two-phase organic liquid-liquid reactions, due to their tunable properties by various cation-anion combinations (Wasserscheid and Welton, 2003). As a consequence, significant interest to implement catalysts based on ionic liquids into technical applications has arisen from chemical industry (Rogers and Seddon, 2003). However, for industrial utilization a solid catalyst is usually preferred instead of liquid catalyst systems due to the ease of catalyst separation by filtration and the possibility for applying fixed-bed technology leading to, e.g. continuous-flow operation mode, avoidance of solvent handling and tedious – but required - catalyst recycling.
Inspired by the demand for solid, ionic liquid-based catalyst systems we have in the last years contributed to the development of novel homogeneous catalyst systems

comprised of ionic liquids containing transition metal complexes on porous high-area supports, i.e. *Supported Ionic Liquid-Phase (SILP) catalysts* (Riisager et al., 2006a). In SILP catalysts the reaction takes place in the diffusion layer of the highly dispersed ionic liquid catalyst phase, thereby offering significant advantage of relatively short diffusion distances compared to conventional two-phase catalysis and an efficient use of the catalyst components. Moreover, SILP catalysts benefit from unique advantages which are not provided by analogous supported catalyst systems containing traditional solvents (i.e. SLP catalysts) such as, e.g. non-volatility, large thermal-/liquid-phase window and adjustable properties. Consequently, processes applying SILP catalysts can be conducted at flexible reactions conditions using preferred fixed-bed reactor designs in continuous-flow operation mode, thus offering simple and complete product separation under solvent-free conditions.

In this work, catalytic and spectroscopic results obtained from our studies of Rh-SILP catalysts for fixed-bed, gas-phase hydroformylation of C_3-C_5 alkenes (Riisager et al., 2006a; Haumann et al., 2007) and methanol carbonylation (Riisager et al., 2006b) are highlighted. Furthermore, technical prospective processes implying SILP catalysts in reaction series are introduced, e.g. hydroformylation of Raffinate II - a mixed C_4 fraction from petrochemical refinering – where a reaction sequence has been established in which internal butenes are isomerized and hydroformylated in two designated reactors, as shown in Figure 1.
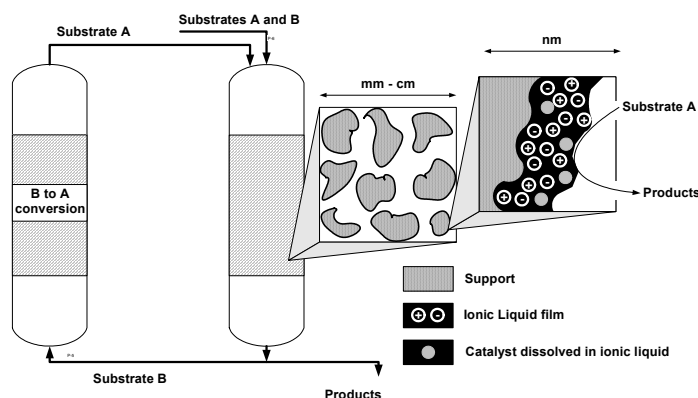
Figure 1: Schematic representation of a novel, fixed-bed SILP catalyzed reaction sequence.

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Computer-aided solvent selection for increased reaction rate

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1. Summary

A hybrid experimental/computer-aided methodology for the design and selection of solvents for increased reaction yield has been developed. It is based on the use of a few reaction rate measurements to build a reaction model, followed by formulating and solving an optimization-based computer-aided molecular design (CAMD) problem in which the logarithm of the reaction rate constant under given conditions is maximized. Since very few measurements are used to build the reaction model, the reliability of the reaction model is checked by solving the problem again using multi-parametric programming in order to assess the impact of uncertainty. The final output consists of a list of robust candidates which can be targeted for experimentation. Step by step, the methodology is illustrated through solvolysis reaction and complex reaction schemes case studies. The promising results obtained are presented.

Keywords: reaction yield, solvent selection, computer-aided molecular design (CAMD), multi-parametric programming

2. Extended Abstract

Solvents are widely used as reaction media in the fine chemicals and other industries where they serve to bring solid reactants together by dissolving them, to control temperature, and to enhance reaction rate. Reichardt (1988) reports that the solvolysis of 2-chloro-2-methylpropane is 335,000 times faster in water than in ethanol. In spite of the importance of solvent choice on productivity, there has been little work on systematic approaches for the selection of solvents for reactions.

Therefore, we propose an iterative approach that combines experimental work with computations for the design of solvents for a reaction. Such a tool can be adapted to plant-wide process integration and enable balancing reaction rate against other processing requirements. A key issue when tackling this problem is to identify a relationship that links certain specific solvent properties to the reaction rate in a way that can quantify solvent effects on a particular reaction. We propose the use of the multi-parameter solvatochromic equation (Abraham *et al.*, 1987), simple and easily

applicable, which correlates solvent properties (empirical solvatochromic parameters and cohesive energy density parameter) with the logarithm of the reaction rate constant. We obtain the values of the solvent parameters used in this equation by group-contribution prediction techniques using first-order UNIFAC groups which make further integration with previous solvent design approaches easier.

The proposed methodology consists of three steps. The first step is concerned with the development of a model of solvent effects on the reaction. It involves gathering the necessary data for eight predetermined solvents and generating the solvatochromic equation by fitting the coefficients by linear regression. The solvents should be chosen in such a manner as to cover a wide range of polarity and classes of chemicals. The second step is an optimization step in which the design problem is formulated as an MILP and solved using standard techniques. The first objective we consider is to identify a solvent in which the reaction rate constant under given conditions is maximized. Implementation of integer cuts enables generation of successive candidate molecules.

Since we build our model based on kinetic data in a few solvents only, and then use it for further extrapolation, we believe there is uncertainty associated with the model coefficients. This is confirmed by wide 95% confidence intervals obtained for each coefficient. We investigate the impact of uncertainty through multi-parametric (mp) programming. Solving the mp-MILP (Dua and Pistikopoulos, 2000) provides a complete map of optimal solutions in the uncertainty space. The optimal solutions are given as a function of the varying parameters, and the most robust solution is the one found to be optimal for the widest range of parameters. Comparing that solution against the one arrived at by deterministic optimization proves the robustness of the MILP solution.

The methodology is illustrated through application to a solvolysis reaction. The proof of concept is also presented for more complex reaction schemes, such as competing parallel and consecutive reactions.

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Session T1-3: Environmental Engineering & Management

Abstract Number	Paper Title & Authors	Included
312	Improving the heat transfer properties of waste activated sludge by advanced oxidation processes R Dewil, L Appels, J Baeyens	Yes
746	Influence of temperature in the continuous pyrolysis of waste tyres in a conical spouted bed reactor G Lopez, G Elordi, M Arabiourrutia, R Aguado, M Olazar, H Altzibar	Yes
1696	Ecological Studies and Dynamic Parameter Estimation for Eutrophication Models V Estrada, E. Parodi, M S Diaz	Yes
1752	Possibility of the Use of Hollow Fiber Membrane Contactors for Phenol Biodegradation in Saline Solutions Ruey-Shin Juang	No
3356	First year operation experience with a 1 t/h CO2 absorption pilot plant at Esbjerg coal-fired power plant J N Knudsen, J N Jensen, P J Vilhelmsen	Yes

Improving the heat transfer properties of waste activated sludge by advanced oxidation processes

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1. Summary

The present paper studies and quantifies the influence of Advanced Oxidation Processes (AOPs) on the thermal properties of waste activated sludge i.e. its thermal conductivity and heat transfer coefficient during indirect contact drying, as commonly applied in sludge drying equipment. Key-design parameters of these dryers will be outlined. The AOPs which were used in the experiments include the well-known Fenton and the novel peroxymonosulphate peroxidations. It was seen that both treatment methods significantly improve the heat transfer properties of the sludge, with the Fenton peroxidation giving superior results. This observation, together with an improvement in mechanical dewaterability of the sludge, results in an increased dryer efficiency and hence smaller dryer dimensions for a given drying rate.

Keywords: sludge drying, advanced oxidation process, heat transfer coefficient, thermal conductivity

2. Extended Abstract

The Waste Activated Sludge (WAS) process has the inherent drawback of producing large amounts of sludge, which should be disposed of. The drying of excess sludge presents an interesting intermediate stage in sludge handling since it stabilises and hygienises the sludge and reduces its volume. Dried sludge can moreover readily be used as a secondary fuel in energy plants (Baeyens and Van Puyvelde, 1994).
In this study, the sludge was subjected to two advanced oxidation processes (AOPs), namely the common Fenton peroxidation (H_2O_2 with Fe^{2+} activation at low pH values) and the peroxidation with peroxymonosulphate (POMS) under neutral pH. It was already demonstrated that these treatments improve the mechanical dewaterability of WAS (Neyens et al., 2003). Since they change the structure of the sludge flocs, an influence on the heat transfer is also expected.

Figure 1 presents the values of the apparent thermal conductivity (k_e) for untreated (blank) sludge and sludge subjected to the peroxidation treatment as a function of the dry solid content (%DS). An increase of k_e is clearly observed when applying either of the methods.
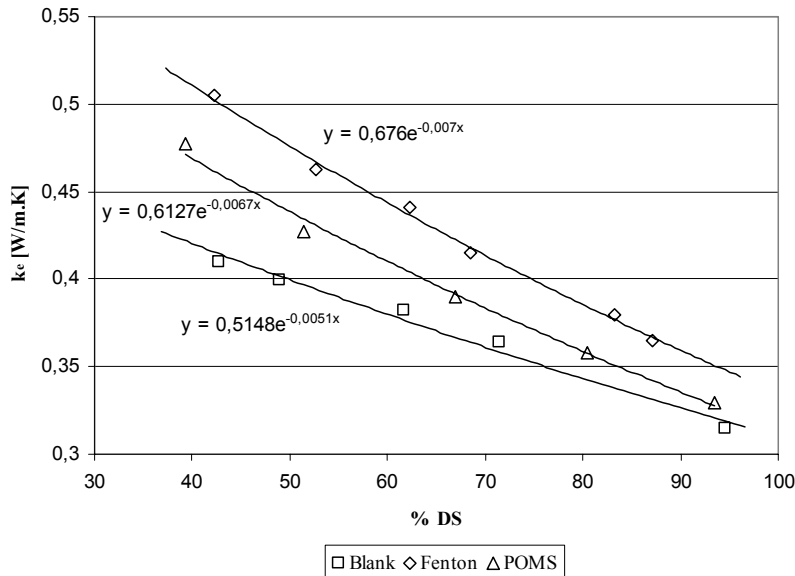
Figure 1: Apparent thermal conductivity of untreated and treated sludge as a function of %DS

As a result of the higher k_e, the heat transfer coefficient h_s also increases, meaning that heat is more easily transferred into the sludge mixture and hence the total dryer surface can be decreased.

In combination with the improved mechanical dewaterability, a significant reduction of the dryer's dimensions is achievable. As an example, both a multiple hearth dryer and a fluidized bed dryer with a sludge drying capacity for 300000 IE were considered. For the multiple hearth dryer a reduction from 12 plates for the untreated sludge to 3 plates for the Fenton treated sludge and 5 plates for the POMS peroxidation could be achieved. The heat exchanging surface of the fluidized bed dryer is reduced from 65.7 m^2 for the untreated sludge to 24.4 m^2 for the Fenton treated sludge and to 32.72 m^2 for the POMS treated sludge respectively.

The decrease in investment costs and in energy consumption represents a considerable economic benefit and largely compensates the cost of the chemicals. The proposed methods are hence technically and economically very attractive.

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Influence of temperature in the continuous pyrolysis of waste tyres in a conical spouted bed reactor

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1. Summary

The conical spouted bed reactor (CSBR) is an interesting technology for the pyrolysis of scrap tyres, due to the excellent hydrodynamic qualities and to the efficient heat transfer between phases. Continuous operation at the 425-600 ºC range gives way to a yield of 1.8 to 8.2% of gases, 55 to 44.4% of liquid fraction (C5-C10 range hydrocarbons), 9.2% to 11.5% of tar and 33.9 to 35.8% of char. The liquid fraction is of suitable quality for its use as fuel but the char requires activation for its upgrading

Keywords: Pyrolysis, waste tyres, spouted beds

2. Extended Abstract

At present, 2.5 million tonnes per year of waste tyres are generated in Europe, a similar amount in USA and approximately 1 million tonnes in Japan [1]. Pyrolysis is considered to be one of the more feasible solutions at large scale. The interest is centred on the fact that the products obtained by this process may be easily handled, stored and transported and, consequently, they may be transformed in other units that are not near the recycling plant [2]. Pyrolysis liquid products may be used directly as fuel or they may be added to a refinery feed. In addition the pyrolysis liquid is a source of light aromatics such as benzene, toluene and xylene [3,4]. Similarly, the oils have been shown to contain limonene, a high value product used in industrial applications including formulation of industrial solvents, resins and adhesives and as an environmentally acceptable solvent [5].

In this work, the pyrolysis of scrap tyres has been studied in the 425-600ºC temperature range. The experimental runs have been carried out in a pilot plant conical spouted bed reactor provided with a system for continuous feeding of scrap tyres. In order to ensure stable spouting, the nitrogen flowrate has been set at 1.2 times the minimum spouting velocity, 9.5 Nl/min. Continuous operation has been carried out by feeding 3 g/min of scrap tyres and the mass fed in each run was 100 g.

The main components of the tyre material studied are (in %wt): natural rubber (SMR 5CV), 29.59; styrene-butadiene rubber (SBR 1507), 29.59; carbon black (ISAF N220), 29.59; zinc oxide, 2.96; phenolic resin, 2.37; sulphur, 0.89 and other less important components.

The products obtained in this process can be divided into five different fractions:
Gases containing C1-C4 hydrocarbons whose yield varies from 1.8% at 425ºC to 8% at 600ºC. The gases can be burnt to provide energy for the endothermal pyrolysis process. The non-aromatic liquid fraction consists of hydrocarbons in the C5-C10 range and decreases from 36% at 425ºC to 13% at 600ºC as a result of the thermal cracking.. The C5-C10 aromatic hydrocarbon fraction increases from 13% to 23%. The yield of aromatics in the pyrolysis of tyres is favoured by high temperatures and by the presence of aromatics in the original formulation of the tyre, as is our case. The C5-C10 fraction contains valuable tyre monomers, such as isoprene, limonene (isoprene dimmer) and styrene. The tar fraction is made up of hydrocarbons heavier than C10, this fraction does not have a clear tendency in the studied range of temperatures and its yield varies from 9% to 11%. Figure 1 shows the evolution with temperature of the fractions described.
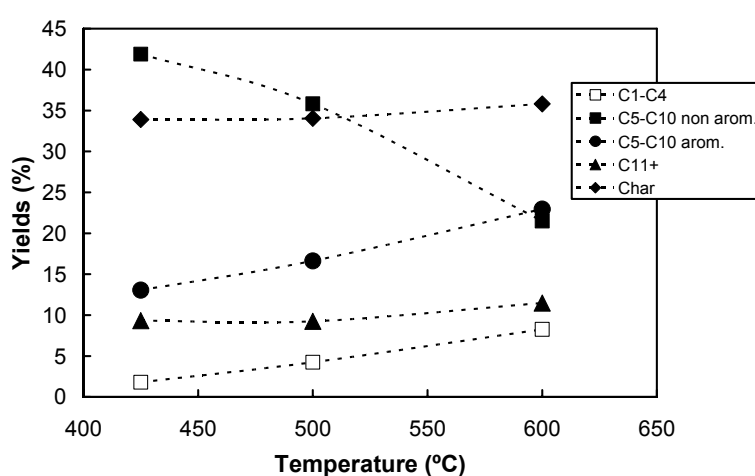
Figure 1: Evolution of the yields of the lumps in the temperature range studied.

Finally, the char yield increases from 33.9 at 425ºC to 35.8% at 600ºC. These values are slightly higher than that corresponding to the sum of carbon black and the other solids in the original tyre. This carbonaceous material may be used as a quality fuel, or as a suitable raw material for carbon black or active carbon once activation has been carried out.

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Ecological Studies and Dynamic Parameter Estimation for Eutrophication Models

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1. Summary

In this work, we address the parameter estimation problem for in a lake eutrophication model. It is a dynamic parameter estimation problem, which is solved with a simultaneous approach with an nonlinear programming solver. Gradients of state variables are considered along the column height, rendering a partial differential equation problem which is transformed into a differential algebraic (DAE) one by spatial discretization. Main biochemical and chemical parameters have been obtained, which allow a close representation of the lake dynamics.

Keywords: ecological model, eutrophication, dynamic parameter estimation, nonlinear programming

2. Extended Abstract

The increasing inflows of nutrients into lakes and reservoirs, mainly due to agricultural activities, have intensified eutrophication of water bodies, which has in turn paved the way to the development of detailed ecological water quality models. These models provide a representation of major physical, chemical and biological processes that affect the biomass of phytoplankton and nutrients throughout periods of time and, once calibrated, they allow the prediction of the system evolution and consequent actions for remediation can be taken.

Eutrophication models comprise a set of complex nonlinear partial differential algebraic equations, with rate coefficients that require calibration to suit site-specific conditions. Consequently, the first step in an eutrophication model development is the resolution of a parameter estimation problem. Zhang et al. (2004) have proposed a sequential procedure to determine phytoplankton and zooplankton parameters using exergy as the objective function and calibrating both physical and chemical parameters by trial and error. More recently, Shen (2006) proposed a least-squares objective function and the resolution of the dynamic parameter estimation problem through the application of a modified Gauss-Newton method capable of handling

upper and lower bounds on parameters and the Hessian being approximated with information from the sensitivity matrix calculated by finite differences.

In this work, we have formulated a parameter estimation problem with a least-squares objective function subject to a partial differential algebraic equations (PDE) model resulting from temporal and spatial dynamic mass balances in the phytoplankton groups diatoms, green algae and cyanobacteria; dissolved oxygen and nutrients, such as nitrate, ammonium, organic nitrogen, silica, phosphate and organic phosphorus. Algebraic equations represent profiles for temperature, solar radiation and river inflows, in addition to the calculation of most factors that affect rate equations, such as effect of solar radiation, nutrients, etc. The PDE is transformed into an ordinary differential equation system by applying the Method of Lines to spatially discretize the PDE into sets of ordinary differential-algebraic equations (DAE) (Rodriguez and Diaz, 2006). The DAE optimization problem is then transformed into a large nonlinear programming (NLP) problem by representing state and control variables profiles by polynomial functions over finite elements in time. The NLP problem has been solved with a successive quadratic programming algorithm.

Field data with a twice a week frequency throughout a year have been obtained by the authors (Parodi et al., 2005) in Paso de las Piedras Reservoir (38° 22´ S and 61° 12´ W), which supplies drinking water to more than 400,000 inhabitants in Bahia Blanca, Argentina. At present, the trophic level of this lake corresponds to eutrophic category and it undergoes repeated blooms of algae (Parodi et al., 2004). Additional data are being obtained to validate the current calibrated model.

Numerical results show good agreement with values from the literature for similar lakes. Confidence intervals have also been determined for parameters.

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First year operation experience with a 1 t/h CO_2 absorption pilot plant at Esbjerg coal-fired power plant

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1. Summary

As a part of the EU integrated project CASTOR a 1 t/h CO_2 absorption pilot plant has been erected at the 400 MW coal-fired Esbjerg power plant in Denmark. The main purpose of the pilot plant is to demonstrate the post combustion capture technology in conjunction with a coal-fired power plant. Additionally, the pilot plant will be used to test the performance of new energy efficient solvents and to verify modelling work. During the pilot plant's first year, two 1000 hours test campaigns using monoethanolamine were conducted. This paper summarises the initial operation experience and some of the first results obtained during these campaigns.

Keywords: CO_2 absorption, clean coal combustion, post combustion capture, pilot plant

2. Extended Abstract

CASTOR is an integrated project under the Sixth Framework programme under Sustainable Energy Systems, "Capture and sequestration of CO_2, associated with cleaner fossil fuel plants" under the European Commission. One of the key targets of CASTOR (see webpage: www.co2castor.com) is to reduce the costs of post-combustion capture by development of an absorption solvent with lower energy requirement and optimise the integration of a CO_2 absorption plant into a modern power plant. A major element of the CASTOR project is to construct and operate a CO_2 absorption pilot plant that operates on coal derived flue gas. The purpose of the pilot plant is to test novel solvents developed in the CASTOR project and to gain hands on experience with the CO_2 capture technology on real coal flue gas. Furthermore, the pilot plant will be used to validate the modelling and laboratory results obtained by the different CASTOR partners. Within the framework of the CASTOR project, DONG Energy and Vattenfall Nordic have carried out the tasks of

engineering, purchasing, installation and commissioning of a CO_2 absorption pilot plant as well as planning and conducting tests at the facility.

The CO_2 absorption pilot plant is placed at the Esbjerg power station, Esbjergværket (ESV). ESV is owned and operated by DONG Energy Generation and is located at the West coast of Denmark. ESV is a 400 MW pulverised coal-fired power plant equipped with deNOx (high dust SCR), cold-sided ESP and FGD plants (wet limestone scrubber).

The design of the pilot plant is based on the design of a standard amine-based CO_2 production plant with minor modifications. A flow diagram of the pilot plant is shown in Figure 1. The pilot plant operates on a slipstream of the flue gas, taken immediately downstream the FGD plant. The flue gas does not undergo any pre-treatment before supplied to the CO_2 absorption plant.
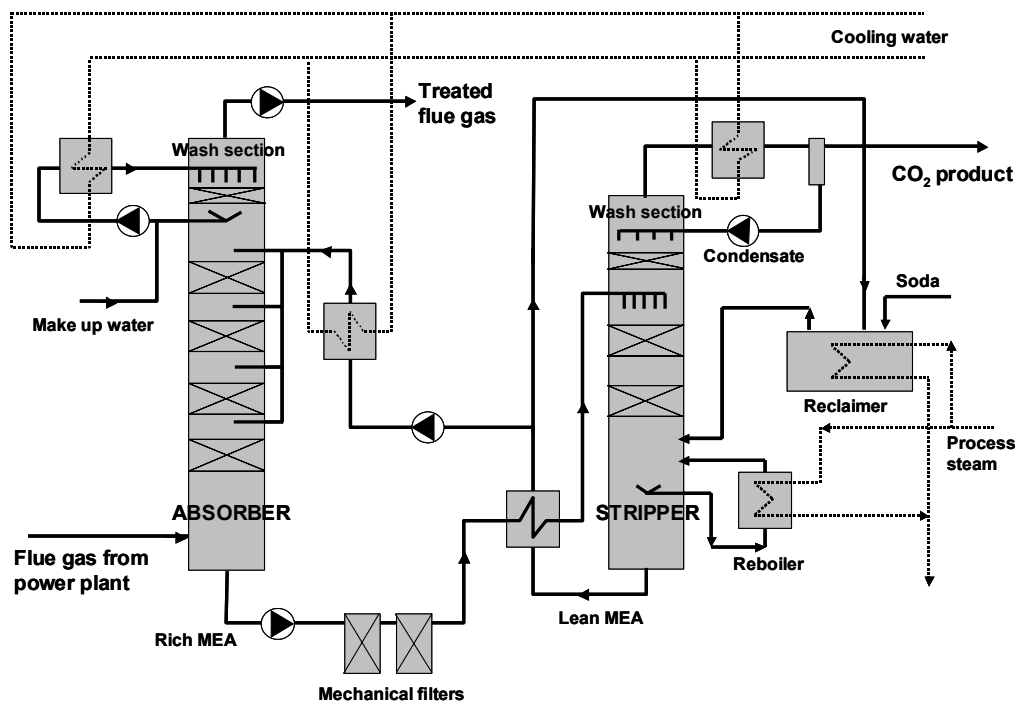
Figure 1: Flow diagram of the CASTOR CO_2 absorption pilot plant at ESV.

In late 2005, the CASTOR CO_2 absorption pilot plant was erected and commissioned. During 2006, two 1000 hours test campaigns were conducted using a conventional solvent, 30 %-weight monoethanolamine (MEA) solution. Among others, the campaigns included tests to verify plant functionality and stability as well as a more detailed parametric study.

MEA was chosen as the start-up solvent because of its well-known performance and the general availability of kinetic and thermodynamic data for simulations. Validation of models by the experimental results obtained from the pilot plant is an important task in the CASTOR project.

Session T1-4a: Sustainable & Clean Technologies - Ia: Extraction & Remediation

Abstract Number	Paper Title & Authors	Included
1332	Treatment of waste oil-in-water emulsions from a copper metalworking industry by vacuum evaporation: Effect of operating conditions G. Gutierrez, A Cambiella, J M Benito, C Pazos, J Coca	Yes
2013	In situ stimulation and remediation of contaminated fractured soils C Tsakiroglou, D Tzovolou, C Aggelopoulos, K E Klint, B Nilsson, W Slack, F Haeseler, Y Benoit, P DeLaplace, D Blancet, T Broeker, T Kasela, M Jeczalik	Yes
2399	Electrokinetic remediation of copper mine tailings H K Hansen, A Rojo, L M Ottosen	Yes
2563	Absorption of pure carbon-dioxide gas in a foam-bed reactor A Gaikwad, A N Bhaskarwar	Yes
2948	The influence of the chelating on the oxidation of phenol catalysed by chelated iron at mild conditions I Sanchez, F Struber, J Font, A Fortuny, A Fabregat, C Bengoa	yes

Treatment of waste oil-in-water emulsions from a copper metalworking industry by vacuum evaporation: effect of operating conditions

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1. Summary

Three different waste oil-in-water (O/W) emulsions from a copper metalworking industry, generated in different parts of the process, were treated by vacuum evaporation and the effect of operating variables on oil removal was analysed. The treatment by a previous coagulation/centrifugation stage, with $AlCl_3$ as coagulant, was also studied. A comparison of laboratory-scale experimental results and those obtained in an industrial evaporator, shows a good agreement.

Keywords: O/W emulsions, vacuum evaporation, metalworking, coagulant, pH

2. Extended Abstract

Oil-in-water (O/W) emulsions are used as metalworking fluids in many industries for lubrication and cooling purposes. These fluids lose their functional properties with aging and generate waste oily emulsions that must be properly treated before disposal. Vacuum evaporation is an efficient treatment for these waste emulsions, and the use of a previous emulsion destabilisation stage might improve the quality of final aqueous effluent, reducing energy costs. The operating parameters, such as heat transfer rate and operating pressure, have an important role in the evaporation process, because if the emulsion components have a vapour pressure similar to water, the evaporation condensate may be polluted.

In the present research, three different waste O/W emulsions were treated by vacuum evaporation. The emulsions were provided by a local copper manufacturing company and they were generated in different parts of the process: a synthetic emulsion (Multiroll) from the melting process, and two semi-synthetic emulsions from smoothing (Unopol) and wire drawing (Divinol) operations, respectively.

Vacuum evaporation experiments were conducted in a Büchi R205 evaporator. The effect of the operating pressure and the temperature difference between the heating bath and evaporation temperature (ΔT_{HE}) were selected as main variables. The highest evaporation temperature was observed for the Unopol emulsion, because of its high

oil content, and the chemical oxygen demand (COD) of the condensates increased when pressure and ΔT_{HE} also increased. Furthermore, a decrease of both the evaporation temperature and COD was observed when a coagulation/centrifugation stage, adding 0.05 M AlCl$_3$, was used prior to evaporation. The addition of coagulant lowers the emulsion pH as a result of Al(OH)$_3$ precipitation, affecting the evaporation rate and leading to a quality decrease of the aqueous effluents. A COD removal increase was observed when the emulsion pH was raised by adding NaOH after centrifugation, as shown in Fig. 1.
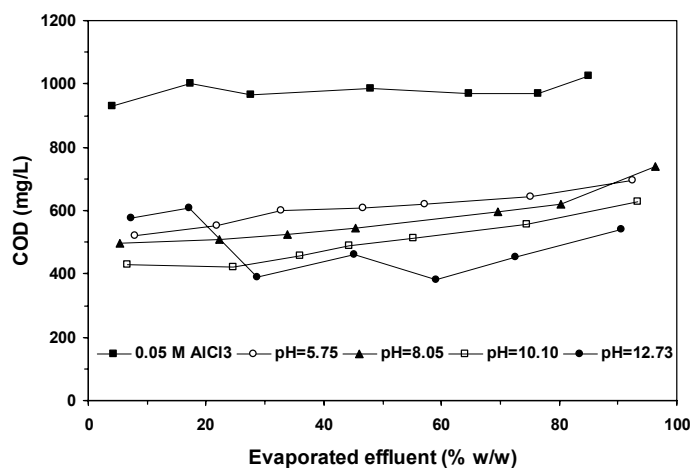
Figure 1. COD values of aqueous effluents obtained during Divinol emulsion evaporation after a previous coagulation/centrifugation stage using 0.05 M AlCl$_3$ followed by pH neutralisation with NaOH.

The characteristics of the feed emulsion and aqueous effluents obtained by evaporation at laboratory and industrial scale (with an evaporator of 60 L/h capacity) are shown in Table 1. No significant differences are observed between the two aqueous effluents obtained: low pH's and high conductivities reveal that probably a small amount of acid is present in the industrial evaporator, because of the difficulty to clean properly the evaporator tubes.

Table 1. Parameters of the aqueous effluents obtained by lab scale and industrial scale compared with the feed.

	Conductivity (µS/cm)	pH	Turbidity (NTU)	COD (mg/L)	BOD$_5$ (mg/L)
Feed	5550	9,13	7600	11500	103
Lab Scale	31,1	9,16	9,55	2670	37
Industrial Scale	119	6,30	12,7	2820	25

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In situ stimulation and remediation of contaminated fractured soils

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1. Summary

Fractured and low permeable sediments / soils comprise a major part of the subsurface especially in Northern and Central Europe. In such porous media, the transport pathways on non-aqueous pollutant liquids (NAPLs) are controlled by vertical fractures, and target contaminants that have been accumulated in the matrix porosity may be bypassed if site remediation is based on vertical wells. An effective in situ remediation of such a site could be done if the horizontal conductivity was enhanced by stimulating the subsurface with hydraulic fracturing.

2. Extended Abstract

The goal of the present work is to design an efficient stimulation set-up and remediation strategy to cleanup a NAPL-contaminated unsaturated zone of fractured and low permeable soils. The test site is an abandoned military airport (Kluczewo), situated in North Poland and contaminated by jet fuel during a long period (1927-1992). The detailed geological characterization of the site revealed that the unsaturated zone is a fractured porous medium (clayey/silty/sandy soil) consisting of five zones (Units) where the lower one (Unit 4) has highly been contaminated. Before initiating remediation (t=t0), the chemical characterization of the site, was carried out by analyzing a great number of soil and water samples with a variety of chromatographic techniques (PollutEval, GC-FID, GC-MS, etc). Hydraulic fractures were installed and tested on five highly contaminated areas (cells). Two remediation technologies were selected and implemented on the site: (i) bio-ventilation by injecting air for a long period of time (Fig.1a); (ii) thermal treatment by injecting steam for a short period of time (Fig.1b). Each remediation scenario was monitored by collecting soil samples and analysing the total concentration and composition of hydrocarbons (HC) with GC-MS (t=t1).
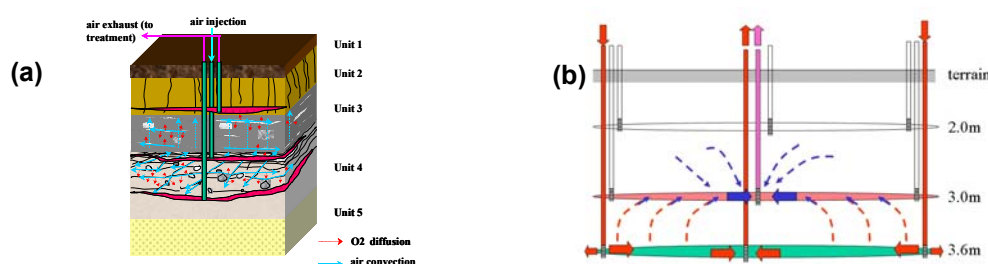
Figure 1: (a) Bio-ventilation setup (cell 1a). (b) Steam injection setup (cell 4).

During bio-ventilation, a significant reduction of HC concentration occurred in the bottom of Unit 4 (Fig.2a). Given that the HC composition was not changed, the increased HC concentration at the top of Unit 4 (Fig.2b) may be due to the upward immiscible displacement of jet fuel by gas through preferential flow paths (Fig.2b).
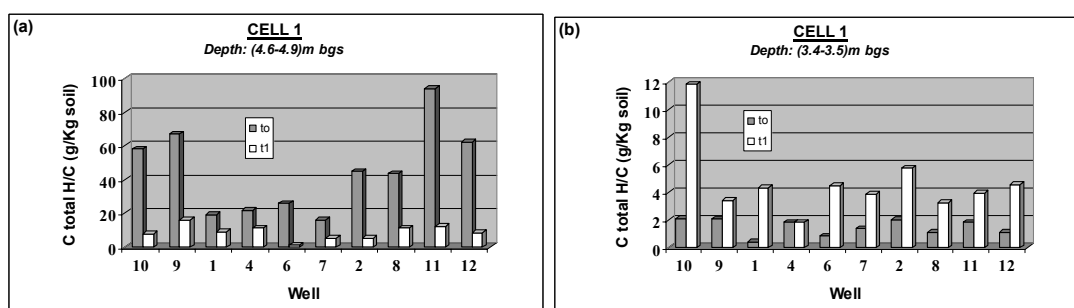
Figure 2: Total hydrocarbon concentration (g/kg soil) measured in the various wells of Cell 1a (bio-ventilation); (a) lower part of Unit 4; (b) upper part of Unit 4 (bgs=below ground surface)

In Cell 4, a significant reduction (>75%) of the total HC concentration occurred in the bottom of Unit 4 Fig.3a). However, at the top of Unit, no significant change of HC concentration occurred (Fig.3b), and this may be associated with the low efficiency of HC displacement by the condensation front in highly heterogeneous media.
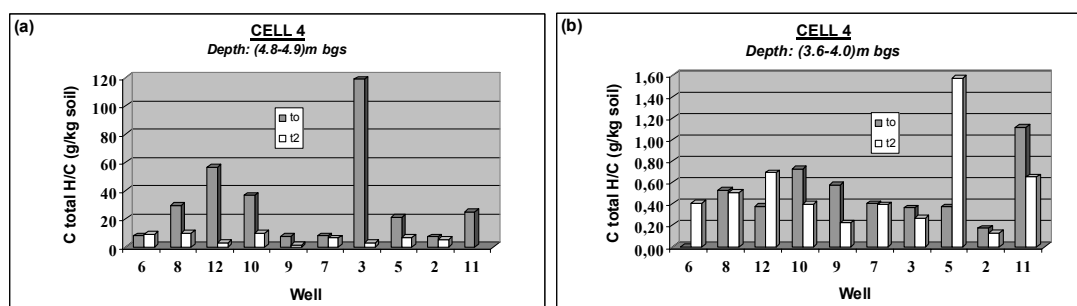
Figure 3: Total hydrocarbon concentration (g/kg soil) measured in the various wells of Cell 4 (steam injection with vapor extraction); (a) lower part of Unit 4; (b) upper part of Unit 4

Electrokinetic remediation of copper mine tailings

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1. Summary

This work compares and evaluates sixteen electrodialytic laboratory remediation experiments on copper mine tailings. Different parameters were analysed, such as remediation time, addition of desorbing agents, and the use of pulsed electrical fields.

Key words: tailings treatment, electrometallurgy, waste processing, environmental solution

2. Extended abstract

The heavy metal contamination from mining industry has become a growing problem both in Chile and worldwide. This contamination includes large areas with soil pollution, contaminated rivers and continuous generation of mining waste deposits. The solid waste that will be analysed is mine tailings, which are the residual products after the flotation process in conventional sulphide copper mining. These tailings are known to contain considerable amounts of different heavy metals.

In the last 20 years, electrokinetic remediation has proved to be a possible way to remove heavy metals from fine-grained porous solids such as soil, clay, fly ash and sludge (Lageman, 1993, Acar and Alshawabkeh, 1993). Soils and mine tailings have similarities regarding the porous structure, electrical conductivity, and adsorption/precipitation processes, and therefore theoretically positive results could be expected using the electrodialytic remediation method on mine tailings. Hansen et al. (2005) demonstrated initially that copper could be removed from mine tailings by electric fields.

On the other hand, due to the semiconductor nature of the mine tailings, the electrical resistance in the remediation cell increases quickly with time. This polarization phenomenon results in a continuous depletion of the current. For this reason, the use of pulsed electric fields in order to speed up the remediation process has also been analysed. Electrodialytic remediation with watery tailing was considered as the baseline for analysis of this process. The effect of additives was investigated considering sulphuric and citric acid. Both acids are strong, and citric acid forms cationic complexes with copper. In the case of pulsed electric fields, a time ratio (electric field "ON" / electric field "OFF") of 20 was used only in tailings pre-treated

with sulphuric acid. Table 1 shows experimental conditions and results (expressed as copper removal).

Experiment	Pre-treatment	Voltage drop (V)	Pulsed electric field frequency (cycles/day)	Remediation time (hours)	Copper leaving cathode side (mg)	Total copper removal (%)
1	dist. Water	20	-	504	0	0
2	dist. Water	40	-	504	0	0
3	1 M H_2SO_4	20	-	504	700	39
4	1 M H_2SO_4	20	-	5	0	0
5	1 M H_2SO_4	20	-	22	30	2
6	1 M H_2SO_4	20	-	72	160	9
7	1 M H_2SO_4	20	-	96	155	8
8	1 M H_2SO_4	20	-	144	180	10
9	1 M H_2SO_4	20	-	200	245	12
10	1 M $C_6H_8O_7$	20	-	5	290	16
11	1 M $C_6H_8O_7$	20	-	10	255	15
12	1 M $C_6H_8O_7$	20	-	20	460	27
13	1 M $C_6H_8O_7$	20	-	40	455	24
14	1 M H_2SO_4	20	14	72	350	19
15	1 M H_2SO_4	20	28	72	315	19
16	1 M H_2SO_4	20	56	72	330	19

* < 0, copper accumulation

Table 1. Electrodialytic remediation results

The results show that electric current could remove copper from watery tailings slowly. With addition of sulphuric acid, the process was enhanced due to a pH decrease from 6.7 to around 4, and the copper by this reason was released in the solution. However, with citric acid addition the process was further enhanced because besides the pH decrease a formation of copper citrate complexes occurred. The use of pulsed electric fields enhanced the remediation process. It was found that for 72 hours of remediation time and voltage drop of 20 V, the use of pulsed electric fields with a time ratio (electric field in position "ON"/"OFF") of 20 improves the copper removal. With 14 cycles/day the copper removal in the anode side was nearly equivalent to DC experiments but increasing to 28 or 56 cycles/day the copper removal was increased by 50 % in the anode side of the remediation cell.

It was found that electrochemical remediation of mine tailings and soil contaminated from mining industry could be an alternative to depositing the waste. To positive aspects are generated by this remediation technology: 1) an environmental friendly solid waste without elevated concentrations of metals, 2) a profit consisting of dissolved copper that can be used directly in the copper refinery process meaning that natural copper containing minerals can be saved, and 3) a possible tool to recover copper from minerals with low grade.

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Absorption of pure carbon-dioxide gas in a foam-bed reactor

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1. Summary

Removal of carbon dioxide by treating it with aqueous barium-sulfide solution has been experimentally investigated in a semi-batch foam-bed reactor. Compared to all conventional gas-liquid reactors, foam-bed reactors offer higher interfacial area per unit volume of the liquid. Foam-bed reactor now seems to be the promising gas-liquid reactor by virtue of its additional characteristics of moderate pressure drop, high gas-to-liquid ratio, low liquid hold-ups, and defiant life of foam bubbles which makes the contact times long. All these characteristics are very desirable for the treatment of large quantities of gases, as in the case of smoke-stack furnaces or power-plant exhausts, or contaminant separation from toxic-gas streams.

Keywords: gas absorption, desorption, barium sulfide, foam-bed reactor, pure gas

2. Extended Abstract

Carbon dioxide is the most important of greenhouse gases. The "Global Warming Theory" predicts that increased amounts of carbon-dioxide gas in the atmosphere tend to enhance the greenhouse effect and thus contribute to the global warming. Around 24,000 million tons of carbon-dioxide gas, equivalent to about 6,500 million tons of carbon, are released per year worldwide. As per the data collected by United Nations in 2002, around 5,872 million tons of carbon-dioxide gas (24.3% of total carbon-dioxide emission) are released in the US, 3,682 million tons (15.3%) in the European Union, and 1,220 million tons (5.1%) in India. Removal of carbon-dioxide gas from large-scale gaseous emissions as from thermal power plants, etc. is a real challenge.

Foam-bed reactor offers a novel method of removal of carbon-dioxide gas. Removal of carbon-dioxide gas by treating it with aqueous barium-sulfide solution has been experimentally investigated here in a semi-batch foam-bed reactor. This carbonation reaction can be carried out using carbon-dioxide gas obtained from smoke-stack furnaces or power-plant exhausts, thereby reducing the air pollution arising from

these major sources. The hydrogen-sulfide gas produced in the reaction reacts faster with amines as compared to carbon-dioxide gas, and thus it can be removed with a relative ease. It can also be converted into sodium hydrosulfide by reacting with caustic solution (possibly in another foam-bed reactor), or converted into elemental sulfur in a Claus sulfur-recovery unit. Alternatively, the hydrogen-sulfide gas can be split to produce hydrogen gas. These end products would have a good market value too.

Experimental data have been generated and analyzed in this investigation to assess the role of the reverse diffusional flux of the desorbed hydrogen-sulfide gas in the actual performance of a foam-bed reactor. The experiments are carried out using pure carbon-dioxide gas, to focus on liquid-phase and interfacial resistances. The variables studied are height of foam bed, initial concentration of barium sulfide in aqueous solution, gas-flow rate, volume of the barium-sulfide solution charged into the reactor, and the surfactant type, and its concentration in the aqueous solution.

The experimental results indicate that the conversion in the reactor increases with an increase in the initial concentration of barium sulfide in the aqueous solution, and with gas-flow rate. The conversion decreases with an increase in the volume of the solution charged into the reactor. The variation of two main parameters, viz. the height of foam bed and concentration of surfactant, reveals the important role of desorption of hydrogen-sulfide gas in governing the observed performance of the foam-bed reactor. The optimum foam height was found to be 0.4 m, and the optimum surfactant concentration to be 1000 ppm. Three different types of surfactant were explored during the experimentation, namely, non-ionic (Triton X-100), cationic (CTAB), and the anionic (like SDS, LABS, stearic acid, Monoxol OT and Teepol). The aqueous solutions of barium sulfide did not foam with any of the anionic surfactants. Comparison of the performances for the non-ionic and cationic surfactants shows that the nature of surfactant does not appreciably affect the performance of the foam-bed reactor.

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The Influence Of The Chelating On The Oxidation Of Phenol Catalysed By Chelated Iron At Mild Conditions

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1. Summary

This work presents the preliminary results obtained for the oxidation of phenol using metallic iron in presence of different chelating agents as Ethylene Diamine Tetra acetic Acid (EDTA), Ethylene Diamine Diacetic Acid (EDDA), Nitrilo Triacetic Acid (NTA), Imino Diacetic Acid (IDA), Diethylene Triamine Pentaacetic acid (DTPA), and Hydroxyethyl Ethylene Diamine Triacetic Acid (HEDTA). The experimental results of this study demonstrated that the efficiency of the process depended on the chelating agent used. After 360 min with an initial concentration of the chelating agent of 0.30 mM, in terms of conversion, the reactivity order observed was: 99% NTA > 96% HEDTA > 84% EDTA > 81% EDDA > 63% IDA > 37% DTPA. The intermediates of the reaction has been identified and differed in some cases, showing a close dependence with the chelating agent utilized; the pH of the process depended also of the chelating agents used, in this sense, the effect of this variable is currently under research.

Keywords: Chelated agents, Mild conditions, Oxidation, Wastewater

2. Extended Abstract

The elimination of organics compounds from wastewater is of interest due to their biotoxic properties. Several catalysed oxidation techniques carried out at low temperature present some limitations in their operational use. To overcome this inconvenient, a chelator is added in the reaction system; as a result, the oxidation potential of the catalyst decreases (Miller et al., 1999). The aminopolycarboxylic acids are ones of the most important groups able to capture metal ions. The formation of these metal complexes have advantages, they are stables, water-soluble and restrict the metal ions from playing their normal chemical role. The used of these compounds could be applied to the degradation of refractory aromatics compounds such as phenol or its derivatives (Noradoun et al., 2003; Sanchez et al., 2007). This work presents the

preliminary results obtained for oxidation of phenol using metallic iron in presence of different chelating agents (ChA) as EDTA, EDDA, NTA, IDA, DTPA, and HEDTA.

The reaction was carried out in a stirred tank reactor under extremely mild conditions, temperature of 20ºC and atmospheric pressure, in the presence of 150 ppm of phenol, zero valent iron particles (10 g), 0.30 mM of the selected ChA and air. The pH value was monitored throughout the experiment. The samples were filtered and analysed by HPLC using a tailored method for the determination of phenol and the possible reaction intermediates. The efficiency of the process has been evaluated based on the degree of conversion.

The ChA used had a direct influence on the initial pH values and were probably the cause of the differences observed on the induction period (Fig.1). The experimental results of this study demonstrated that the feasibility of the process depended on the chelating agent used to promote the reaction. The best results were obtained using NTA reaching a 99% of phenol conversion after 6 hours, and the worst was DTPA, with only a 37% of phenol conversion.
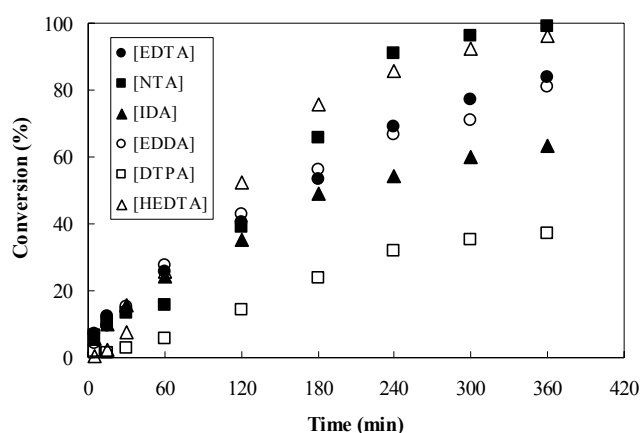
Figure 1: Phenol conversion evolution for different chelating agents (ChA). $[Ph]_0 = 150$ mg·l^{-1}, $mFe_0 = 10$ g, $[ChA] = 0.30$ mM and $T = 20$ºC

On the other hand, HPLC analyses showed that the intermediates also depends on the ChA used; some of the identified compound were hydroquinone, benzoquinone, catechol, maleic, malonic, fumaric, oxalic and formic acids.

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Session T1-4b: Sustainable & Clean Technologies - Ib: Extraction & Remediation

Abstract Number	Paper Title & Authors	Included
715	A modified UCT method for enhanced biological phosphorus removal E Vaiopoulou, A Aivasidis	Yes
1600	Characterization of a granular-immobilised laccase bioreactor for the conversion of synthetic dyes M E Russo, P Giardina, A Marzocchella, P Salatino, G Sannia	Yes
1955	The sustainable potential of enzymes within detergency V S Nielsen, S Elisson, P Skagerlind	Yes
1970	The influence of novel disinfection strategies in the removal of humic substances U Iriarte-Velasco, Jon I Alvarez-Uriarte, J R Gonzalez-Valesco	Yes
3116	Dynamic modeling of a continuously moving bed biofilter performing tertiary nitrification and filtration G Sin, J Weijma, H Spanjers, I Nopens	Yes
4048	Kinetics of fluoxetine and triclosan oxidation during municipal wastewater ozonation S Suarez, M Dodd, F Omil, J M Lema	Yes

A Modified UCT Method for Enhanced Biological Phosphorus Removal

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1. Summary

A pilot-scale prototype activated sludge system is presented, which combines both, the idea of University of Cape Town concept and the step denitrification cascade for removal of carbon, nitrogen and phosphorus. The experimental set-up consists of an anaerobic selector and stepwise feeding in subsequent anoxic and oxic tanks. Raw wastewater with influent flow rates ranging between 48 – 168 L/d was fed to the unit at hydraulic residence times of 5 – 18 h and was distributed at percentages of 60/25/15, 40/30/30 and 25/40/35 % to the anaerobic selector, 2nd and 3rd anoxic tank respectively (influent flow distribution before the anaerobic selector). The results show high removal efficiencies of organic matter of 89% as total COD removal and 95% removal for BOD5, 90% removal of TKN and total nitrogen removal through denitrification of 73%, mean phosphorus removal of 67%, as well as excellent settleability. An alternative influent flow distribution pattern was also investigated by applying influent flow distribution after the anaerobic selector. In any case, the highest removal efficiency and the optimum performance are recorded for influent flow distribution before the anaerobic selector at HRT of about 9 hrs and influent flow rate of 96 L/d, which is distributed by 60% to the anaerobic selector, by 25% to second anoxic tank and by 15% to the last anoxic tank.

Keywords: UCT, wastewater, nutrients, phosphorus, step feeding, BNRAS

2. Extended Abstract

Biological Nutrient Removal Activated Sludge (BNRAS) systems remove carbon, nitrogen and phosphorus by biological means with low costs and less waste sludge production. One of the most commonly applied BNRAS methods for urban wastewater treatment relies on the University of Cape Town (UCT) concept. The UCT process was designed to minimize the effect of nitrate to the anaerobic contact zone, which is crucial for maintaining truly anaerobic conditions and thus, allowing biological phosphorus release. Step feeding is an attractive process to eliminate the need for internal recycling and optimize organic carbon utilization for denitrification, and thus it results to energy savings. Multiple stage cascades optimize removal efficiency with minimum reactor volume and provide operational safety. On this basis, the UCT approach could be enhanced by combining multiple stages of anoxic and oxic zones with the step feeding process.

The pilot-scale prototype BNRAS system presented here combines both, the idea of UCT concept and the step denitrification cascade for integrated removal of carbon, nitrogen and phosphorus. The experimental set-up of 44 L operational volume consists of an anaerobic selector and stepwise feeding in subsequent anoxic and oxic tanks. Raw wastewater with influent flow rates ranging between 48 – 168 L/d was fed to the unit at Hydraulic Residence Times (HRT) of 5 – 18 h and specific BOD_5 loading rates of 0.08 – 0.82 kg BOD_5/ (kg MLVSS· d). Influent flow rate (Q_F) is distributed at percentages of 60/25/15, 40/30/30 and 25/40/35 % to the anaerobic selector (AN), 2nd (DN2) and 3rd (DN3) anoxic tank respectively. The overall Sludge Retention Time (SRT, θc) was kept constant at 10 d and temperature at 20˚C.
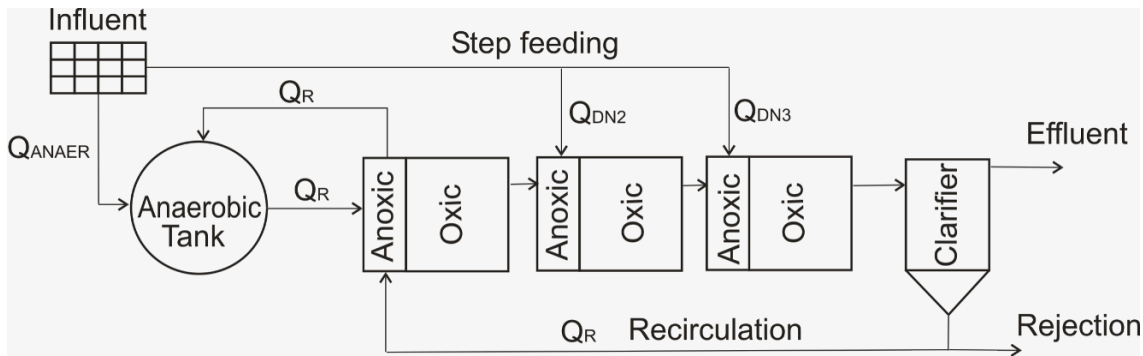
Figure 1. Experimental set-up of the BNRAS system.

Theoretical expectations were confirmed since the proposed flow scheme does not permit nitrate introduction to the anaerobic selector, whereas step feeding to anoxic tanks adds essential carbon compounds for the denitrification process and no internal recycling is necessary. The results of two year operation show high removal efficiencies of organic matter of 89% as total COD removal and 95% removal for BOD_5, complete nitrification (95% removal of ammonium-nitrogen), 90% removal of Total Kjeldahl Nitrogen (TKN) and total nitrogen removal through denitrification of 73%. Phosphorus removal attains a mean value of 67% but ranges intensively because of fluctuations in the incoming phosphate concentration. All removal efficiencies receive constantly the highest values at the feeding ratio of 60/25/15. Moreover, plant configuration provides operational conditions that suppress filamentous bacteria and favour growth of floc-formers, and thus leads to high sludge settleability characteristics (Sludge Volume Index ≈ 100 ml/g).

The highest removal efficiency and the optimum operation are recorded at HRT of about 9 hrs and influent flow rate of 96 L/d, which is distributed by 60% to the anaerobic selector, by 25% to second anoxic tank and by 15% to the last anoxic tank. Removal efficiency of organic substrate is 94% and 98% for COD and BOD_5 respectively, 99% for ammonium nitrogen, 94% for TKN, 83% for total nitrogen and 93% for orthophosphates. Nitrate nitrogen effluent concentration is about 7 mg/L.

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Characterization of a Granular-Immobilised Laccase Bioreactor for the Conversion of Synthetic Dyes

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1. Summary

The present paper reports on the assessment of an enzyme-based process for the bioconversion of polyaromatic hydrocarbons (synthetic dyes, polyphenols, …). A crude laccase mixture, obtained from *Pleurotus ostreatus* cultures, was covalently immobilized on granular supports - EUPERGIT C 250L$^{©}$, an acrylic resin with epoxy functionalities. The resulting biocatalyst was used in the conversion of an anthraquinonic dye. The activity was focused on: i) the optimization of the immobilisation protocol of the biocatalysts; ii) the kinetic characterization of both dye conversion and biocatalyst deactivation under controlled operating conditions. Two fixed bed reactors were purposely designed, set-up and operated to assay the activity of the supported biocatalyst and to characterize the dye conversion kinetics. Kinetic data have been worked out in order to compare the performance of a Continuous Fixed Bed Reactor (CFBR), operated with granular-immobilized laccases, with that of a Stirred Tank Reactor (STR), operated with free laccases. The analysis takes into account the immobilisation efficiency, the dye conversion kinetics and the laccases deactivation kinetics.

Keywords: laccases, enzyme immobilisation, dye, fixed bed

2. Extended Abstract

Technologies based on immobilised enzymes can benefit improved resistance of enzymes to denaturation and proteolysis, improved enzyme recovery and recycling, enhanced process throughput and intensification. Additional savings may be achieved if crude preparations of enzymes can be used rather than expensive highly purified ones (Cowan and Tombs, 1999). Despite these advantages, industrial processes based on immobilised enzymes represent still a very limited fraction of the current enzyme-based industrial operations. One key to the limited diffusion is represented by the limited information available to support design and optimization of immobilized enzyme-based bioreactors.

The present study regards the development of intensified enzymatic bioreactors for the bioremediation of liquid streams containing a synthetic dye (Remazol Brilliant Blue R – RBBR - an anthraquinonic dye). The activity was focused on: i) the optimization of the immobilisation protocol of the biocatalysts; ii) the kinetic characterization of both dye conversion and biocatalyst deactivation under controlled

operating conditions; iii) the comparison of the performances of bioreactors operated with either free or immobilized laccases.

Enzyme immobilization. A crude laccase mixture, obtained from *Pleurotus ostreatus* cultures (Palmieri et al., 2003), was covalently immobilized on granular EUPERGIT C 250L$^{©}$, an acrylic resin bearing epoxy functionalities (Katchalski-Katzir and Kraemer, 2000). The efficiency of the immobilisation protocol was assessed in terms of the immobilization yield, i.e. the ratio between the laccase activity per unit mass of carrier and the activity initially available in the liquid mixture. The activity of the enzyme immobilised on the granular resin has been measured in a fixed bed operated as recycle reactor (36 mm long, 6 mm ID) with respect to the substrate adopted in the free enzymes activity assay. Optimization of the immobilisation protocol led to a maximum yield of about 7% under the following immobilization conditions: i) 50 mM sodium phosphate buffer pH 7.5; ii) ratio (initial activity)/(mass carrier) of 80 IU/g; iii) 4 h incubation at room temperature under gentle shacking; iv) rinsing and saturation of the residual epoxy groups by albumin.

Dye conversion and enzyme deactivation. Granular biocatalysts were tested to characterize their ability to promote conversion of RBBR, an anthraquinonic dye. The study addressed both the determination of kinetic parameters of dye conversion and the rate of enzyme deactivation along with conversion. Experiments were carried out in a continuous fixed bed reactor operated at constant liquid flow rate. Dye conversion rate was measured under steady state conditions over wide ranges of space-times and dye concentrations in the feeding. Data were worked out to assess kinetic parameters of a Michaelis-Menten kinetic equation. Dye conversion data measured during prolonged runs (lasting a few days) were worked out to characterize the biocatalysts deactivation rate. The activity of immobilized laccases decreased with time according to a nearly linear trend.

Comparison of the performance of free vs immobilized enzyme bioreactors for bioconversion of a synthetic dye: A simple theoretical analysis has been developed to compare the performances of two ideal enzymatic reactors: a) a Continuous Fixed Bed Reactor (CFBR), operated with granular-immobilized laccases, and b) a batch Stirred Tank Reactor (STR), operated with free laccases. The model takes into account: i) the immobilisation yield (7%); ii) the residual laccases recovered in the liquid phase after the immobilisation process (about 60% of the initial activity); iii) laccases deactivation, expressed as linear decay of the maximum reaction rate for both free and immobilised laccases. The comparison between the two options has been carried out in terms of the total amount of dye-bearing stream that can be remediated for a given initial amount of laccases available. The maximum productivity of the STR is limited by the reactor size. The maximum productivity of the CFBR is instead governed by enzyme deactivation. For the operating conditions investigated, the simplified analysis indicates that option b), i.e. continuous operation of a fixed bed reactor with immobilized enzymes, performs better from the standpoint of the maximum amount of dye-bearing stream that can be remediated. The volume of the CFBR is about one order of magnitude smaller than the remediated liquid.

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The sustainable potential of enzymes within detergency

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1. Summary

Enzymes have the potential of partially substituting classical detergent ingredients like surfactants. This study presents an example of such potential. Wash performance is presented with a detergent composition having varying amount of surfactants compensated with an enzyme cocktail at cost neutrality. Overall superior performance is observed when the surfactant level is lowered and enzymes added.

Keywords: enzyme, detergent, LCA, green chemistry

2. Extended Abstract

Enzymes have been used for stain removal and fabric maintenance for more than four decades. Over the years, many types of enzymes have been developed and continuously optimized for better performance to fit the requirements of modern wash products and procedures. Today a wide range of enzyme products are available for removal of proteins, lipids, starch and other types of carbohydrates. Also, enzymes for removal of particulate matter and fabric care are available today.

Detergent manufacturers have began widening their view on application of enzymes. Today's enzymes have the potential of partially substituting classical detergent ingredients like surfactants (Schäfer et al., 2007). There are several drivers for this new way of looking at enzymes. First of all the escalating price of crude oil have helped increase the focus on technologies which are not linked to the oil price. Furthermore, from a sustainability point of view enzymes are very attractive ingredients. They work catalytically so only very minute amounts of active material are needed in the wash. Enzymes typically work very well at low temperature. Therefore, they are key ingredients when formulating products effective at lower wash temperatures.

Wash performance is shown below in a detergent composition having varying amount of surfactants adjusted for cost neutrality with an enzyme cocktail. Four wash temperatures, 20, 30, 40 and 60˚C normal wash, were used showing overall superior

performance of detergent with reduced surfactant level and enzymes added versus a detergent with 100% surfactant and no enzymes added at all four wash temperatures (Figure 1).

Enzyme levels adjusted to keep total formula costs neutral
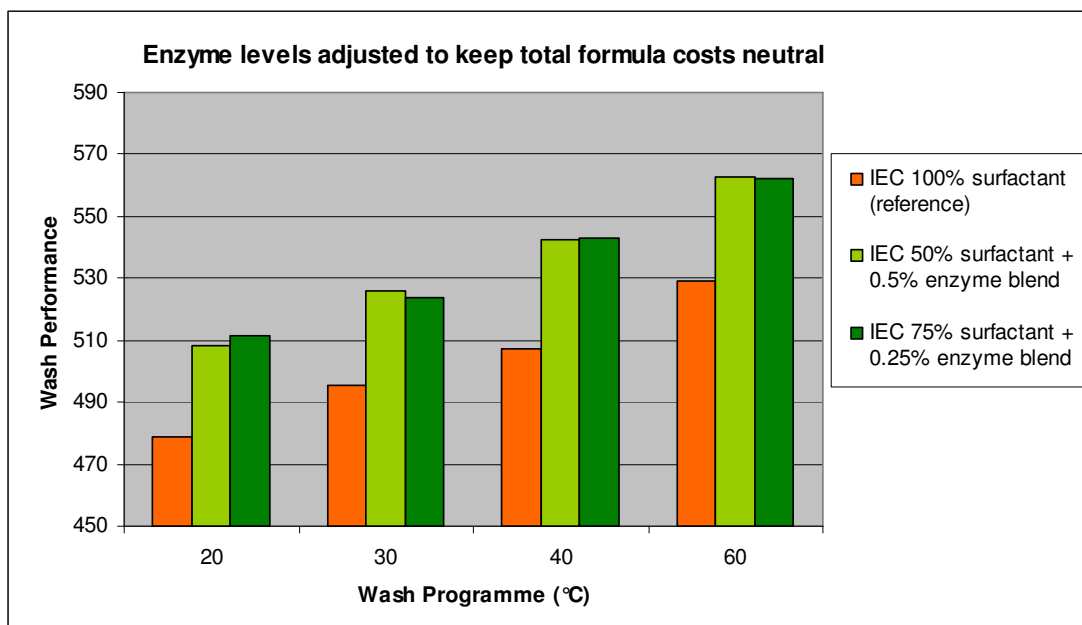
Figure 1: Comparison of wash performance at 4 different wash temperatures of IEC-A detergent with 100% surfactant and no enzymes (orange bars) and IEC-A with reduced surfactant level and enzyme cocktail added (green bars). Experimental details: Stains defined by EU ECOLABEL; Detergent: IEC-A with bleach; Enzyme blend: protease, amylase, lipase and cellulase

A life cycle assessment study is also described comparing the environmental impact of lowering the wash temperature while maintaining the overall wash performance unchanged by addition of enzymes (Nielsen, 2005).

Looking into the future, there is no doubt that biotechnology will offer new opportunities for the detergent industry. Beyond new and better detergent enzymes, biotechnology is expected to influence the detergent industry both directly with new types of ingredients and also indirectly by biotechnological routes for production of chemical ingredients.

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The influence of novel disinfection strategies in the removal of humic substances

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1. Summary

Conventional drinking water production includes coagulation-flocculation, settling followed by sand filtration and chlorine disinfection. In order to avoid algae proliferation, pre and intermediate chlorination is usually effected. During these previous oxidation steps, water contains higher loads of organics; thus formation of chlorinated disinfection by products (DBP), such as trihalomethanes (THM), is favoured. The nascent chlorine, ozone and chlorine dioxide combination generated in "CETOLAR" system presents greater oxidative power (synergy) than conventional chlorine. By the sum of oxidizers' power, this "CETOLAR" system confers greater capacity of disinfection and it is possible, with a smaller dosage, to eradicate the pathogenic germs and avoid the presence of resistant germs; at the time, less DBPs are formed. However, very little is known about its effect over NOM. The present paper studies the effect of such a pioneering oxidation strategy on the content, nature and reactivity to form THMs of natural organic matter (NOM).
Keywords: Drinking water; Nascent chlorine; Humic substances, Trihalomethanes

2. Extended Abstract

Selected water treatment plant (WTP) uses nascent chlorine as primary and secondary oxidant. Treatment includes preoxidation, coagulation-flocculation, intermediate oxidation, sand filtration and disinfection. NOM characterisation was achieved by separation into hydrophobic acid (HPOA-DAX8), transphilic acid (TPHI), hydrophilic acid (HPIA-XAD4) using XAD resins. DEAE resin was used to obtain the so called HPOA-DEAE and HPIA-DEAE fractions. THM formation capability, defined as the THM formation potential (THMFP), of each fraction was studied by different standarized chlorination tests ($THMFP_{3h}$, $THMFP_{15h}$, $THMFP_F$, SDSTHMFP). THMs precursor content of raw water, measured as $THMFP_F$ was 367 µgTHM/L, high enough to exceed maximum contaminant level of 100 µg/L established by European Directive. SUVA value (2.4 L/mg m) denotes low to moderate aromaticity of NOM in sample. Based on UVA_{254nm}, DOC and $THMFP_F$ measurements, DEAE absorbs almost 90, 82 and 80% of raw water. The sum of DAX8 and XAD4 extracts accounts for 50, 57 and 40% of raw water. It is noteworthy the contribution of non-humic material to $THMFP_F$. Its contribution strongly varies depending on the used absorbent. DEAE extract accounts for most of the THMFP (for all chlorination times and conditions). Within first 24 hours of reaction 85-96% of THM production stems from substances extractable with DEAE. DAX extracts showed less reactivity with chlorine. THM production profile of DAX8 extracts accounts for 48-55% of the THM formed during source water chlorination. Treatment

removes up to 70% of UVA, reflecting a high reduction in aromatic structures. DOC progressively decreased throughout treatment; 1.9, 1.3 and 1.2 mg/L for raw, settled and filtered water. However, $THMFP_F$ reduction is minimal. Its value descends from 113 µgTHM/L in raw water to 105 µgTHM/L at outlet stream. Figure 1 shows the contribution of each humic/non-humic extracts. Both hydrophilic fractions (HPI-DEAE and HPI-XAD) showed similar behavior. HPI-DEAE contribution significantly increased along WTP, while HPI-XAD remained at same level. For the latest, hydrophobic substances conversion into transphilic was observed as deduced from HPO-DAX decline and increase of TPHI fraction. Similar results (not shown) were obtained when "quick formers", simulated plant ($THMFP_{15h}$) and simulated distribution system (SDSTHMFP) chlorination tests were applied. Ozone application is known to destroy NOM aromaticity. The ozone present in nascient chlorine system is effective in reducing hydrofhobic susbtances while hidrophilic and neutral fractions are unaltered. This fact gains special relevance on view of the high THM formation capability shown by hydrophilic fraction. Coagulation-flocculation was the most effective step in $THMFP_F$ removal. However, HPI fractions were not removed. In order to optimise operational conditions 96 Jar-Test experiments have been systematically carried out with raw water. Independent variables were pH, coagulant type and dosage, mixing rate and water alkalinity-hardness. Multivariable general linear models were used to explain the variance in $THMFP_{15h}$, $THMFP_F$, UVA and DOC removal. Post hoc analysis showed that coagulation with 40 mg/L polyaluminium chloride at pH 6 was most effective. Under these conditions process performance doubled compared to that achieved in WTP. THM production during first 15 hours decreased from 15 to 11% of $THMFP_F$. Molecular weight distribution (MWD) studies confirmed that higher molecular

Figure 1. Contribution of NOM fractions to $THMFP_F$ along full scale WTP.

weight molecules (>10,000 Da) were preferably removed. Thus, lower MW and more hydrophilic molecules turned into main DBP source during disinfection. Monitoring NOM character by measuring the HPI fraction will allow operators to better control coagulant dose and pH to minimize DBP production. Sand filtration in WTP was not effective in removing THM precursors. Even more, sand-filtering increased THM formation capability of water. Systematic investigations with activated carbon filtering media are currently under progress in our laboratory to address this issue.

Dynamic modeling of a continuously moving bed biofilter performing tertiary nitrification and filtration

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1. Summary

A mathematical model with adequate complexity integrating hydraulics, biofilm processes and microbial conversion processes is successfully developed, calibrated and validated for a particular continuously moving bed biofilter (ASTRASAND®) performing tertiary nitrification. It can now be used reliably for design and process optimization purposes. Overall, the general model development method used here is expected to be useful for developing such models for other biofilm processes and applications. The use of dedicated simulation software having user friendly model coding language facilitated significantly this work.

Keywords: biofilm modeling, moving bed sand filter, nitrification, tertiary treatment

2. Extended Abstract

The interest in tertiary treatment within wastewater treatment plants has increased recently due to strict effluent legislation introduced by European Water Framework Directive (EWFD, 2000/60/CE). This requires a significant improvement of the existing treatment plant performance. Moving bed sand filter such as ASTRASAND® can help existing sewage treatment plants comply with particularly nitrogen and suspended solids discharge limits. The process removes suspended solids physically through sand-filtration and performs nitrification by specialized bacteria enriched in the biofilm developed on the sand particles. Finally, the sand particles are recycled continuously in the reactor bed using an airlift to control clogging in the sand filter. To help better design and operate such systems, this study sets out to develop a dynamic model to mainly describe nitrification.

2.1 Model development

WEST® (MOSTforWATER N.V., Kortrijk, Belgium) is used for the modelling and simulation. For the hydraulics part of the model, the mixing in bulk water (also the biofilm thickness and composition along the filter bed) is described using 6 tanks-in-series based on an evaluation of ammonium measurements in the filter bed. The airlift

recirculation of the sand particles is described using a dedicated algorithm written in WEST®. The biofilm compartment was described using Rauch model (Rauch *et al.*, 1999) – a 1-D numerical model describing substrate diffusion, attachment and detachment processes. The microbial transformations (mainly nitrification but also decay) are described using the standard ASM1 model (Henze *et al.*, 2000).

2.2. Model calibration and validation results

The model was calibrated using data from Nether Stowey pilot plant in the UK with a capacity of 1.4 m^3 bed-volume and 0.7 m^2 surface area. Three months data of influent and effluent ammonium and solids load have been used for the calibration of the model. First a steady-state calibration was done using 3-months average performance data (ammonium and suspended solids removal). For that, it was sufficient to change only a few system specific parameters such as biofilm thickness, attachment and detachment coefficients (default values were used for the remaining parameters (Wanner et al., (2006)). Using the initial conditions and the calibrated parameters of the steady-state, the model was then dynamically calibrated to a set of one-month effluent ammonium measurements by slightly changing the autotrophic maximum growth and yield parameters (0.81 and 0.22 for μ_A (d^{-1}) and Y_A (gCOD/gN), respectively). The resulting model fit was found to have a bias (mean absolute error) of 0.8 mgNH4-N/l. This is often found acceptable for many engineering applications (Figure 1-left). To validate the model, a 10-days long independent data set was used (Figure 1-right). The model fits well to the measurements. These fits were statistically assessed by Janus coefficient, which was found 0.9 close to unity. This indicates that the model structure remain largely unchanged (hence valid) in both calibration and validation periods. Hence this reinforces our confidence in the model.
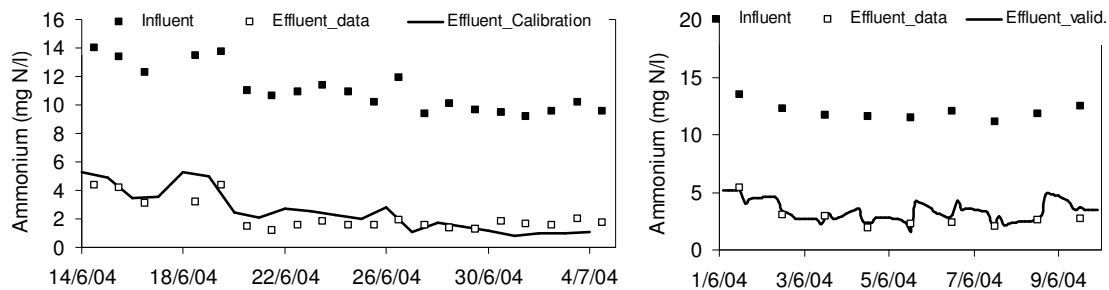
Figure 1 – Dynamic model fits to ammonium data: calibration (left), validation (right)

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Kinetics of Fluoxetine and Triclosan Oxidation during Municipal Wastewater Ozonation

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1. Summary

The oxidation of the antimicrobial agent triclosan (TRI) and the antidepressant drug fluoxetine (FLX) during conventional ozonation has been investigated in this work. In a first step, second-order rate constants for the reaction of the selected compounds with ozone (k_{O3}) were determined. Although very high maximum k_{O3} were measured for both compounds, at neutral pH only TRI showed to be fast reacting. In the second part of this work, oxidation of the selected compounds in wastewater was investigated, considering the effluent of two conventional activated sludge treatment plants with different water quality parameters. For TRI ozonation showed to be quite effective for the two types of wastewaters. Due to the slower reactivity of FLX at the pH of the wastewater, the transformation could be followed as a function of time. Therefore, measured data could be compared with modelled values, to check if the k_{O3} determined in pure aqueous solution can be used to predict the behaviour of FLX in wastewater.
Keywords: fluoxetine, triclosan, ozone, hydroxyl radicals, organic matter

2. Extended Abstract

Triclosan (TRI), 5-chloro-2-(2,4-dichlorophenoxy)phenol, is used as an antimicrobial agent in a large number of skin and oral care medical and household products (soaps, creams, toothpaste, mouthwash). The second considered compound, fluoxetine (FLX), N-methyl-8-14-(trifluoromethyl)phenoxylbenzenepropanamine, is an antidepressant drug, commercially sold as Prozac®, characterised by its widespread use. Both compounds have been detected in wastewater at concentrations in the range of 0.4-1.3 µg/L (Lindstrom et al., 2002; Brooks et al., 2003). Although TRI and FLX concentrations appear to be significantly reduced during biological wastewater treatment (Singer et al., 2002; Boethling et al., 1994), residual concentrations detected in surface water may still be a matter of concern (Kolpin et al., 2002). Ozonation, which has proven to be a very effective post-treatment technique for other pharmaceutical and personal care products (Huber et al., 2005), presents one possible option for wastewater post-treatment, since TRI and FLX are expected to react rapidly with ozone.

In the present work, reaction kinetics for the oxidation of TRI and FLX by aqueous ozone (O_3) have been investigated. Second-order rate constants, k_{O3}, were determined for reaction of O_3 with each of TRI's and FLX's acid-base species (Figure 1). Although very high values of k_{O3} were measured for the deprotonated species of each

target compound (k_{O3} = 5.1 ($\pm$ 0.1) $\times$ 10^8 M^{-1}s^{-1} for anionic TRI and k_{O3} = 1.1 ($\pm$ 0.1) $\times$ 10^6 M^{-1}s^{-1} for neutral FLX), only TRI was fast reacting at circumneutral pH (the pH-dependent, apparent second-order rate constants, $k_{app,O3}$ were 3.8 $\times$ 10^7 M^{-1}s^{-1} for TRI and 9.6 $\times$ 10^2 M^{-1}s^{-1} for FLX at pH 7).
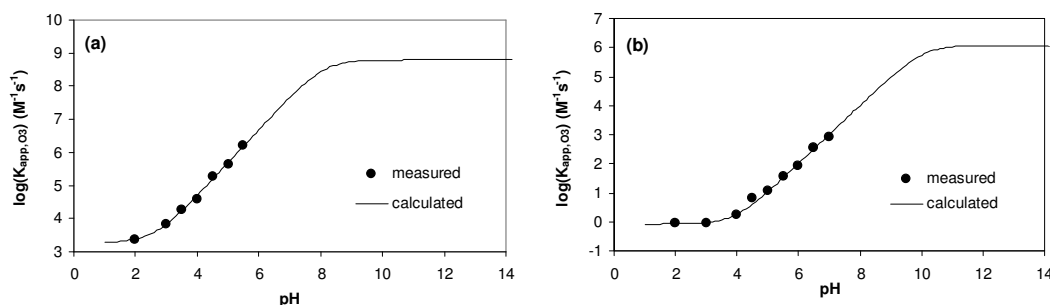
Figure 1: Apparent second-order rate constants for (a) triclosan and (b) fluoxetine as a function of pH.

Kinetic modelling indicates that O$_3$ reacts with TRI and FLX via electrophilic attack at their phenol and neutral amine moieties, respectively. TRI and FLX oxidation during ozonation of secondary effluent samples from two conventional activated sludge treatment plants were also investigated. TRI was oxidized with relatively high efficiency during wastewater ozonation, due to its high reactivity toward O$_3$. Nearly 100% TRI depletion was achieved for a 4 mg/L O$_3$ dose applied to a wastewater containing 7.5 mg/L of DOC, and ~58% TRI depletion for dosage of 6 mg/L O$_3$ to a wastewater containing 12.4 mg/L of DOC (Suarez et al., 2007). However, FLX transformation was less efficient, due to its low reactivity toward O$_3$ at the circumneutral pH. Generally, the contributions of •OH to FLX oxidation were higher than for TRI, also primarily due to FLX's lower reactivity toward O$_3$. In any case, ozonation appears to provide an effective technique for enhancing the removal of TRI and FLX after biological treatment, with the objective of minimizing their discharge into receiving surface waters.

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Session T1-5a: Sustainable & Clean Technologies - IIa: Energy Production

Abstract Number	Paper Title & Authors	Included
40	Operating parameters for the circulating fluidized bed (CFB) pyrolysis of biomass M va de Velde, J Baeyens, I Boukis	No
348	Biodiesel characterization using electronic nose and artificial neural network D Giordani, H F Castro, P C Oliveira, A F Siqueira	Yes
176	Havesting Straw Bio-Oil on the Field N Bech, P A Jensen, K Dam-Johansen	Yes
700	Immobilized *thermomyces lanuginosus* lipase for methyl ester production from sunflower oil D Y Koseoglu, N Dizge, B Keskinler	Yes
1068	Novel strategy for the production of a generic fermentation feedstock based on particulate bioprocessing C Botella, R Wang, A Koutinas, C Webb	Yes
1412	Pre-treatment processes of lignocellulosic material for bioethanol conversion: Steam explosion M T Garcia-Cubero, S Bolado, G Gonzalez, I Catalina, I Lopez, A Miranda	Yes
2296	Transesterification of different vegetable oils to produce biodiesel L Rodriguez, A Perez, M J Ramos, A Casas, C M Fernandez	Yes
3802	Ethanol Production from Waste Sweet Potatoes Using Recombinant *Zymomonas mobilis* M N Karim, B Han	Yes

Biodiesel characterization using electronic nose and artificial neural network

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1. Summary

Biodiesel is an alternative to mineral diesel which has been studied worldwide due to its great applicability. Such as any commercial combustible, it must be characterized in many steps of its production chain. In this work, a new characterization method is proposed using an electronic nose coupled to artificial neural networks. Four biodiesels from different sources and one commercial pretoleum diesel were analysed and could be recognized by the e-nose. Besides, an innovative semiquantitative method is proposed entirely based on the smellprints correlated by feed forward artificial neural network. The promising results of this work indicate that e-nose can be used to identify the origin of biodiesel and even as a pre-analysis method when expensive equipments are not available.

Keywords: biodiesel, electronic nose, artificial neural network, green chemistry

2. Extended Abstract

Biodiesel are alkyl ester obtained from vegetal or animal oils by transesterification reaction. A lot of feedstocks can be used to produce the parent oils and this usually varies with geographic availability. It is obvious that the ester obtained varies with the parent oils, because it will contain the corresponding fat acid from the oil (Khote, 2005).
There are some important reasons to characterize a biodiesel in terms of its parent oils, probably the most important is due to fiscal laws. Some countries apply different policies depending on the feedstock. The quantitative analysis in terms of the quantity of biodiesel in mixture with petroleum diesel is also important due to the necessity of supervising the correct application of environmental laws.
A great quantity of authors have reported chromatographic and spectroscopic methods to classify biodiesel on its mono-, di-, or triacylglycerol composition (Freeman et al. 1986; Foglia et al., 1987). However few articles are found reporting the determination of the parent oils from which a biodiesel has been produced.
Electronic noses measurements are based on a change in resistance in an array of chemical sensors when exposed to a chemical vapor. Its use has been reported in the

literature, coupled to neural networks resources, to determine the origin of a variety of stuffs such as wine (Lozano et al., 2005) and olive oil (Cosio et al., 2006).

Experimental

In this work, the Cyranose 320 e-nose was used to recognize the origin of four different biodiesels, obtained from babassu oil, palm oil, beef tallow, chicken grease and also the commercial petroleum diesel. The e-nose was capable to recognize the smellprints of each biodiesel and to group them based on principle components analysis techniques, as can be seen on figure 1.
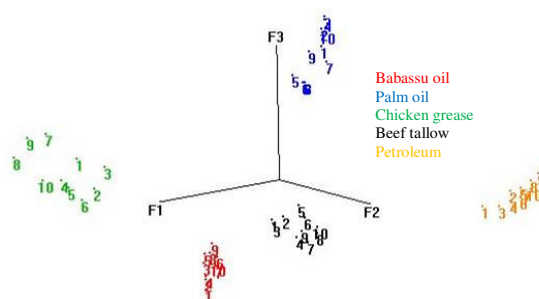
Figure 1: Principal Components Analysis distribution of different biodiesels in terms of their parent oil

Additionally, the B20 mixture (20% of biodiesel with 80% of Petroleum diesel) of the four biodiesel were well recognized as well by the same method, with exception of the chicken grease and beef tallow B20 mixtures that constituted near groups, but could yet be recognized one from another when they were treated as a separate class.
Finally, a semiquantitative technique was proposed to determine the quantities of biodiesel in the mixtures B0 to B20 of babassu biodiesel. The baseline of the smellprints had to be conditioned with the pure petroleum diesel in order to enhance the sensitiveness of the sensors regarding to biodiesel. A feedforward neural network was successfully developed to correlate the smellprints to their corresponding proportion of biodiesel in the BX mixture.

Conclusions

E-nose coupled to artificial neural networks is a very promising technique to identify the origin of pure biodiesel and its mixtures with petroleum diesel, especially if it is considered the portability and the price of the equipment compared to the traditional techniques.

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Harvesting Straw Bio-Oil on the Field

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1. Summary

This study presents experimental results from bench-scale runs with the Pyrolysis Centrifuge Reactor, a novel reactor designed to convert straw to bio-oil on the field.

Keywords: Flash pyrolysis, straw, biomass-to-liquid, bio-oil, harvest

2. Introduction

Bioenergy in the form of straw represents a significant energy source on a world-wide scale but is today largely unutilized due to a cost disadvantage and increased operational demands on power stations and district heating facilities. Straw is by itself not expensive but the cost associated with especially logistics, increase the price seven fold from field to a regional processing facility. Further, the five to ten percent ash content of straw is a source of solid waste which can form slag and promote corrosion if the straw is burned in conventional boilers. Our efforts to develop the mobile pyrolyzer/harvester [Bech *et al.*, 2006a] may drastically increase the attractiveness of straw as an energy source. Harvesting straw bio-oil on the field will concentrate the energy content in an energy-dense versatile liquid product and directly recycle inorganic nutrients/ash, without the expenses from baling and transportation of bulky straw. The conversion can be accomplished with flash pyrolysis within a fraction of a second by rapidly heating the organic material to 500 to 600 °C. Heat is provided by combusting the small incondensable pyrolysis gas fraction, whereas the ash is concentrated in the char fraction which may be distributed on the field behind the pyrolyzer/harvester (figure 1). Bio-oil is the principal product which may be transported from the field to power stations or refineries for further upgrading (*e.g.* to transportation fuels).

3. Pyrolysis Centrifuge Reactor

In order to incorporate a flash pyrolysis reactor in a moving agricultural implement, it has been necessary to develop and refine a suited reactor technology. This study

presents bench scale (1.5 kg straw pr. hour) results from operation of a Pyrolysis Centrifuge Reactor (PCR), a novel ablative flash pyrolysis reactor with a high capacity/volume ration, well suited for operation in a rough environment [Bech *et al.*, 2006b]. The focus of the study is on the yield of products from flash pyrolysis, *i.e.* liquid, char and gas with changes of the operational parameters. In the PCR, straw particles are forced centrifugally (4,900 to 17,000 times gravity) against the heated (470 to 620 °C) inner wall of a horizontally arranged pipe by introducing a swirling motion to the gas phase through the action of a centrally located rotor. Experimental runs have identified an optimum for bio-oil yield at a reactor temperature of approximately 520 °C. For the investigated rotor speeds bio-oil yield increases with the centrifugal force applied to the particle. Furthermore, it was established that solid residence time was controlled by straw feed rate and was independent of rotor speed and gas residence time.
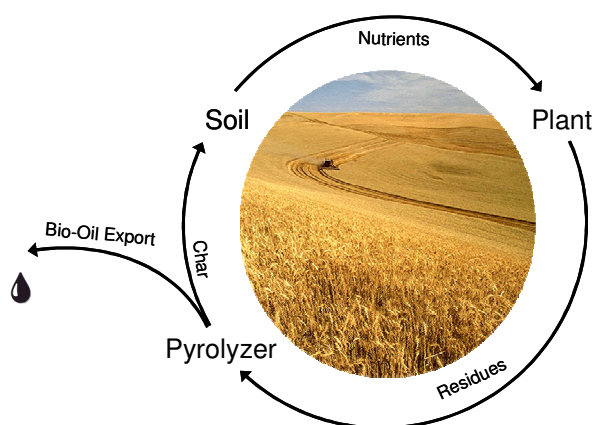
Figure 1: On-field conversion of straw to bio-oil and char.

The results obtained in the laboratory with the PCR have proven our technology to be robust and able to obtain a high yield of bio-oil. Further developments of the PCR to include stationary or semi-stationary applications in the forestry and solid waste industries are foreseen.

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Immobilized *Thermomyces lanuginosus* lipase for Methyl Ester Production from Sunflower Oil

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1. Summary

In this study, lipase-catalyzed transesterification of sunflower oil using immobilized matrix was investigated both continuous and batch reactors. Some key parameters were explored to determine the optimal transesterification conditions. Additionally, we showed how three-step reaction with alcohol is effective for efficiency of biodiesel production. In view of industrial processing, the stability of immobilized lipase during repeated runs was also investigated. During enzymatic transesterification of sunflower oil in the continuous and the batch reactors, the maximum biodiesel yields were found to be 76% and 69% after 1 hour and 97% and 95% after 3 hours, respectively.

Keywords: Transesterification, Styrene-divinylbenzene copolymer, *Thermomyces lanuginosus* lipase, polyglutardialdehyde, immobilization.

2. Extended Abstract

Biodiesel fuel is produced by methanolysis of vegetable oil, animal fats and waste edible oil. Conventional esterification for biodiesel production has used strong alkalis or acids as a chemical catalyst in water and high temperature [1]. In recent years, the lipase-catalyzed transesterification of vegetable oils using a solvent free system has become of great interest. In this study immobilized lipase enzyme was studied on biodiesel production. The effect of pH and the immobilization time, stability and reusability of immobilized enzyme were investigated. The STR-DVB (polystyrene-divinylbenzene) copolymer was used as lipase-immobilizing support and a micro porous polymeric enzyme reactor (MPPER). It includes aldehyde functional groups. It was produced as block then it was cut into small pieces for using at the first study and for the second one it was placed in a holder. *Thermomyces lanuginosus* lipase (it was purchased from Novo Nordisk) was immobilized on the matrix with 48% and 44% yields for continuous and batch reactors, respectively. The reaction media consist of 0.92 g of sunflower oil and 24 mL of methanol was circulated in the holder during 3 hours. Methanol (oil:methanol molar ratio is 1:6) was added in the reaction systems at three steps. By product glycerol on matrix was extracted by tertiary butanol.

The effect of pH on the immobilization of lipase was investigated both acetate (25mM) and phosphate (25mM) buffer (5.0 and 6.0 for acetate, 7.0, 8.0 and 9.0 for phosphate buffer).The highest immobilization efficiency (48%) was obtained at pH 6.

The immobilization time was investigated the range from 6 to 48 h, increasingly. It was observed that the highest immobilization efficiency was determined 48% at 24 h.

2.1. Immobilized enzyme: stability and reusability

After each transesterification reaction, lipase-containing MPPER was washed with tertiary butanol subsequently reused. This procedure was repeated 30 times to examine the extent of the stability of the immobilized enzyme. As seen in Fig. 1, the activity of the immobilized lipase upon repeated uses showed a stable trend. Since the process is simple and enzyme does not leak out from polymer, this method can be used for industrial scale applications.

Figure 1. Reusability of immobilized lipase
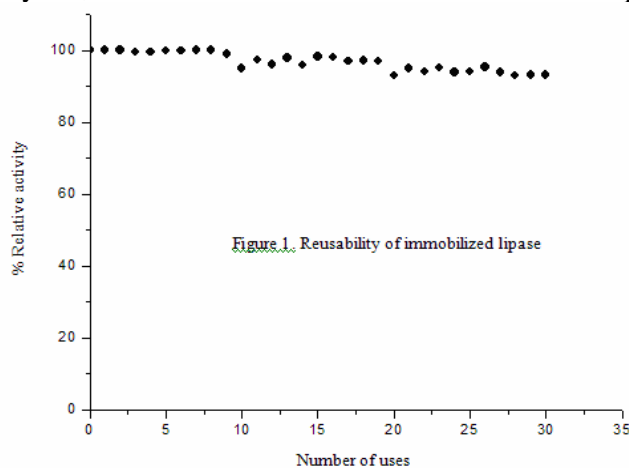
2.2. Conversion in MPPER

Aliquots of the reaction mixture were withdrawn and the ester content and glycerol and glycerids contents of the product were determined by DIN EN 14103 and DIN EN 14105 methods, in respectively [2,3]. A 6890 N gas chromatograph (Agilent) equipped with a capillary column and a flame ionizing detector (FID) was used for analysis.

| Operation (number of uses) | Composition of reaction product in the MPPER (wt.%) ᵃ: Monoacylglycerol ᵇ: Diacylglycerol ᶜ: Triacylglycerol | | |
	FAME(wt.%)	MAGᵃ	DAGᵇ	TAGᶜ
1	97.4	0.445	0.312	0.010
5	97.2	0.444	0.315	0.015
10	97.0	0.450	0.319	0.018
20	97.1	0.447	0.317	0.015
30	97.3	0.448	0.318	0.015

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Novel strategy for the production of a generic fermentation feedstock based on particulate bioprocessing

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1. Summary

A novel process strategy based on particulate bioprocessing has been developed for the production of value-added chemicals and biofuels. The process which involves two main units operations: fungal fermentation and discontinues extraction, leads to the production of generic fermentation feedstocks from cereals. Partially pearled whole wheat grains were used as substrate for the growth of *Aspergillus awamori* in a packed bed reactor in solid state fermentation conditions. Water was circulated through the bed of particles every 6 h to remove glucose and other nutrients and to maintain optimum moisture and temperature levels. The feedstocks obtained through this system with high glucose (up to 190 g/L) and FAN concentrations (up to 1.7g/L), have been used for subsequent fermentations by *Wautersia eutropha* to produce the biodegradable plastic PHB (Polyhydroxybutyrate) and by *Sacharomyces cerevisiae* for ethanol production. This presentation describes results obtained in the development of this process and the introduction of this novel concept, particulate bioprocessing, which has also been introduced to stress the particulate nature of the substrate. Some experimental results from the major unit operations are presented to provide a more detailed description of the process proposed.

Keywords: solid state fermentation, generic feedstock, cereals, biofuels, bioplastics.

2. Extended Abstract

There is an increasing social and political demand to establish renewable feedstocks for chemical and fuel production which can decrease our dependency on dwindling oil reserves, and reduce greenhouse gas emissions. At the same time there is a growing desire to replace traditional chemical processes with more benign and sustainable, biotechnology based, processes. However biotechnological processes generally require the use of relatively expensive raw materials and large amounts of water and are therefore often uncompetitive. Research in the Satake Centre for Grain

Process Engineering is aimed at overcoming these limitations through the development of generic fermentation feedstocks using cereals as raw material. As part of this goal we are developing a novel process strategy (particulate bioprocessing) based on solid state fermentation (SSF) for the production of a generic microbial feedstock that can be used for the production of value-added chemicals or biofuels.

The process proposed involves two main fermentation steps. In the first one a packed bed of partially pearled whole wheat grains is used for fermentation by the fungus *Aspergillus awamori*. Intermittent addition of water during the cultivation helps to maintain moisture and temperature levels, and is also used to extract soluble components. The extracts obtained have high glucose and free amino nitrogen (FAN) concentrations and have been used for subsequent fermentations by *Wautersia eutropha* to produce the biodegradable plastic PHB (Polyhydroxybutyrate) and by *Sacharomyces cerevisiae* for ethanol production

Preliminary studies on the effects of pearling, initial moisture content and addition of water have been carried out, followed by more detailed studies on mixing, scale up, and the duration between extractions. Extracts with high glucose (190 g/L) and FAN (1.7g/L) concentrations were successfully produced with starch to glucose conversion yields of up to 70%.

Results of subsequent fermentations using the extracts have already shown that they can be used successfully for the production of both PHB and ethanol and therefore contain the full range of nutrients required by a variety of microorganisms. The processing strategy based on particulate bioprocessing therefore has the potential to produce through, simple *in-situ* extraction, a generic feedstock that could be used for the production of a wide range of petrochemical replacements.

Pre-treatment Processes of Lignocellulosic Material for Bioethanol Conversion: Steam Explosion

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1. Summary

Preliminary results achieved for the wheat straw steam explosion are presented. The aim of this study is to obtain both, the greatest recovery in a later enzymatic hydrolysis of fermentable sugars (hexoses and pentoses) present in the selected raw material, and a high fermentability of the recovered monosaccharide. This is because owing to the effect of inhibitors on yeast fermentation, high sugar yields do not necessarily result in high ethanol yields. To evaluate these optimal conditions, the experiments were arranged as a 2^4 factorial design which factors are temperature (188ºC, 210ºC), residence time (4 min, 10 min), and particle size (0.2cm, 3cm) and the use or not of an acid catalyst.
Steam explosion pre-treatment was carried out in a 5L stainless steel batch reactor (Masonite technology) in which lignocellulosic material was loaded at the top of the reactor and heated to the desired temperature with saturated steam until 20 bar. After pre-treatment, the water-insoluble fibre is enzymically hydrolyzed in standard conditions previously established to determine the maximum sugar yield.

Keywords: Lignocellulosic biomass, steam explosion, bioethanol

2. Extended Abstract

The presented work is part of a project researching different pre-treatment alternatives of several plant source materials that allow us to exploit the lignocellulosic material and to optimize the yield in the bioethanol process from crops suitable in Castilla y León (Spain). Steam explosion, wet oxidation, AFEX and Ozonolysis were the processes selected as pre-treatments. The research involves the optimization of the parameters which show the higher influence in the recovery of fermentable sugars present in the selected materials.

The comparative analysis of the raw materials and products obtained in the later enzymatic hydrolysis step, applying different operational pre-treatment conditions and alternatives will permit to choose, from a technical point of view, the most suitable pre-treatment to process each one of the raw materials proposed in this project.

This work presents the preliminary results achieved in the study of steam explosion pre-treatment in order to obtain both, the greatest recovery in a later enzymatic hydrolysis of fermentable sugars present in the selected raw material, and a high fermentability of the recovered monosaccharide. A factorial design of experiments has been planned to minimize the number of experiments and to establish the effect of the parameters in the process yield. Once the optimal conditions are determined, a number of different raw materials (oats, wheat, barley, rye and triticale straw, sorghum s.p. and prunning waste) will be steam exploded in order to analyse the yield obtained in the enzymatic hydrolysis for the diverse materials after the treatment.

The steam explosion pre-treatment is carried out in a 5L stainless steel batch reactor (Figure 1). Lignocellulosic material (at the desired size) is loaded at the top of the reactor and heated to the desired temperature with saturated steam until 20 bar. When the pre-set residence time has concluded, the steam-treated biomass is released from the reactor by rapid depressurization of the vessel. After the pre-treatment, the product is washed with warm water and the residual solid is separated by filtration and analysed for acid insoluble lignin, acid-soluble lignin and carbohydrates and possible inhibitors formed. The liquid portion is analyzed for carbohydrates and other compounds generated during steam explosion (organic acids, furfural and HMF). The experiments arrange as a 2^4 factorial design which factors are temperature (180ºC, 210ºC), residence time (4 min, 10 min), particle size (0.2cm, 3cm) and the use or not of an acid catalyst (4,5% w/w SO_2).

After both pre-treatments, the water-insoluble fibre is enzymically hydrolyzed in standard conditions previously established to determine the maximum sugar yield.
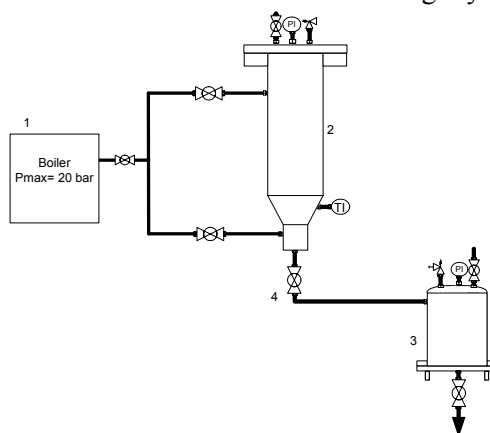
Fig 1. Diagram of the lab-scale plant for steam explosion pre-treatment. 1 – Boiler ;
2 – steam reactor; 3 – depressurization vessel; 4 – depressurization valve.

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Transesterification of different vegetable oils to produce Biodiesel

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1. Summary

In this work, seven refined vegetable oils were transesterificated to produce biodiesel. The transesterification process was made in a thermostated batch reactor. The alkaline catalyst used in the transesterification process was CH_3OK. Experimental conditions were at atmospheric pressure as follows: reaction time, 1 h; weight of catalyst, 1 % wt of initial oil weight; molar ratio methanol/oil, 6/1; reaction temperature, 60 ºC. The following parameters were used to characterize the biodiesel obtained: methyl ester, linolenic acid methyl ester, mono-, di- and triglycerides, free glycerol, total glycerol and methanol contents, viscosity, flash point, oxidation stability, acid value, iodine value and cold filter plugging point. In addition, the fatty acid content of the vegetable oils was measured. Finally, the influence of the vegetable oils nature on the quality of biodiesel, according to the European Standard EN 14214, was discussed.

Keywords: Vegetable Oil, Degree of Unsaturation, Biodiesel, Fuel Properties, Critic Parameters.

2. Extended Abstract

Biodiesel, an alternative diesel fuel, is made from renewable biological sources such as vegetable oils and animal fats [1]. Nowadays, most biodiesel is produced by the transesterification of triglycerides of refined/edible type oils using methanol and an alkaline catalyst [2]. The fatty acid profile of the seven vegetable oils used in this work was measured following the International and European Standards ISO 5509 and EN 14103. These compositions are summarized in Table 1. Degree of unsaturation (DU) was obtained from the empirical equation:

$$DU = \text{monounsaturated (weight percent)} + 2 \cdot \text{polyunsaturated (weight percent)}$$

Table 1. Fatty acid composition (% by weight) of the vegetable oil. Degree of Unsaturation.

Fatty acid	Palm	Olive	Peanut	Rapeseed	Soybean	Sunflower	Grape seed
Saturated	44.7	15.7	15.6	6.5	15.3	11	11.7
Monounsaturated	46.4	76.0	55.7	65.3	25.6	26	19.1
Polyunsaturated	8.9	8.4	28.7	28.3	59.1	63	69.3
Unsaturated	55.3	84.3	84.4	93.6	84.7	89	88.3
Degree of Unsaturation	64.2	92.8	113.1	122	144	152	158

Next, the quality of the Biodiesels synthesized was tested according to the European Standard EN 14214. Most of the parameters satisfied legal limits. However, some of them were out of specification. These critic parameters were Cetane Number, Oxidation Stability, Iodine Value and Cold Filter Plugging Point. Its limits are: CN ≥ 51; OS at 110 ℃ ≥ 6 hours; IV ≤ 120 mg I$_2$/100 g. In Spain CFPP limits are 0 ℃ in summer and – 10 ℃ in winter.

The longer the fatty acid carbon chains and the more saturated the methyl esters were, the higher the cetane number (Figure 1a). According to this, palm, olive and peanut biodiesels reached the highest Cetane Numbers. All the biodiesels obtained did not achieve the minimum limit of six hours for OS. Relative rates of oxidation given in the literature [3] were 1 for oleates, 41 for linoleates, and 98 for linolenates. Methyl esters obtained from Soybean, Sunflower and Grape seed showed the worst OS. Moreover, Iodine Value of these methyl esters is higher than 120 (Figure 1a).

CFPP increases with the presence of methyl esters of long-chain saturated fatty acid. Biodiesels obtained from peanut and palm oils had the poorest cold flow properties. The Figure 1b shows this tendency. The long-chain saturated factor was calculated with the following equation:

$$LCSF = 0.1 \cdot C16:0(\%) + 0.5 \cdot C18:0(\%) + 1 \cdot C20:0(\%) + 1.5 \cdot C22:0(\%) + 2 \cdot C24:0(\%)$$
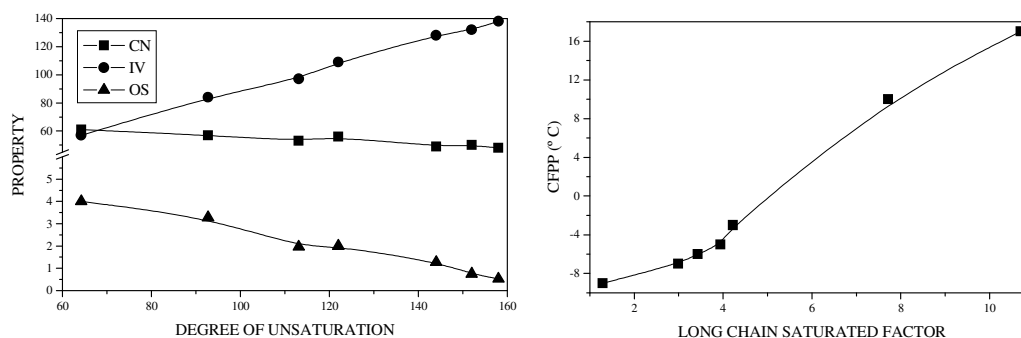
Figure 1. Critic parameters of biodiesel

Summarizing, the rapeseed and the olive Biodiesels have the global better properties, because they have the greater monounsaturated content and their DU and LCSF are balanced.

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Ethanol Production from Waste Sweet Potatoes Using Recombinant *Zymomonas mobilis*

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1. Summary

Ethanol production from waste sweet potatoes, which are left in the fields and cannot be marketed for various reasons, has been investigated. Sweet potatoes collected from a family-owned farm in western Texas contain 4.35% sucrose, 2.68% glucose, and 2.21% fructose, respectively. However, since the dry mass content is only around 21.9%, the average mono and disaccharides content based on the dry biomass is close to 50%. Other components in the dry biomass are mainly starch, which can be effectively converted to monosaccharides (glucose and fructose) using amyloglucosidase as the enzyme at 55 ^{o}C. Two strains of recombinant *Zymomonas mobilis*, 8b and AX101, from National Renewable Energy Laboratories, have been tested, to convert the enzyme treated sweet potatoes to ethanol. Prior to the sweet potato fermentation, the efficiency of these two strains to convert ethanol from four individual sugars, including glucose, xylose, fructose and sucrose, has first been evaluated. The results show that, these two strains have different efficiency in converting these four sugars to ethanol. Fermentation experiments using the enzyme treated sweet potato as the raw material, were conducted in a 1 L fermentor at 30 ^{o}C, pH 6 and an anaerobic condition. More than 90% of the total sugars can be converted into ethanol within 18 hours.

2. Extended Abstract

Sweet potatoes (*Ipomoea batatas*) have been domesticated for at least 5000 years. The world production of sweet potato in 2004 was approximately 1.27×10^8 tons, while in USA, the production of sweet potato in 2005 was close to 7.14×10^8 tons. Fresh sweet potatoes contain approximately 80% of water. For dried sweet potatoes, in which the water has been removed, starch is the major components, being more than 50%. Sweet potatoes also contain mono and disaccharides, mainly sucrose, glucose and fructose. The content of these sugars could be up to 20% based on the dried mass. Further, fibres (digestible and non-digestible) can also be found in sweet potatoes with a typical a content of approximately 10%. In addition, sweet potatoes

also contain many other valuable nutrients e.g. amino acids, proteins, vitamins, lipids and minerals, which may be useful for the fermentation operation.

In Texas, there are some farms which produce sweet potatoes, which are mainly used as foods. During the harvesting season, some sweet potatoes which are difficult to market for various reasons, such as small in size or damaged from the harvesting process, will be left in the fields. The total quantity is huge. However, after collection, these sweet potatoes may be excellent raw materials to produce valuable by-products, such as bio-ethanol. This study intends to develop an efficient and economical technology to convert the starch and sugars in the sweet potatoes into ethanol, thus to significantly increasing the profit of these local farms producing sweet potatoes. Various microorganisms have been reported in the literature, which convert starch and sugars into ethanol. In this study, two strains of *Zymomonas mobilis,* 8b and AX101, both obtained from National Renewable Energy Laboratories, Colorado, have been used to convert sugars into ethanol. The strain 8b is tetracycline and chloramphenicol resistant, while the strain AX101 is not . Further, the strain 8b does not contain arabinose utilizing genes, whereas strain AX101 does. In this study, medium containing a given type of sugar was first fermented with these two strains, to investigate the efficiency of these two strains in converting a single sugar into ethanol. Further, homogenized sweet potato suspensions have also been enzymatically pre-treated to convert starch to consumable sugars, which can then be consumed by these two strains. The enzymatically treated sweet potato suspension has been subjected to these two strains. It is found that more than 90% of the total sugars could be converted into ethanol within 18 hours.

Figures:
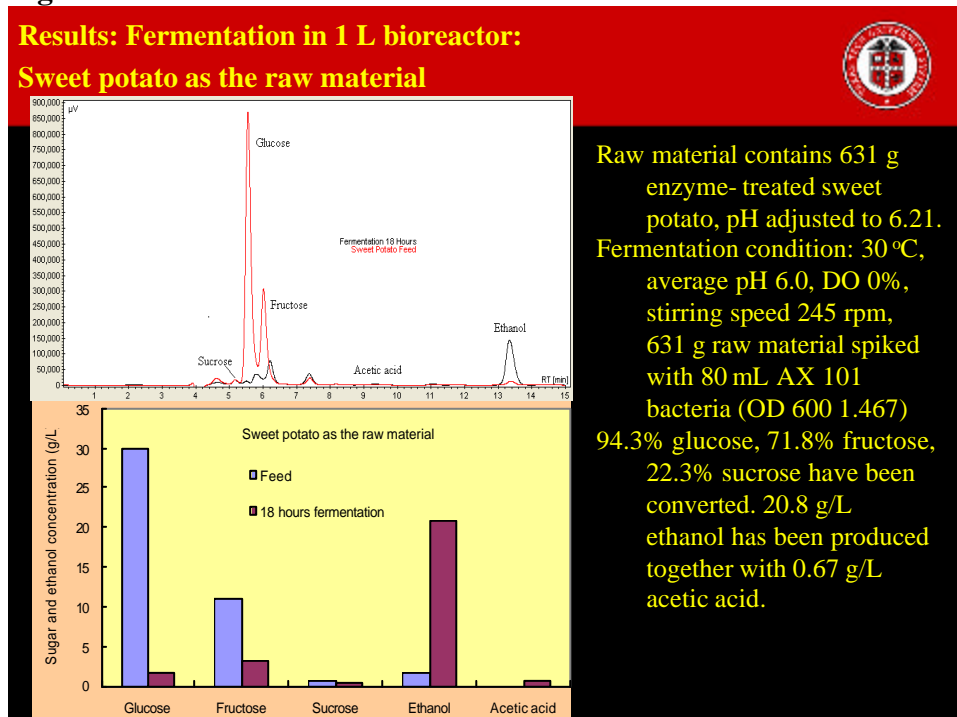
Session T1-5b: Sustainable & Clean Technologies - IIb: Energy Production

Abstract Number	Paper Title & Authors	Included
2210	Development of a tubular-flame burner for a fuel processing system in fuel cell systems K Yagi, K Nakagawa, S Nojima	Yes
2381	Sustainable hydrogen production via reforming of bio-oil using a novel spouted bed reactor P N Kechagiopoulos, S S Voutetakis, A A Lemonidou, I A Vasalos	Yes
2707	Enhanced hydrogen production from biomass when coupled with carbon dioxide capture using CaO N H Florin, A T Harris	Yes

Development of a Tubular-Flame Burner for a Fuel Processing System

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1. Summary

As one of the power generation systems that can contribute to decrease emission of carbon dioxide (a greenhouse gas), polymer electrolyte fuel cell (PEFC) has been highlighted in Japan. We have developed 1kW-50kW power generation systems using our PEFC and fuel processing system (FPS), which generates hydrogen from various fuels: kerosene, liquefied petroleum gas (LPG), city gas, dimethyl ether (DME) and so forth. (Yagi 2005) A burner of kerosene is dramatically improved with tubular flame in this study. The developed burner is lower NOx emissive and more axisymmetric than conventional burners.

Keywords: tubular flame, fuel cell, fuel processing, burner, power generation

2. Extended Abstract

A tubular flame can be established in a tube into which fuel gas and air are supplied in tangential directions. It has been demonstrated experimentally and numerically that the tubular flame burner has a unique characteristic of low-NOx emission. (Ishizuka et al. 2006) Also, it can be easily inferred that it has axisymmetric temperature distribution due to its shape. The purpose of this study is to confirm the advantage of the non-premixed tubular flame burner for the FPS over the conventional non-premixed co-annular burners from the viewpoint of low emission of NOx and axisymmetric heating. The target FPS shown in Fig.1 generates hydrogen of maximum $9.0 Nm^3/h$ from kerosene, which corresponds with 10kW electricity.

The combustion characteristics of the tubular flame burners are significantly influenced by various dimensional parameters including tube diameter, slit thickness and width, back space length and stabilizing tube length. In this study, an experimental approach was implemented using Taguchi method, one of experimental design methods, in order to elicit an innovative performance of the tubular flame burner for combustion of Kerosene. Kerosene is preliminarily vaporized and heated. Air is also preheated and both gases are supplied separately into the tube. The temperature of air in addition to the dimensional parameters are adopted as control factors of Taguchi method.

In consequence, Taguchi method was successfully utilized to derive an optimal set of parameters minimizing emission of NOx as well as CO. As shown in Fig. 2, the

maximum NOx concentration over a range of equivalent ratio (λ) is lower than the allowable value for the FPS, which is 70ppm at 0% O_2. Lower equivalent ratio dramatically decreases NOx emission without losing combustion stability. According to the sensitivity analysis of the parameters, it was clarified that high swirl number inducing recirculation is most effective on the emission of NOx. Also, circumferential dispersion of gas temperature is less than 50K as demonstrated in Fig. 3. It is inferred that low NOx emission is achieved due to decrease in temperature and homogenization of temperature distribution due to the recirculation. In this study, the potential performance of the tubular flame was well elicited and verified. It can be expected that tubular flame is a promising combustion technology in various industrial areas including furnaces, chemical reactors and fuel cell systems. (This research was financially supported by the New Energy and Industrial Technology Development Organization (NEDO).)
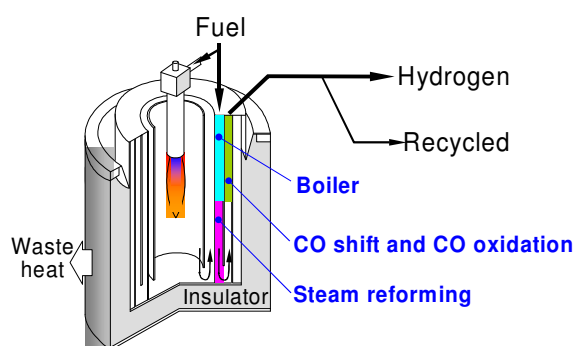
Fig. 1. A schematic of the fuel processing system. Three kinds of catalysts, installed in the multiple-layered reactors are thermally controlled by a burner.

Fig. 2. NOx emission of the developed burner. NOx concentration over a wide range of combustion load and equivalent ratio is kept at a low level.

Fig. 3. Temperature distribution of the flame. Temperature distributions measured at 38mm below the burner tip in two directions indicate the axisymmetric heating of the burner.
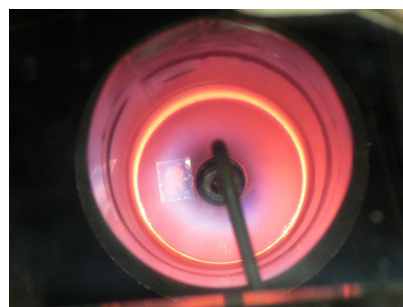
Fig. 4. Flame appearance. A tubular flame of kerosene is formed inside. Flow rate of kerosene is 7g/min. λ = 0.91.

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Sustainable hydrogen production via reforming of bio-oil using a novel spouted bed reactor

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1. Summary

Hydrogen produced from renewable energy sources is of great interest as an alternative to fossil fuels and as a means for clean power generation via fuel cells. In this paper we present the experimental work carried out in a novel spouted bed reactor for the reforming of the aqueous fraction of bio oil. The use of a specially designed injection nozzle in combination with the particular hydrodynamic characteristics of the spouted bed resulted in efficient processing of the organic feed. Olivine, when associated with nickel, proved to be a very suitable catalytic material combining high reforming activity, anti-coking characteristics and exceptional mechanical strength.

Keywords: hydrogen, bio-oil, reforming, spouted bed reactor, Ni/Olivine catalyst

2. Extended Abstract

Hydrogen is emerging as the energy carrier of the future, since it can be used as a clean transport fuel, as well as a means for the production of electricity via fuel cells. Necessary requirement is its production from renewable energy sources, such as biomass, so as not to cause additional CO_2 emissions to the environment. Reforming of the aqueous phase of bio-oil is one of the promising routes for the production of renewable hydrogen. One of the major hurdles to be overcome is the elimination of coke formed via thermal and/or catalytic reactions (Kechagiopoulos, et al., 2006, Wang, et al., 1998).

In the current work we present the experimental results of reforming of bio-oil using a novel spouted bed reactor. The particular type of reactor is characterized by the short residence time of the gas phase and the almost perfect mixing of the catalytic particles. Immediate contact and reaction between catalyst and bio-oil is achieved using a properly designed injection nozzle. The first phase of the experimental work was carried out using ethylene glycol as a model compound. Parameters investigated

were temperature and H_2O/C ratio in the feed under the presence of sand, olivine and a Ni/Olivine catalyst.

The thermal decomposition of ethylene glycol was investigated by loading the reactor with inert sand (SiO_2). Runs were conducted in the absence and presence of steam. In the entire range of conditions studied, the main gaseous products were CO, CO_2, CH_4 and H_2. The presence of steam did not seem to influence noticeably the selectivity of gaseous products or the total conversion, proving that ethylene glycol is thermally decomposed in the presence of SiO_2. The production of coke was especially limited demonstrating the rapid and effective mixing of solid particles and reactants achieved using the spouted bed reactor. Increase of temperature from $650^{o}C$ to $850^{o}C$ led to an increase of ethylene glycol conversion to gases from 55% to 85%. H_2 yield compared to the maximum possible for the case of full reforming was very low fluctuating at 10-15%. The highest percentage of H_2 was lost bound in CH_4 and the liquid compounds produced.
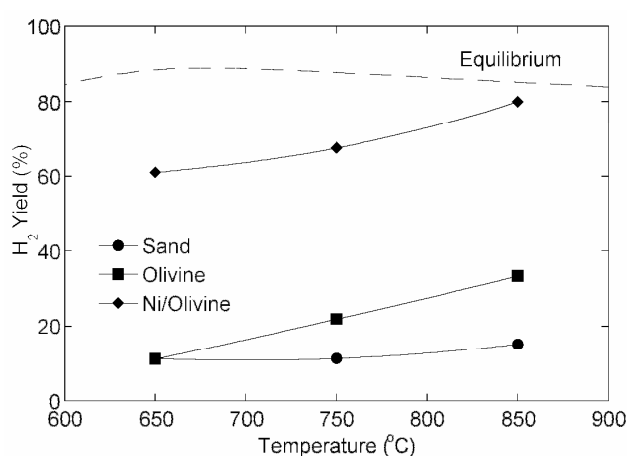
Figure 1: H_2 yield versus temperature for various catalytic and non-catalytic particles tested at $H_2O/C=4.6$.

A relative improvement was observed upon loading the reactor with olivine ($(Mg,Fe)_2SiO_4$), a mineral known to present catalytic action, mainly due to the presence of Fe species. At equivalent conditions to the experiments using sand and in the presence of steam, C-to-gas conversion of ethylene glycol increased from 70% at $650^{o}C$ to 95% at $850^{o}C$. H_2 yield at the highest temperature reached 35%.

Coke deposition on olivine was low averaging at 0.15 wt% of the bed for a typical experiment, percentage equivalent to 0.5 wt% of the total incoming carbon.

Catalytic results over Ni/Olivine are especially promising. Conversion of ethylene glycol to gaseous products was complete for all temperatures studied. Apart from a small percentage lost in CH_4, ethylene glycol was converted completely to CO_x and H_2. This resulted in high H_2 selectivity that averaged at 90-95%. As a result, H_2 yield was much higher as well, reaching 80% at $850^{o}C$. Coke generation was practically nil (~0,02 wt% of the bed after 6h TOS). The unique hydrodynamic features of the spouted bed combined with the reforming activity, the low coking tendency and the attrition resistance of the Ni/Olivine particles clearly demonstrate the prospects for successful processing of actual bio-oil. The suitability of the reactor will be further investigated, conducting tests in a wide range of operating conditions and model compounds, concluding with the use of actual bio-oil.

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Enhanced H$_2$ production from biomass when coupled with CO$_2$ capture using CaO

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1. Summary

The steam gasification of biomass and non-recyclable combustible wastes, coupled with in situ carbon dioxide (CO$_2$) capture using calcium oxide (CaO) is a promising process for the renewable production of hydrogen (H$_2$). In this paper we present a simultaneous thermogravimetric-mass spectrometric study of the thermal decomposition of pure cellulose, in the presence of CaO. Measurement of the pyrolytic weight loss and simultaneous recording of the mass spectra for evolved gas species is used to elucidate the role of CaO during the decomposition of pure cellulose, a model biomass fuel.

Keywords: biomass, CaO sorbent, CO$_2$ capture, gasification, H$_2$

2. Extended Abstract

The production of energy from biomass is receiving considerable interest, particularly due to concerns regarding regional energy security and the need to reduce greenhouse gas emissions. A highly promising way to exploit biomass resources involves converting biomass to a H$_2$ rich gas. H$_2$ produced from biomass could be used as a direct replacement energy carrier for fossil fuels in the transport, industrial, commercial and residential sectors.

A number of processes can be utilised to convert biomass into H$_2$, including biological, chemical and thermochemical pathways (Nath and Das, 2003). In this work we investigate a thermochemical conversion process - steam gasification. In this process, biomass is converted to a mixture of gases, including H$_2$, CH$_4$, CO, CO$_2$, and trace amounts of higher hydrocarbons, at moderate temperatures (500-800°C) and in the presence of steam. This conversion process may be considered simply according to the important reactions shown in Table 1, Eqns. (1&2)
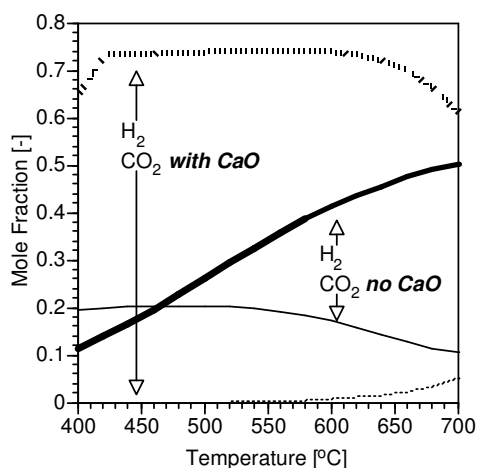
Table 1. Important chemical reactions for the thermal decomposition of biomass

Chemical Equation	ΔH°_{673} [kJ/mol]	No.
Steam reforming $C_nH_mO_p+(n\text{-}p)H_2O\rightarrow$ $(n + m/2\text{-}p)H_2+nCO$	endothermic	(1)
Water-gas shift $CO+H_2O\rightarrow CO_2+H_2$	-38.1	(2)
Carbonation $CaO+CO_2\rightarrow CaCO_3$	-174.0	(3)

Figure 1. Predicted H$_2$ and CO$_2$ concentration in the product gas for biomass gasification.

The output of H_2 can be maximised by integrating the biomass conversion process with in situ CO_2 capture using CaO, according to Eqn. (3). The removal of CO_2 from the reaction system shifts the equilibrium balance according to Eqn. (2), enhancing H_2 output. This equilibrium process is clearly demonstrated with thermodynamic modeling predictions, displayed in Figure 1 (Florin and Harris, 2007). However, significant practical challenges prevent the attainment of thermodynamic equilibrium in real biomass gasifiers, due to heat and mass transfer limitations. In this paper we examine the effect of key variables, including: i) CaO loading; ii) heating rate, and residence time, with a specific focus on obtaining fundamental data relevant to the design and scale-up of novel gasification reactors.

The experimental apparatus consisted of a modified thermogravimetric analyser coupled with a mass spectrometer (TG-MS). The TG-MS measures the pyrolytic weight loss using a thermobalance. The mass spectra of the evolved gas species are simultaneously recorded as a function of temperature using the mass spectrometer. Pure cellulose was selected as a model biomass species because it is the main component of biomass, ie typically greater than 50% (weight basis).

A comparison of the rate of weight loss with the mass spectra for the evolved species was used to elucidate the mechanistic pathways during cellulose decomposition. For example, Figure 2 shows the rate of decomposition of cellulose (wt-%/°C) without, and with, CaO and the corresponding mass spectra of the major product gases - H_2 (m/e=2), CH_3^+ (m/e=15), H_2O (m/e=18), CO (m/e=28) and CO_2 (m/e=44).
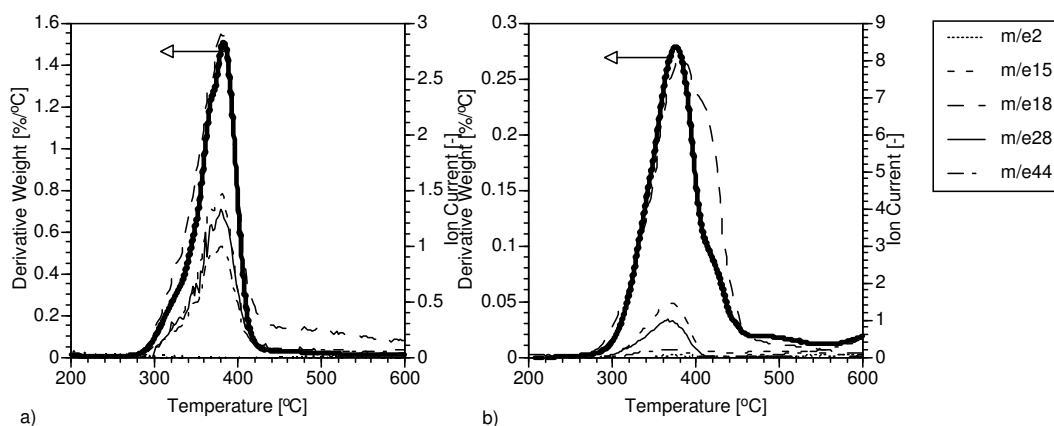
Figure 2. TG-MS measurement of the pyrolytic weight loss for the decomposition of cellulose, superimposed with mass spectra of the evolved gases recorded as a function of temperature - a) no CaO; b) CaO present (C:Ca=1molar basis).

The single and uniform decomposition peak and the close correspondence of the mass spectra, shown in Figure 2 a), suggest a single decomposition step for cellulose without CaO, consistent with the literature (Varhegyi et al., 1988). In comparison the decomposition peak for cellulose and the corresponding mass spectra indicates a more complex mechanistic pathway. T_{peak}, defined as the temperature corresponding with the maximum rate of decomposition, is shifted downwards by ~10°C compared to decomposition without CaO. The decomposition peak is considerably broader, reflecting a decrease in the rate of weight loss, commencing at ~405°C. The difference in the relative intensities of the mass spectra is consistent with equilibrium modeling predictions, demonstrating enhanced H_2 output and the effective capture of CO_2 by CaO.

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Session T1-6: Sustainable & Clean Technologies - III: Combustion & Emission

Abstract Number	Paper Title & Authors	Included
568	Membrane contactors for post-combustion CO_2 capture: Progress towards pilot plant operation R Klaassen, P H M Feron	Yes
1528	Biomass combustion in fluidized bed boilers: Potential problems and remedies A A Khan, W de Jong, P J Jansens, H Spliethoff	Yes
1806	Particle formation from gas cookers A Yilmaz, P Glarborg, H Livbjerg	Yes
2163	Nature and combustion of the coke deposited over a Ni-HZSM-5 catalyst in the transformation of methanol/bio-oil mixtures into hydrocarbons B Valle, A G Gayubo, A Atutxa, A Alonso, J Bilbao	Yes

Membrane contactors for Post-Combustion CO2 Capture: Progress towards pilot plant operation

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1. Summary

It is becoming clear that to halt the change in the global climate, CO2 emissions need to be reduced by more than 80% in the middle of this century. Capture and storage of CO2 (CCS) is a technology which enables large reductions of CO2-emissions from fossil fuel fired power plants. As part of a balanced technology portfolio for emission reductions, it is at present receiving considerable attention, because other methods to reduce CO2-emissions (e.g. renewable energy) will take considerable time before they can impact on the required large scale. CCS is also attractive because it can be implemented directly in current power plants, by using post-combustion capture of CO2. The leading technology for post-combustion capture is a chemical solvent which reacts reversibly with CO2. Increasing the solvent temperature will lead to the release of CO2. The process is, however, rather expensive not in the last because of the high costs of absorbers.
Membrane contactors represent a novel way to contact gas and liquid streams, which can reduce costs due to the fact the equipment is rather compact. Its advantages lie in the fact the equipment can be made more compact and with a smaller footprint. This presents advantages in terms of investment cost reduction.

Keywords: CO2 capture, post-combustion, solvents, absorption, membrane contactors

2. Extended Abstract

Membrane contactors represent a novel way to contact gas and liquid streams. In solvent processes for post-combustion capture of CO_2, they can be used for in the absorption step and the desorption step. The essential element in a membrane absorber is a solvent repellent, polymeric membrane. The gas phase remains separated from the liquid absorbent as a result of the hydrophobicity of the membrane. The components to be removed from the gas stream will diffuse through the gas filled pores to the other side. There they will be absorbed into the absorption liquid.
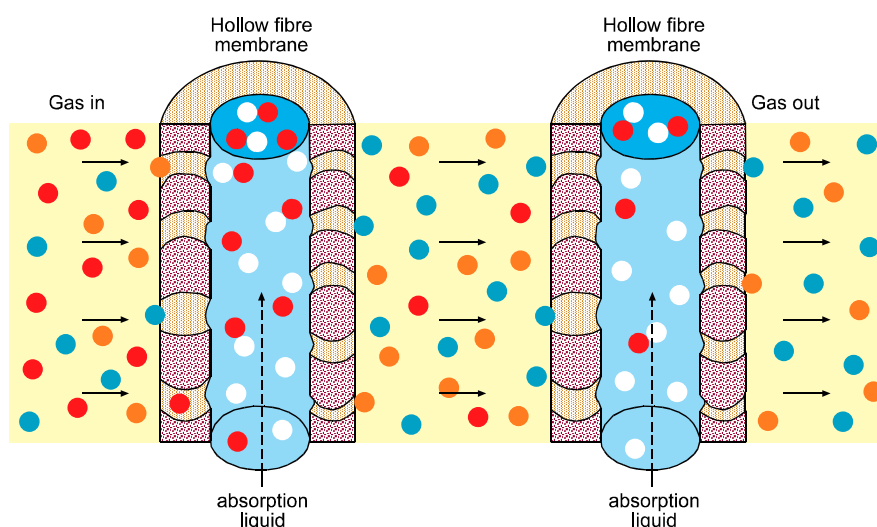
Figure 1:   Membrane gas absorption principle

TNO has been developing this process successfully for a number of small-scale applications. The technology is based on combinations of dedicated solvents with cheap polypropylene membranes. The presentation will focus on the following items:
1.   Principles and benefits of membrane contactors.
Membrane contactors will enable the establishment of a compact apparatus for gas separation based on absorption processes.
2.   Selection and characterisation of membranes for membrane contactors
Membranes should fulfill requirements regarding their porosity, thickness, pore size, permeability to be useful for contacting applications.
3.   Development of dedicated solvents for CO2-capture.One of the most critical development items is the system stability, i.e. whether the gas-liquid interface can be fixed at the membrane surface for a sufficiently long period without wetting the membrane pores.
4.   Development of dedicated membrane modules for use as contactors
Membrane modules should exhibit good fluid distribution and low gas-side pressure drop and this leads to module concepts based on transversal flow.
5.   Performances of membrane contactors in laboratory conditions
Results from laboratory set-ups will be presented for a variety of conditions.
6.   Pilot plant operation with power plant flue gases
The application of membrane for reduction of CO2-emissions from power stations will be presented. TNO is building a pilot plant at a coal fired power station, which will be the largest pilot plant for testing membrane contactors for gas absorption.

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Biomass combustion in fluidized bed boilers: Potential problems and remedies

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1. Summary

This review article presents the major issues concerned with biomass combustion with special reference to the small scale fluidized bed systems. The range of issues including market status, feasibility, availability, cost competitiveness, physical, chemical, and combustion properties, and technical difficulties (gaseous and particulate emissions) related to biomass combustion have been addressed. Attempts have been made to provide the most updated review to date. The major technical issues i.e., environmental concerns (emissions) and operating problems, associated with biomass have been dealt with especial emphasis. Problems have been identified, mechanisms explained and solutions have been indicated.

Keywords: Fluidized bed, combustion, biomass

2. Extended Abstract

Due to increasing environmental concerns especially related with the use of fossil fuels, new solutions to limit the greenhouse gas effect are continuously sought. Among the available alternative energy sources, including hydro, solar, wind etc. to mitigate greenhouse emissions, biomass is the only carbon based sustainable option. Not only is the biomass renewable but increasing its share in heat and electricity production can reduce the total CO_2 emissions and decrease our dependency on fossils fuels. Furthermore, its relatively easy applicability in the existing heat and power producing units makes it very attractive for plant owners and delivers huge environmental dividends with low to occasionally almost no investment costs. Although present biomass economics are a bit more expensive than fossils fuels but trends show that with an efficient bio-cycle including cultivation, transportation and combustion, biomass can also compete economically.

On one hand, the versatile nature of biomass enables it to be utilized in all parts of the world, and on the other, this diversity makes biomass a complex and difficult fuel. Especially the high percentages of alkali (potassium) and chlorine, together with high ash content, in some brands of biomass prove to be a major source of concern.

However, mechanisms leading to corrosion and high dust emissions problems have been identified and a range of possible solutions is already available.

Among the available technologies, fluidized beds are proving to be one of the best because of their flexibility, stability and efficiency. They provide the necessary window of variability needed to handle this diverse renewable fuel.

Apart from small-scale green house or community boilers, the use of biomass as a sole energy source is unimaginable especially for electricity production. At least for now, the most feasible way of increasing the share of this sustainable energy fuel in world energy supply is through co-firing. Comparing with other available renewable energy sources, co-firing offers the lowest risk, most efficient and shortest term option for renewable based electrical power generation. However, there are still some obstacles that need to be removed to run this sustainable bioenergy engine at full throttle.

In general, first category pollutants including PAHs, PCDDs/Fs, CO, and particulate carbon can be easily handled with operating variables and combustor design consideration. Good combustion practices with optimized design considerations are in most cases enough to keep unburnt pollutants emissions under environmental norms. Fuel based pollutants (NO_x, SO_x, dust and metal emissions) however may need secondary measures. For NO_x, air-staging or together with SCR, SNCR, and reburning deliver high reduction rates (upto 95%). The lower sulfur content in most biomass make SO_x emissions irrelevant, however, sulfur becomes important for its role in corrosion and deposition problems.

The biggest technical challenges that biomass today faces are all related to its ash content. Comparatively higher percentages of alkali metals (potassium) in biomass ash together with chlorine content (especially in herbaceous biomass) are probably the biggest disadvantage associated with this fuel. Biomass ashes melt and sinter at lower temperature due to high potassium and silicon content and in combination with other elements like chlorine and sulfur, they cause the well known biomass related problems, fouling, deposition, corrosion, slagging, and agglomeration.

For fluidized beds, they are especially detrimental as agglomeration leads to abrupt shutdowns. Different remedies including extracting these problematic elements from fuel to different bed additives and use of different bed material (agglomeration) have been suggested and successfully implemented at few units. High dust and metal emissions problems related to few bio-fuels (Greenhouse Residues, Demolition Wood etc.) have already been rectified with efficient but still expensive solution (Electrostatic precipitators, Bag House Filters).

This review article presents the major issues concerned with biomass combustion with special reference to the small scale fluidized bed systems. Problems have been identified, mechanisms explained and solutions have been indicated. In conclusion, a range of concerns including environmental, economical and technical associated with biomass exist but none of these issues represent an insurmountable obstacle for this sustainable energy source. The focus, based on environmental and economical objectives, is broadening the spectrum by adding new possibilities, bridging the gaps, and bringing continuous improvement in the existing ones.

Particle Formation from Gas Cookers

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1. Summary

A recent hypothesis on the epidemiological associations between illness and nitrogen dioxide (1) is that it may be the consequence of confounding by particle numbers. It was communicated that like many other phenomena in nature, the presence of carbon nano-tubes in blue combustion flames went virtually unrecognized because it was essentially unexpected (2-3).

In this PhD study, particle formation from gas cookers is investigated. The present findings of this study are partly in agreement with the ranges reported by Dennekamp et al (4) in that ultra-fine particle (UFP) concentrations rise to ~10^5 UFP/cm^3 by turning on a single gas ring; and with Bang et al (2) and Murr et al.(3) that the average diameters of these particles are 3-30 nm.

Keywords: particles, aerosols, gas cookers, gas burner

2. Extended Abstract

When particles are measured as mass the greatest contribution comes from the largest particles, but the greatest number of particles by far are the submicron ones. These ultrafine particles are generated, as is nitrogen oxides (1,4), by the combustion process, and therefore the two pollutants are likely to correlate closely. Bang et al (2) and Murr et al (3) reported aggregated multi-wall carbon nano-tubes with diameters ranging from 3 to 30 nm and related carbon nano-crystal forms ranging in size from 0.4 to 2μm (average diameter) in the combustion streams for methane/air, natural gas/air, and propane gas/air flames from domestic (kitchen) stoves. These observations suggests that the proliferation of so-called clean- burning gaseous fuel sources, particularly methane-series gases ($C_nH_{2(n+1)}$); n=1,2,3…etc) may, in fact, make a significant contribution of carbon nano-crystal forms to both the indoor and outdoor air environment. In this PhD study, the objective is to provide new results on particle generation from gas cookers together with their size distribution, nature and origin.

Samples are collected using a gas ejector probe developed for particle analysis in a research program instigated to study fine particles (5). Particles are classified using a TSI Model 3080 Electrostatic Classifier with a TSI Model 3081 LDMA (Long Differential Mobility Analyzer), and/or a TSI Model 3085 NDMA (Nano Differential Mobility Analyzer). Particle concentrations are measured with a TSI Model 3775 Condensation Particle Counter (CPC). Electron microscopy methods (SEM and TEM, coupled with EDA) are addressed to identify the nature of particles. Chemical kinetic modelling is addressed together with experimental measurements to determine the origin of the particles.

Preliminary experiments are carried out using the gas cooker in its normal procedure - natural gas supplied from the city line and air supplied from the surroundings. The elevated particle concentrations did not go beyond sharp peaks observed once in a while, which would indicate a release of high amount of fine particles at some instant during gas combustion. Since the repeatability of this type of experiments was not likely due to changing gas and air quality over time, a controlled set-up is prepared. The burner is installed in a compartment which is supplied with particle free air at its bottom; keeping the partial premixed flame structure of the burner unchanged. The compartment functions as a steady state reactor with no mechanical mixing. Particle concentrations, size distributions, gas concentrations (CO, CO_2, O_2, NO, NO_x) and temperatures are measured at the reactor outlet and/or along the reactor. Natural gas from the city line is used as the fuel supply. Experiments are repeated with methane to observe the differences; as well as addition of minor amounts of hydrogen sulphide and acetylene to methane. Natural gas resulted in higher particle concentrations than methane. Addition of hydrogen sulphide to methane resulted in an increase in particle concentrations while no affects were observed from acetylene. The present findings of this study concerning the particle concentrations and size distributions are partly in agreement with the ranges reported by Dennekamp et al (4) in that UFP concentrations rise to $\sim 10^5$ UFP/cm^3 by turning on a single gas ring; and with Bang et al (2) and Murr et al.(3) that the average diameters of these particles are 3-30 nm. Future studies will focus on morphology studies.

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Nature and combustion of the coke deposited over a Ni-HZSM-5 catalyst in the transformation of methanol/bio-oil mixtures into hydrocarbons

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1. Summary

In the upgrading of bio-oil by transformation into hydrocarbons, the NiHZSM5 catalyst undergoes a rapid deactivation by coke deposition. In this paper, the nature of this coke has been studied by combustion with air. From the DTG (mass variation) curves, two combustion peaks have been observed: one corresponding to "thermal" coke (which burns at lower temperature and is associated with the thermal degradation of bio-oil components) and the other corresponding to catalytic coke formed by coke precursors evolution in the reactions of hydrocarbon formation. Dilution with methanol has been proven to attenuate both types of coke (mainly the thermal coke), which contributes to increasing catalyst life.

Keywords: bio-oil upgrading, NiHZSM-5 zeolite, coke combustion.

2. Extended Abstract

2.1. Introduction

The liquid (bio-oil) obtained by fast pyrolysis of vegetable biomass is an interesting alternative to conventional fuels, but its instability and composition (oxygenated nature) make it advisable to carry out catalytic reforming upon acidic catalysts, prior to its combustion in turbines or combustors [1]. A Ni-HZSM-5 zeolite catalyst is suitable for this purpose, because it is hydrothermally stable at high temperatures (up to 500 ºC) in the presence of high water content in the reaction medium [2], which is a requirement in order to attain high conversion of bio-oil in this process. Nevertheless, this catalyst undergoes a rapid deactivation by coke deposition, and must be regenerated by coke combustion. In this paper, a study has been carried out on the nature and combustion kinetics of the coke deposited over a NiHZSM-5 catalyst in the transformation of bio-oil performed in a fluidized bed reactor. The bio-oil has been previously stabilized by dilution in methanol at different proportions.

2.1. Experimental

The catalyst based on a Ni-HZSM-5 zeolite (1 wt% Ni) has been prepared by impregnation of a commercial HZSM-5 zeolite (from Zeolytst International with

Si/Al=30). The final catalyst has been prepared by agglomerating the active phase (25 wt %) with a binder (bentonite, 30 wt %) and an inert solid (alumina, 45 wt %), in order to provide the catalyst high mechanical resistance to attrition. The bio-oil has been stabilized by dilution in methanol in different proportions in order to minimize the plugging problems due to the deposition of carbonaceous material caused by thermal degradation-polimerization of bio-oil components [3]. The kinetic runs have been carried out in a fluidized bed reactor on-line with a Micro GC 3000 from Agilent for reaction products analysis. The feed preheating zone of the reactor is refrigerated with water in order to minimize the problems of plugging in this zone. Coke combustion with air has been carried out in a thermobalance (SDT 2960 TA Instruments) by following a temperature ramp (3 ºC min -1) from 300 to 550 ºC.

2.2. Results and discussion
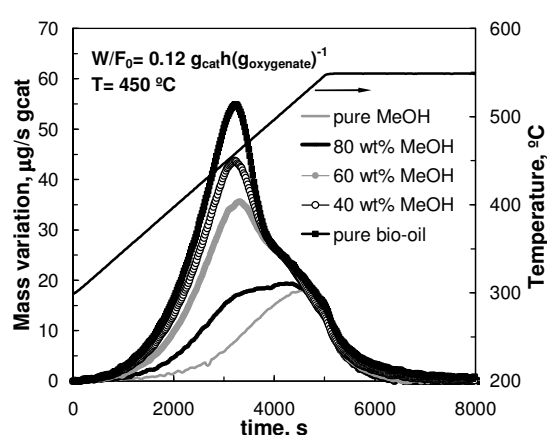
Figure 1: Mass variation (DTG) during combustion of coke deposited upon the catalyst in the transformation of bio-oil/methanol mixtures

Two combustion peaks have been observed in the DTG (mass variation) curves corresponding to combustion of cokes deposited in the transformation of bio-oil dissolved in different proportions of methanol (Figure 1): one corresponding to "thermal" coke (which burns at lower temperature and is associated with the thermal degradation of bio-oil components [4]) and the other corresponding to catalytic coke formed by coke precursors evolution in the reactions of hydrocarbon formation.

By means of a deconvolution program (Matlab), which assumes a first order kinetics with respect to oxygen and coke content for both types of coke, their content has been quantified and the effect of dilution of bio-oil with methanol upon both types of coke has been analised. It has been observed that, as the content of MeOH in the feed is increased, the coke content in the catalyst is considerably lower, mainly the "thermal" coke fraction. Consequently, dilution of bio-oil in MeOH favours its catalytic transformation not only by minimizing the problems of reactor plugging in the feed preheating zone, but also by extending considerably the catalyst life as a consequence of a lower coke deposition, which is an important requirement for the viability of bio-oil upgrading processes by catalytic transformation.

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Session T1-7: Selection & Use of Organic Solvents

Abstract Number	Paper Title & Authors	Included
389	Solvent reduction in an industrial solid-liquid contactor R Poirot, L Prat, C Gourdon, C Diard, A M Autret	Yes
1741	Development of systematic procedures for the evaluation of solvent selection at an early stage in pharmaceutical process S Perez Vega, P Sharrat	Yes
3134	Propane + CO2 mixtures as near critical solvents, properties and mixture design P Hegel, G Mabe, S Pereda, E A Brignole	Yes
3827	A methodology for the design and selection of green solvents for organic reactions M Folic, R Gani, C Jimenez-Gonzalez, D C Constable	Yes
3886	3886 - Biodiesel production using cosolvent E Çağlar	No

Solvent reduction in an industrial solid-liquid contactor

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1. Summary

Solid-liquid extraction represents an important part of many industrial processes. Extraction from plant is common in perfume industry, pharmaceutical sector and food field (Schwartzberg, 1980). The vegetable substrates are complex. The raw material is non-homogeneous and the hydrodynamic behaviour changes from one plant to another according to the storage, the harvesting time, etc… In industry, the difficulty lies also in the variation of plant lots. Furthermore in one lot, the plant is not homogeneous. The extraction process must then takes into account all these constraints (Prat, 2006). In the present work, the solid-liquid extraction is performed in a Pierre Fabre Company's industrial unit using a counter-current continuous extractor. Advantages over the conventional batch extraction methods include a decrease in solvent consumption and shorter handling time. However, continuous extractor implementation at industrial level requires preliminary laboratory tests in order to optimise the operating conditions (Poirot, 2007). Each material-solvent system shows a different behaviour, which cannot be easily predicted (Pinelo, 2004). The objective is then to propose a method for fast transposition of information from lab scale to the industrial process.

Keywords: solid-liquid extraction, vegetable, solvent reduction

2. Extended Abstract

This study has been integrated in a classical pharmaceutical industry methodology as the first step of the batch to continuous process transfer. A methodology has been extracted from this study on leaves as raw material and is based essentially on batch tests. The objectives are to answer at three questions about continuous extractor: what filling rate? what retention time? and what policy of solvent management to applied?
In the continuous extractor, the raw plant is transported by single-screw. Then the plant transport is considered like a plug flow. So the filling rate depends on hydrodynamic behaviour of plant in the unit (Poirot, 2007).

The retention time and the policy of solvent management depend on the plant-solvent couple. Two mains information are necessary in order to determine them: the kinetic and the saturation data.

The global extraction kinetic was measured in batch. Liquid samples were taken at different times and analysed by HPLC. The extraction yields are also measured in the continuous extractor. Figure 1 shows the evolution of the extracted percentage versus time, for the two cases. Data are normalized by the plant potential value. Extraction kinetics are similar. The retention time of raw material is determined according to desired yield and batch kinetic.
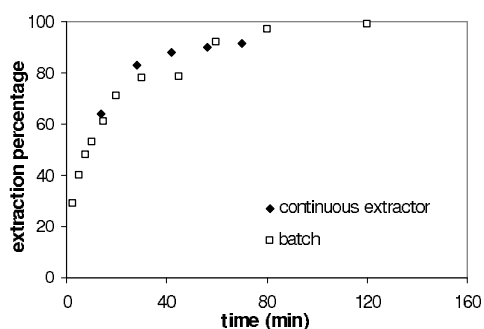
Figure 1: batch and continuous extraction kinetics
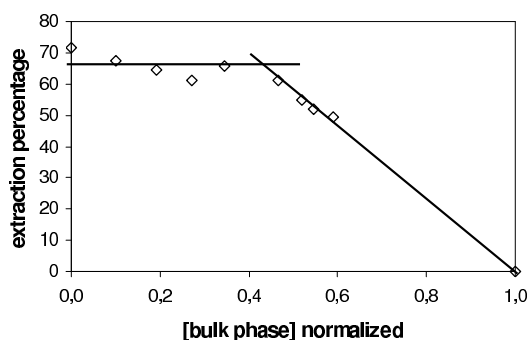
Figure 2: Extraction percentage evolution according to the bulk phase concentration

The policy of solvent management represents the choice of solid-liquid ratio function of time. A saturation study of solute is carried out in batch. Different plant lots were extracted in the same bulk phase. Figure 2 shows the evolution of extraction percentage according to the bulk concentration normalized by saturation concentration. The extraction percentage is constant until a point, called rupture point, and then it decreases linearly until limit concentration. The limit concentration is obtained at equilibrium between solid and the only liquid necessary for solid impregnation. Over the rupture point, the extraction is not altered by the bulk phase concentration. In the unit, the outlet concentration must be as close as possible of rupture point. So the flux is maximum without altering the extraction.

In the study case, the solid-liquid ratio has been decreased by a third compared to usual conditions. This change of ratio decreases the solvent amount used and its recovery. And in following treatment operations, solvent come more concentrated. So the concentration phases will be less important, and then less energy will be necessary.

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Development of systematic procedures for the evaluation of solvent selection at an early stage in pharmaceutical process

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1. Summary

Three levels of evaluation for the selection of solvents on a system where developed, where considering the lack of information is one of the main characteristics. Tools to aided the evaluations and capable to be applied at an early stage where identified. A first level is based on system properties analysis. A second level considers the impact of the potential streams to be formed on the system. A third level exploits process simulation in order to evaluate industrial scale issues of the solvents on the system. A case study based on the synthesis of propanol is presented, where solvents such as water, isopropylamine, diethyl ether and cyclohexane are used for different operations. Through the evaluations solvents such as isopropylamine and diethyl ether presented high cost implications related with their management and containment. On the other hand, some of their characteristics are necessary for the successfully performance of operations such as reaction and extraction. Water also contributes to the formation of great amount of aqueous wastes, which can represent higher disposal costs. Since the yield of the reaction is not very high and some implications arise on the system, the chemist and chemical engineer can think about alternatives at very early stages.

Keywords: evaluations, system, solvents, early stage, cost implications

2. Extended Abstract

Solvent are one of the main raw materials applied in the pharmaceutical process. This is because a huge range of operations commonly applied in this industry need the application of a solvent. At these days, organic pharmaceutical processes consist on series of reactions followed by a great number of separation and purification stages. As a result, great deals of solvents are applied during the processing of a drug. It is considered that solvents represent between 80% and 90% of the total mass utilization in a pharmaceutical industry (Constable et al. 2007). This reflects the great

importance that solvents have in the complete process. Moreover, all the issues (Fig. 1) arising with the use of solvents are reflected on high cost implications for the industry.
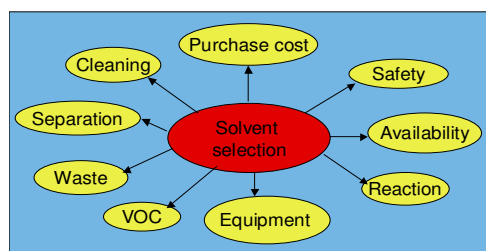
Figure 1: Common solvent issues on a system

There levels of evaluation where introduced (Table 1) to evaluate the impact of the issues presented in Fig.1. Each level starts with a question that can be answered by the chemist. This answer is the starting point of the evaluation. The main objectives and some of the identified tools are shown in Table 1.

Question	Main Objectives	Tools to employ
1)What solvents are you planning to employ?	Properties based analysis on aspects such as: SHE, solubility, chemical reactivity, compatibility, and purchase cost.	Chemicals databases, software for the simulation of properties, web services consultation, development of experiments, and contact with stakeholders.
2)What are the potential conditions?	Determine the most important streams formed on the system. Establish the cost implication of handling these mixtures along the process.	Solvent databases, process design heuristics, development of experiments, stakeholders contact.
3)What is the lab recipe?	Determine industrial scale mass balance in order to evaluate issues with solvents at industrial scale. Determinate cost implications related with the solvents selected.	Batch process simulators, cost estimation, process design heuristics, contact with contractors.

Table 1: Approach behaviour.

The evaluation steps where integrated into systematic evaluation procedures, where different algorithms for the evaluation of each level where developed. An interactive tool containing such algorithms was created in order to guide the chemist through the evaluations. As a result, the approach can interact with the chemist in a friendly environment.

The *Propranolol* synthesis was treated as an early stage synthesis with the aim to probe our approach. As a result, cost implications related with VOC and waste disposal arise very early on design. Also the tool provides insight into where the efforts should be aimed in order to replace or reduced the impacts on the system.

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Propane + CO2 mixtures as near critical solvents, properties and mixture design

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Planta Piloto de Ingeniería Química (PLAPIQUI – UNS – CONICET), CC: 717, Bahía Blanca, Argenitna

1. Summary

The use of mixtures of propane + CO2 for the extraction of natural products can offer special properties regarding solvent power, selectivity and safety. For the case of extraction of vegetable oils from grounded seeds, previous studies have shown that it is possible to obtain complete miscibility of the vegetable oil with the propane + CO2 mixture keeping the mixture below the flammability limits (Hegel et al, 2006). A strategy for mixture design at different temperatures to comply with the requirements of complete miscibility and non flammability is presented, on the basis of the phase equilibrium properties of the mixtures of vegetable oils + propane + CO2.

2. Extended abstract

The solvent properties of mixtures of CO2 + Propane for the extraction of grounded seed were studied for the extraction of soy oil, sunflower oils and hiprose oil. In a previous work was observed a reduction in mass transfer rate at increasing CO2 concentrations, even in the complete miscibility region (Hegel et al, 2007). Figure 1 shows the experimental observation of this effect for soy oil extraction from grounded seeds. Complete extraction for soy oil is obtained at 298.15K, when the solvent/seeds mass ratio is around 10, at 95% propane concentration in the CO2–propane solvent mixture. On the other hand, when the solvent mixture contains only 40% of propane, less than 10% of the total oil can be extracted at the same solvent/seeds mass ratio. In this case partial miscibility between the oil and the solvent takes place.
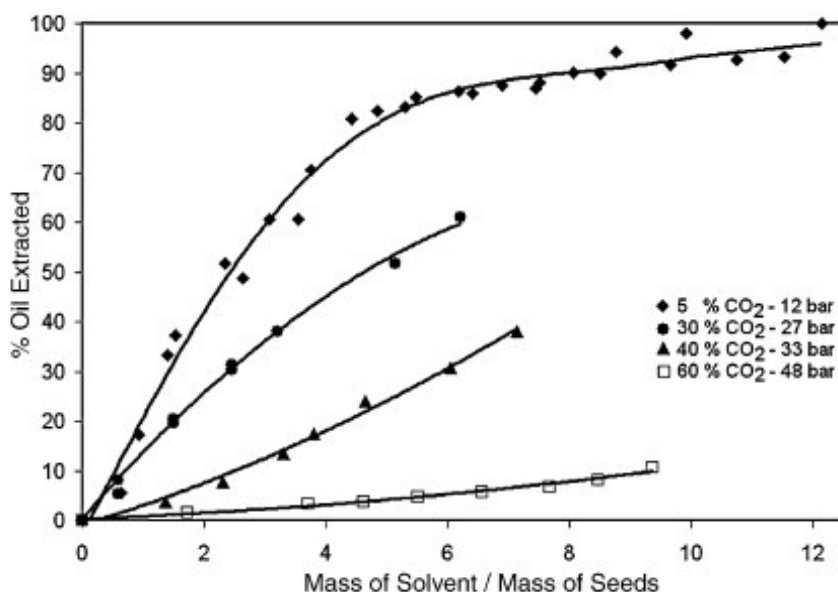
Figure 1: Effect of solvent CO2 concentration on the oil extraction yield of milled soy seeds as a function of the solvent/seeds mass ratio, at 298.15 K. Solvent: CO2–propane mixtures. Markers: raw experimental data (this work). The solid lines are the result of smoothing the raw experimental data. (Hegel et al, 2007)

This behaviour is explained in the present work on the basis of the nonideality effects on the effective diffusion coefficients and a mass transfer model for the extraction experiments based on transient diffusion phenomena is presented to quantify the observed experimental results. The phase equilibrium predictions are based on an extended version of the Group Contribution Equation of State (Skold-Jorgensen, 1988).

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A methodology for the design and selection of green solvents for organic reactions

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1. Summary

The solvent selection methodology developed by Gani *et al.* (2005) is extended with application to complex case studies inlcluding multi-step organic synthesis reactions. Also, it has been modified so as to allow taking into account the effect of solvent on the reaction rate and yield. Promising results have been obtained that are in good agreement with the observations and results obtained by the industrial partner.

Keywords: pharmaceutical synthesis, green chemistry, green engineering, solvent selection

2. Extended Abstract

Solvents are widely used in fine chemicals and pharmaceutical industry where they serve to facilitate reaction-based processes by, for example, dissolving reactants and/or bringing them together in suitable concentrations. Reichardt (1988) reports that the reaction between trimethylamine and trimethylsulfonium ion is 119 times faster in nitromethane than in water which is a dramatic influence pointing out the need for knowledge-based choice of solvents for reactions. However, the excessive consumption of solvents leads to disposal of millions of tons of solvents every year. Given this situation, we aim to design and select solvents that, when used as inert media for liquid phase organic reactions, will lead to an increase in reaction rate and simultaneously minimize the environmental impact. Provided the details of an organic reacting system (reactants, products and reaction conditions) are known, our objective is to find solvents that can promote the reaction and rank them according to an established scoring/evaluation system.

The basis for this work is the method developed by Gani *et al.* (2005) that incorporates industrial practice knowledge in the currently available computer-aided

tools for solvent design and property estimation. Essentially, it is a multi-step algorithm, with the solvent selection process occurring in two stages. In the first stage, a list of well-known solvents, if available, is used to identify the solvents that match a sub-set of specified requirements (constraints) and based on this a score is allocated to each solvent. Simultaneously, a computer-aided molecular design (CAMD) technique can also be used to generate a list of solvent candidates, which are then ranked with respect to the corresponding scores. The needed reaction data is provided by the user while the solvents data can either be retrieved from a list of 75 most common solvents or using the hybrid computer aided molecular design (CAMD) technique of Harper and Gani (2000). In the latter case, chemically stable molecules that satisfy the solvent-property requirements are generated and tested. In the second stage, the candidate solvents are further evaluated through more detailed property calculations or by checking the properties databases.

The original method has been extended with application to several case studied of increased complexity involving multi-step organic synthesis reactions. It has also been combined with a CAMD-based methodology for the selection of reaction media developed by Folić *et al*. (2006) in order to quantify the increase in reaction rates. The methodology of Folić *et al*. (2006) consists of a simple reaction model based on empirical parameters embedded within the CAMD framework. The model uses as input kinetic data for a small number of solvents for a specific reaction and can then be extrapolated to predict values of reaction rate constants for nearly 8000 molecular structures based solely on their structural parameters. Given the large search space, the optimal potential candidates are easily found.

Results obtained agree well with the solvents commonly used by the user but also give innovative ideas for solvents yet to be tried out. The method allows easy integration process-wide allowing the product recovery operations to potentially be taken into account.

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Session T1-8: SCF as Solvent Substitutes

Abstract Number	Paper Title & Authors	Included
502	Supercritical antisolvent micronization of minocycline hydrochloride M A Tavares Cardoso, G A Monteiro, J P Cardoso, T J V Prazeres, J M F Figueiredo, J M G martinho, J M S Cabral, A M F Palavra	Yes
508	Properties and characterization of silica aerogel-metal composites produced by a supercritical impregnation process G Caputo, E Reverchon	Yes
587	Continuous selective oxidation of alcohols in supercritical carbon dioxide By Dr J-D Grunwaldt, M Caravati, A Baiker	Yes
1372	Kinetics and specificity of lipozyme-catalysed oil hydrolysis in supercritical CO2 H Sovova, M Zarevucka	Yes
2964	The role of pressure at the limit of the dispersion stability in the polymerization of methyl methacrylate in supercritical carbon dioxide C Mantelis, T Meyer	Yes
3402	3402 - Micro-encapsulation of particles with chitosan R Carvallo, A K Sunaol	No

Supercritical Antisolvent Micronization of Minocycline Hydrochloride

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1. Summary

Micronization of minocycline hydrochloride solubilized in ethanol and with supercritical carbon dioxide as antisolvent was successfully performed using a recently built SAS apparatus. Amorphous particles of minocycline ranging from 100 to 1000 nm (depending on the operating conditions) were obtained. The mean particle size and the particle size distribution were determined by Dynamic Light Scattering. Images were obtained by Scanning Electron Microscopy (SEM) to verify the shape and the size of the micronized particles. The quality of the micronized minocycline was analyzed by HPLC. Experiments were carried out in order to study the effects of the pressure (75–130 bar), temperature (35-50 ºC) and concentration of the liquid solution (1-20 mg.mL^{-1}). Furthermore, the effect of antisolvent/solvent flow ratio on the mean particle size and particle size distribution of the obtained final product was also analyzed.

Keywords: Supercritical antisolvent, Micronization, Minocycline, Ethanol, Antibiotic.

2. Extended Abstract

Minocycline (Mcc) [1] is a second-generation long-acting tetracycline that penetrates well into the central nervous system (CNS) via blood-brain barrier. In addition to its actions as antibiotic, Mcc has other biologic effects, recently researched, such as affecting inflammation, proteolysis, angiogenesis, apoptosis, metal chelation, ionophoresis and bone metabolism [2,3]. In all biological applications of Mcc,

particle size and particle size distribution are important parameters that can influence the bioavailability, the delivery route and the pharmacokinetics of this drug.

The utilization of supercritical CO_2 (SC-CO_2) to micronize pharmaceutical compounds has become important in recent years [4]. Advantages such as high purity and low (or none) content of residual solvent in final products, environmental protection and experimental versatility justify the large application of SC-CO_2 to pharmaceutical compounds [5].

Among the several micronization techniques based on SC-CO_2, the supercritical antisolvent process (SAS) is the most suitable to bioactive substances. This technique uses both the high power of supercritical fluids to dissolve the organic solvents and the low solubility of the pharmaceutical compounds in supercritical fluids [6] to induce their precipitation from the initial liquid phase.

In this work, the micronization of minocycline hydrochloride by the SAS process, with ethanol as organic solvent and SC-CO_2 as antisolvent has been studied. Several experiments were carried out in order to evaluate the effects of pressure (75–130 bar), temperature (35-50 ºC) and concentration of the liquid solution (1-20 mg.mL^{-1}) Another effect analyzed was the ratio SC-CO_2 flow rate/ liquid flow rate that was tested for values of 5, 15 and 50 on a mass basis.

The mean particle size and particle size distribution were determined by Dynamic Light Scattering in a suspension of the micronized Mcc in water. The obtained results were amorphous particles of Mcc with mean particle sizes between 100 and 1000 nm (depending on the operating conditions) and with narrow particle size distributions.

The Mcc was subject to HPLC analysis before and after micronization and images of the corresponding powder were obtained by Scanning Electron Microscopy (SEM) in order to compare the effect of the process in the quality and morphology of the antibiotic.

The experimental evidences lead to the conclusion that SAS micronization of minocycline hydrochloride with ethanol as solvent and SC-CO_2 as antisolvent, above approximately 80 bar (the only region where it occurs), is a Q-type mixture according to the classification proposed by Reverchon et al [7], where a homogeneous supercritical phase is formed in the precipitator and particle formation results from gas-phase nucleation and sub-micrometric particles are usually obtained.

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Properties and characterization of silica aerogel-metal composites produced by a supercritical impregnation process

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1. Summary

In the present work, silica aerogel has been loaded with ruthenium acetyl acetonate ($Ru(acac)_3$) by impregnation from a supercritical carbon dioxide phase. After depressurization, the impregnated metallorganic compound has been reduced to elemental ruthenium by heat treatment. The effects of precursor concentration, pressure and depressurization mode on impregnated aerogel were studied by optical and scanning electron microscopy (SEM), X-ray microanalysis (EDX) and thermogravimetric analysis (TGA). First results showed that $Ru(acac)_3$ can be uniformly dispersed into the aerogel in the form of nanoparticles up to 6 wt%. Moreover, precursor loading and particle size are controllable by properly changing operating conditions.

Keywords: supercritical fluids, impregnation, aerogel, metal composite, ruthenium

2. Extended Abstract

Supported metal nanocomposites have attracted increasing attention in recent years due to their unique physical and chemical properties, which are suitable for a wide range of industrial applications. In particular, metals particles dispersed in a porous matrix can find use in areas as catalysis, microelectronics, magnetics, and optics. One kind of materials effectively used as substrate are silica aerogels (SA) because they have unique properties such as high porosity (90-99%), high surface area (400-1000 m^2/g), extremely low density (0.003-0.15 g/cm^3) and good thermal resistance (500 °C). A promising method to deposit metals into porous substrates is supercritical (SC) deposition that involves the dissolution of an organometallic precursor in $SC-CO_2$ and the impregnation of the substrate by exposure to this solution [1]. Subsequent chemical treatment of the impregnated substrate can result in the formation of a metal loaded matrix. The various SC-impregnation methods have been recently reviewed [2]. In this work, an autoclave loaded with accurately weighed amounts of SA monolith and $Ru(acac)_3$ was pressurized with CO_2 at 80 °C and 200 bar or 280 bar. For each run, 100 mg of $Ru(acac)_3$ were dissolved in 100 cm^3 of CO_2 with impregnation times up to 24 h. After controlled depressurization of CO_2, impregnated

SA was weighed and analyzed. The amount of precursor that can be impregnated in SA depends both on the kinetics and on the thermodynamics of adsorption of the precursor from SC-CO_2. The thermodynamics of adsorption is generally quantified by an adsorption isotherm, which relates to the concentration of the precursor in the SC-CO_2 phase to the concentration of the precursor in the solid phase. To determine the time precursor takes to reach equilibrium under given conditions of temperature and pressure, the kinetic of adsorption was first investigated. The kinetic data were obtained by determining the $Ru(acac)_3$ loading within SA at various times. As shown in figure 1, the kinetic of adsorption was relatively fast. In about 2 h the loading was 70% of the equilibrium value, and in 5 h the loading was almost equal to that at equilibrium. This fast kinetic is basically due to the high diffusivity of the supercritical phase. As shown in figure 2, the red colouring of SA after impregnation is uniform and its intensity increases with precursor loading.
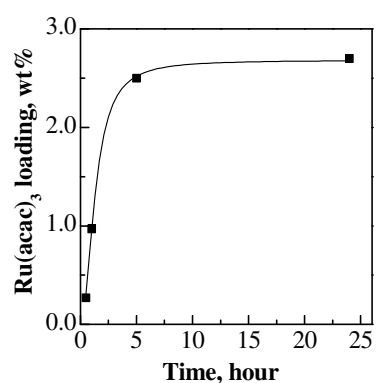
Figure 1. Kinetic curve for the adsorption of $Ru(acac)_3$ on silica aerogel in SC-CO_2 at 80 °C and 20 MPa.
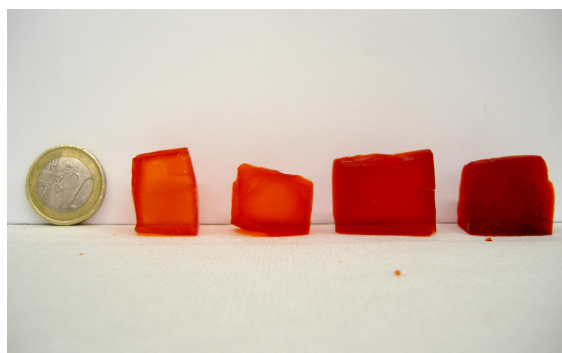
Figure 2. $Ru(acac)_3$ loaded on silica aerogel in SC-CO_2 at 80°C, 20 MPa at different loadings. From the left: 0.28, 0.97, 2.5 and 2.7 wt%.

TGA which is a precise measurement of the weight change of a solid as it is heated at controlled rate, was carried out to investigated the decomposition of the precursor and to determine the appropriate reduction temperature. First results suggested that almost all of the ruthenium in the precursor was deposited into SA in reduced form. The difference in TGA between the adsorbed and pure $Ru(acac)_3$ showed that decomposition of the precursor must be occurring in its adsorbed state without volatilization. EDX showed that elemental Ru is dispersed within the SA even after decomposition; optical and electronic microscopy revealed that the structure of composites is made by nanoparticles uniformly dispersed in the SA porous network. The particle dimensions strongly depends on the initial loading of $Ru(acac)_3$ in the SA, which depends on the concentration of the precursor in the SC-CO_2 phase according to the adsorption isotherm.

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Continuous selective oxidation of alcohols in supercritical carbon dioxide

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1. Summary

The selective oxidation of benzyl alcohol to benzaldehyde and of cinnamyl alcohol to cinnamaldehyde in supercritical carbon dioxide over Pd/Al_2O_3 was performed a continuous fixed-bed reactor. Both reactions strongly depended on the pressure and the oxygen concentration. Phase behaviour and spectroscopic studies using X-ray absorption spectroscopy and ATR-IR spectroscopy were used to gain further insight into the reaction mechanisms. Whereas the oxidation of benzyl alcohol occurred best under single phase conditions and could be improved by co-solvents such as toluene, the oxidation of cinnamyl alcohol was best performed in a CO_2-expanded liquid.

Keywords: supercritical fluids, aerobic alcohol oxidation, supported noble metal catalysts, in situ spectroscopy

2. Introduction

Supercritical fluids (SCFs) have gained considerable attention in various technical applications, particularly in extraction, separation, crystallization, and polymer technologies. More recently, their unique physical properties, which lie between those of liquids and gases, have also been exploited in the field of heterogeneous catalysis[1]. Particularly, the improved mass transport properties at the solid/fluid interface, the elimination of the gas/liquid interface compared to conventional gas/liquid reactions and the process intensification appear attractive. Along with the unique physical properties and the environmental and technical benefits, carbon dioxide, with its low critical temperature and pressure, its non-toxic behaviour and its ready availability, is the solvent of "choice". In oxidation reactions, it can additionally be regarded as a relatively "safe" reaction medium.

3. Results and Discussion

In the first part, the selective oxidation of benzyl alcohol in $scCO_2$ as an important example for a mild selective oxidation reaction is described[2,3]. Different noble metal

catalysts were tested in a continuous process and compared to conventional gas-liquid operations. A strong dependence on the pressure was observed when using $scCO_2$ as a solvent (Fig. 1) and the reaction rates greatly exceeded those observed in conventional liquids, e.g. toluene. For the selective oxidation of benzyl alcohol over $0.5\%Pd/Al_2O_3$ a turnover frequency higher than 2000 h^{-1} (rate related to the number of Pd-surface atoms) was measured.

Figure 1: Pressure dependence of the reaction rate during selective oxidation of benzyl alcohol in $scCO_2$

This rate is significantly higher than those reported up to now for selective oxidation of alcohols in liquid phase and it is attributed to improved mass transport both in the bulk fluid phase and at the solid/fluid interface. In addition, a characteristic dependence on the oxygen concentration was observed, with a maximum at about 5 – 8 mol% oxygen. The studies were supported both by kinetic investigations as well as *in situ* spectroscopic studies applying attenuated total reflection infrared spectroscopy (ATR-IR) and X-ray absorption spectroscopy (XAS)[3]. They show that the mass transport is improved and that metallic palladium is the active species in alcohol oxidation.

To widen the scope of supercritical carbon dioxide application, we have extended the approach investigating the effect of co-solvents and expanded liquids[4]. Small amounts of toluene significantly improved the catalytic performance. Moreover, continuous processing of a solid alcohol, cinnamyl alcohol, was studied[5]. Also in this case a characteristic dependence on the phase behaviour was found, but not the single phase region but a CO_2-expanded dense liquid-like phase was beneficial.

These results show that supercritical fluids and CO_2-expanded solvents may exhibit advantageous properties for heterogeneous catalytic reactions. A proper understanding using phase behaviour and spectroscopic studies is, however, required.

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Kinetics and specificity of Lipozyme-catalysed oil hydrolysis in supercritical CO_2

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1. Summary

Blackcurrant seed oil is rich in linoleic and linolenic acids. The aim of the study was to obtain by partial hydrolysis a mixture of free fatty acids of different composition than that of the hydrolyzed oil. The oil was dissolved in supercritical carbon dioxide flowing through a packed bed reactor. The catalyst was Lipozyme$^{®}$, a 1,3-specific lipase from *Mucor miehei* immobilised on a macroporous ion-exchange resin. The operating conditions were temperature 40 °C, pressure 15-28 MPa, and superficial velocity 0.1-0.7 mm s^{-1}. The composition of the hydrolyzate was determined using colorimetric method and chromatographic methods PTLC, GC, HPLC, and LC-NMR. The maximum reaction rate per unit amount of enzyme 2.6 10^{-3} mol s^{-1} kg^{-1} was achieved at maximum flow velocity and at maximum pressure. The mixture of liberated fatty acids contained higher percentage of saturated fatty acids than the hydrolyzed oil, in accordance with the fact that saturated acids occupy in triacylglycerols of vegetable oils the *sn*-1 and *sn*-3 positions. According to analytical methods PTLC+GC and HPLC (but not according to LC-NMR) the concentration of γ-linolenic acid in the mixture of free fatty acids in the hydrolyzate was by order of magnitude lower than its concentration in the oil.

Keywords: blackcurrant oil, lipase, hydrolysis, supercritical carbon dioxide, mass transfer

2. Extended Abstract

Oil hydrolysis takes place in three stages:

$$TG + H_2O \rightarrow DG + FFA$$
$$DG + H_2O \rightarrow MG + FFA$$
$$MG + H_2O \rightarrow G + FFA$$

where TG, DG, FFA, MG and G represent triacylglycerols, diacylglycerols, free fatty acids, monoacylglycerols and glycerol, respectively.

Dense carbon dioxide at the inlet of a continuous-flow packed bed reactor was saturated with oil and water. The reactor contained immobilized enzyme mixed with glass beads. As water was in surplus, the only substrate affecting the kinetics of the reaction was oil, which concentration at the enzyme is c_e. The rate of enzymatic liberation of fatty acids is simulated by Michaelis-Menten kinetics

$$v = v_{max} \, c_e/(K_m + c_e)$$

and is equal to the rate of substrate transport to enzyme

$$v = k_f \, a(c - c_e)$$

where c is the oil concentration in bulk fluid. As shown in Fif. 1, the reaction rate increased with increasing flow velocity u, which suggests that the reaction was controlled by mass transfer because the mass transfer coefficient k_f is known to increase with increasing u. The reaction rate increased with increasing pressure, too, as the oil concentration in the solvent was increasing.
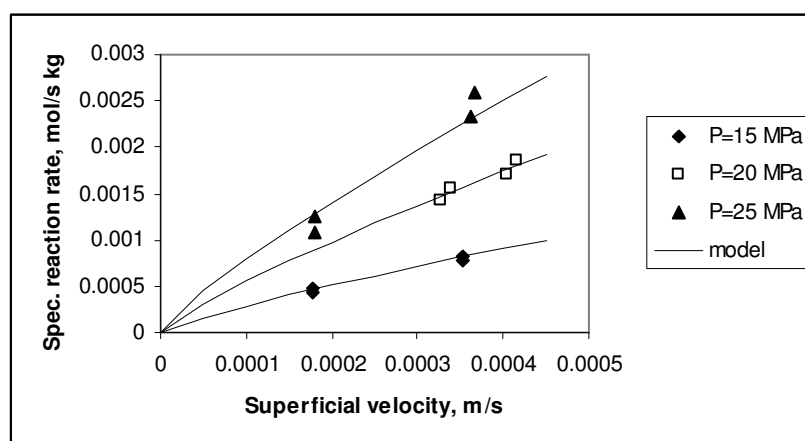
Fig. 1. Reaction rate per unit amount of enzyme versus flow velocity and pressure.

Different analytical methods (preparative thin layer chromatography followed by gas chromatography of methylesters, liquid chromatography with UV and NMR detection, and colorimetric method indicating sum of FFA) were combined to quantify the composition of the hydrolyzates. Compared to the oil, the mixture of FFA contained more palmitic and stearic acids. After PTLC separation it also contained slightly more α-linolenic acid and substantially less γ-linolenic acid. As the LC-NMR method indicated no change in the composition of lnolenivc acids, this aspect will be further examined.

The Role of Pressure at the Limit of the Dispersion Stability in the Polymerization of Methyl methacrylate in Supercritical CO2.

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1. Summary

In the quest for the development of sustainable chemical processes including supercritical fluids we have employed the technique of reaction calorimetry to monitor the evolution of the free-radical dispersion polymerization of methyl methacrylate in supercritical carbon dioxide. Considering the particularities of supercritical fluids, this technique proves to be very robust, as shown by the direct comparison of the results during the nucleation period with previous reported results from other techniques. A series of experiments at marginal dispersion stability reveal the effect of the pressure in the monomer partitioning between the two formed phases and in the dissolution of the stabilizer macromolecules. These in turn are found to affect the pressure evolution during the reaction. The experimental results are combined with a theoretical approach to provide a comprehensive explanation of this evolution.

Keywords: supercritical, calorimetry, MMA, polymerization, high pressure

2. Extended Abstract

The past two decades have seen an unprecedented scientific interest on the application of supercritical fluids as solvents for polymerization reactions. The motivation has been the effort to substitute many of the organic solvents used today, having been classified as volatile organic compounds, by more environmentally friendly substances like supercritical carbon dioxide. Numerous systems have been investigated but the dispersion polymerization of methyl methacrylate is without doubt the one that has attracted the most attention.

In our study we have employed the well-established technique of reaction calorimetry to monitor the evolution of the polymerization reaction of methyl methacrylate in supercritical carbon dioxide. The results are in very good agreement with the previously reported particle formation mechanism and allow for the first time the measurement of the heat released by the reaction during the nucleation period. Figure 1 shows a qualitative comparison between the average particle diameter evolution measured by O'Neill et al. using turbidimetry and the reaction heat rate (O'Neill 1998).

A series of experiments have been also explicitly designed to investigate the region where the dispersion is at its limit of formation. The latter was initially observed as a step in the reaction acceleration. It was shown that this deceleration is strongly connected to the balance between the reaction rates in the two formed phases, namely the CO2-rich phase and

the polymer-rich phase. This balance is determined by the monomer partitioning in the reaction phases, which in turn is affected by the pressure.
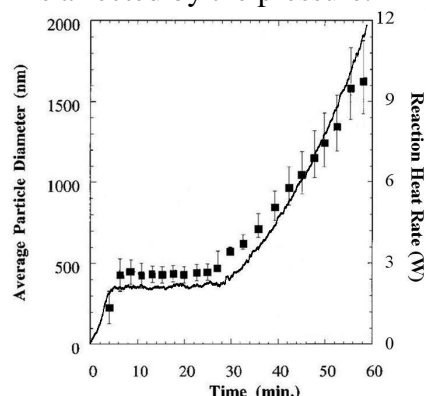
Figure 1. Qualitative comparison of the Average Particle Diameter (filled squares, MMA in scCO2, at 65°C, 5% PDMS-mMA/MMA, ~20% MMA/CO2, (O'Neill 1998)) and the Reaction Heat Rate evolution (line, MMA in scCO2, at 65°C, 10% PDMS-mMA/MMA, 25% MMA/CO2 (this study)) during the nucleation phase.

During the same experiments the pressure variation was also monitored and based on the experimental results and theoretical considerations by Lepilleur and Beckman it is explained why at low initial pressures the final pressure is higher and vice versa (Figure 2) (Lepilleur, 1997). During the polymerization reaction, the net volume contraction is estimated to be around 20% of the original monomer volume, thus a decrease in the system pressure should be expected. However, the pressure evolution has been found to depend on the monomer partitioning between the two phases, which affects the non-ideal mixing molar volumes of the reactants.
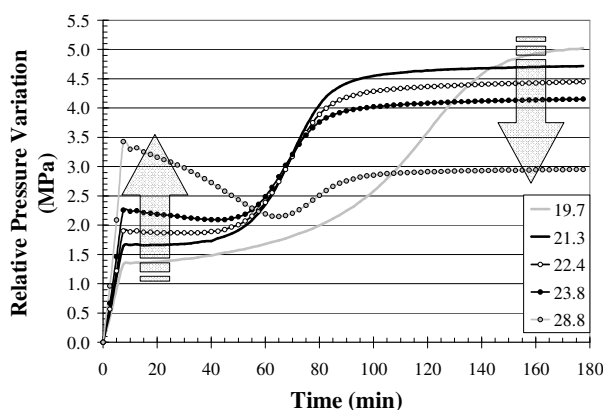
Figure 2. Relative pressure variation for different initial reaction pressure experiments.

In conclusion, important information can be obtained from, monitoring the polymerization with the reaction calorimetry technique. The experimental results serve not only for kinetics analysis but also for performing safety analysis studies.

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Session T1-P: Theme-1 Poster Session

1. Modelling, Design & Analysis of Processes with Ionic Liquids (T1-1P)

Abstract Number	Paper Title & Authors	Included
3884	Equilibria in the mixed solvent system Glycol-NaOH-CO2-Water applied to corrosion modelling P L Fosbøl, K Thomsen, E H Stenby	Yes
803	Selection of ionic liquids for aromatic/aliphatic separations and determination of LLE data supported by COSMO-RS A B Hansmeier, M M Ruiz, G W Meindersma,A B de Haan	No
2036	The se of ionic liquids as efficient media in olefin/paraffin separations A Ortiz, A Ruiz, D. Gorri, I Ortiz	Yes
2048	Amino-acid recovery using ionic liquids: Partitioning in water + ionic liquid systems O Rodríguez, P P Madeira, E A Macedo	Yes
2967	Multi-functional catalysts for process intensification R Knapp, T. Müller, J A Lercher	No
3205	Ionic liquids as clean alternative to organic solvents for lipase-catalyzed ester synthesis in non-conventional media F J Hernandez-Fernandez, A P de los Rios, D Gomez, F. Tomas-Alonso, M Rubio, G Víllora	Yes
4137	Density prediction for ionic luquids using COSMO-RS J Palomar, V R Ferro, J Torrecilla, F Rodriguez	Yes

2. Environmental Engineering & Management (T1-3P)

Abstract Number	Paper Title & Authors	Included
121	Reduction in toxicity of the slag generated during the secondary lead process G M F Gomes, L D Zen	Yes
331	The use of an oxidative pre-treatment method for increasing the efficiency of anaerobic digestion of waste activated sludge R Dewil, L Appels, J Baeyens	yes
456	Power consumption in a mineralization of direct red 23 azo	Yes

dye in a sequencing batch reactor
F Morales-Guzman, R M Melogza-Aleman, R J Romera

1593	Mineralization of organic compounds in wastewater by O3 & O3/H2O2 advanced oxidation systems A Rodriguez, R Rosal, J A Perdigon, E Garcia-Calvo, P Leton, K Boltes, S Gonzalo, A L Petre, A Fernandez-Alba, M J Martinez Bueno, M Mezcua	Yes
579	Basic dyes biosorption onto Azolla filiculoides: equilibrium and kinetic modelling By Dr TVN PADMESH (Sathyabama Univeristy, India)	No
683	Double-pass flat-plate solar air heaters with external recycle C D Ho, R C Wang, T C Chen	Yes
792	Carbonization of empty fruit bunch using hydrothermal method S Inoue	Yes
1043	Application of self-organising map (SOM) artificial neural networks for the chemical assessment of sediment quality M Alvarez-Guerra, C Gonzalez-Pinuela, A Andres, J R Viguri	Yes
1115	1115 - Green technology for conversion of food scraps to biodegradable thermoplastic polyhydroxyalkanoates R Maddali	No
1430	Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of uranium ions onto Cystoseria indica algae biomass M H Khani	No
1732	Treatment of textile dyes effluents by laccase mediator system A P M Tavares, R O Cristovao, J M Loureiro, R R Boaventura, E A Macedo	Yes
1774	Treatment of oil waste water toolkit A Troyankin, O Akhacheva, N Menshutina, O Sidorkin, Y Avramenko	Yes
2376	Release of K from the system: K-Ca(-Si)-P – The Effects of the Ca/Si- and Ca/P-ratios A Novakovic, F Frandsen, P A Jensen, S van Lith, L B Holgersen	Yes
2456	Information system for phosphorus-containing compounds P Seferlis, J Klemes, I Bulatove, P Kapustenko, L Puigjaner, A Bojarski, R Suleymanov, E Koltsova	Yes
3138	Towards sustainability in conceptual process design: Petroleum refinery F Emun, M Gadalla, L Jimenez	No
3491	CWAO of phenol over activated carbon catalysts with hydrogen peroxide as promoter A Quintanilla, J A Casas, J J Rodriguez	Yes
4014	4014 - Arsenite Adsorption Upon Activated Carbon And Its Pva-composite N Deveci, A Aydin	Yes

3. Sustainable & Clean Technologies-I: Extraction & Remediation (T1-4P)

Abstract Number	Paper Title & Authors	Included
265	Removal of acid orange 7 (AO7) by UV/H2O2 oxidation in the presence of dye auxiliaries A Anglada, M J Rivero, A Uritaga, I Ortiz	Yes
323	Optimal water purification using low grade waste heat – an ecological proposal R J Romeroa, A Rodrígueza, M L Domíngueza, A Huicocheab	Yes
454	Removal of heavy metals by ultrafiltration X Bernat, I Sanchez, F Stuber, C Bengoa, A Fortuny, A Fabregat, J Font	Yes
765	Evaluation of the capacity of adsorption of CO2 in commercial zeolites on PSA pilot plant Y Lima, P Guimaraes, S Bello, L Carvalho, D Lisboa, R Carvalho, E. Santos	Yes
1957	Color removal from textile effluent using Azadirachta indica leaf powder as an adsorbent A P S Immich, S G Ulson de Souza, A A Ulson de Souza	Yes
2158	Catalytic wet oxidation for abetement of textile dyes S Rodríguez, A Santos, P Yustos, M de Gracia, F Garcia-Ochoa	Yes
2361	Impact of non-biodegradable contaminants on long term performance of semi-industrial-scale MBR (membrane bioreactor) for dilute swine wastewater with direct reuse of treated water N Prado	No
2364	Removal of benzalkonium chloride by polymeric adsorbent I Turku, T Sainio, E Paatero	Yes
2437	Modeling of the imbition of polypropylene fiber cloth with emulsions J Sek	Yes
3701	Aplicability of the spouting regime for drying of biomass wastes in conical spouted beds with a draft tube M J San Jose, S Alvarez, A Ortiz, A Morales, J Bilbao	Yes
3851	Removal of As, Cd, Cr, Cu, Ni and Zn from polluted water using an iron based sorbent H Genç-Fuhrman, P Wu, Y Zhou, A Ledin	Yes

4. Sustainable & Clean Technologies-II: Energy Production (T1-5P)

Abstract Number	Paper Title & Authors	Included
790	Biodiesel production by thermomyces lanuginosus and rhizomucor miehei immobilised in hydrophilic polyurethane foam N Dizge, D Y Koseoglu, B Keskinler	Yes
1035	Enzymatic transesterification of Hungarian rapseed and sunflower oils M Krár, S Kovács, M Neményi, J Hancsók	Yes

2020	Lipase-catalyzed synthesis of biodiesel J M Cerveró, J R Alvarez, S Luque, J Coca	Yes
3292	Reduction of stillage 's volume in the production of ethanol by recirculation G A Castro, L A Caicedo	Yes
3561	Development of an ethanol production process with stillage recycling at bench-scale G A Castro, I D Gil	Yes

5. Sustainable & Clean Technologies - III: Combustion & Emission (T1-6P)

Abstract Number	Paper Title & Authors	Included
882	Modeling and prediction of ammonia emission from field-applied animal manure Y-I Lim, Y-S Moon	Yes
1486	1486 - Wood in pulverized fuel power plants: Char characterization and char combustion M Dall'Ora, P A Jensen, A D Jensen	Yes
1747	Production and CO2 adsorption characteristics of activated carbon from Bamboo by CO2 activation method Y-Cl Bak, J-H Choi	No
1999	Reduction of NO by acetylene soot T Mendiara, m U Alzueta, a Millera, R Bilbao	Yes
2178	Catalyst selection for the coupled methanol/paraffins cracking process D Mier, A T Aguayo, J Ereña, A Alonso, J Bilbao	Yes
3320	How to deal with one of the main obstracles for an increased use of CO2 neutral biomass in power plant boilers - Optimal ash deposit removal in straw fired boilers P A Jensen, H Zhou, F Frandsen	Yes

6. SCF as Solvent Substitutes (T1-8P)

Abstract Number	Paper Title & Authors	Included
2879	Novel PVDF-HFP membranes tailored by supercritical drying process S Cardea, A Gugliuzza, C Rapuano, M Sessa, M C Aceto, E Drioli, E Reverchon	Yes
356	Supercritical extraction of valeriana officinalis L. roots. Mathematical modeling and experiments A R Salimi, S Fatemi, H zakizadeh, A Safaralie	No
528	528 - Supercritical fluid extraction, Hydrodistillation and Soxhlet extraction of the aerial part of winter savory: Comparative evaluation of the extraction method on the chemical composition A C Grosso, M A Tavares-Cardoso, A C Figueiredo, M Moldào-martins, J Burillo, J S Urieta, J G Barroso, J A	Yes

	Coelho, A M Palavra	
559	Acid heterogeneous catalysis in supercritical media : application to isobutane alkylation by light olefins M Montillet, D Guillaume, N Essayem	Yes
741	Predicting solubility of tributyl phosphate in supercritical carbon dioxide R Orouj, H Abolghasemi, M Mahdavian, M Tabasi	Yes
2471	2471 - Extraction of heavy metals from CCA treated wood by supercritical fluids E G Søgaard, D A Ankrah	No
2804	Extraction of phytoecdysones with ethanol-modified supercritical CO2 H Sovova, M Sajfrtová, M Pavlik	Yes
3344	Comparison of predictive models for determination of supercritical fluids solubility in heavy oils C E P Siqueira Campos, P W Falcào, F L P Pessoa, A M C Uller	Yes

Equilibria in the mixed solvent system Glycol-NaOH-CO_2-Water applied to corrosion modelling

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1. Summary

Gas produced in oil production is saturated in water (also known as wet gas). It contains CO_2 and the water condenses at the cold pipe wall during transportation. NaOH and glycol (MEG) or methanol is injected to prevent gas hydrates and corrosion. CO_2 dissolves in the water-MEG-NaOH liquid phase and the electrolytes will corrode the lower peripheral part of the pipeline. Various protective corrosion products are produced, depending on the chemical environment.

Results will be shown of modelling the corrosion products using the extended UNIQUAC activity coefficient model to predict dissolution of corrosion products and corrosion under diffusion control showing the stability of the products and the concentrations at which diffusion control may prevent pipeline corrosion.

Keywords: CO_2 Corrosion, Glycol phase equilibria, carbonate solubility, extended UNIQUAC modelling

2. Modelling CO_2 corrosion

CO_2 corrosion products are the focus of this study. It is known that $FeCO_3(s)$ forms as a product and behaves as a diffusion barrier of the corrosive components and prevents iron from dissolving.

The chemical environment of a typical pipeline has an ionic strength (I) of approximately 0.1 to 10 which clearly indicates high non-ideality of the liquid phase. Electrolytic diffusion processes deviate strongly from ideal conditions at ionic

strengths above 1. All existing corrosion models, both simple electrochemical and mechanistic models assume ideal liquid phase. All lack the correct description of the diffusion processes, bulk activities, and surface activities/concentrations.

It is clear that an advanced electrolytic model is required, but most existing models do not produce accurate results at ionic strengths higher than 6 mol/kg. The extended UNIQUAC has proven to be able to do this.

In this work we seek to get a better understanding of the CO_2 corrosion through experimental work and modelling.

The experimental work focuses on the corrosion products in the complicated CO_2-NaOH-H_2O-MEG-Fe system. SLE (Solid-Liquid-Equilibrium) experiments have been carried out in the mixed solvent electrolyte subsystem $NaHCO_3$-Na_2CO_3-H_2O-MEG.

The modelling is done through correlation of the experimental VLE (Vapour –Liquid-Equilibrium) and SLE data using the Extended UNIQUAC activity coefficient model for electrolytes.

The use of ionic liquids as efficient media in olefin/paraffin separations.

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1. Summary

In this work we have consider in one hand the separation of olefins from corresponding paraffins which has been investigated widely in literature (the most promising alternative appears to be π-complexation with silver ions) , and in the other hand the substantial potential as diluents in separations of RTIL (room temperature ionic liquids). Combining both concepts we have proposed two different study´s case on the basis of two industrial real situations

Keywords: Ionic liquids, π-complexation, separation, olefins, paraffins

2. Extended Abstract

The separation of alkenes from hydrocarbon mixtures is one of the most important processes in the petrochemical industry. Their separation, a difficult process due to the similarity in molecular sizes and physical properties, is currently carried out by distillation, a high energy intensive process (Safarik and Eldridge, 1998). Hence, there is a strong incentive to develop new processes for their separation with lower energy cost. To improve the energy efficiency of this separation process, absorption using chemical complexing agents such as copper or silver salts for selective olefin removal has been investigated .

 Separation by π-complexation is a subgroup of chemical complexation where the mixture is contacted with the second phase, which contains a complexing agent. The advantage of chemical complexation is that the bonds formed are stronger than those by van der Waals forces alone, so it is possible to achieve high selectivity and high capacity for the component to be bound; at the same time, the bonds are still weak enough to be broken by using simple engineering operations such as raising the temperature , decreasing the pressure or use a sweep gas (Wentink et al., 2005).
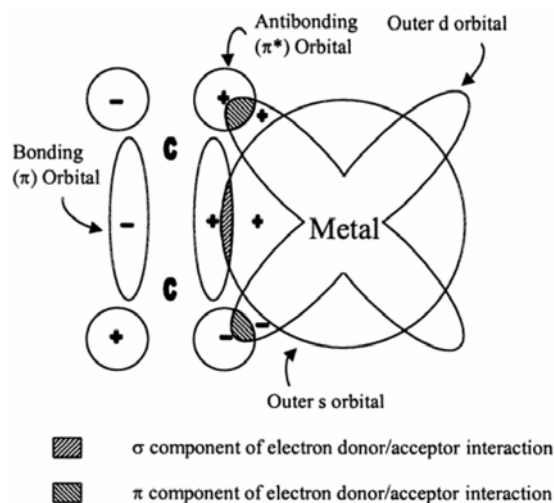
Figure 1. Model for silver ion-olefin complex (Safarik and Eldridge, 1998)

Recently, considerable attention has been drawn to room temperature ionic liquids (RTIL) as green alternative to common organic solvents. RTIL are organic salts with melting points at or below room temperature. They have substantial potential as diluents in separations and their application is an important step in the design of environmentally safe separation processes, because ionic liquids are considered to be non-flammable, non-toxic and non-volatile.

In this work we present two study cases. The first one is the removal of a diolefin (cyclopentadiene) solved in a paraffin (cyclohexane, which is used as a solvent and reaction medium in the manufacture of different types of synthetic rubbers where cyclopentadiene is an impuritie´s process), both in liquid fase. The second one is the separation of propane/propylene mixtures, of great commercial importance to the chemical and petrochemical industry. In our work it was found that the recovery of the olefins via silver complexation can be carried out in both aqueous and ionic liquid media. On the other hand, it was shown that BmimBF$_4$ containing silver ions has higher sorption capacity for olefins than the corresponding aqueous solution.

Acknowledgements

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Amino-acid recovery using ionic liquids: Partitioning in water + ionic liquid systems

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1. Summary

Partitioning of a series of dinitrophenylated amino-acids was studied experimentally in the system ionic liquid + water, at 23 ºC, using 1-hexyl-3-methylimidazolium tetrafluoroborate, [C_6mim][BF_4]. The pH of the initial aqueous solution was fixed at 7.4 using a universal phosphate buffer. From the partitioning of this series of solutes the free energy of transfer of a methylene group was calculated. This provides an effective measurement for the relative hydrophobicity of the equilibrium phases. DNP-amino-acids partition preferentially to the ionic liquid phase and this partition increases with the size of the alkyl chain of amino-acid. The relative hydrophobicity of conjugated phases is higher than in other biphasic systems used in biotechnology.

Keywords: ionic liquids, partitioning, amino-acids.

2. Extended Abstract

Ionic liquids are defined as electrolytes with melting points around or below ambient temperature. Research with ionic liquids has been growing in the last 10 years, especially as reaction media and as solvents for separations. Biomolecules (proteins, enzymes…) are usually produced at industrial scale using enzymatic or fermentation processes. Separation and purification steps are difficult and expensive, but high purity is often needed for biomolecules' applications. Information regarding the use of ionic liquids as solvents for the separation and/or purification of biomolecules is still scarce. We present here some preliminary results on the partitioning of a series of dinitrophenylated amino-acids between aqueous and ionic liquid phases.

2.1. Experimental

N-(2,4-dinitrophenyl)glycine, N-(2,4-dinitrophenyl)-L-alanine, N-(2,4-dinitrophenyl)-DL-n-valine, N-(2,4-dinitrophenyl)-DL-n-leucine, and N-(2,4-dinitrophenyl)-DL-α-amino-n-caprylic acid were obtained from Sigma. Ionic liquid [C_6mim][BF_4] was provided by Green Solutions (Vigo, Spain). Water (GR for analysis) was obtained

from Merck. Universal phosphate buffer, NaPB, $0.11m$ was prepared with reagent-grade Na_2HPO_4 and NaH_2PO_4 (pH = 7.4). Aqueous stock solutions of DNP-amino-acids were prepared with a concentration of ~0.2 wt%.

Partitioning experiments were performed in 2 ml tubes, mixing 1.4 g of NaPB and 0.27 g of ionic liquid. Five replicates were prepared and 0 to 40 µl of amino-acid stock solution were added. Tubes were thoroughly vortex mixed for 2 min. and centrifuged at 10^4 rpm for 30 min. Samples of top and bottom phases were pipetted and diluted conveniently for analysis by UV-Vis spectroscopy. The partition coefficient was calculated as the slope of the straight line obtained when the absorbance in top phase (aqueous) is plotted against that in bottom phase (ionic liquid), corrected with dilution factors. The increasing concentration of solutes allowed to check aggregation effects. Preliminary experiments in water + $[C_6mim][BF_4]$ systems showed aggregation effects for total concentrations of DNP-amino-acids >0.004 wt% (Figure 1). Thus, solute concentrations in partitioning experiments were below 0.004 wt%.

2.2. Results and Discussion

Figure 2 shows the logarithm of partition coefficient K obtained against the number of equivalent methylene groups in the aliphatic side-chain of the DNP-amino-acids, n^oCH_2. Their negative value indicate the preference for ionic liquid phase, which increases with the size of the amino-acid. The free energy of transfer of a methylene group between the equilibrium phases, $\Delta G(CH_2)$, can be calculated from the slope in Figure 2 using the following equations[1]:

$$ln\ K = C + E·n(CH_2) \tag{1}$$

$$\Delta G(CH_2) = -R·T·E \tag{2}$$

where C and E are constants, R is the universal gas constant and T is the absolute temperature. The free energy of transfer obtained, -0.367 kcal/mol, is of the same magnitude than for polymer-salt aqueous two-phases systems and ~20 times that for polymer-polymer aqueous two-phases systems[2].
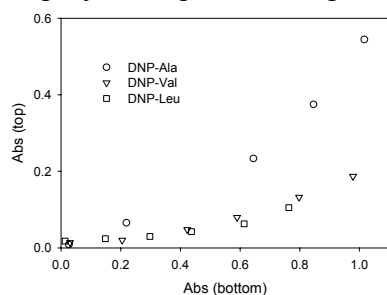
Figure 1: Aggregation effects for DNP-amino-acids.
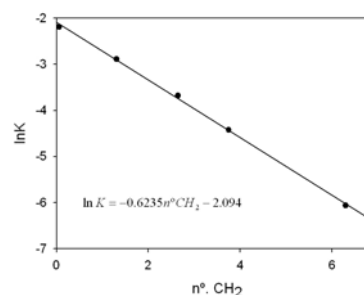
Figure 2: Partition coefficients for DNP-amino-acids.

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Ionic liquids as clean alternative to organic solvents for lipase-catalyzed ester synthesis in non-conventional media

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1. Summary

This work studies the synthesis of aliphatic esters by transesterification from 1-butanol and vynil esters using *Candida antarctica* lipase B (CALB) in ionic liquids. The effect of various parameters such as pH, temperature, acyl-donor and additives on the enzymatic activity and selectivity was studied. The IL medium selected for this study has been 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim$^+$][PF$_6^-$]). The reaction was also carried out in a common water-immiscible organic solvent, n-hexane, in order to use it as reference solvent to study the suitability of this IL for the proposed reaction.

Keywords: ionic liquids, lipase, ester synthesis, additives, stability.

2. Extended Abstract

In nature, enzymes act as catalysts of living systems and are designed to function in aqueous solutions. However, anhydrous conditions are needed for synthetic transformations using enzymes. The use of organic solvents as non-aqueous environments offers the possibility of carrying out synthetic reactions by hydrolytic enzymes, increasing the solubility of organic substrates [1]. However, organic solvents are usually volatile liquids that may evaporate into the atmosphere with a detrimental impact on the environment and human health. The use of ionic liquids in biocatalytic processes has recently gained much attention as an environmentally attractive alternative to classical organic solvents [2], and they have been seen to be good solvents in a wide variety of biochemical processes [3]. Ionic liquids are organic salts that are liquid close to room temperature. They normally consist of an organic cation, being the most commonly used dialkylimidazolium and tetraalkylammomiun salts, and a polyatomic inorganic anion (e.g. BF$_4^-$, PF$_6^-$). From an environmental point of view, the most important properties of ionic liquids are their negligible vapour pressure and their good chemical and thermal stabilities.
This work studies the synthesis of aliphatic esters by transesterification from 1-butanol and vynil esters using *Candida antarctica* lipase B (CALB) in ionic liquids. The efficiency of the catalytic action was measured by two parameters, the synthetic rate and the ratio between this

parameter and the acyl-donor consumption rate (selectivity). The effect of various parameters such as pH, temperature, acyl-donor and additives on the enzymatic activity and selectivity was studied. The IL medium selected for this study has been 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim$^+$][PF$_6^-$]). The reaction was also carried out in a common water-immiscible organic solvent, n-hexane, in order to use it as reference solvent to study the suitability of this IL for the proposed reaction. It has been observed that at all assayed operating conditions, the enzymatic activity in [bmim$^+$][PF$_6^-$] was higher than that obtained in hexane. It was also found a strongly influence of the pH on the synthetic activity and selectivity of the lipase in [bmim$^+$][PF$_6^-$], showing a maximum at pH 7, while an increase in the reaction temperature lead to an increase in both parameters in the experimental interval (30 - 70 ºC).

A strong influence of the nature of different vinyl esters (RCOOCHCH$_2$, R= CH$_3$-, CH$_3$CH$_2$-, CH$_3$(CH$_2$)$_2$-, CH$_3$(CH$_2$)$_8$-, CH$_3$(CH$_2$)$_{10}$-, CH$_2$CH-, CH$_2$C(CH$_3$)-, Ph-) used as acyl-donor on both activity and selectivity was found. When the alkyl chain length of the acyl donor was increased, the synthetic activity of CALB showed a bell curve, with a maximum at an 4-carbon chain length of the vinyl ester (vynil butyrate).

In order to improve the use of this solvent as reaction media, different treatments were carried out on the ionic liquid, such as equilibration with NaHCO$_3$ or Na$_2$CO$_3$ solution until neutral pH, or adding triethylamine to the reaction mixture. The lipase activity was greatly enhanced in the IL treated in these ways.

Finally, the study was extended to seventeen water-immiscible and water-miscible 1,3-dialkylimidazolium based ionic liquids using vinyl butyrate as acyl donor at 30 ºC and pH 7. It has been observed that in all the water-immiscible ionic liquids assayed the enzymatic activity and selectivity were higher than the obtained in hexane. However, in water-miscible ionic liquid the activity result to be smaller than that in hexane. In general, for the ILs based on the same anion, the synthetic activity were gradually enhanced by the increase in hydrophobicity of the ILs, Furthermore, it has been observed that the activity of CaLB is greater in ionic liquids containing anions with lower nucleophilicity.

Moreover, to know the direct influence of the IL medium on the enzyme, the stability of the lipase has been studied by the incubation of the enzyme at 30 ºC. It has been observed that the increase in the enzyme´s half-life seemed to be in agreement with the increase in the hydrophobicity of the ionic liquid. In addition, the enzyme showed potentiality of recycled use in the ionic liquid.

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Density prediction for ionic liquids using COSMO-RS

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1. Summary

The specific density of forty imidazolium based ionic liquids were predicted using COSMO-RS model, a thermodynamic model based on quantum chemistry calculations. A molecular model of ion-pairs was proposed to simulate the pure ionic liquid compounds. These ion-paired structures were generated at B3LYP/6-31++G** by combining the cations 1-methyl- ($Mmim^+$), 1-ethyl- ($Emim^+$), 1-butyl- ($Bmim^+$), 1-hexyl- ($Hxmim^+$) and 1-octyl-3-methylimidazolium ($Omim^+$) with the anions chloride (Cl^-), tetrafluoroborate (BF_4^-), tetrachloroferrate ($FeCl_4^-$), hexafluorophosphate (PF_6^-), bis(trifluoromethanesulfonyl)imide (Tf_2N^-), methylsulfate (MSO_4^-), ethylsulfate ($EtSO_4^-$) and trifluoromethanesulfonate ($CF_3SO_3^-$), using the quantum chemical software Gaussian03. Excellent agreement with the available experimental measurements was obtained, showing the capability of current computational approach to describe the effect of the anion nature and cation substituent on the volumetric properties of this family of ionic liquids. Thus, calculated and experimental density values of ionic liquids (and also other common solvents) were fitted by linear regressions with correlation coefficients $R > 0.99$ and standard deviations $SD < 20$ kg/m^3. The good predictions of COSMO-RS indicated the suitability of the ion-pair model to describe intermolecular interactions of pure ionic liquids.

Keywords: Ionic liquids, COSMO-RS, ion-pair model, property prediction, density.

2. Extended Abstract

The room temperature ionic liquids (ILs) have gained popularity in the last years as suitable green solvents (Welton, 1998). At current stage of development of ILs, the application of predictive theoretical models to estimate their thermophysical properties is of great interest. Recently, Klamt (2005) have developed a quantum chemical approach (COSMO-RS) for the prediction of the thermodynamic properties of pure and mixed fluids using only structural information of the molecules. In this work, we perform for the first time COSMO-RS calculations to predict the density of

pure ionic liquid solvents. For this purpose, we use the ion-paired structures as molecular model to simulate the pure ionic liquids, which are optimized at high quantum-chemical level. In order to validate the capability of COSMO-RS computational approach, density predictions for ten 1-alkyl-3-methylimidazolium ionic liquids (XmimBF$_4$ and XmimPF$_6$ series) are compared to those of common organic solvents (alcohols and water) in Figure 1A. As can be seen, the correspondence between experimental and COSMO-RS predictions is very good, for which the root-mean-square deviation (RMSD) is lower than 1.7 %. The linear regression fit presents an excellent correlation coefficient, R=0.999, and a slope of 1.01. When the analysis is generalized to the wide collection of 1-alkyl-3-methylimidazolium ionic liquids (Figure 1B), we also observe an excellent prediction for twenty three ILs whose experimental density is available in the bibliography (http://ilthermo.boulder.nist.gov), obtaining a value of RMSD of 3.0 %. The linear relationship between experimental and COSMO-RS density values shows a correlation coefficient of 0.995 and a slope of 1.14. It is important to note that current predictions of ionic liquid densities are able to reproduce the tendencies related to anion and cation nature effects. Thus, the increase of the alkyl chain length of the cation rise to significant lower densities, while the choice of the anion has also a noteworthy effect on ionic liquid densities, increasing for a fixed cation in the sequence $Cl^- < BF_4^- < EtSO_4^- < MeSO_4^- < CF_3SO_3^- < PF_6^- < FeCl_4^- < Tf_2N^-$ for each 1-alkyl-3-methylimidazolium series studied. In sum, accurate specific density of forty ionic liquids has been calculated using COSMO-RS method with a molecular model which simulates the pure compound in terms of ion-paired structures. The capability of the volumetric property prediction for ILs by the proposed computational approach is reported as high as that for common organic solvents.

Figure 1: Comparison of experimental and COSMO-RS calculated values of specific density for some common solvents (alcohols and water) and imidazolium based ILs at 298 K.
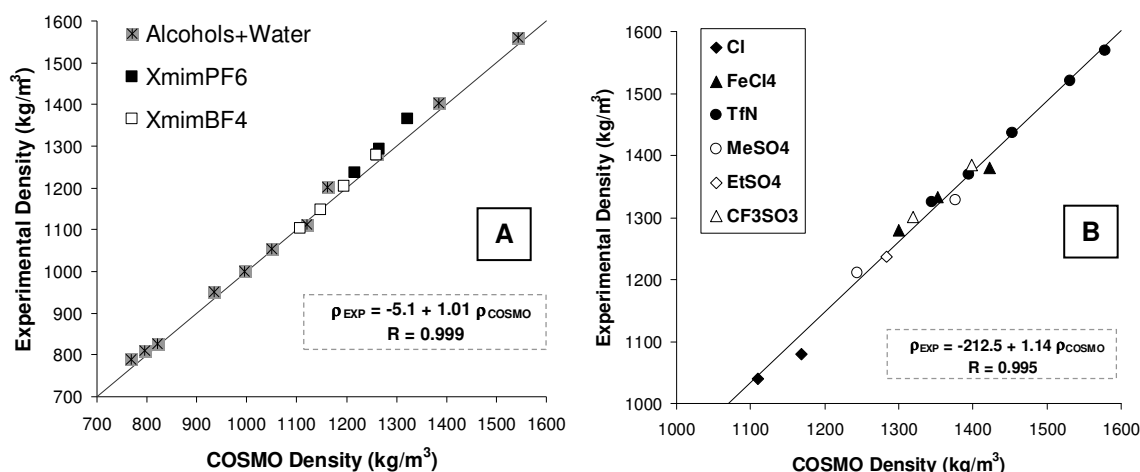
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Reduction in Toxicity of the Slag Generated during the Secondary Lead Process

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1. Summary

The secondary lead process in lead-acid battery scrap recycling generates a large amount of waste during the foundry stage, when lead is re-obtained in its metallic form. In this work, an analysis of the slag was carried out in order to determine its chemical, mineralogical and structural composition, and to measure its effect on the environment. As a result of this, it was possible to identify certain deficiencies in the recycling process, and suggest ways of improving it. The overall aim was to optimize the process in order to reduce the toxicity of the slag, and, subsequently, its environmental impact.

Keywords: secondary lead, slag, characterization, toxicity

2. Extended Abstract

On the basis of three different charges that usually compose a batch for the rotary furnace, it was done the characterization of the slags and the optimization of one charge.

2.1 Slag characterization

Table 1 presents the results for the main elements according to their elemental composition by means of ICP-AES on a Spectro (Spectroflame Modula). The leaching test results for the lead, performed slag in accordance with Brazilian norm ABNT NBR 10005, are given in Table 2, as well as the pH values when the slag is generated (initial pH), and with a storage period over 6 weeks (final pH).

Mineralogical analysis was carried out using a Siemens D5000 X-ray diffractometer. The predominant form found was FeO and Fe_3O_4. Lead was found in its metallic form and as $PbSO_4$. Sulphur was found associated to iron and sodium, as FeS and $Na2S$. Some samples of the slags were subjected to scanning electron microscopy (SEM) in conjunction with energy-dispersive spectroscopy (EDS). The presence of $PbSO_4$ and PbO was detected.

Type	G		PG		P	
Elem.	% in mass	Std. Dev.	% in mass	Std. Dev.	% in mass	Std. Dev.
Pb	1,3	0,4	1,7	0,7	3,1	2,7
Fe	57,8	3,3	50,8	4,4	42,4	3,0
S	7,1	1,3	6,9	1,0	7,6	2,1
Na	8,6	1,9	5,0	0,9	10,4	3,1

Table 1: Elemental analysis of the slags

Slag	G	PG	P
Pb (mg/L)	0,40	0,78	0,18
initial pH	13,2	12,8	13,5
final pH	11,2	11,1	11,4

Table 2: Pb leaching test results

2.2 Optimization of the process

In order to improve the process, the coke (carbon) and flux additions (Na_2CO_3) to the PG charge were optimized. Figure 1 compares the average for the previous PG slag and the one that had the generating batch optimized.
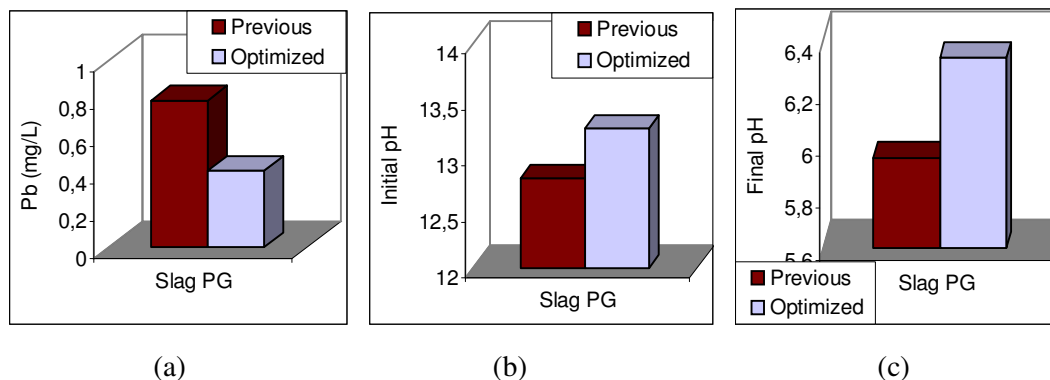
Figure 1: (a) Pb leaching results for previously generated and optimized slags; (b) Initial pH; (c) Final pH (storage period over 6 weeks).

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The use of an oxidative pre-treatment method for increasing the efficiency of anaerobic digestion of waste activated sludge

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1. Summary

During the anaerobic digestion of sewage sludge an energy rich biogas is formed which can be valorized for the production of heat or electricity. The total biogas yield of this process is however limited due to the presence of a large amount of non-biodegradable (refractory) organic material in the sludge. In this study several advanced oxidation processes (AOPs) are tested for their use as a chemical pre-treatment step. The results show that these methods have the ability to degrade and solubilise the refractory components to a large extent and hence increase the biogas production. The methane concentration in the gas (and hence its calorific value) remains moreover unchanged.

Keywords: anaerobic digestion, advanced oxidation process, biogas, waste activated sludge

2. Extended Abstract

The Waste Activated Sludge (WAS) process has the inherent drawback of producing large amounts of sludge, which should be disposed of. The anaerobic digestion of sludge is widely applied because of several advantages: the sludge quantity is decrease by 25-30% due to the decomposition of organic material, part of the pathogenic micro-organisms are destroyed and an energy rich biogas is produced.

During anaerobic digestion, the rate limiting step is the hydrolysis reaction, which breaks down insoluble high molecular weight organic molecules into small, soluble and readily available material. Pre-treatment methods which achieve a significant breakdown of refractory COD hence have the potential to enhance the biogas production (Tiehm et al., 2001).

In this study, the sludge was subjected to three advanced peroxidation processes (AOPs), namely reactions with the common Fenton reagents, with peroxymonosulphate (POMS) and using dimethyldioxirane (DMDO). Previous studies revealed that AOPs effectively disintegrate sludge flocs by affecting the extracellular polymeric substances (Neyens et al., 2004).

The results show that the concentration of soluble BOD and COD significantly increased, as well as the BOD/COD ratio. This observation confirms the disintegration of organic material during the treatment and the conversion of COD into BOD.

Examining the biogas production during digestion, a considerable increase is observed. The evolution of biogas production of sludge pre-treated with POMS and DMDO, compared to untreated (blank) sludge is represented as example in Figure 1. The figure clearly shows that an increase by a factor 3 is possible. The surplus biogas which is formed largely compensates the costs of chemicals involved.
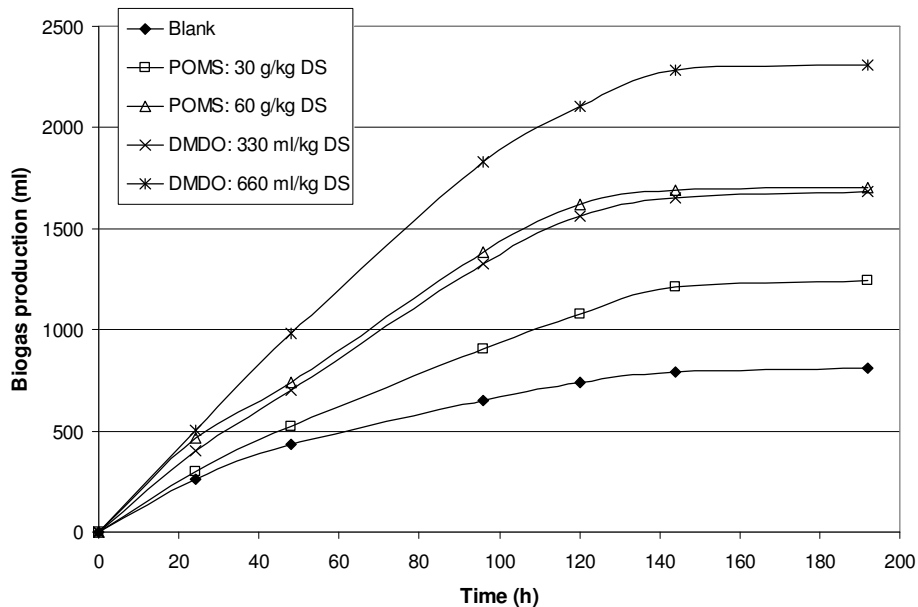
Figure 1: Evolution of biogas production for blank and pre-treated sludge

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Energy consumption in the mineralization of the azo dye C.I. direct red 23 in a sequencing batch reactor

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1. Summary

The main objective of this work was to study the energy consumption in the start–up of an anaerobic/aerobic sequencing batch pilot reactor (SBR an/ae) for the mineralization of the azo dye C.I. Direct Red 23 (DR23). The reactor was packed with granular activated carbon as carrier medium of the biomass. A mixture 50/50 of activated sludge from two treatment plants was used like inoculums. It was used synthetic wastewater with 25 mg/L DR23 as substrate, 15 mg/L acetic acid as co-substrate and medium mineral nutrient. For the acclimatization of the biomass to the DR23 and to the changes of environmental anaerobic/aerobic, the reactor used the strategy of fixed efficiencies. The thermodynamic evaluation was made. The reactor was operated 253 cycles. The acclimatization was reached in the cycle 27 with an initial concentration of 25 mg/L of DR23. The reaction time was reduced from 72 h to 24 h. The removal efficiency of COD was stayed between 75 and 80 %. The concentrations of DR23 were increasing of 25 to 200 mg/L with a global removal efficiency of 90 %. The reactor pilot of expanded bed SBR anaerobic/aerobic was evaluated for the treatment of the DR23 azo dye. Finally, the total energy balance of the start – up process during the first 27 cycles was of 544 MJ added to the SBR.

Keywords: Energy evaluation, sequencing batch reactor (SBR), RD23 azo dye, Anaerobic/aerobic process, textile effluent

2. Extended Abstract

The textile processes generate large volumes of wastewaters that contain great variety of recalcitrant compounds used in their production. Some of the present compounds in the wastewaters are the azo dyes. In the case of the DR23, it is used in the dyed of cotton fibers, linen and rayon; it is stable to the light and it is absorbed easily in the water, its fixation grade in the fiber is from 70 to 95% (O'Neill *et al.*, 1999).

Experimental system
It was installed a sequencing batch reactor (SBR) at pilot level, that consisted of a cylinder of acrylic with double wall and cover, of 58 cm of height and 14 cm of internal diameter, with an useful volume of 9 L. Three peristaltic pumps of variable

speed (Master Flex) and an aeration pump were connected to a programmable clock (Timer Chrontol), with the purpose of controlling the load, recirculation and the unload. The temperature was controlled to 30 °C, by a recirculation and heating of the water system (Poly Science Model 210). Electrodes of pH, potential redox, nitrates, nitrogen amoniacal and dissolved oxygen were installed to the reactor.

Start up energy consumption.
The exchange volume of the SBR was of 6 L of synthetic wastewater prepared with DR23 as substrate, acetic acid (co-substrate) as source of carbon and of electrons to complement the reduction reactions in the anaerobic phase and a mixture of mineral nutrient medium was necessary for the growth of the microorganisms. The process of start-up was of 27 cycles, considering that has been reached an 80% of removal of the DR23 in the anaerobic phase and of 80% of amine removal in the aerobic phase, as recommends the strategy of fixed efficiencies (Melgoza *et a*l., 2000). The energy consumptions of the beginning are based on the estimate of the energy that goes into to the system so that the phases anaerobic and aerobic can be made. In each cycle, is not considered useful energy that goes out of the system because they do not supply energy to the pumps and heating recirculator. The consumptions were: At the beginning, 15.54 kJ are consumed by filling, later to this one are consumed 10.74 MJ by the process of anaerobic recirculation. The aeration has consumption under relative of 48.88 kJ and finally the unload with an identical consumption of the load is made, of 15.54 kJ. During the anaerobic and aerobic process, the temperature of the SBR was controlled to 30.0 °C by means of heating recirculator with a nominal power of 750 W, operating by a 24 cycle of h. Nevertheless, the controller is not permanently on, it has periods (in average) of 14.37 % of the time of operation and the rest of the time stayed off, therefore the consumption by each cycle of 24 h was of 9.32 MJ. The thermodynamic analysis of the variation of the temperature indicates that it were contributed to the jacket of the system, a total amount of 1, 8 MJ in the process of 24 h, with a pumping of 0, 05 kg/s of water for the heating, reason why the rest of the considered energy dissipates in heat form to the atmosphere. This process can have a significant variation of energy because to the measurements of temperature were performed without heat insulation.

Conclusions
Start-up consists of 27 cycles defined by the strategy of fixed efficiencies, reason why the total of energy consumed in this process was of 544 MJ, for a volume of 6 L to a removal efficiency average of 80% of DR23 in the anaerobic phase and a mineralization efficiency of aromatic amines of 93 % in the aerobic phase.

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Mineralization of organic compounds in wastewater by O_3 and O_3/H_2O_2 advanced oxidation systems

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1. Summary

The scarcity of fresh water will be a dramatic reality in the near future making it necessary to improve the management of this no renewable resource. Wastewater reuse is a reasonable option for extending the available water resources, but it is necessary to develop reliable treatment processes which guarantee the disinfection and elimination of POPs and PCPs. Ozone and ozone/hydrogen peroxide have been used for the treatment of samples from two municipal wastewater (urban and domestic) effluents that had previously undergone a biological treatment by activated sludge and later clarifying. 57 PCPs and POPs regularly present in municipal wastewater and the TOC values have been checked before and after the treatment to assess that ozonization could be a successful option to face the reuse of wastewater

Keywords: wastewater reuse, ozone, wastewater treatments, POPs, PCPs, mineralization

1. Abstract

With the aim of developing wastewater treatment processes to make the reuse of wastewater possible, ozone and ozone/hydrogen peroxide have been used for the treatment of two municipal wastewater (urban and domestic) effluents that had previously undergone a biological treatment by activated sludge and later clarifying. The ozone treatments were made in a semi continuous mode in a 5 L stirred tank reactor (1000 rpm) of work volume, where a gas flow of 204 NLh^{-1} with a 49 gm^{-3}ozone concentration was bubbled through a volume of wastewater. In the case of the ozone/hydrogen peroxide treatment, volumes of 0.15 mL of hydrogen peroxide (30 % w/v) were injected by pulses every 5 min to reach values of hydrogen peroxide concentration equal to half the saturated ozone concentration. During the treatments the pH was not controlled but it was maintained between 7.8 – 8.2 values in a natural way. Ozone was produced from oxygen by Ozomatic SWO100. The concentration of ozone in the liquid was monitored using a Rosemount 499AOZ amperometric sensor and checked against the Indigo Colorimetric Method (SM 4500-O3 B). The concentration of

ozone in gas was determined with UV Photometer Anseros Ozomat GM6000, calibrated and tested against a chemical method. Total organic carbon was measured with a Shidmazu TOC-VCSH apparatus.

To test the efficiency of these two treatments, pollutants regularly present in the effluents from conventional biological treatments as: Erythromycin, Ciprofloxacin, Sulfamethoxazole, Mepivacaine, Caffeine, Omeprazole, Carbamazepine, Codeine, Cefotaxime, Urbason, Keterolac, Nicotine, Paraxanthine, Atenolol, Naproxen, Indomethacine, Propanolol, 4-MAA, Diazepan, Metoprolol, Fenofibrate, Ranitidine, Paroxethine, Fluoxethine, Acetaminophen, Trimethoprim, Metronidazole, 4-FAA, 4-AA, 4-AAA, 4-DAA, Ofloxacin, Salbutamol, Ketoprofen, Mefenamic Acid, Sotalol, Terbutaline, Octocrylene, Carbamazepine-10,11 Epoxide, Isoproturon, Chlorpyriphos Methyl, Chlorfenvinphos, Atrazine, Simazine, Diuron, Biphenylol, Fenofibric Acid, Furosemide, Diclofenac, Benzafibrate, Gemfibrozil, Clofibric Acid, Fenoprofen, Hydrochlorothiazide, Chlorophene, Ibuprofen and by-products, were checked before and after the ozonization treatments. The concentration of these pollutants was reduced from thousand to tens of ngL^{-1}, or they were totally eliminated, after 20 minutes of treatment. The use of ozone/hydrogen peroxide improves the elimination of pollutants although there are not significant differences with the use of ozone solely. These differences are more evident when the objective is to mineralise the organic matter. Very few TOC is eliminated if ozone is used only, but on the contrary more than 85 % of TOC is eliminated with ozone/hydrogen peroxide.

Ozone and Ozone/hydrogen peroxide wastewater treatment could be successful options to face the reuse of wastewater but it is necessary to develop models of ozone consumption and elimination of TOC and specific pollutants to optimize the ozonization processes. Considering that the municipal wastewaters are real matrix the models proposed are focused on determining a kinetic constant of decomposition of ozone (k_d) and a kinetic parameter (R) of TOC elimination related with the ozone exposure. Due to the variability of the wastewater, samples of domestic and urban municipal wastewaters were collected twice per month during a year with the object of undergoing ozonization treatments and to check these two parameters: k_d and R. Two stages of elimination of TOC and decomposition of ozone and a variability of R from 0.8 $mM^{-1}min^{-1}$ to 1.8 $mM^{-1}min^{-1}$ and kd from 0.87 min^{-1} to 1.00 min^{-1} have been determined in the two first months of work

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Double-Pass Flat-Plate Solar Air Heaters with External Recycle

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1. Summary

A new device of inserting an absorbing plate to divide a flat-plate channel into two channels with fins attached and external recycling at the ends, resulting in substantially improving the heat transfer efficiency, has been investigated both experimentally and theoretically. The agreement of the theoretical predictions with those measured values from the experimental results is fairly good. The experimental and theoretical results are represented graphically and compared with that in the downward-type single-pass solar air heaters of the same size without recycling. Considerable improvement in heat transfer is obtained by employing double-pass operations with external recycling and fin attached over and under the absorbing plate. The influences of recycle ratio and absorbing plate location on the heat-transfer efficiency enhancement as well as on the power consumption increment have been also delineated.

Keywords: Solar air heaters; flat-plate type; double-pass operations; collector efficiency.

2. Extended Abstract

Flat-plate solar collectors which absorb the solar radiation, transform it into heat, and to heat passing air are mechanically simpler than concentrating collectors to be used in domestic and industrial needs. The flat-plate solar air heaters are constructed with the blackened absorber to transfer the absorbed energy to the flowing medium, transparent cover to reduce convection and radiation losses to atmosphere, and back and side insulation to reduce conduction losses. The main application of solar air heaters are space heating and drying. The recycle-effect concept in double- and multi-pass operation can effectively enhance the heat transfer rate and lead to improved device performance (Ho et al., 2001; Ho and Yang, 2003). An alternative design device for improving collector efficiency by increasing heat transfer coefficient has been studied with experiment and theoretical predictions.

The double-pass solar air heater with fins attached of channel width W, channel length L, and height of both upper and lower channels H, may be illustrated by the schematic diagram of Fig. 1 with artificial simulation. The total heat flow from the absorber plate with attaching fins to a passing airflow may be written as

$$q' = h_1 \left(A_t + \tanh m_f h_f A_f / m_f h_f \right) \left(T_p - T_i(z) \right), i = a, b \tag{1}$$
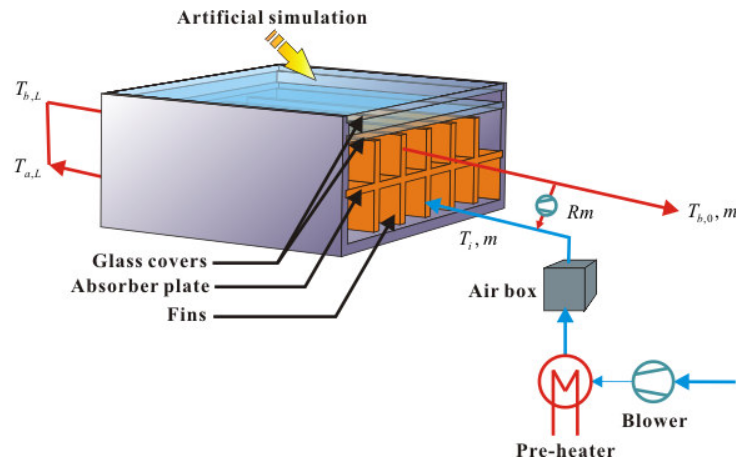
Fig.1 Schematic diagram of a solar air heater with artificial simulation

After solving the outlet temperature of solar air heater, the collector efficiency η may be given

$$\eta = Q_u / A_c S_0 = \tau_g^2 \alpha_p - U_L (T_{p,m} - T_s) / S_0 = m C_p (T_{b,0} - T_i) / A_c S_0 \tag{2}$$

The collector efficiency improvement can be obtained by defining the percentage of collector efficiency improvement

$$I_D = \frac{\eta - \eta_D}{\eta_D} \times 100\% \tag{3}$$

The comparison of collector efficiencies between the devices with recycle and the one of single-pass operation without recycle is readily observed from Table 1. It is seen from Table 1 that the recycle double-pass solar air heater with fins attached has good performance.

Table 1 The collector efficiency improvement of solar air heaters

I_D	$S_0 = 830$ W/m^2 (Theo.)			$S_0 = 830$ W/m^2 (Exp.)		
	$R = 0$	$R = 0.5$	$R = 1.0$	$R = 0$	$R = 0.5$	$R = 1.0$
$m = 0.0107$ kg/s	30.42	68.93	86.41	13.27	56.31	72.82
$m = 0.0161$ kg/s	21.08	55.41	68.11	20.27	49.46	67.30
$m = 0.0214$ kg/s	15.70	46.62	56.28	21.98	35.99	52.17

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Carbonization of Empty Fruit Bunches Using Hydrothermal Method

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1. Summary

We have been carried out research for the utilization of Empty Fruit Bunches (EFB) as a fuel. To produce charcoal, EFB was treated under hydrothermal condition at 423-623 K without a catalyst, and then compared it with carbonization under dry nitrogen condition. The charcoal yields were 31.4% under hydrothermal condition at 573 K and 27.8 % under dry condition at 873 K, respectively. The carbon content of charcoal was almost equal value between under hydrothermal condition at 573 K and under dry condition at 873 K. The heating value of charcoal obtained from hydrothermal condition at 573 K was high (25.8 MJ/kg), compared with it obtained from dry condition at 873 K (22.0 MJ/kg). It is suitable as an energy feedstock. The studies clarified that the carbonization of EFB was promoted at low temperature under hydrothermal condition.

Keywords: carbonization, hydrothermal, empty fruit bunches

2. Extended Abstract

The disposal of empty fruit bunches (EFB) is an important problem in palm oil production industry. Regularly, it is produced from palm oil mills after the removal of oil palm fruits for the oil production. More than 8 million ton of EFB is generated annually in Malaysia and Indonesia. A part of the EFB is used boiler fuel and fertilizers. However, most of it is unused. Consequently, the valuable energy contained in woody waste is lost without utilization in the energy cycle.

In general, charcoal is made from solid wood, which is carbonized at high temperature, at higher than 873K, under dry conditions, such as a nitrogen atmosphere. It is reported that the carbonization of wood was promoted at low temperature, at 573-623 K, using the hydrothermal method (Inoue *et al.,* 2002; Mochidzuki *et al.,* 2004). One of the advantages of hydrothermal method is no drying process. It is suitable for wet biomass.

We have been carried out research for the utilization of EFB as a fuel. To produce charcoal, EFB was treated under hydrothermal condition at 423-623 K without a catalyst, and then compared it with carbonization under dry nitrogen condition.

Solid yields and their carbon contents obtained from EFB under hydrothermal and dry conditions are shown in Table 1. The yield of the solid materials decreased with increasing reaction temperature. It was almost an equal value between 623 K under hydrothermal conditions and 873 K under dry conditions.

The carbon concentration of solid remarkably increased at 573 K. It is reported that dehydrogenation and deoxygenation during the carbonization process of wood begin under dry conditions at temperature of 573 and 573-873 K, respectively (Nishiyama *et al.,* 1998). Dehydrogenation and deoxygenation began at a temperature of 573 K using hydrothermal condition and the carbonization of EFB was promoted. The heating values are dependent on the increase in the carbon ratio and the decrease in the oxygen ratio in the solid. The heating value of solid increased at 573 K, remarkably. It was high (25.8 MJ/kg), compared with it obtained from dry condition at 873 K (22.0 MJ/kg).

Table 1 Solid yields and their carbon contents obtained from EFB under hydrothermal and dry conditions

	Solid [wt%]	Carbon content [wt%]
423 K, 0 h	80.9	47.8
473 K, 0 h	66.8	50.3
523 K, 0 h	57.6	52.0
573 K, 0 h	31.4	66.9
623 K, 0 h	28.3	72.4
623 K, 1 h	26.1	76.7
573 K, 1h	38.6	64.1
873 K, 1 h	27.8	71.2
1173 K, 1h	26.8	76.5

We found that the charcoal could be obtained from EFB using hydrothermal method. The hydrothermal method can be expected to be a new method to produce charcoal from high moisture biomass because no drying process.

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Application of Self-Organising Map (SOM) Artificial Neural Networks for the Chemical Assessment of Sediment Quality

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1. Summary

In this work, the suitability of Self-Organising Map (SOM) for the assessment of sediment quality was investigated using data from 3 estuaries of Cantabria (Spain). The results obtained with the SOM were compared to those of multivariate statistical techniques, emphasising the better visualisation tools offered by the SOM that allowed a more useful classification of the sediment samples according to their levels of contamination in order to prioritise management actions.

Keywords: sediments, sustainable management, chemical assessment, self-organising map (SOM), artificial neural network (ANN)

2. Extended Abstract

Sediments comprise an essential component to take into account when analysing the environmental status of marine ecosystems [1]. The physico-chemical characterisation of estuarine sediments is a basic initial step in the design and implementation of environmental management actions in coastal zones. However, due to the fact that many variables have influence on the sediment quality [2,3], the use of tools that allow the analysis and interpretation of these variables becomes necessary in a global characterisation approach; thus, this will also be useful in a decision-making framework for determining the application of the best engineering processes that lead to the sustainable management of sediments.

The Kohonen Self-Organising Map (SOM) is one of the most well-known artificial neural networks (ANNs) with unsupervised training algorithms. The aim of this work is to apply the SOM for the integrated assessment of physico-chemically characterised sediments from different zones and with different levels of contamination, as well as to compare the results of the SOM with those of traditional multivariate statistical techniques (hierarchical cluster (HC) and principal component

analysis (PCA)). The SOM Toolbox 2.0 for Matlab® was used to create and visualise the SOMs, and all statistical analyses were performed using SPSS 14.0 for Windows. The data used in this study included 40 samples of superficial sediments from 3 estuarine zones of Cantabria (Northern Spain): Santander, Suances and Santoña, exposed to different levels of anthropogenic pressure due to urban, industrial and port activities. A set of 12 physico-chemical variables were studied in each sample: % of silt+clay, Total Organic Carbon (TOC), 8 metals (As, Cr, Cu, Fe, Mn, Ni, Pb and Zn) and 20 polycyclic aromatic hydrocarbons (PAHs), grouped in sum of 7 low molecular weight PAHs, (Σ7LPAHs) and in sum of 13 high molecular weight PAHs (Σ13HPAHs).

A 42-unit SOM (7x6) allowed a proper classification of the 40 sediment samples into 4 groups according to their different level of contamination. The HC analysis, which was carried out as a comparison, identified 3 clusters; although two of the groups were very similar to those found in the SOM, HC grouped in a third cluster both contaminated and clean samples that the SOM was able to separate appropriately into two groups. As well as providing a better classification of the sediment samples than HC, it should be emphasized that SOM allows an easier visualisation of multidimensional data; the very useful graphic representations that SOM offers help in the task of interpreting the data involved in the sediment quality assessment and management.

The SOM was also applied to look for associations of variables analysed in the sediments. In the 14-unit map (7x2) that was obtained, 3 groups of variables could be distinguished: 1) the heavy metals Fe, Mn, Cr, Ni and Cu; 2) Pb, Zn, As and Σ13HPAHs; 3) the physical variables (silt+clay and TOC) and Σ7LPAHs. The application of HC led to a dendrogram where these same 3 clusters were identified. However, the results obtained using PCA were slightly different and perhaps showed the interrelations between the variables more clearly; specifically, PCA discovered a component that included Pb, Zn, As and Σ7LPAHs, but the three metals with positive coefficients and Σ7LPAHs with a negative one.

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Treatment of textile dyes effluents by laccase mediator system

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1. Summary

A screening using several laccase mediators (2,2-azinobis(3-ethylbenzthiazoline-6-sulfonic acid (ABTS), 1-hydroxybenzotriazole (HBT), *N*-hydroxyacetanilide (NHA), 2,2,6,6-tetramethylpiperidin-1-yloxy (TEMPO) and violuric acid (VA)) was performed on the degradation of three reactive textile dyes: Reactive Black 5 (RB5), Reactive Blue 114 (RB114) and Reactive Yellow 15 (RY15). ABTS was the most effective mediator and its efficiency depended on the type of dye and also on the pH, temperature and ABTS concentration. The optimum temperature and pH values were found at 35ºC and 5.0, respectively. ABTS has no effect on the decolourisation at low dyes concentrations, except for RB114 where at lower concentrations it promotes the best decolourisation (93%). High concentrations of ABTS inhibited the decolourisation.

Keywords: laccase, mediator, reactive textile dyes, decolourisation

2. Introduction

In textile industry, colour is applied to finished products through dyeing, resulting in the generation of different wastewaters. During the textile process, industries release large quantities (about 10% of the global wastewater) of intensely coloured and toxic effluents [1], which cause serious environmental pollution. A number of biotechnological approaches have been suggested with potential interest to eliminate this pollution source in an eco-efficient manner [2]. It is known that lignolitic enzymes (laccase) can be used to decolorize dyes [3]. The range of laccase substrates can be extended to nonphenolic compounds by inclusion of a specific compound, called mediator [4].

The aim of this work is to optimize the dye degradation of three reactive dyes typically used in Portuguese textile industries. For this purpose five traditional laccase mediators, temperature, pH and mediator concentrations were tested in order to evaluate the decolourisation by laccase-mediator system (LMS).

3. Materials and methods

Decolourisation experiments were carried out with three industrial textile dyes supplied by DyStar (Portugal): RB5, RB114 and RY15. The commercial laccase (DeniLite Base II; 800 U/g) was kindly supplied by Novozymes. Five redox mediators ABTS, VA, NHA, HBT and TEMPO were employed in order to evaluate the LMS. The experiments were carried out in 25 mL Erlenmeyer flasks at 20-50ºC and pH of 3.0-7.0, under stirring during one day, with 50 mg/L of each dye, laccase (0.2 U/mL) and a redox mediator (0.001-0.5 mM). A control without mediator was carried out in parallel. Dye decolourisation was determined spectrophotometrically.

4. Results and Discussion

The experiments with laccase and without a mediator did not decolourise any dye along incubation time. However when a redox mediator was introduced, the catalytic mechanism of decolourisation started depending on the dye and on the mediator. The mediator screening showed that ABTS was a more effective mediator than the others for the oxidative degradation of the reactive textile dyes (table 1).

Table 1 – Mediator screening for reactive dye degradation by laccase.

Reactive Dye	Dye degradation (%)					
	No mediator	HBT	ABTS	TEMPO	NHA	VA
RB114	ND[a]	0.3	**70**	ND	1.5	5.0
RB5	ND	0.2	**42**	1.5	ND	2.5
RY15	ND	2.7	**21**	2.0	0.8	0.2

[a] ND, not detected.

The decolourization by LMS is very sensitive to temperature and pH, depending on the kind of dye. The optimum temperature and pH for decolourisation were 40ºC and pH 5.0, respectively, with a maximum decolourisation above 80% for RB114. At lower temperature (20ºC) no decolourisation was observed, except for RB5 (36%), as well as at lower pH (pH 3.0).

The decolourisation of all dyes was very dependent on ABTS concentration. When high ABTS concentrations were employed (above 0.2 mM), lower or none dye degradation was observed. The optimum ABTS concentration for RB5 and RY15 decolourisation by LMS was 0.1mM with colour reductions of 73% and 76%, respectively. The best absorbance spectrum for RB114 was obtained with ABTS 0.001mM where a very low absorbance was detected over all spectrum, with a decolourisation of 87%.

These results are very promising and reveal the high potential of LMS to reactive dye decolourisation. So, LMS can be used for treating textile dying wastewaters, particularly as a polishing process for water recycling.

5. Acknowledgments

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Treatment of oil waste water toolkit

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1. Summary

Present system was developed to provide process engineers with an opportunity of fast search of the necessary treatment equipment, information about water purification systems and elimination methods of consequences of oil spills and other accidents; and by means of integrated expert part given system depending on drain properties and other sufficient characteristics is able to search for and analyze proper water treatment technology, equipment etc.

Keywords: oil-wastewater, treatment, environmental engineering

2. Extended Abstract

Treatment of oil waste water toolkit is a set of modules integrated in one computer application. It consists of Informational System module and two modules combined in expert part.
The Informational System consists of 5 databases with built-in search engine, developed in terms of algorithm full-text fuzzy search.

Databases include the following information:
• on equipment and schemes of waste water treatment at petroleum and refining;
• elimination methods of oil spill and consequences of damage;
• patent information;
• general reviews;
• reviews of investigations.

The factografic data model is used in database design, that in comparison with relational data model allows user to add, store and use the information not depending on file format.

Capabilities of the search system are:
• flexible search algorithm;
• Russian or English languages for search request;
• search engine uses the annotation of documents.

Informational system allows user to search the necessary information, store new data in the system and it is intended to provide a complex informational environment to support the work of process engineers, environmental engineers and other people concerned with water treatment area.

Expert part includes two main modules: Case module and Adviser.
Case module provides previously stored information about treatment sequences that was obtained from real-life situations. It utilises the case-based reasoning approach in solving new design task. The aim of this module is to retrieve and rank relevant cases from the current user's problem. Once relevant cases have been retrieved from the case base, the user can browse through those cases on order to select the most applicable ones for the current situation. The representation of the case includes description of water characteristics, type of industry, description of used technology, and technical parameters of treatment operations such as flow rate, cost of treatment, water supply etc. The module is capable of defining a similarity between cases containing both numeric and textual-symbolic information.
The Case module provides facilities for reviewing, deleting, and editing existing cases, as well as possibilities for adding new one.

The Adviser module can generate a sequence of treatment technologies for given water characteristics. This is based on an analysis of influent characteristics and the recommended methods for the removal of specific contaminants. Each harmful factor can be treated by specific set or several sets of methods that are able to remove the factor from wastewater. The stream may contain a number of harmful factors that can be processed by many sets of treatment methods. As a result of analysis, one or several entire treatment sequences are generated and then evaluated by economical and treatment efficiency criteria.

Developed system was aimed to support the solving of common problems in water treatment area. It can also be used as an educational tool for training on wastewater treatment technologies and be applied to different areas such as chemical / civil / environmental engineering, environmental sciences and management. The development of present System for oil-wastewater treatment was supported by BP.

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Release of K from the system: K-Ca(-Si)-P – The Effects of the Ca/Si- and Ca/P-ratios

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1. Summary

The presence of relatively high amount of volatile inorganic matter in biomass, K above all, is one of the major contributors to the operational problems occurring during the combustion of biomass in boilers for heat and power production. Synthetic blends of K-Ca-Si and K-Ca-P compounds, resembling straw and wood ash chemistry, were heated at 900°C and 1000°C to investigate transformations and release of K to the gas phase. Experiments were performed in fixed-bed reactor. Increased Ca/Si-ratio in the sample results in increased K-release rate, while decrease of the Ca/P-ratio leads to the decreased K-release rate from the samples.

Keywords: Ash, biomass, combustion, release, potassium

2. Extended Abstract

In biomass-fired grate boilers, ash formation is strongly influenced by the release of volatile alkali metals. Ash from biomass may cause a number of different operating problems, such as deposition and corrosion. This is due to the high content of alkali metals, causing a low melting point of the ash. Release studies on annual biomass have shown that a Ca-Si – chemistry is responsible for controlling the release of K to the gas phase. In the case of wood biomass, a matrix rich in Ca and P is left behind in the residual ash after pyrolysis and char burnout. Thus, these elements may also influence the release of K from wood fuels.

A reliable method for studying the alkali release rate from model species was developed and tested. The effect of Ca on the release of K- species from a mixture of K-, Ca- and Si-species was studied. Two K-sources, KCl and K_2CO_3, were investigated, while Quartz was applied as Si-source, and CaO and $Ca(OH)_2$ were applied as Ca-sources. The release of K- species from the mixtures was quantified in a fixed-bed reactor. The experiments were done in N_2 with 2%(v/v) H_2O, at 900°C and 1000°C. The residue left in the crucible was investigated by scanning electron microscopy and energy dispersive X-ray mapping. The results showed that in the

ternary system K-Ca-Si, mixing between the compounds occur, causing a higher K-species release rate, while the presence of Ca alone does not influence the K-release.

Further experiments were performed in order to investigate the system: K-Ca-P, i.e. the new aspect was the effect of different amounts of P and effect of different Ca-species on the release of K-species from mixtures of K-, Ca- and P-species. KCl and K_2CO_3 were again used as K-sources, $Ca(PO_3)_2$ was used as P-source, while $CaCO_3$ and $Ca(COO)_2$ were applied as additional Ca-sources. Experimental conditions were the same as stated above.
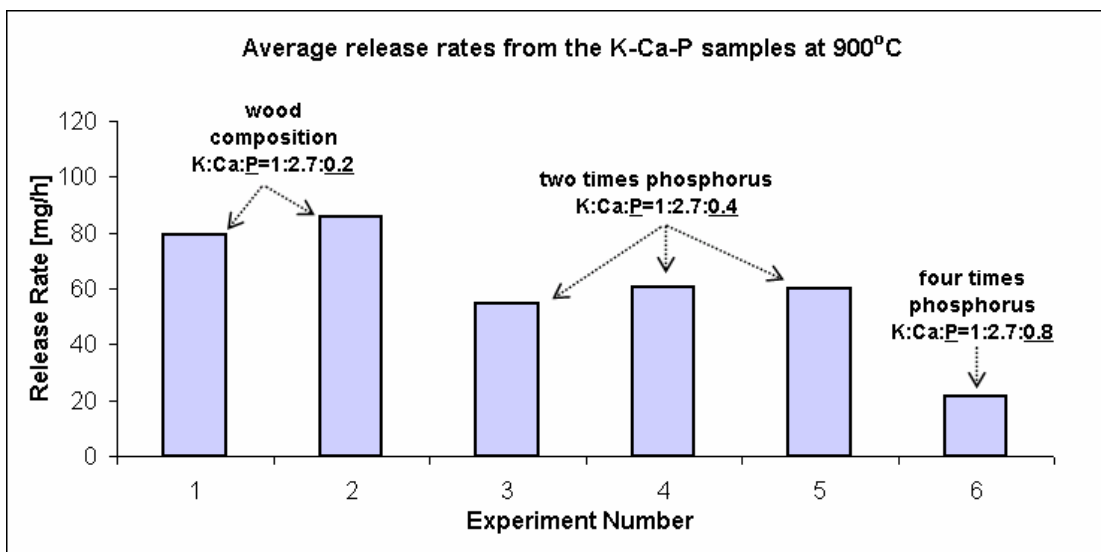
Figure 1: Average release rates from the $K_2CO_3+CaCO_3+Ca(PO_3)_2$ samples at 900°C

The average release rates for the K-Ca-P system, excluding initial CO_2 release, are shown in Figure 1. These experiments were performed on $K_2CO_3+CaCO_3+Ca(PO_3)_2$ mixtures with molar ratios closely resembling the wood composition (K:Ca:P=1:2.7:0.2), or wood with two and four times the amount of P-source (K:Ca:P=1:2.7:0.4 and K:Ca:P=1:2.7:0.8). It is evident that the decrease of the Ca/P-ratio in the blends leads to the significant decrease of the release rate from the samples. The same trend has been observed regardless of the applied Ca-source or the applied temperature. The observed behaviour can be explained by the ability of P-species to react with K- and Ca- species, i.e. due to the increase of the P-content in the sample, more K and Ca can be incorporated into non-volatile $(K_2O)_k(CaO)_l(P_2O_5)_m$, leaving less K available to be released to the gas phase.

The residue left in the crucible after the heat treatment will be investigated by STA/EDX. These experimental techniques will provide information on sample morphology and mixing of different species in the sample. Furthermore, a simultaneous thermal analysis (STA) instrument will be used to characterize the behaviour of K-Ca-P-synthetic blends with respect of the melting and gas-phase release behaviour. The STA will provide information on mass loss and exothermic/endothermic reactions as a function of sample temperature.

Information system for phosphorus-containing compounds production

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1. Summary

According to the prediction of the UN Food Organisation, consumption of mineral fertilisers in the world will be 310 Mt, including phosphorus-containing products – 77 Mt. Phosphorus-containing fertilisers are produced on the basis of phosphoric acid. Over 2,000,000 t of phosphoric acid (in P_2O_5) are produced only in Europe. Serious pollution of surface and subterranean waters, atmosphere, soil, damage to human health and green plantations damages are registered for discharged wastes of phosphorus-containing products. In Russian Federation alone, the annual discharge of these wastes in environment is:

- into atmosphere 80,000 t
- shedding into the water – 70 Mm^3
- storage of solid wastes – 16 Mt

Keywords: information system, information technologies, phosphorus, phosphorus-containing compounds, mathematical modelling

2. Extended Abstract

Sustainable development of the society requires the phosphorus industry to significantly boost its environmental performance which needs radical technological improvements. Those requirements are comprehensively addressed in EC supported FP6 INCO ECOPHOS Project. The project focuses on new technologies for (a) the production of useful phosphorous salts (fodder, food and pharmaceutical phosphates), phosphorous acid and phosphates in a cost efficient and ecologically sustainable way, (b) the improvement of existing methods in the phosphoric acid production for the

drastic minimisation of waste, (c) the utilisation and processing of industrial solid waste from the production of phosphoric acid and (d) the production of a new generation of phosphoric fertilizers.

One of the key aspects of the work is the development of an integrated toolbox for production of the wide class of phosphorus-containing products with information and data on waste minimising processes, safety, resource- and energy saving, exchange of information about advanced technologies of these chemical productions. The advanced processes developed during the work cover (i) sodium phosphite production, (ii) phosphorous acid production, (iii) dibasic lead phosphite production, (iv) upgraded dihydrate method for phosphoric acid production, (v) dihydrate-semihydrate method, semihydrate method and (vi) ortho-phosphoric acid purification, and they will constitute the core of the open-type advanced technologies toolbox. The toolbox is based on mathematical models of those processes which are incorporated into mathematical model block of the toolbox. Also these toolbox models will be used for development of training systems.

The toolbox also contains a number of technologies (including process flowsheets and relevant data) for waste minimisation by utilisation such as: (i) phosphogypsum utilisation, (ii) cadmium containing phosphate ores processing and production of fodder, (iii) production of fodder, food and pharmaceutical phosphates and (iv) production of prolonged and aqua-accumulating fertilizers.

Databases within the integrated toolbox include:

- Advanced technologies of phosphorus-containing products manufacturing;
- Phosphogypsum disposal and its impact on the environment;
- Phosphogypsum processing technologies;
- Producers of phosphorus-containing products;
- Substance physicochemical properties;
- Raw materials and their producers;
- Equipment and its manufacturers;
- Expert system knowledge;
- Models for phosphorus-containing substance production;
- Phosphorus-containing products production flowsheets
- and some other auxiliary databases

The information available from various sources is fed into the toolbox, including the data from projects such as CAPE-OPEN (1997-1999), GLOBAL CAPE-OPEN and CO-LaN 2001-2004 for the chemical industry and will follow the standards established in these projects. Thus particular emphasis will be placed in order to promote the use and the development of the CAPE-OPEN standard in Computer-Aided Process Engineering (CAPE) software, and more generally to encourage all actions aiming at facilitating the use of CAPE software tools in industry, administration and academia.

The toolbox being developed has a multilevel structure (three-level architecture). The system consists of following components: database server, application server and client application.

CWAO of phenol over activated carbon catalysts with hydrogen peroxide as promoter

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1. Summary

The study of the catalytic wet air oxidation (CWAO) of phenol with activated carbon catalysts in presence of hydrogen peroxide as promoter has been accomplished. The effect of the addition of hydrogen peroxide to CWAO processes has been analyzed in terms of both initial activity and effluent toxicity. To this purpose, the experimental profiles for phenol and TOC conversions were obtained, also the toxicity of the effluents were measured. The results were compared to those found in absence of hydrogen peroxide. The experiments were carried out in a trickle-bed reactor at given operating conditions ($C_{inlet\ phenol}$= 1 g/L, $C_{inlet\ H2O2}$= 5g/L, T=127 ºC, P_T=8 atm and W_{CAT}=2.5 g) in a wide range of space time values (W/Q_L=20-320 g_{CAT}·h/L). Results show that due to hydrogen peroxide the initial activity in the oxidation of phenol can be increased from 3 to 42 $g_{Phenol}/(kg_{CAT}·h)$ and toxicity effluent can be abatement at relatively short space times which indicates that a reduction on the reaction times or on operating conditions are possible.

Keywords: wet air oxidation; hydrogen peroxide; activated carbon; wastewater; phenol

2. Extended Abstract

Catalytic wet air oxidation (CWAO) is an effective technology to treat aqueous hazardous wastes, especially when these are too dilute to incinerate and too concentrated for a biological treatment (COD:10-100 g/L). CWAO occurs through a radical mechanism. It uses molecular oxygen as oxidant and operates at T<200 ºC and P<100. The employ of heterogeneous catalysts allows reducing the operating conditions, the issues is to find long term stable catalysts. Bare activated carbons have been successfully employed as catalyst (Tukac and Hanika, 1998) but restrictions in the operating conditions has to be considered (T<160 ºC and P_T< 10 atm) in order to avoid carbon combustion (Mundale et al. 1996). The employ of a promoter to initiate the reaction can improve the activity of the carbon. Lin and Wu (1998) reported that the addition of hydrogen peroxide to the non-catalytic WAO systems enhances phenol reaction rate.

In this work, we have studied the effect of hydrogen peroxide in the CWAO of phenol with activated carbon catalysts also on the mineralization rate and toxicity of the effluent. The experiments were carried out in a trickle-bed reactor (L=80 mm and φ=8.5 mm) at $C_{inlet\ phenol}$= 1 g/L, $C_{inlet\ H2O2}$= 5g/L, T=127 °C, P_T=8 atm, W_{CAT}=2.5 g and Q_{O2}=92 NmL/min in a wide range of space time values, W/Q_L=20-320 g_{CAT}·h/L. Complete hydrogen peroxide consumption was observed at any space time.

Evolution of phenol and TOC conversions upon space time are shown in Figure 1. Higher phenol and TOC conversions are obtained in presence of hydrogen peroxide. Initial reaction rates for phenol are 3 and 42 g_{Phenol}/(kg_{CAT}·h) and for TOC 1.8 and 12 g_{carbon}/(kg_{CAT}·h) in absence and presence of hydrogen peroxide, respectively. Moreover, phenol oxidation route was different since the carboxylation of phenol to p-hydroxybenzoic acid does not occur, reaction that has been always reported in the CWAO with based-activated carbon catalysts. The addition of hydrogen peroxide gives preference to phenol hydroxylation route. These most toxic intermediates, hydroquinone and p-benzoquinone, were detected in far lower amounts. The oxidation of hydroquinone to p-benzoquinone was instantaneous and the oxidation of p-benzoquinone to CO_2 and low molecular weight acids (maleic, oxalic, formic and acetic acids) was also faster in presence of hydrogen peroxide. As a consequence of the different rates and, therefore, intermediate distribution, toxicity of the effluent will be also affected (Figure 2). Toxicity of the effluent, expressed as TU_{50}, determined by a bioassay in a Microtox M500 Analyzer, significantly decreases in addition of hydrogen peroxide. The curves follow the same profile as p-benzoquinone concentration. The reason for this beneficial effect is the preferential decomposition of hydrogen peroxide on activated carbon into oxygen and water, and also into hydroxyl radicals due to both the operating conditions and metallic reactor walls.
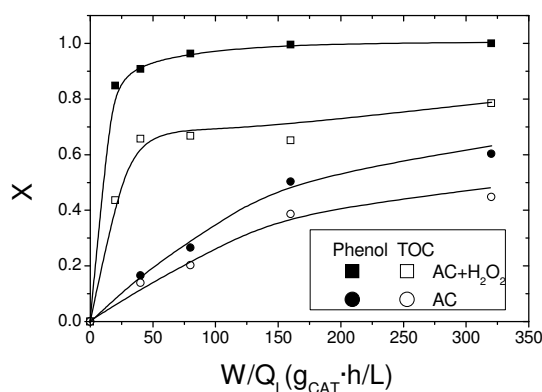
Figure 1. Influence of addition of hydrogen peroxide on phenol and TOC removal.
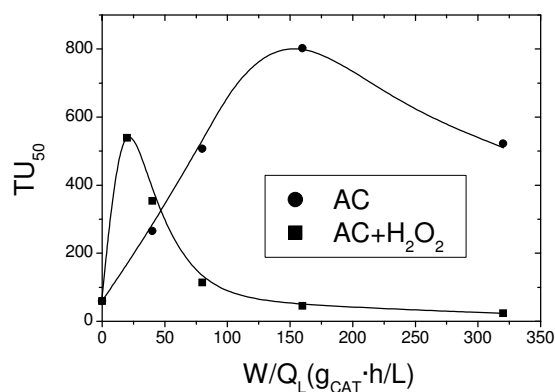
Figure 2. Influence of addition of hydrogen peroxide on toxicity of the effluent.

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Arsenite adsorption upon activated carbon and its pva-composite

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1. Summary

In this study, the removal of As(III) ions from aqueous solutions by adsorption onto activated carbon and its pva composite has been investigated as a function of pH, adsorbent dosage, contact time and temperature. Accordingly, the extent of removal was maximized after 16 hours of operation at pH of 4.5 and with 13 g/L adsorbent. Adsorption of arsenite was characterized by Langmuir isotherm. Kinetics of adsorption was described by Lagergren equation and thermodynamic analysis showed that the process had endothermic nature. Operation conditions leading to maximum arsenite removal were tested using effluent from a galvanization facility. The arsenite adsorption capacity was improved by preparation of carbon-pva composite beads. Desorption studies showed that the adsorbents could be regenerated up to 95% of original capacity.

Keywords: arsenite adsorption, carbon-pva composite, thermodynamics, kinetics

2. Extended Abstract

2.1 Introduction

Heavy metal ions introduced to the environment through industrial activities have a tendency towards accumulation in the biosphere [1]. Being one of the heavy metals in the list of priority pollutants, arsenic has been gaining public and scientific concern pertaining to its high toxicity. Among its five oxidation states, As(III) is the most toxic and persistent one [2]. Chemical precipitation, membrane filtration, ion exchange, and adsorption are amongst the conventional methods applied for reduction of the concentrations of arsenic in polluted waters. Adsorption upon activated carbon is recognized as the most preferred and advantageous method mainly due to the high surface area, well developed porosity and structural features of the activated carbon, *i.e.* distribution and variety of heteroatoms and functional groups in its structure. However, the high cost of material constitutes a major drawback and therefore, research has focused recently on modification of carbon so as to increase its efficiency [3].

The aims of the present study can be listed as: (i) determination of the set of operation conditions at which efficacious removal of arsenite could be attained; (ii) characterization of adsorption by isotherms and calculation of isotherm parameters; (iii) evaluation of the process in terms of kinetics and thermodynamics and calculation of the related parameters; (iv) enhancement of adsorption capacity by preparation of carbon-polymer composites.

2.2 Experimental

All experiments were conducted batchwise in 100 mL stoppered glass flasks in triplicates to ensure accuracy of results. Experiments were conducted first by synthetic solutions involving only arsenite and then by real effluents contaminated with copper, lead, cadmium and nickel besides arsenite. The parameters pH, contact time, adsorbent dosage and temperature were investigated in the ranges 2-11, 0.5-24h, 0.5-20 g/L and 20-40°C respectively. Arsenite concentration was analysed by either AAS or ICP. Carbon-pva composite beads were prepared by sedimentation polymerization at 90°C with the cross-linking effect of glutaraldehyde.

2.3 Results

The arsenite adsorption capacity of granular activated carbon was determined as 33.3 mg/g in its raw form. Maximum capacity was attained after 16 hours operation at pH 4.5 and at 313 K with an adsorbent dosage of 13 g/L. The adsorption data was found to follow Langmuir isotherm with regression coefficient of 0.99. Kinetic analysis showed that the adsorption of arsenite on activated carbon could best be represented by first order Lagergren expression. Calculated rate constants of adsorption and pore diffusion suggested that the rate of adsorption of As(III) was limited by both film and intraparticle diffusion steps. Thermodynamic analysis proved that the adsorption of arsenite was endothermic with ΔH being calculated as 18.51 kJ/mol.

The As(III) adsorption capacity was further increased to 34.5 mg/g with pva-carbon composites. The modification procedure applied to activated carbon leaded to increased surface area however, it also caused clogging of large pores at high concentrations of cross-linking agent. Raw and modified materials were tested in removal from wastewater. Raw activated carbon could utilize only 17.3% of its arsenite adsorption capacity, while with the composite bead this ratio increased to 51.4%. The decrement in capacity was attributed to existence of competing ions, especially copper and zinc in wastewater.

Desorption studies showed that both activated carbon and its pva composite could be regenerated up to 95% of original capacity. The capacity of modified material reduced to 33% after 5 successive adsorption cycles.The results were 97% reproducible.

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Removal of Acid Orange 7 (AO7) by UV/H$_2$O$_2$ oxidation in the presence of dye auxiliaries

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1. Summary

In the present study, the effect of dye-auxiliary chemicals such as NaCl, Na$_2$SO$_4$, Na$_2$CO$_3$ and CH$_3$COOH on the advanced oxidation of Acid Orange 7 (AO7) by UV/H$_2$O$_2$ process has been investigated. Addition of NaCl and Na$_2$SO$_4$ decreased the removal efficiency of AO7, though no significant effect of Na$_2$CO$_3$ was observed. The effect of NaCl is higher than that of Na$_2$SO$_4$. A 10gL^{-1} acetic acid concentration decreased the oxidation kinetic constant by 50%.

Keywords: Advanced oxidation processes, UV/H$_2$O$_2$, Acid Orange 7, dye-auxiliaries, colour removal.

2. Extended Abstract

Color removal from textile wastewater has been a matter of considerable interest, not only because of the potential toxicity of certain dyes but often due to their visibility in receiving waters and to their low biodegradability. Advanced oxidation processes (AOP) employing hydrogen peroxide with UV-light have been found to be very effective in the degradation of dye pollutants (3) and are therefore one of the Best Available Techniques (BAT) for the treatment of waste waters from the textile industry (1), affected by the IPPC Directive 96/61/EC.

A large percentage of the total emission load from textile industry activities is attributable to salts and carboxylic acids employed in the finishing mills. Although the effect of some dye auxiliary chemicals (2, 4) has already been investigated on the removal of reactive dyes by AOP, their effect on the destruction of acid dyes needs to be evaluated. The aim of this study is the analysis of the effect of auxiliary chemicals highly used in dyeing processes, such as NaCl, Na$_2$SO$_4$, Na$_2$CO$_3$ and CH$_3$COOH, on the treatment by UV/H$_2$O$_2$ of aqueous solutions containing Acid Orange 7 (AO7).

All experiments were carried out in a batch cylindrical glass photoreactor equipped

with a medium-pressure Hg vapour lamp emitting at 200-450nm immersed in a quartz sleeve placed within the reactor. The temperature was maintained at 25ºC. An initial AO7 concentration of $150 mgL^{-1}$ and a mass relation of H_2O_2/AO7 of 10/1 were employed. The individual effect of dye auxiliary chemicals (NaCl, Na_2SO_4, Na_2CO_3, CH_3COOH) was investigated at three different concentrations (1, 5 and $10 gL^{-1}$). The initial pH of the simulated dyehouse effluent was adjusted to a value of 3 with HCl.

The effect of acid dye auxiliary chemical concentration was assessed through the variation of the pseudo-first order kinetic constant of the decolouration reaction of AO7. Reaction rate constants were evaluated using linear regression of the plot of the logarithmic variation of dye concentration with UV irradiation time [Fig.1a]. In Figure 1b, the rate constant divided by the kinetic constant value of the removal reaction of AO7 in the absence of auxiliary compounds (k_{obs}^*) is plotted versus the concentration of the four auxiliary compounds. Regarding the effect of inorganic salts, no significant effect was observed upon addition of Na_2CO_3. The effect of NaCl is higher than that of Na_2SO_4. In both cases, the degradation rate diminished as the concentration of dye-auxiliary compound increased in the range $1-5gL^{-1}$. Higher amounts of Na_2CO_3 and Na_2SO_4 had a minor effect on the kinetics of AO7 degradation. A $10 gL^{-1}$ acetic acid concentration decreased the rate constant by 50%.

(a)   **(b)**
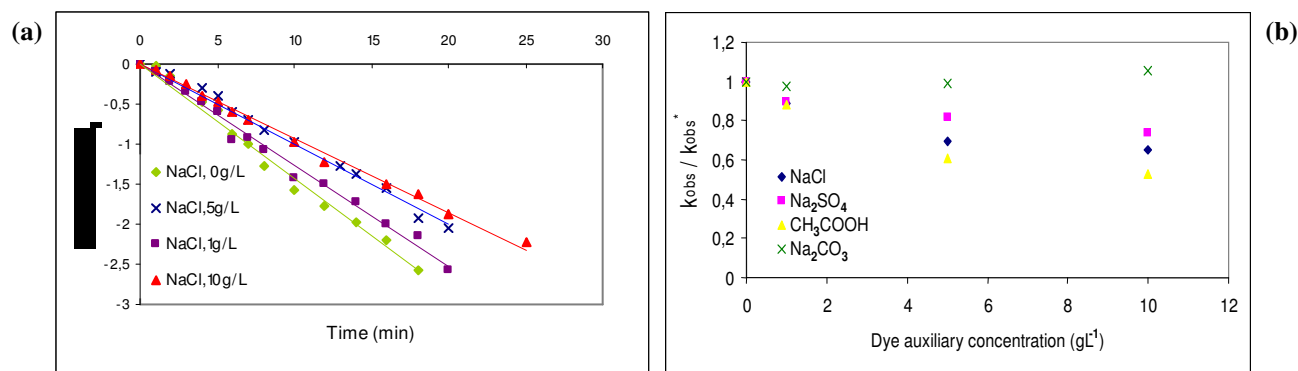
Figure 1: Effect of dye-auxiliary chemical concentration on the UV/H_2O_2 decolouration of AO7; semi-logarithmic plot of the disappearance of AO7 upon irradiation (a) k_{obs} dependence with dye auxiliary concentration (b).

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Water purification using low grade waste heat

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1. Summary

Water purification can be a rational energy save using wasted heat, as shown the present paper. Thermodynamic - mathematical model is presented like an effort for water purification from waste heat. This paper describes computing results of heat absorption pump operation for water purification using low grade waste heat. Equations, parameters and simplifications used in the model are briefly described. The main parameter of the carried out study is the coefficient of performance (COP) defined for reversed heat pumps and the second main parameter is absorber temperature, both parameters has been showed and correlated between them. Main objective of this work is to show the optimal operating condition for different process witch deliver low grade waste heat and requires water purification. Assisted computing simulation was used for obtain these results. The main result is a proposal for optimal recover of low grade waste heat. Many operating conditions are showed in graphical form and discussed for different environment conditions.

Keywords: heat pump, lithium bromide, energy save, water, waste heat

2. Water purification model for waste heat

The proposal of water purification process consists in a simple distillation powered by waste heat, where the heat obtained by the heat pump is recycled when the steam is condensate, this increase the temperature of the heat source. Figure 1 shows a simplified diagram. The impure water to be distilled is heated in absorber, water steam is condensated (loosing heat) and it is collected in auxiliary condenser. In the water purification system, heat supply can be proportionated by the heat pump.

Then the enthalpy based coefficient of performance for to it single stage heat transformer is defined in (eq. 1) and the water purification coefficient of performance for the proposal [Romero et. al., 2006] water purification system using low grade waste heat is the eq. 2

$$COP_{Ent} = \frac{Q_{AB}}{Q_{GE} + Q_{EV}} \quad \text{(eq. 1)} \qquad COP_{WP} = \frac{Q_{AB}}{Q_{GE} + Q_{EV} - Q_{AB}} \quad \text{(eq.2)}$$

(a)   (b)
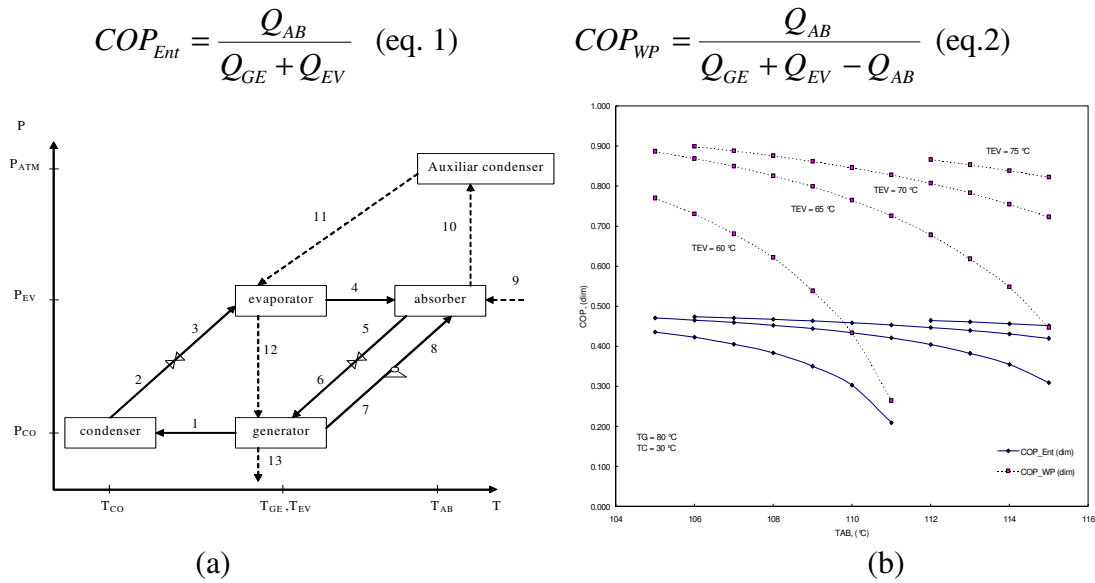
Figure 1(a) Schematic diagram water purification system assisted single stage heat pump and (b) COP_{Ent} and COP_{WP} against T_{AB} for $T_{GE} = 80$ ºC, $T_{CO} = 30$ ºC for four different constant values of T_{EV}.

In figure 1b the water purification and enthalpy based coefficients of performance are shown for constant generator and condenser temperatures of 80 and 30 °C respectively, for evaporator temperatures from 60 to 75 °C.

3. Conclusion

Theoretical behavior of possible operating conditions for an ecological water purification system was shown. The proposal system for lithium bromide was theoretically evaluated with low grade energy with inlet temperatures from 65 to 80 °C, could be from a source of industrial waste heat. Surroundings for condensate the working fluid remain for the calculations between 25 and 30°C, for guarantee absorber temperature higher than 100 °C water purification. Absorber temperature for the system is the power for simple distillation of impure water, with values from 105 to 115°C which can be able for purification of brackish water. The recycled energy for latent heat of purified water purification system has a benefit effect in coefficient of performance, with the relative rise value. Enthalpy based coefficient of performance can arise from 0.3 to 0.43 water purification coefficient of performance.

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5. Acknowledgements

Evaluation of the Capacity of Adsorption of CO_2 in Commercial Zeolites on a PSA Pilot-Plant

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1. Summary

This study is concerned with the capacity of CO_2 adsorption on commercial zeolites in a Pressure Swing Adsorption (PSA) pilot-plant. The determination of the equilibrium CO_2 adsorption capacity of these adsorbents has been carried out through gravimetry. The isotherms obtained for both zeolites were adjusted to the models proposed by Langmuir, Freundlich and Tóth and have shown a particularly good agreement to the Langmuir model. The equilibrium isotherm for zeolite 13X has then been used to determine the optimum operating conditions for the PSA pilot-plant, with regard to temperature and adsorbent moisture content, so as to maximize CO_2 adsorption.

The breakthrough experiments in the PSA pilot-plant, using zeolite 13X as adsorbent, have been undertaken at 300 K and flow rate of 3.0 mL/min , for a gaseous mixture containing 11,5 % CO_2, 87,5 % N_2 and 1.0 % O_2, and resulted in an adsorption capacity of 10.38 g of CO_2 / 100 g of adsorbent. This is in agreement with the equilibrium adsorption isotherms obtained through gravimetry (10.4 g of CO_2 / 100 g of adsorbent), and shows that, at these operating conditions, the adsorption of CO_2 in the PSA pilot-plant is very close to equilibrium.

Keywords: zeolite, adsorption, PSA.

2. Extended Abstract

The experimental evaluation of the CO_2 adsorption capacity of zeolites 13X and 5A involved the physicochemical characterisation of these adsorbents, followed by determination of equilibrium data through gravimetry and finally, breakthrough runs on a PSA pilot-plant. The results indicate a very good agreement with other data already reported in scientific literature.

The characterisation of the zeolites involved techniques such as X-Ray diffraction (XRD), electronic scanning microscopy (ESM) and BET. The adsorption equilibrium data were obtained through gravimetry for several CO_2/Argon mixtures, using an

apparatus composed of mass flow meters, an adapted muffle, a high precision micro scale and a gas chromatograph. For these tests the zeolites have been previously treated at 403 K and 673 K for moisture removal.

The breakthrough runs were performed on a custom designed PSA pilot-plant, and were undertaken on zeolite 13X only, since this adsorbent gave better results on the equilibrium adsorption tests, as shown in Figure 1. It can also be observed that the experimental data for both zeolites are well represented by the isotherm models of Langmuir, Tóth and Freundlich, with a better adjustment for the first two, as indicated by the respective correlation coefficients (R^2)

Fig. 1. Adsorption isotherms at 298 K for CO_2 on zeolites 5A (a) and 13X (b), treated at 673 K, for the Langmuir, Tóth and Freundlich models.

Following activation, the adsorbent has been submitted to a continuous flow of a gas mixture composed of 11.5% de CO2, 87.5% N2 e 1.0% O2, supplied by Air Products, at 523 K, 150 kPa and a 3.0 cm3/s flow rate, for 98.1 min. These runs resulted in the breakthrough curve shown in Figure 2.

Fig. 2. Breakthrough curve for zeolite 13X at 298 K.

The adsorption capacity of the 13X fixed-bed, determined through Ruthven's equation (Equation 1), was 10.71 g/100 g_{ads}, which is in agreement with equilibrium adsorption previously determined through gravimetry (10.41 g/100 g_{ads}).

$$t' = \frac{L}{V}\left[1 + \left(\frac{1-\varepsilon}{\varepsilon}\right)\left(\frac{q'}{Co}\right)\right] = \int_{0}^{t'}\left(1 - \frac{C}{Co}\right)dT \qquad (1)$$

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Color removal from textile effluent using Azadirachta indica leaf powder as an adsorbent

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1. Summary

The removal of dyes present in industrial effluent has received great attention in the past few years. Adsorption is one of the techniques used for the effective removal of dyes (GUARATINI & ZANONI, 1999). However, the efficiency of the adsorption process depends on the choice of a suitable adsorbent (FIGUEIREDO *et al.*, 2000). Because of the high cost of some conventional adsorbents, researches have been seeking alternatives, such as Neem tree leaves. These leaves have polar groups on the surface, which gives it a high cationic exchange capacity (DOHAREY & SINGH; 1989). The Langmuir model was applied to adjust the experimental data. The aim of this study was to investigate the use of Neem leaves as an alternative adsorbent for the removal of dyes present in textile effluents. As this removal showed good results, this adsorbent could be used in industries for the treatment of textile effluent.

Keywords: Reactive dye, *Azadirachta indica,* Remazol Blue RR, dye removal.

2. Extended Abstract

In order to remove the dye Remazol Blue RR, the influence of different parameters were verified, such as pH of the aqueous solution, batch agitation, salt addition, temperature and adsorbent grain size.

After verifying the influence of different parameters on the removal of Remazol Blue RR, the best conditions for this dye removal were obtained, as given in Table 1.

Table 1: Best conditions for Remazol Blue RR dye removal.

Parameters	Agitation	pH	Sodium sulfate	Temperature	Particle size
Best condition	No agitation	10	4%	60°C	40-70 mesh

The results obtained using all of the best conditions given in Table 1 in one experiment for color removal are shown in Figure 1.
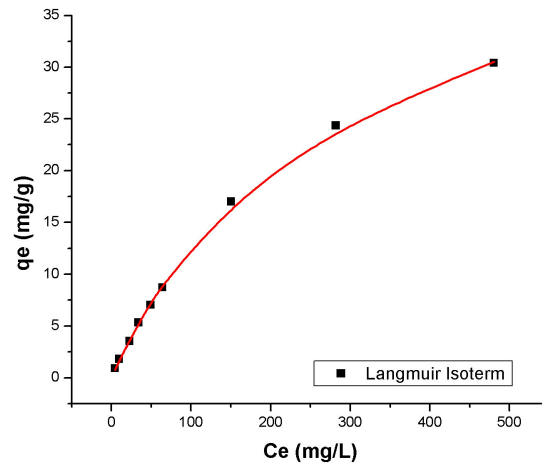
Figure 1: Langmuir adsorption isotherm for Remazol Blue RR dye – best conditions.

In order to study the NLP efficiency for the removal of different dye classes, the conditions given in Table 1 were used for the removal of Lanaset Blue 2R dye (class: acid) and Maxilon Blue GRL dye (class: basic) from aqueous solution.

The maximum adsorption capacity, q_m, calculated for the dyes Remazol Blue RR, Lanaset Blue 2R and Mazilon Blue GRL were 33.898 mg/g, 36.323 mg/g and 41.66 mg/g, respectively.

According to experimental data, Maxilon Blue GRL dye removal using NLP as the adsorbent was over 99%. For the other dyes, Lanaset Blue 2R and Remazol Blue RR, the removals were approximately 97 and 90%, respectively. On the basis of the results obtained, it is possible to observe that the use of NLP as an adsorbent showed good efficiency in the removal of the textile dyes studied. Thus, the use of NLP as an adsorbent could be applied as one of the stages in textile effluent treatment processes.

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Catalytic wet oxidation for abatement of textile dyes.

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1. Summary

Catalytic Wet Oxidation (CWO) of three dyes commonly found in textile wastewaters, Orange G (OG), Methylene Blue (MB) and Brilliant Green (BG) has been carried out using a commercial activated carbon without impregnation of any metal.

Runs were carried out in a three phase fixed bed reactor by feeding concurrently an aqueous phase containing 1000 mg/L of the dye. Temperature was set to 160ºC and the pressure in the reactor was fixed to 16 bar. The catalyst showed high catalytic activity in dye conversion and the catalyst kept stable during the time tested on stream (200 h). Total dye removal is obtained at short residence times but some refractory organic intermediates are obtained (mineralization achieved an asymptotic value about 40-60% depending on the dye). The toxicity of the inlet and outlet effluent was measured by the Microtox bioassay.

Keywords: Catalytic wet oxidation, Dye, Decolorization, Activated carbon, Toxicity

2. Extended Abstract

Synthetic dyes with great structural diversity are commonly found in textile industrial wastewaters (1). These effluents cannot be treated through conventional biological processes because of their poor biodegradability (2). Abatement of three dyes commonly found in textile wastewaters, such as OG, MB and BG has been accomplished by CWO. CWO has been studied in a three phase Fixed Bed Reactor using a commercial activated carbon, Industrial React FE01606A, as catalyst. Runs were carried out at 160 ºC of temperature and 16 bar of oxygen pressure. The initial

pollutant concentration was 1000 mg/L and the oxygen gas flowrate was 90 mL/min. The pollutant conversion was quantified by HPLC using a Diode Array detector, and the remaining total organic content (TOC) was measured. The toxicity of the liquid samples at the reactor outlet was determined by means of a bioassay following the standard Microtox test procedure (ISO 11348-3, 1998).
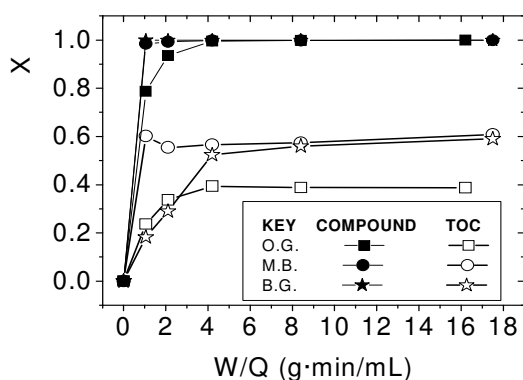
Figure 1. Conversion and mineralization of OG, MB and BG using CWO. T=160ºC, P_{O2}=16 bar.
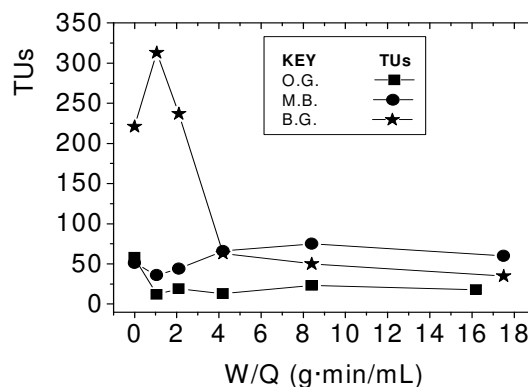
Figure 2. Toxicity Units of O.G., M.B. and B.G. using CWO. T=160ºC, P_{O2}=16 bar.

Figure 1 shows pollutant and TOC conversion. As can be seen, the catalyst showed high catalytic activity in dye conversion and colour removal. Catalyst stability was good during the time on stream tested (200 h). TOC conversion reached asymptotical values of 40 % in OG and 60 % in MB and BG. The Toxicity Units at the reactor effluent are shown in Figure 2. Toxic intermediates are obtained when CWO of MB is carried out, while non toxic effluents are obtained for CWO of OG. A maximum in the toxicity of the CWO of BG is achieved due to nitrogen containing aromatic intermediates.

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Removal of benzalkonium chloride by polymeric adsorbents

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1. Summary

Removal of benzalkonium chloride (BKC) from aqueous streams by polymeric resins XAD-7 and XAD-16 was investigated. Adsorption equilibrium isotherms of BKC from water were measured in a batch adsorber at different temperatures and ionic strengths of the external phase. In addition, the influence of an organic solvent (ethanol) on the phase equilibrium was studied. The experimental data was correlated with the Langmuir isotherm, and thermodynamic parameters for adsorption process were determined. Mass transfer kinetics were investigated in a batch adsorber and correlated with a Fickian diffusion model. Finally, removal of BKC in an adsorption column and regeneration of the column was investigated. It was found that a three-step process is necessary: after break-through, the column could be efficiently regenerated only with an aqueous ethanol solution (20% – 50% EtOH), followed by a short washing stage.

Keywords: cationic surfactant, adsorption, polymer, thermodynamic parameters

2. Extended Abstract

Cationic surfactants are widely used in many industries, household products, and hospitals as bactericides. Because of their toxic properties and very large production volume, their efficient removal from wastewaters is very important.

Polymeric resins have recently been widely investigated as an alternative to activated carbon for the removal of organic pollutants from wastewater (1, 2). Their benefits include more uniform surface chemistry and pore structure as well as the possibility of regeneration under mild conditions. In this work, adsorption of cationic surfactants onto non-ionic polymeric resins is investigated by using benzalkonium chloride (BKC) as a model substance. Two types of adsorbents are used: XAD-7 is an acrylic ester polymer, whereas XAD-16 is a styrenic polymer.

Adsorption equilibrium isotherms were measured at various ionic strengths (0.1, 10 and 100 mM NaCl) and temperatures (23 ^{o}C, 37 ^{o}C and 50 ^{o}C). In addition, the influence of an organic solvent (ethanol) on the phase equilibrium was studied. Adsorption kinetics experiments were conducted in a batch adsorber at pH 5, an ionic strength of 0.1 mM NaCl, and a temperature of 23 ^{o}C.

The adsorption equilibrium isotherms were successfully correlated with the Langmuir isotherm. It was found that the adsorption efficiency was strongly dependent on the ionic strength of the external phase. Higher sorption capacity per mass (and volume) of adsorbent were obtained in the case of the XAD-16 polymer. On the other hand, adsorption capacity per surface area of adsorbent was higher in the case of XAD-7.

Considering the chemical structures of the adsorbents, it seems probable that, in the case of XAD-16, the adsorption mechanism involves hydrophobic interaction. The stronger interaction observed with XAD-7 stems most from hydrogen bounding and possibly electrostatic interaction. Thermodynamic parameters for the adsorption process were determined using adsorption equilibrium parameters calculated for different temperatures. The heat of adsorption was found to be relatively low and had a negative value, indicating that interaction between adsorbent and adsorbate molecules is physical and of exothermic nature. The adsorbed amounts were found to decrease strongly with increasing amounts of ethanol in the external phase.

Removal of BKC from aqueous streams in a single-column adsorption process was studied experimentally and by means of mathematical modeling. As expected from the batch adsorption kinetics data, intraparticle mass transfer resistance was found to be significant, reducing the working capacity of the column. Due to very high affinity of BKC towards the adsorbents, desorption was found to be not feasible by using water as the eluent. Instead, aqueous ethanol solutions (20 wt-%, 50 wt-%) were found to regenerate the column efficiently. Under typical conditions, the duration of the regeneration step was approximately 10 % of the adsorption step. A short washing step prior to the next adsorption cycle was found to be necessary.

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Modeling of the imbibition of polypropylene fiber cloth with emulsions

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1. Summary

This study concerns adsorption of emulsions by polypropylene pneumothermic fiber cloth. A theoretical model was proposed for prediction of the imbibition rate. This model was verified positively for the cases of adsorption of pure kerosene and kerosene in water emulsions of different concentration of the inner phase.
Keywords: porous media, emulsions, imbibition, soaking,

2. Extended Abstract

Emulsion sewage that contains emulsified substances, mainly oil derivatives: oils, fats and lubricants, are extremely arduous to the natural environment. They disturb the processes of both biological and mechanical sewage treatment and have a negative effect on sewerage network. So, oil must be removed from sewage and especially from industrial wastewater. One group of sorbents used to adsorb oil and oil derivatives from water are the polypropylene fibers [1, 2]. They are used in the form of cloth, pillows or sleeves. Their sorption properties are dependent on the thickness of fibers and their structure. The rate of sorption is also dependent on the properties of the emulsions – their viscosity and concentration.

The theoretical model was developed for prediction of the velocity of soaking of the polypropylene strips immersed vertically with one end in the tested liquid as presented in Fig. 1.
Three forces acting on the rising liquid [3, 4] were taken into account: the capillary force F_1, the gravitational force F_2 and the resistance to flow force F_3 resulting from the theory of flow through granular. They can be calculated using the following equations

$$F_1 = 2\pi r_h \sigma \cos\theta \tag{1}$$

$$F_2 = \pi r_h^2 h \rho_c g \tag{2}$$

$$F_3 = 2K_0 \pi h v_c \eta_c \tag{3}$$

where: σ – surface tension, [N/m], θ – wetting angle, [rad], g – gravitational acceleration, [m/s^2], ρ_c – liquid density, [kg/m^3], h – height of the liquid, v_c – velocity of rising of the liquid along the strip, [m/s], η_c – viscosity of the liquid, [Pas], K_0 – constant dependent on the shape of the capillary cross – section, [-]
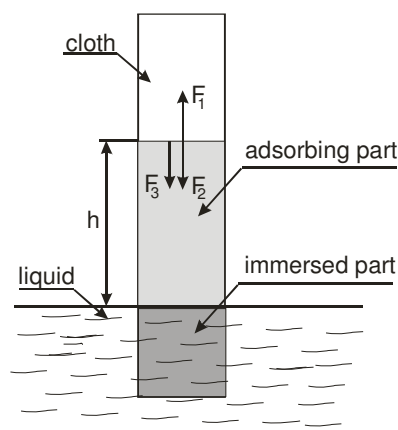
Fig. 1 Forces acting on the rising liquid during imbibition

In the conditions of the steady state flow the balance between these forces allows to write the following formula which allows to predict the velocity of the liquid soaking the fiber cloth

$$v_c = \frac{1}{K_0}\left(\frac{\sigma r_h \cos\theta}{h\eta_c} - \frac{r_h^2 \rho_c g}{2\eta_c} \right) \quad (4)$$

The accuracy of the proposed model was verified positively for the cases of the imbibition of polypropylene stripes with pure kerosene and two kerosene emulsions with the inner phase concentration of 33 and 50 percent as presented in Fig. 2.
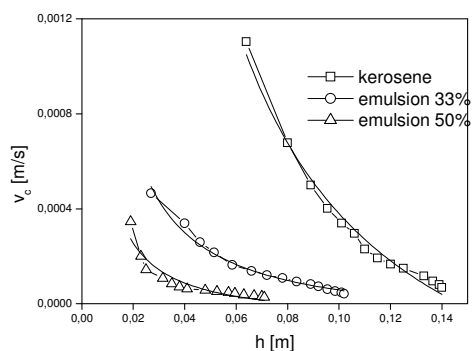
Fig. 2 Soaking velocity changes as a function of the height

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Applicability of the spouting regime for drying of biomass wastes in conical spouted beds with a draft tube

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1. Summary

The operating conditions in spouted bed regime of uniform beds consisting of different biomass wastes dry and wet have been studied to determine the applicability of conical spouted beds with a draft tube in the drying of biomass wastes. This experimental study has been carried out at room temperature and the effect of the solid humidity on the stability of beds of biomass wastes has been determined.

Keywords: conical spouted beds, draft tube, wastes, drying

2. Extended Abstract

Since biomass and agroforestal wastes usually have high humidity content is necessary to reduce this one before the treatment methods, so it is necessary to make a previous drying to other treatment operations. The spouted bed technology is very useful for applications where a vigorous movement of the solids is required, as happens in the handling of solids that are sticky, of irregular texture and with a wide particle size distribution (San José et al., 1993). The first application of spouted beds was drying of grain. Several authors (Passos et al., 1987; Mujumdar, 1984; Strumillo et al., 1980; Viswanathan, 1986) have used spouted bed in drying of granulated materials.

It is proven the great stability of beds of moist sawdust (up to wt % 50) and that system stability decreases as solid moisture increases.

The experimental unit design at pilot plant scale is provided with a blower that supplies a maximum air flowrate of 300 Nm^3/h at a pressure of 15 kPa.

Figure. Diagrammatic representation of the equipment.
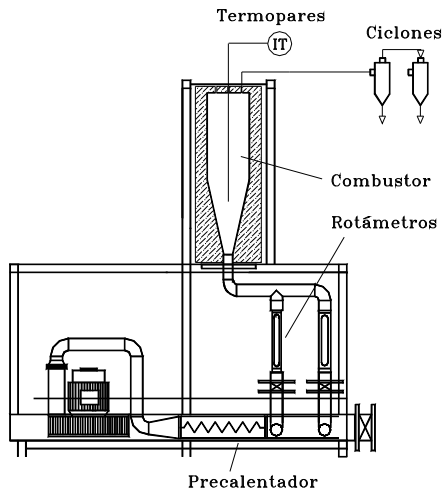
Five conical contactors of poly(methyl methacrylate) with the following dimensions: column diameter, 0.36 m; cone angle, γ, between 28 and 45°; base diameter D_i, 0.62 m, gas inlet diameter D_o= 0.03, 0.04 and 0.05 m. The values of the stagnant bed height Ho, used are between 0.05 and 0.30 m. The values of length of the central draft tubes, l_t, are between 0.010 to 0.30 m and the distance between the base of the contactor and the lower level of the device, h_t, between 0.01 and 0.10 m, respectively. Solid moisture has been measured by means of a hygrometer AQUA-Boy KPM HM III.

The solids studied have been pine bark of Sauter average particle diameter, d_S= 1.5 and 3.5 mm, pine sawdust of Sauter average particle diameter, d_S= 0.95, 1.5 y 4.2 mm, pine shavings of dimensions between 5x15x0.05 y 15x35x0.05 mm and cork wastes of Sauter average particle diameter d_S= 1.5 and 2.5 mm.

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Removal of As, Cd, Cr, Cu, Ni and Zn from polluted water using an iron based sorbent

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1. Summary

In this study a fixed-bed sorption filter is filled with an iron based sorbent (ferrosorp plus, FP) and tested to remove As, Cd, Cr, Cu, Ni, and Zn from polluted water. It is found that FP is very effective at simultaneous removal of the heavy metals, and the magnitude of heavy metal removal in a decreasing order is: Cd, Ni, Cr, Zn, Cu and As. A mathematical model (i.e. Thomas model) is employed to study the data further and to predict the breakthrough adsorption capacities. The capacities of 10.57, 21.85, 15.96, 12.86, 17.54, and 11.07 μmol/g are found for As, Cd, Cr, Cu, Ni and Zn, respectively at an average inflow pH of 6.8 and influent heavy metal concentration of $\approx$2.8 μM. It is concluded that FP has high affinity to heavy metals and it can be used (e.g. as a filter medium) to treat waters containing a wide range of heavy metals e.g. stormwater and industrial wastewater.

Keywords: adsorption, ferrosorp plus, column tests, heavy metals, humic acid, light

2. Extended Abstract

Ferrosorp plus (FP) has been previously tested in batch tests, and found to be one of the most effective sorbents for the combined removal of As, Cd, Cr, Cu, Ni and Zn [Genç-Fuhrman et al., 2007]. Therefore, the current study is designed to test the heavy metal removal in continuous flow experiments to investigate the possibility of using FP as a filter material, and to model the experimental data using Thomas model [Reynolds and Richards, 1996] to estimate breakthrough capacities.

3. Materials and Methods

The FP was supplied by Ingenieurgesellschaft Prof. Dr. Sieker, Germany, and the surface area of the sorbent was found to be 173 m^2/g. Analytical grade heavy metal stock solutions (Perkin-Elmer, Denmark) at 1000 mg/L were used for the study. All the heavy metals were measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The detection limits were 0.4, 0.2, 0.1, 0.8, 0.2 and 1.1

µg/L for As, Cd, Cr, Cu, Ni and Zn, respectively. The column used here, as given in Fig. 1 was custom made for the study and made of Perspex tubes.

Fig. 1. Diagram of the adsorption column and the column detail; arrows show the water feeding direction.
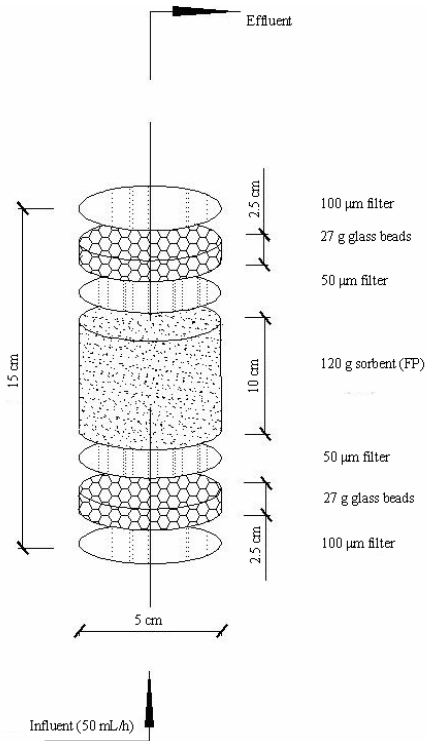
4. Results and Discussion

The results of the heavy metal removal in column experiments are given in Fig. 2, where it can be seen that the full breakthrough (i.e. C_e/C_0 = 1) is not observed within the experimental running time of 100 days. Indeed, the C_e/C_o value was around 0.1 after ≈800 bed volumes. The data suggest that FP has high affinity for all tested heavy metals and the magnitude of the sorption is: Zn>As> Cu>Ni>Cr>Cd.

The predicted adsorption capacities at the breakthrough points from Thomas model are 10.57, 21.85, 15.96, 12.86, 17.54, and 11.07 µmol/g for As, Cd, Cr, Cu, Ni and Zn, respectively. It is noted that significantly higher sorption capacities are observed in column experiments for FP compared to the previously reported batch results [Genç-Fuhrman et al, 2007].

5. Conclusions

- The results suggest that FP is highly efficient for simultaneous removal of As, Cd, Cr, Cu, Ni, and Zn from water with estimated breakthrough capacities of 10.57, 21.85, 15.96, 12.86, 17.54, and 11.07 µmol/g for As, Cd, Cr, Cu, Ni and Zn, respectively. It is foreseen that FP can be developed as an effective filter media for the removal of heavy metals from contaminated water.

Fig. 2. Comparison of the experimental data on the adsorption of As, Cd, Cr, Cu, Ni, and Zn onto FP at average flow rate of 50 ml/h, feeding water pH of 6.7 and using 0.003 M NaHCO$_3$ buffer, and I = 0.01 M NaCl.

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Biodiesel Production by *Thermomyces lanuginosus* and *Rhizomucor miehei* lipase Immobilised in Hydrophilic Polyurethane Foam

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1. Summary

In this study, lipases from *Thermomyces lanuginosus* and *Rhizomucor miehei* were immobilized by covalent binding in polyurethane foam to produce biodiesel using crude soybean and sunflower oils. Polyurethane foam was selected to immobilization, because it has got many advantages. The immobilization method is easy, matrix structure is firm and it has fitting pore size. The highest biodiesel yields were found 98.7% and 98.5% for *Thermomyces lanuginosus* lipase at sunflower and soybean oil, respectively. It was not seen a difference between soybean and sunflower oils for enzymatic biodiesel production.

Keywords:*Rhizomucor miehei* lipase, Styrene-divinylbenzene copolymer, *Thermomyces lanuginosus* lipase, polyglutardialdehyde, immobilization.

2. Extended Abstract

Methyl and ethyl esters of fatty acids, better known as biodiesel, are nontoxic, biodegradable, and an excellent replacement for petroleum diesel. Biodiesel's cetane number, energy content, viscosity and phase changes are also similar to those of petroleum-based diesel fuel [1]. The conventional biodiesel technology involves the use of an inorganic base or acid catalyst at or near the boiling temperatures of the triglyceride/alcohol mixture. The removal of catalyst is through neutralization and eventual separation of salt from the product, which is difficult to achieve. Enzymatic conversion of triglycerides has been suggested as a realistic alternative to the conventional physiochemical methods. Enzymatic transesterification of triglycerides offers an environmentally more attractive option to the conventional process. However, the high cost of the enzymes often makes the enzymatic processes economically unattractive. The key step in enzymatic processes lies in successful immobilization of the enzyme, which will allow for its recovery and reuse [2].

In this study, immobilized lipases from *Thermomyces lanuginosus* and *Rhizomucor miehei* were studied on production of fatty acid methyl ester (biodiesel). The effect of pH and PGA (polyglutardialdehyde) on immobilization efficiency, stability and reusability of immobilized enzyme were investigated. The polyurethane foam including PGA was used for lipase-immobilizing support. The PGA was utilized cross-linking agent for enzymes because it increased enzyme immobilization

efficiency. The reaction solution consists of 46 g of oil, 9.87 g of methanol and 1.5 g polyurethane foam (was cutted 0.5 cm x 0.5 cm). Methanol (oil:methanol molar ratio is 1:6) was added in the reaction systems at three steps. By product glycerol on matrix was extracted by tertiary butanol. The immobilization yields measured by Bradford method were obtained 53% for *Thermomyces lanuginosus* and 50% *Rhizomucor miehei*. The alcoholysis reactions were carried out in a 250 mL-shake flask and heated to 40°C. The immobilized lipase in the polyurethane foams proved to be stable after even 10 reused and lost little activity when was subjected to repeated use. The ester contents of product were determined by DIN EN 14103 method. The effect of pH on the immobilization of lipase was investigated both acetate (25mM) and phosphate (25mM) buffer (5.0 and 6.0 for acetate, 7.0, 8.0 and 9.0 for phosphate buffer). The highest immobilization efficiencies were obtained at pH 6 for both enzymes. The effect of PGA was investigated the range from 0 to 1.6 mL, increasingly. It was observed that the highest relative enzyme activity was determined at 0.2 mL PGA.

After each 9 h transesterification reactions, lipase-containing polyurethane foam was washed with tertiary butanol subsequently reused. This procedure was repeated 10 times to examine the extent of the stability of the immobilized enzyme. The activity of the immobilized lipase upon repeated uses showed a stable trend.

2.1. Conversion in batch reactor

Aliquots of the reaction mixture were withdrawn and the ester content of the product was determined by DIN EN 14103 method [3]. A 6890 N gas chromatograph (Agilent) equipped with a capillary column and a flame ionizing detector (FID) was used.

Operation (number of uses)	Ester content of reaction product (wt.%)			
	Thermomyces lanuginosus		**Rhizomucor miehei**	
	Soybean oil	Sunflower oil	Soybean oil	Sunflower oil
2	98.5	98.7	96.9	97.2
5	98.4	98.7	96.8	97.1
10	98.5	98.6	96.8	97.0

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Enzymatic transesterification of Hungarian rapeseed and sunflower oils

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1. Summary

Hungarian vegetable oils produced by pressing were refined under identical conditions. Biodiesels were produced by batch technology of enzymatic catalysis (Novozym 435) from the refined oils using identical process conditions. Quality properties of biodiesels were determined by standard test methods according to EN 14214. Monoester content of the biodiesels produced with the above described method was above 98.5%, the other properties satisfied the requirements of the EN 14214 standard. The most favorable results, except for CFPP were observed in case of the biodiesel of highest oleic acid methyl ester content, which was produced from the sunflower oil, obtained from an improved type of sunflower species.

Keywords: Hungarian vegetable oils, enzymatic transesterification, biodiesel

2. Extended Abstract

2.1. Introduction

The European Union facilitated the penetration of biofuels with the establishment of Directive 2003/30/EC, which resulted in a biofuels share of 1% in the EU by 2005, calculated on the total amount of transportation fuels consumed [COM(2006) 845]. The most recent proposal of the European Union is to raise the share of biofuels to 10% by 2020. This target can be achieved with the application of biodiesel, which is produced from triglycerides. Quite a number of feedstocks are available for the production of biodiesel (Körbitz, 1999). Out of them a very important one is the rapeseed oil obtained from rape, which can be cultivated with high yield in the western part of Europe. Another important raw material is the sunflower, which can be efficiently cultivated in the climate and geographical conditions of the Central European Region. The two vegetable oils are reasonable for Hungary as feedstocks for biodiesel production (Bélafi-Bakó, 2002; Hancsók, 2005).

2.2. Experimental

In our research work, the possibility of the transesterification of different vegetable oils was investigated by using Candida antartica lipase enzyme. Furthermore, the effect of fatty acid composition of the feeds on the characteristics of biodiesel products was studied. Suitability of biodiesel products considering the requirements of the standard (EN 14214) was also investigated.

2.1. Materials and apparatus

The experiments were carried out at 50°C in New Brunswick G24 type shaking incubator. Vegetable oils of various fatty acid composition, which had been pressed from plants cultivated in Hungary, were used as feeds together with Candida Antartica lipase enzyme and methanol of analytical grade.

2.3. Results and discussion

After the reaction time of 16 hours we found only a few percent of difference in the methyl-ester content of the different samples. Highest methyl ester content was achieved with the transesterification of the sunflower oil of high oleic acid content. The kinematical viscosity at 40 °C, the density and the flash point of all feedstock types were only slightly different, and decreased significantly during the transesterification reactions.

Biodiesel containing high amount of oleic acid and low quantity of saturated fatty acids has the most favourable cold filter plugging point (CFPP). The samples prepared from the conventional sunflower had the worse CFPP value due to their unfavourable fatty acid composition (high content of saturated fatty acids). Although CFPP values of all the samples comply with requirements of the summer grade (grade A) biodiesel standard for temperate climate regions; they are inappropriate as a winter grade biodiesel. Iodine numbers of biodiesels prepared from the sunflower oil of high oleic acid content and from conventional rapeseed oil have met the specification (max. 120 g I_2/ 100 g) of EN 14214 biodiesel standard. Those prepared from conventional sunflower oil, however were off-scarification from the point of view of iodine number. Thus they are not suitable to be used directly as a biodiesel fuel.

2.4. Conclusions

Through the transesterification of vegetable oils of various fatty acid contents, it was concluded that fatty acid composition does not significantly affect enzymatic transesterification. Iodine number and CFPP value of the biodiesel based on conventional sunflower oil is less favourable than those originated from conventional rapeseed oil or from improved sunflower rich in oleic acid. Summarized, biodiesels produced from improved sunflower oils rich in oleic acid had better properties than the conventional sunflower oils and conventional rapeseed oils.

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Lipase-catalyzed synthesis of biodiesel

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1. Summary

This work is focused on the catalytic transesterification of sunflower and soybean oils with methanol and ethanol, employing enzymes as catalysts. Moreover, alkali-catalyzed reactions were also carried out, using NaOH and KOH, and the results were compared to those obtained by the biocatalyzed reaction.

Keywords: Biodiesel, lipases, FAME, green chemistry, enzyme.

2. Extended Abstract

Among the alternative energies that could be produced from biomass, the use of vegetal oils and their derivatives, such as mixtures of fatty acids esters, the so-called biodiesel, is one of the most promising routes (Ma and Hanna, 1999). Biodiesel has similar energy efficiency as the conventional diesel, and a reduced pollution load. Moreover, it can be used in the conventional diesel engines without the need of modifications. Since it can be obtained from low-cost raw materials, the resulting fuel may also be economically feasible (Van Gerpen, 2006)

Biodiesel is produced at large scale by transesterification of the triglycerides present in animal fat or vegetable oils, by displacing glycerine by a low molar mass alcohol (typically methanol), using alkali catalysts. These resulting methyl esters are rather similar to the hydrocarbons that are present in the diesel (Fukuda *et al.*, 2001).

This research work has been focused on the catalytic transesterification of sunflower and soybean oils with methanol and ethanol, employing enzymes as catalysts. Although the methyl esters are currently the only ones produced at industrial scale, the use of ethanol, which can be obtained from renewable resources, would generate a cleaner and more biocompatible fuel (Peterson *et al.*, 1996).

From a preliminary enzyme screening, the lipase B from *Candida antarctica* was found to give the highest yield. Reaction conditions, such as enzyme/substrate ratio, alcohol/oil ratio, and temperature were then optimized. Methanol caused enzyme deactivation even when used at moderate excess, thus, a fed-batch system has been implemented. Ethanol transesterification proceeds at a slower reaction rate, but with less alcohol excess. Although enzyme catalysis is slower than alkali catalysis, it results in a simpler downstream purification process.

Acknowledgements

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REDUCTION OF STILLAGE's VOLUME IN THE PRODUCTION OF ETHANOL BY RECIRCULATION.

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1. Summary

The recirculation of the stillage (or vinasse) to the stage of fermentation, in the production of alcohol, is a technique of source reduction very applied in this industry, but it presents the inconvenience of it turns limited because with her they can feed to the process by-products of the fermentation that remain in the stillge after the distillation they are inhibitory for the yeast and they also go accumulating when applying several recirculations in series. In this work was defined the acetic acid, as the main inhibitor of the yeast and the effect of different concentrations of this on the fermentation was evaluated, it was observed that any level of the acid affects the biomass and starting from 2.5 g/L it begins to diminish the production of alcohol. The extraction liquid-liquid was applied, on the stillage, as separation technique of this acid, with that were improved the recirculation possibilities, since, without the separation and after five recirculations, the biomass diminished until in 70% and the productivity of alcohol until in 30%, while when the extraction was applied, the biomass was affected in 42% and the productivity of alcohol didn't diminish; during the five recirculations, a descent in the consumption of water of dilution of 56% was achieved and in the generation of stillage of 44%.

Keywords: Ethanol production, fermentation, distillation, stillage, vinasse, liquid_liquid extraction.

2. Extended Abstract

The used culture was a Saccharomyces cerevisiae ATCC26603, with which there prepared the mother culture, it was renewed monthly, the inoculate for the fermentation, was a 15 % of the total fermentation broth, the time of preparation of inoculate was of 14 h and that of the fermentation of 20 h, in a reciprocant shaker with control of temperature for 30ºC and 110 rpm; of the fermented mash obtained, was distilled 15 %. The stillage obtained in every distillation, was centrifuged and used to replace 70% of the dilution wáter in the next fermentation. In the cases in which extraction was not applied, with this one the following fermentation broth, was prepared, in other case it was carry on to the extraction stage, the solvent used was the palm oil methyl ester in relation 1:1, the vinasse like that treated was re-circulated to prepare the following fermentation medium, 4 recirculations were carried out. The fermentation kinetic was verify following-up of sugars and ethanol, in a HPLC as well as the quantification of the acetic acid in the stillage. To determine the biomass there was used the Neubawer's chamber. The statistical analysis was realized using the software SPSS, with a significance up to 95 %, for all the results.

To study the inhibitor extraction effect on the stillage recirculation, five fermentations in series were carried out, each of which used 70 % of the vinasse of the previous fermentation, to dilute the molasses, parallely to these five fermentations, were carried out another ones, this time applying an liquid - liquid extraction to the stillage, before recirculate it.
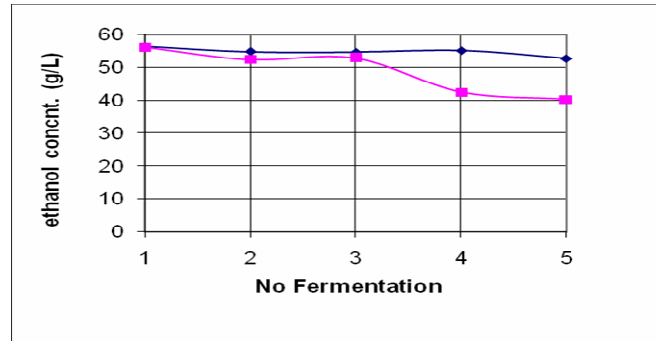
Figure 1 Ethanol final concentration in the fermented mashes prepared with vinasse, with and without extraction

The figure 1 shows changes in the ethanol concentration in each of five fermentations, with recirculation of 70 % of the stillage, could be seen that the recirculation with extraction applied to the vinasse, does not have a clear effect on the ethanol concentration reached, there is no a decrease in the concentration of ethanol in the fermented final broth, in the successive fermentations; for the case of the fermentations without extraction (low curve), it is possible to estimate a similar behavior in the first three fermentations, comparablly also with the observed for the case with extraction, since there are reached close values of concentration of ethanol to 55 g/L. For the last two fermentations one presents a decrease in the concentration of ethanol to values of 40 g/L, similar results were obtained (Kim et al., 1997) applying 8 recycles with only a decrease of 2-3 % in the productivity of ethanol, using an ultrafiltration to the vinasse. Slightly similar to what happens with the ethanol, it happens with the biomass, it presents a decrease from the second fermentation, making well-known that the response of the yeast is more sensitive than that of production of ethanol and when the extraction is not applied in the stillage, with which the corresponding way will be prepared, the quantity of produced biomass is still minor. There achieved a major saving of water, 56 %, that achieved by Shojaosadati (1996), 33 % and a major decrease in the generation of vinasse 44%, that achieved by this investigator, 33 %, owed principally on having re-circulated 70 % of the vinaza in this work, compared with 50 % applied by Shojaosadati.

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DEVELOPMENT OF AN ETHANOL PRODUCTION PROCESS WITH STILLAGE RECYCLING AT PILOT PLANT-SCALE.

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1. Summary

The production of energy from biomass has been object of wide research in the last years, especially the production of fuel alcohol, in Colombia, has increased thanks to laws promulgated by the government; parallel to this the generation of residues increases also, in this case called stillage or vinasse, for a conventional process 13 to 15 liters are obtained of stillage by liter of ethanol, which for the quantity of ethanol projected, of 750 million liters/ year of alcohol, would be generated between 9750 and 11250 million liters of stillage/year, a so big quantity.

An ethanol production process with stillage recycling in bench-scale was developed in order to determine stillage percentage recirculation and the number of successive recycles that can be carried out, without detriment in the ethanol productivity achieved. With the best results obtained in bench-scale will be climbed to pilot plant-scale.

The inhibitors presents in the stillage, as acetic acid and solids, which increase by accumulation, with the continuous recycles, limit the recirculate percentage and the number of recycles that can be carried out, for this reason several alternatives were proposed and evaluated in order to remove them or diminish their harmful effect.

Keywords: stillage recycling, ethanol production, clean technology, pilot plant scale.

2. Extended Abstract

The used culture was a Saccharomyces cerevisiae ATCC26603, with which there prepared the mother culture, it was renewed monthly, the inoculate for the fermentation, was a 15 % of the total fermentation broth, the time of preparation of inoculate was of 14 h in a reciprocant shaker with control of temperature for 30ºC and 110 rpm and the time for fermentation of 28 h in a CE 640 Fermentation & Alcohol Production Pilot Plant / PC (Gunt, Hamburg); the fermented mash obtained, was distilled 15 %. The stillage obtained in every distillation, was centrifuged and used to replace 70% of the dilution wáter in the next fermentation. The fermentation kinetic was verify following-up of sugars and ethanol, in a HPLC as well as the quantification of the acetic acid in the stillage. To determine the biomass there was used the Neubawer's chamber. The

statistical analysis was realized using the software SPSS, with a significance up to 95 %, for all the results.

To study the stillage recirculation effect on the etanol productivity and biomass, five fermentations in series were carried out (Castro, 2006), each of which used 70 % of the vinasse of the previous fermentation, to dilute the molasses.
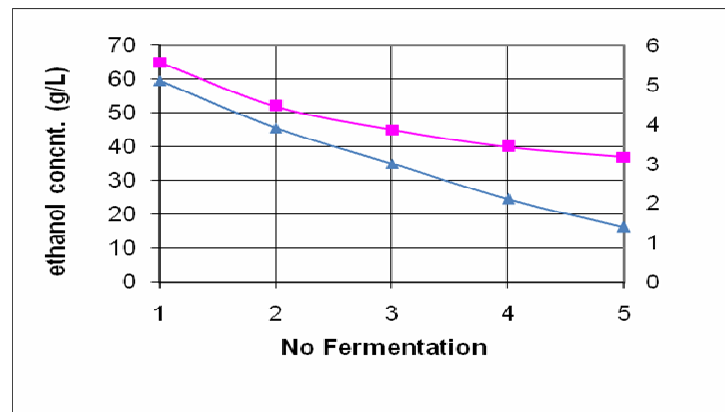
Figure 1 Ethanol final concentration (square marker) and cell number $*10^7$/ml (triangle marker) in the fermented broths prepared with vinasse,

In the figure 1, is clear the behaviour with the succesive fermentations, It is possible to observe a decrease in the productivity of ethanol from 65 g/L to 37 g/L, as well as a decrease in the biomass of 66 % approximately, this as apparent consequence of the sequential increase in the solids (sugars unfermentables, principally) from 15 up to 25 ° Bx after the fifth fermentation in series. Maiorella et al. (1983) presented to the increase in the concentration of solid as one of the three most important inhibitors in the production of ethanol, due to the increase in the osmotic pressure that they can cause. Navarro et al. (2000), showed that the concentration of solid reached, produces inhibition for the yeast, since there comes closer the value of 26 % of solid that they defined as the low limit of the range of high inhibition.

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Modeling and prediction of ammonia emission from field-applied animal manure

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1. Summary

Ammonia emission from field-applied pig manure slurry is studied using Michaelis-Menten equation. The two model parameters (total emission of ammonia and time to reach half of the total emission) of the Michaelis-Menten equation are estimated using a multivariate linear regression (MLR) method and a feedforward-backpropagation artificial neural network (ANN) approach on the basis of ALFAM (Ammonia Loss from Field-applied Animal Manure) database in Europe.

The MLR method well describes the ammonia emission tendency with variation in the emission factor. However, ammonia emission from manure slurry is too complex to be captured in a linear regression model. This necessitates a model which can describe complex nonlinear effects between the ammonia emission variables such as soil and manure states, climate and agronomic factors. In the present study, a ANN approach is proposed to account the complex nonlinear effects.

The ammonia emission is predicted with precision by the 11 emission factors, using the nonlinear ANN approach. The relative importance among the 11 emission factors is identified using the elasticity analysis in the MLR method and using the ANN approach. The relative significance obtained quantitatively by the ANN approach in the present study gives an excellent explanation of the most important processes controlling NH_3 emission.

Keywords: Ammonia emission; livestock manure; Michaelis-Menten equation; Multivariate linear regression (MLR), Artificial neural network (ANN).

2. Extended Abstract

The Michaelis-Menten type equation is one of the widely used model to predict the ammonia emission from field-applied manure (Lim et al., 2007). The Michaelis-Menten equation is:

$$N_{NH3}(t) = N_{max} \frac{t}{t + K_m} \tag{1}$$

where N_{NH3} $[kg/ha]$ is the accumulated ammonia loss at a time (t), $N_{max}[kg/ha]$ is the maximum ammonia loss, and $K_m[hr]$ is the time to reach half of the maximum ammonia loss ($\frac{N_{max}}{2}$). Here, the quantity of ammonia loss is based on the nitrogen weight. The two model parameters (N_{max} and K_m) can be estimated by an empirical equation regressed from experiments.

In this study, the two model parameters are estimated on the basis of ALFAM (Ammonia Loss from Field-applied Animal Manure) database (Sommer, 2000) in Europe, using the feedforward-backpropagation artificial neural network (ANN) approach.

2.1. Artificial neural network approach

The ANN approach is composed of one input layer, one or several hidden layers and one output layer. The neuron numbers of the input and output layers are equal to the input and output variable numbers, respectively. In this work, the neuron numbers of the input and output layers correspond to the 11 independent variables influencing the ammonia loss and the two model parameters of the Michaelis-Menten equation, respectively.

2.2. Results and Discussion

The calculation is performed on the statistics and neural network toolboxes of Matlab (Mathworks, USA, 2005). Table 1 shows the correlation coefficients (R^2) of the two model parameters and the mean square errors (MSE) using the two model parameter estimation methods (MLR and ANN methods). The nonlinear regression method (i.e., ANN approach) shows a higher correlation coefficient value than the MLR method, because nonlinearity between the independent variables (p_i) and the model parameters (K_m and N_{max}) is better considered. It is noted that the ANN approach predicts quasi perfectly the measured K_m and N_{max} values (see Fig. 2) even without information of NH_3 emission factors excluded in the model (e.g., soil moisture, radiation, total nitrogen in manure, etc.). However, the prediction is valid for the used 83 datasets.

Table 1. Correlation coefficient (R^2) and mean square error (MSE) in MLR and ANN approaches.

model		R^2 for K_m	R^2 for N_{max}	MSE
MLR	This study	0.3680	0.6631	141.04
	DIAS	0.77	0.80	-
PWA 11-10-26-2		0.9941	0.9985	0.8333
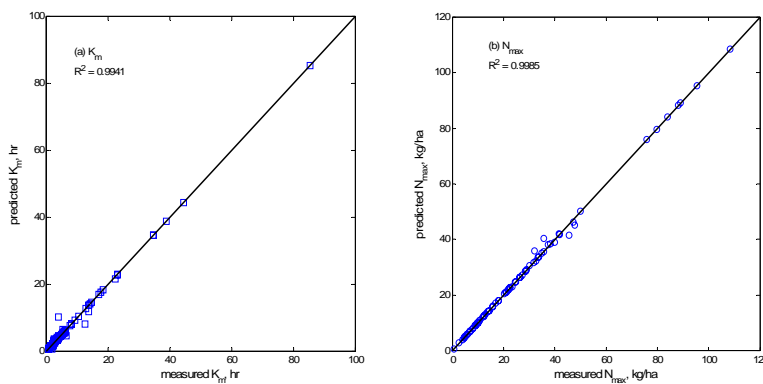
Fig. 1 Comparison of measured and predicted model parameters (K_m and N_{max}).

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Wood in Pulverized Fuel Power Plants: Char Characterization and Char Combustion

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1. Summary

In suspension fired boilers char oxidation is the slowest step in the conversion of wood and thus determines the degree of burnout of the fuel as well as the heat release profile in the boiler, affecting the operation and efficiency of the plant. Chars were produced at different conditions in a pilot-scale entrained flow reactor (EFR) reproducing the conditions in a real suspension fired boiler; for comparison, some wood chars were produced by thermogravimetry (TGA) at much lower heating rate. SEM analyses showed that wood particles subjected to rapid heating had lost completely their characteristic fibrous structure; char particles were spherical and porous, and it seemed likely that during devolatilization the particles had gone though a molten phase. Wood particles exposed at higher temperatures resulted in char particles of smaller size. Chars produced under boiler-like conditions showed significantly higher reactivity than those produced at milder conditions in the TGA apparatus. Kinetic parameters obtained from chars produced at boiler-like conditions can allow a more accurate prediction of fuel burnout in pulverized wood power plants.

Keywords: wood combustion, pyrolysis, char combustion

2. Extended Abstract

The influence of high temperature fast pyrolysis on wood char properties and reactivity was investigated. As illustrated in Figure 1, wood char did not retain the fibrous structure typical of wood when high heating rates and high temperatures were applied, whereas no changes in structure were seen for pyrolysis in a TGA apparatus. Particles may undergo plastic deformation when pyrolysed at severe conditions.

The oxidation reactivity of the produced wood chars was derived by thermogravimetry, assuming a single first order reaction. The activation energy was fixed at a common value for all chars and the derived reactivity is shown in Figure 2. Char produced in inert atmosphere showed a tendency to deactivate when the

pyrolysis temperature increased. For the chars produced in TGA, there exists a pyrolysis temperature interval (1273K – 1373K) where char reactivity does not vary.

As can be seen in Figure 2, all the chars produced in EFR under boiler-like conditions had higher reactivity than those produced in the TGA. This could be due to the major transformation of the particle structure during fast pyrolysis. Vaporization, reaction and re-arrangement of the mineral matter during pyrolysis may also contribute to some extent to the differences in char reactivity.
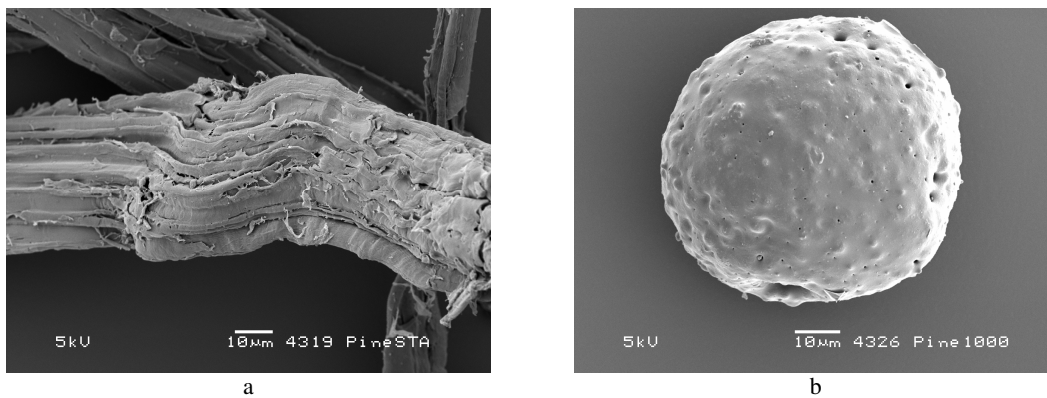
Figure 1: a) Char particle obtained by pyrolysis of pine wood in TGA; the wood sample was heated in N_2 at 10K/min up to 1373K and held at this temperature for 30min. b) Char particle obtained by fast pyrolysis of pine wood in EFR; reactor temperature 1273K, pyrolysis gas 100% N_2.
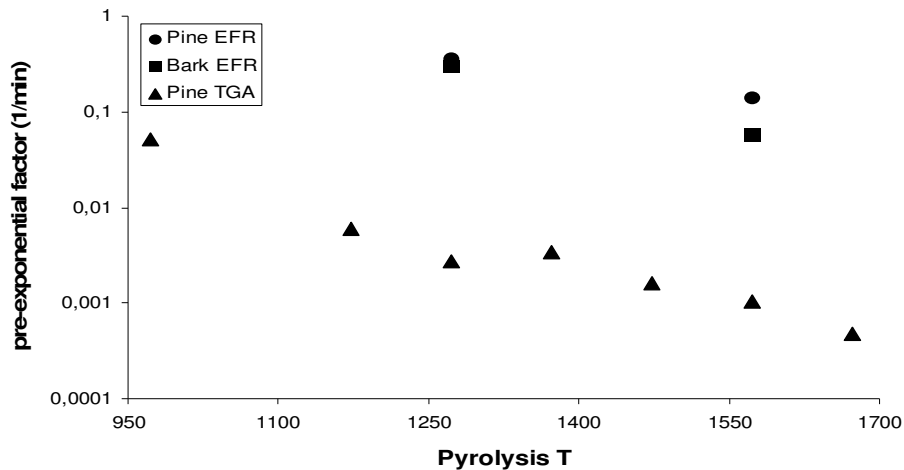
Figure 2: Calculated oxidation kinetics of wood chars. Triangles represent chars produced in TGA by heating pine wood in nitrogen atmosphere at 20 K/min up to the final pyrolysis temperature and holding the sample at this temperature for 20 min. The other chars included in the figure are produced in the EFR reactor at boiler-like conditions.

Reduction of NO by acetylene soot

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1. Summary

Soot formation may occur in high temperature fuel rich areas in combustion processes. To avoid possible fouling and environmental problems, soot particles should be eliminated before exiting the combustion equipment. One of the possibilities is their reaction with NO within the combustion chamber. The study of this reaction conditions could result in a synergistic effect for the reduction of both NO and soot. With the aim of exploring the soot-NO reaction, two different soots were produced from acetylene pyrolysis at 1100ºC using 50000 and 5000 ppmv acetylene, respectively. At 1100ºC, experiments of soot-NO reaction were performed using a wide range of NO concentrations (300-3000 ppmv). Results show the reactivity of both materials to NO, maybe caused by their different structural characteristics. The analysis of these data may contribute to minimize pollutant emissions in combustion devices.

Keywords: acetylene pyrolysis, soot, reactivity, NO reduction

2. Extended Abstract

In a previous study (Mendiara et al., 2005), the experimental setup and the methodology used for the study of soot formation were explained. Acetylene was selected as reactant because it is one of the main precursor species in soot formation from different fuels (Stanmore, 2001). Soots produced by pyrolysis of 50000 and 5000 ppmv acetylene were denoted as soot A and B, respectively. BET area with nitrogen at 77 K was quantified and elemental analysis was made for both soots. SEM, HRTEM and XRD analysis to the soot samples were also carried out. Results obtained in soot characterization showed chemical and structural differences between both materials. Soot A C/H molar ratio was 13.5 and soot B was 10.0. Soot A presented 13.13 m^2/g BET area and soot B 30.25 m^2/g. For soot A, the particle diameter distribution was in the 0.6-0.2 μm range. For soot B, it was in the range of 0.2-0.1 μm. XRD and HRTEM analysis also showed differences in their internal structure. Soot A possesses longer graphitic layers, and so lower ratio of border to

basal sites. Soot B showed a higher percentage of border active sites due to its no aligned short graphitic layers.

Soot-NO experiments were performed in a quartz reactor. This reactor is designed including a bottleneck in its middle, where a quartz wool plug is placed. Soot is mixed with silica sand particles and the mixture is located over the plug, resulting in a thing layer. An amount of approximately 10 mg of soot was introduced in the reactor. The reaction of soot A and B with NO was analyzed at 1100ºC and in the range of 300-3000 ppmv NO. The reactivity of soot A and B to NO is analyzed through the representation of the carbon consumption rate evolution versus carbon weight remaining in the thin layer. Figure 1 shows the values of carbon consumption rate for soot A and B and different NO concentrations**.**
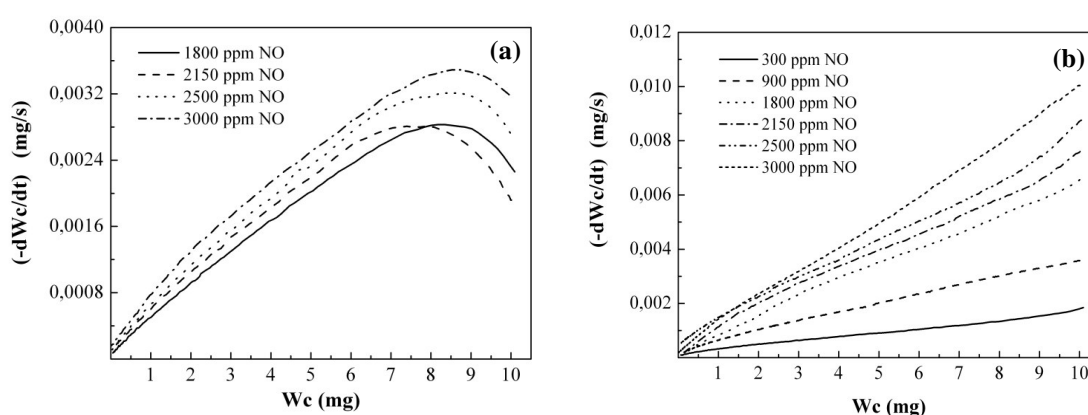
Figure 1: Evolution of the carbon consumption rate versus carbon weight for the reaction soot-NO at T = 1100ºC of (a) soot A and (b) soot B, and different NO concentrations

In figure 1, the values of the carbon consumption rate for the same NO concentration and carbon weight are higher for soot B in all the cases. Therefore soot B can be considered more reactive to NO than soot A.

There are also differences between both soots with respect to the NO conversion values achieved in the same reaction conditions. Conversion values are higher for soot B (close to 30 %) compared to soot A (close to 10%) in all the cases. The differences in carbon consumption rate and NO conversion can be related to the structural differences of soot A and soot B. The highest BET surface area, lowest C/H molar ratio and particle diameter distribution and the shortest graphitic layers of soot B in relation to soot A may explain its higher reactivity to NO.

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Catalyst selection for the coupled methanol/paraffins cracking

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1. Summary

The upgranding of paraffins (propane and butane) into light olefins, over catalyst with shape selectivity, is of great interest due to the olefin demand. However, these kinds of processes give way to low olefin yield and require high temperatures. The energy requirements in the paraffin cracking can be reduced by feeding methanol, (the CMHC process), [1] in order to achieve: i) the energy compensation combining the endothermic cracking with the exothermic stage of methanol dehydration and; ii) the attenuation of catalyst deactivation due to coke deposition [2], and irreversible deactivation. The selection of the catalyst is one of the keys to obtain a viable process, which has to be active, selective and hydrothermally stable. Taking into account this purposes, the properties of different catalysts and their behaviour under different operation conditions have been studied.

Keywords: coupled methanol paraffins cracking, catalyst selection

2. Extended Abstract

2.1 Experimental

The catalyst consists of 25 wt% of active phase agglomerated by wet extrusion with bentonite as binder (30 wt%) and inert alumina calcinated at 1000 ºC as charge, in order to confer a high mechanical resistance to attrition upon the catalyst. HZSM-5 zeolites with different Si/Al rate, Ni/HZSM-5, HY and a silicoaluminophosphate (SAPO-18) have been studied as active phases. The acid properties of the samples (acid strength distribution and total acidity) have been characterized by temperature-programmed desorption of ammonia (TPD, calorimetric-thermogravimetric adsorption) (Setaram TG-DSC 111 connected on-line to a mass spectrometer Balzers Quadstar 422) [3]. The physical properties have been characterized by adsorption-desorption of N_2 (ASAP 2100 Micromeritics). The experiments have been carried out under normal pressure in automated reaction equipment. The reactor is connected on-line to a micro-chromatograph Varian CP-4900. Different experiments have been performed at 550 ºC, feeding n-butane and methanol/n-butane mixtures.

2.2 Results
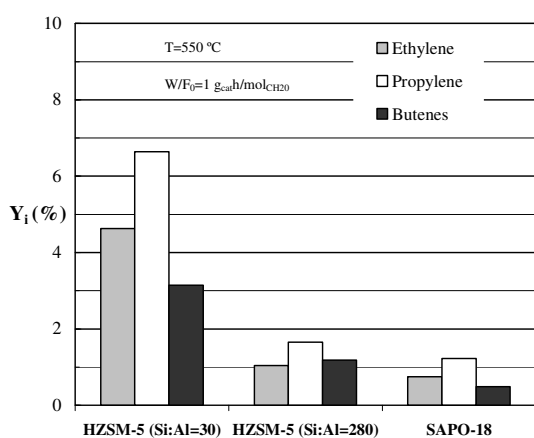
Figure 1.- Individual olefin yield at zero time by feeding n-butane over different catalysts. 1 ($g_{catalyst}$) h^{-1} (mol CH$_{2\ reactant}$)$^{-1}$ and 550 ºC.
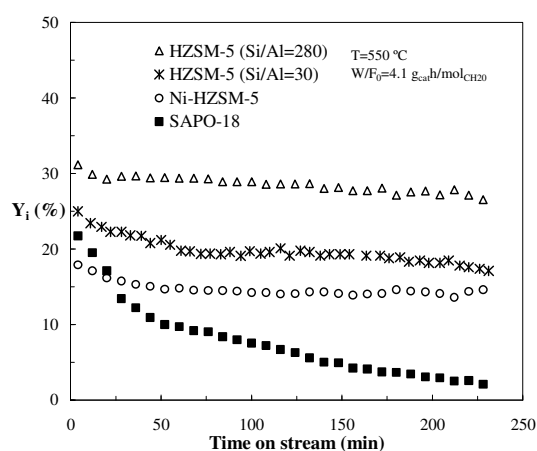
Figure 2.- Evolution with the time on stream of the olefin yield obtained in the CMHC process over different catalyst.

HZSM-5 (Si/Al=30) catalyst has a good behaviour in the n-butane cracking. Thus, a 14 % yield of olefins is obtained practically constant throughout 5 h reaction. This might be a consequence of: i) the high number of acid sites with moderate acid strength (140 kJ/mol) on the catalyst, which give way to catalytic cracking; ii) the low coke deposition in the pores of the catalyst. The HZSM-5 zeolite catalyst with smaller content of Al (Si/Al=280) presents a higher initial yield of olefins (30 %) and a very slow deactivation in the combined cracking, which is attributed to the moderate acid strength (130 kJ/mol) without strong acid sites.

The severe shape selectivity of the SAPO-18 is decisive for the quick deactivation (blockage of pores) by coke deposition of the corresponding catalyst. The results for the HY zeolite catalyst (not shown) are evidence of a low olefin yield, high formation of aromatics and fast coke deposition in the supercages of the Y zeolite. From the point of view of stability (low deactivation) and especially for the regenerability, the Ni containing catalyst give way to remarkable advantages, although high yields of aromatic BTX and thermal coke are obtained as by-products. Regarding olefin selectivity, the propylene is the main product for all the catalysts.

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How to deal with one of the main obstacles for an increased use of CO$_2$ neutral biomass in power plant boilers – Optimal ash deposits removal in straw fired boilers

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1. Summary

An increased use of biomass as fuel in power plant boilers leads to a net decrease of CO$_2$, but the high fuel alkali and chlorine content of biomass induce unwanted ash deposit formation on boiler hest transfer surfaces. Slagging and fouling problems that reduce boiler availability are often observed. The amount of ash deposit present on boiler heat transfer surfaces is influenced by deposit formation and shedding processes. While short time deposit formation measurements often have been performed, well controlled deposit removal experiments have rarely been conducted in biomass power plant boilers. In this study, deposit shedding was investigated by advanced probe measurements and a computer model describing deposit formation and shedding from a superheater tube was developed.

Keywords: Biomass, Combustion, Slagging, Fouling.

2. Extended Abstract

A combined air- and water-cooled probe and support equipment were constructed, so that the weight of probe ash deposit and the heat uptake could be measured in situ in a power plant boiler (see Figure 1.). Equipment for video recording, flue gas temperature measurements and controlled soot blowing were also used. Measurements with the probe were performed in grate power plant boilers. The probe was placed near the superheaters and in the convective pass of a straw fired boiler (The Avedøre power plant) and near the superheaters of a wood and oil fired boiler (The Herning power plant).

The main shedding mechanism (at flue gas temperatures of 900 to 1100ºC) was observed to be melting of the deposit surface and ash droplet detachment. It was observed that the flue gas temperature affects the melt fraction of the deposit and thereby controls the shedding rate. A sequential deposit buildup process was observed on the probe: An initial large increase of deposit mass (deposit formation rate of 300 g/(m^{2}h)) up to 6 hours after the clean probe was inserted into the boiler, was followed by a slow deposit weight increased in

the following 5 days, and finally the deposit weight reached a reasonably stable level, with equal rates of deposit formation and shedding by ash droplet detachment.
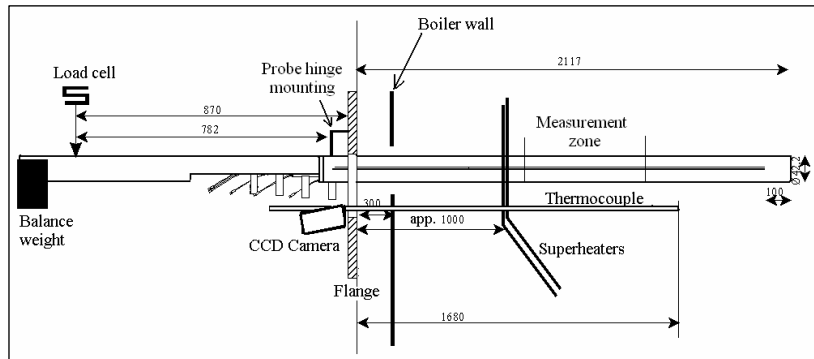
Figure 1. Sketch of the deposit probe system

A computer model describing the deposit formation and shedding process on the probe was developed. The model includes sub-models of mass and heat transfer, as well as calculations of deposit melt fraction and viscosity. The model describes deposit formation processes as condensation, ash particle impaction, and thermophoresis, and shedding by deposit melting and droplet detachment. As seen on Figure 2 the model was validated by the probe measurements and was used to calculate the influence of changed local parameters on the development of the probe deposit and heat uptake.
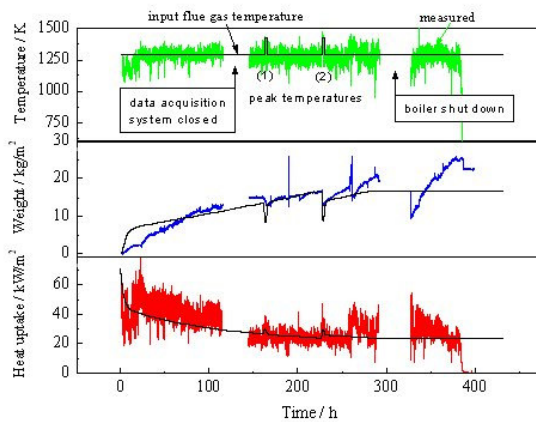
Figure 2. Comparisons of the evolutions of modeled and measured probe deposit weight and heat uptake as a function of time in the furnace. Probe measurements conducted in the furnace chamber.

Well-controlled soot blowing measurements in the second boiler pass (flue gas temperature from 650 to 800°C) of the probe was performed in order to determine the peek impact pressure needed to remove the deposits. The influence of changed probe metal temperature and residence time was investigated. At a probe temperature of 400°C the deposit could easily be removed by the plant soot blowers. At a probe temperature of 500°C the removability of the deposit by soot blowing decreased with time. Based on the investigation recommendations for optimal operation of straw fired boilers with respect to deposit minimization could be provided.

Novel PVDF-HFP membranes tailored by supercritical drying process

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1. Summary

The work is based on the drying of PVDF-HFP gels with a procedure assisted by supercritical CO_2 to obtain nano-sized porous membranes at high quality/low cost ratio. Series of supercritical drying experiments have been performed at 35°C, 200 bar and at various polymer concentrations (from 5 to 12% w/w). In all cases, the membranes exhibit interconnected structures with nano-sized pores and highly porous surfaces.

Keywords: PVDF-HFP, Membranes, Supercritical, Nanostructure.

2. Extended abstract

Poly(vinylidene fluoride) (PVDF) as homopolymer or copolymer with hexafluoropropylene (PVDF-HFP) is a very interesting material largely used in catalytic membrane reactors [1-3], chemical and biomedical applications [4-5] and various filtration processes [6-7]. For this reason, many studies have been performed concerning the formation of porous PVDF-HFP structures by means of traditional phase inversion or gels drying methods [8-10]. The classic gels drying presents some problems. In particular, the surface tension of solvent to be eliminated can cause the collapse of the gel polymeric structure, leading to a partially non-porous structures. This problem can be avoided using supercritical CO_2, which preserves the polymeric network of gels during the drying and aerogels formation [11]. Moreover, this new approach appears advantageous with respect to conventional phase inversion methods [12-15], due to the reduced-solvent manufacturing process.
PVDF-HFP gels have been prepared from polymer/acetone solutions adding ethanol; then, the solutions have been cooled at -20°C for 30 min. Series of supercritical drying experiments have been performed at 35°C, 200 bar and at various polymer concentrations (from 5 to 12% w/w).
Effects of the tailoring conditions on the membrane structural parameters have been evaluated by FE-SEM, AFM, DSC and IR analysis. Contact angle measurements have been performed in order to evaluate changes in the surface properties. Also, pore size, porosity and transport properties have been estimated for all membranes. In all cases,

the membranes exhibit interconnected structures with nano-sized pores and highly porous surfaces as reported in figure 1.
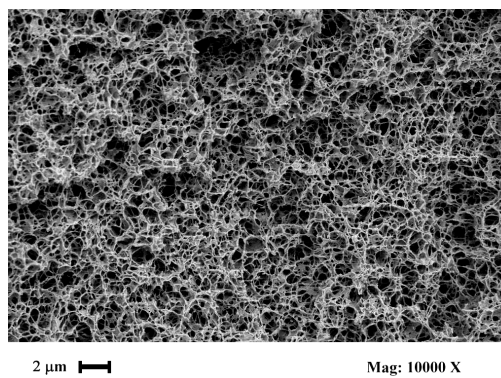
Figure 1: Example of PVDF-HFP membrane obtained by supercritical drying process

These PVDF-HFP membranes can lead to an interesting class of nano-structured films resistant to harsh environments, which can find application in different separation processes that can be useful for chemical and pharmaceutical industry.

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Supercritical Fluid Extraction, Hydrodistillation and Soxhlet Extraction of the Aerial Part of Winter Savory: Comparative Evaluation of the Extraction Methods on the Chemical Composition

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1. Summary

Supercritical fluid extraction of the volatile oil was carried out under different conditions of pressure, temperature, mean particle size and CO_2 flowrate and the results were compared with those obtained by hydrodistillation with a Clevenger-type apparatus and by Soxhlet extraction with different solvent mixtures.
The antioxidant activity of the extracts was assessed by the DPPH method and the results are discussed.

Keywords: supercritical fluid extraction, hydrodistillation, Soxhlet extraction, antioxidants, *Satureja montana* L.

2. Extended Abstract

Winter savory (*Satureja montana* L.) is an aromatic herb frequently used in food industry and in traditional medicine due to its antimicrobial activities (antibacterial and antifungal), as well as its the antioxidant, digestive, laxative, expectorant and sedative properties [1].

Hydrodistillation (HD) and solvent extraction (SE) are the common methods to isolate volatile and non-volatile components from aromatic plants, although they present some problems, such as the thermal degradation and solvent contamination, respectively. On the other hand, supercritical fluid extraction (SFE) can prevent these limitations. Additionally, in this technique the manipulation of parameters, such as temperature and pressure, results in the extraction of different components, which can be useful when a particular component is required [2, 3].

In the present work, SFE of the volatile oil was carried out with a flow apparatus using a two stage fractional separation technique. Different conditions of pressure (100 and 90 bar), temperature (50 and 40ºC), mean particle size (0.8, 0.6, 0.4 mm) and CO_2 flowrate (1.3, 1.1, 0.8 kg/h) were studied to understand the influence of these parameters on the composition and yield of the volatile oil. HD was performed on a Clevenger-type apparatus, for 4 h, using the same mean particle diameters as for the SFE. The chemical composition of the extracts obtained by the different extraction procedures was identified by GC-MS and quantified by GC. The main compounds in all extracts are carvacrol (41-62%), *p*-cymene (6-15%), thymol (6-11%), γ-terpinene (2-8%) and β-bisabolene (2-4%). The major difference between volatiles obtained by these two techniques (SFE and HD) is the relative percentage of thymoquinone, an oxygen-containing monoterpene. This compound occurs in a relative amount that is 10 times higher in the SFE extract than in the HD extract (3-4% vs. 0.2%), which is an advantage to the pharmaceutical industry due to its anti-cancer, antioxidant and anti-inflammatory properties, as well as a neuroprotective effect against forebrain ischemia and alzheimer disease [4, 5, 6].

The non-volatile fraction was isolated after deodorization by SFE at 250 bar, 40ºC, 1.1kg/h of CO_2 flowrate and 0.6 of mean particle size. The yield and composition were compared with those obtained by SE with pentane and acetone for 5h. The extracts were analysed by HPLC and their antioxidant activity was assessed by the DPPH method.

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Acid heterogeneous catalysis in supercritical media : application to isobutane alkylation by light olefins

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1. Summary

Supercritical fluids may improve the catalyst efficiency by preventing the deactivation by coke deposition. This study aims to understand which phenomena account for the benefic effects. The reaction of isobutane alkylation by light olefins illustrate this study. According to the results, the main effects seems to be a physical one.

Keywords: supercritical fluids, isobutane alkylation

2. Extended Abstract

Introduction

The specific properties of supercritical fluids near and above the critical point are the subject of intensive researches and developments in separation processes, material synthesis and also for application to chemical reactions. In the case of heterogeneous reactions, supercritical media are expected to improve the extraction of products from the catalytic surface. This is due to their enhanced transfer properties resulting from a high density and diffusivity combined to a low viscosity (Baiker, 1999).

Objectives of the study

This study aims to understand and elucidate the phenomena which promote the reactions in heterogeneous catalysis and to differenciate physical and chemical effects due to the presence of supercritical phase, during the reaction.

The reaction of isobutane alkylation by olefins seems to be well adapted to demonstrate the supercritical fluid contribution in heterogeneous catalysis.

The alkylation process is used in the refining industry to produce gazoline of a high octane number, using highly corrosive and toxic liquid acid catalyst (HF, H2SO4). The replacement by a solid catalyst has not been industrialized up to now. Indeed, rapid deactivation takes place due to heavier products formation. In the literature, earlier studies have reported the enhancement of the catalyst lifetime in supercritical media (Subramaniam, 2000).

Experimentation conditions
Supercritical alkylation was performed with excess isobutane with addition of a solvent. The reaction was carried out in a continuous flow type fixed bed reactor. Liquid reactants and solvent was fed by mean of two HPLC pumps and the supercritical phase was reached within the reactor by tuning the pressure and the temperature. The reaction products were analysed on-line, in gas phase by two GC equipment.

Results
The use of a solvent with low critical temperature (like carbon dioxide or ethane), allowed to perform the reaction at equivalent temperature in supercritical media (with solvent) and in liquid phase (without solvent). Experiments, using butene or propylene as olefin, confirmed the enhanced activity and longevity of the catalyst (β-zeolite) in supercritical media as regard to the liquid phase. However in those conditions, the supercritical media doesn't seem to have chemical effect (kinetic and mecanism pathway).

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Mathematical representation of Tributyl Phosphate Solubility in Supercritical Carbon Dioxide

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1. Summary

In this work, two methods are developed to estimate the solubility of Tributyl phosphate (TBP) in supercritical CO_2. First method uses Soave Redlish-Kowang (SRK) and Peng-Robinson (PR) equation of states with Huran-Vidal mixing rules while the second method uses based-density models for a direct relation between density of solvent and solubility. While there isn't any variable data for critical properties of TBP, a new method for evaluating of C_2 (mixing rule parameter) is recommended as a function of temperature and pressure. Such function for C_2 has never been in the literature. This method in comparison with other methods such as group contribution methods give a good result, as the solubility of TBP is obtained Average Absolute Relative Deviation (%AARD) of about 9% employing SRK-EOS and 17% using PR-EOS. Also, a based-density modified equation is used with variable coefficients which results %AARD of about 6% (employing Chrastil and semi-empirical method).

Keywords: Solubility, Supercritical fluid, Tributyl phosphate (TBP), cubic equation of state

2. Extended Abstract

TBP has widely employed in solvent extraction of metal ions, particularly in the field of nuclear technology, because of its high extractability toward metal ions from highly acid aqueous solution and high radiochemical stability.
The solubility of solute (2) in the supercritical fluid (1) may be expressed as:

$$y_2 = \frac{P_2^{sat}}{P} \frac{\exp(\frac{v_2^l (P - P_2^{sat})}{RT})}{\varphi_2^V} \tag{1}$$

For equations of state the mixing rules proposed by Huron and Vidal were applied:

$$B_m = \sum_i y_i B_i = y_1 B_1 + y_2 B_2 \tag{2}$$

$$\frac{A_m}{B_m} = \sum_i y_i (\frac{A_i}{B_i} - \frac{\ln \gamma_i^\infty}{\ln 2}) = \sum_i y_i C_i = \frac{A_1}{B_1} y_1 + (\frac{A_2}{B_2} - \frac{\ln \gamma_1^\infty}{\ln 2}) \tag{3}$$

As critical values and acentric factor for the TBP solute are not available, C_2 can not be calculated from Eq. (3). In contrast with most of previous works which have used group contribution methods, this study tries to propose a mathematical model to estimate C_2 values without using critical properties. According to the above illustration C_2 is a function of temperature and pressure. The model which best fits to the experimental results is presented as:

$$C_2(T,P) = (m_1 + m_2 T) - (n_1 + n_2 T)\ln(\frac{P}{P_{ref}}) \tag{4}$$

Also, the co-volume B_2 of the solute can be assumed as equal to the known molar volume of the liquid [1]:

$$B_2 = v_2^L \frac{P}{RT} \tag{5}$$

Using the Huron-Vidal mixing rules with the above approximation, the fugacity coefficient of the solute in gas phase calculated.

Two semi-empirical models have been used for data correlation. The first one, a simple relation as given by Eq. (6) between the solubility of solute (S) and the density of $CO_2 (\rho)$:

$$\ln S = p \ln(\rho) + q \tag{6}$$

The second semi-empirical correlation used, was the Charastil model [2]:

$$\ln S = k \ln \rho + \frac{a}{T} + b \tag{7}$$

In contrast with the previous reports which have considered constant coefficient, we developed a new technique what the values of p, q, and k coefficients are considered as function of temperature and simulation shows that the dependency is linear as follows:

$$p = c_1 T + c_2, \quad q = d_1 T + d_2 \tag{8}$$

$$k = n_1 T + n_2 \tag{9}$$

The errors of Chrastil and Semi-empirical models (constant and variable coefficients) in addition to the errors for PR-EOS and SRK-EOS are listed in Table (1).

Table (1): The amount of %AARD for the prediction of TBP solubility in SC-CO_2

	Equation of state		Chrastil model		Semi-empirical model	
	PR-EOS	SRK-EOS	Modified form	Main form	Modified form	Main form
%AARD	17.01	8.97	5.99	6.40	6.02	7.33

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Extraction of phytoecdysones with ethanol-modified supercritical CO_2

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1. Summary

Biologically active polar substance 20-hydroxyecdysone was extracted with ethanol-modified dense carbon dioxide from roots and leaves of *Leuzea carthamoides*. The effect of operating conditions (pressure 20-27 MPa, temperature 40-60 ºC, ethanol concentration in the solvent 4.3-7.1 wt.%, and solvent-to-feed ratio up to 100 g/g) on the extraction rate and the concentration in extract was examined. The maximum extraction yields were achieved with 7.1 wt.% ethanol in the solvent. Despite the high solvent-to-feed ratios the extraction was not complete; the maximum yield of 20-hydroxyecdysone from the leaves containing 1.50 mg/g dry mass was only 0.19 mg/g and the maximum yield from the roots containing 0.49 mg/g dry mass was 0.30 mg/g. The maximum concentration of 20-hydroxyecdysone in CO_2 extract from the roots, 2.8 wt.%, was higher than in the extracts obtained with 95% EtOH (1.74 wt.%).

Keywords: supercritical extraction, 20-hydroxyecdysone, *Leuzea carthamoides*,

2. Extended Abstract

The study was focused on supercritical fluid extraction of 20-hydroxyecdysone (beta-ecdysterone, 2-beta,3-beta,14-alfa,20R,22R,25-hexahydroxy-5-beta-cholest-7-en-6-on) from roots and leaves of *Leuzea carthamoides* (Willd.) DC, syn. *Rhaponticum carthamoides* (Willd.) Iljin, a large perennial herb growing wildly in Southern Siberia. Its extract, whose biological activity is determined by phytoecdysterone quantity, is an adaptogen with normalizing effect on the central nervous and cardiovascular systems and with wide spectrum of anabolic activities. More than fourteen ecdysteroids from the roots of *L. carthamoides* have been isolated and identified, 20-hydroxyecdysone (20-OH) being the major component (Vokáč *et al.*, 2002). Besides, 20-OH is an invertebrate steroid hormone playing an important role in the regulation of insect growth and morphogenesis. Phytoecdysones as relatively polar substances are commonly extracted from plants with methanol or ethanol. In this work, the supercritical fluid extraction of 20-OH is compared with the extraction with ethanol.

The solvent of choice for the supercritical fluid extraction (SFE) is carbon dioxide which must be modified with polar liquids to dissolve polar substances. Pressurised ethanol used as modifier was mixed with dense CO_2 before entering the extractor filled with 1.5-3.2 g leaves or roots of *L. carthamoides* (feed). The plant material was dried, milled and sieved and the size fraction 0.2-0.4 mm was used for the extraction. The extract was collected at ambient pressure and temperature to 3-4 traps in succession. The samples were dried to constant weight with a stream of nitrogen and the content of 20-OH was determined using HPLC. The extraction conditions were 20-27 MPa, 40-60 ºC, and 0-7.1 wt.% ethanol in the solvent; 85-205 g CO_2 passed through the extractor in an extraction run.

Table 1. SFE: Extraction yield of 20-OH (*Y*) and its concentration in extract (*C*) for different EtOH concentrations at 25 MPa, 50 ºC and solvent-to-feed ratio 55-65 g/g

	Leaves					Roots	
EtOH, wt.%	0	1.5	3.0	4.3	7.1	5.7	7.1
Y, mg/g dry mass	0.006	0.009	0.024	0.070	0.182	0.029	0.137
C, mg/g	0.5	0.6	1.3	2.1	6.8	3.0	16.5

The yield of 20-OH was primarily influenced by ethanol concentration in the solvent (Table 1). The best results were obtained with 7.1 wt.% ethanol at the maximum applied pressure. The temperature had little effect except for the extraction of 20-OH from roots at 7.1 wt.% ethanol where its increase to 60 ºC resulted in the extraction yield of 0.32 mg/g and in the 20-OH concentration in the extract 28 mg/g. Except for this concentration, the results of supercritical fluid extraction are worse than those of the conventional extraction with ethanol (Table 2). The strong effect of ethanol modifier suggests, however, that comparable extraction yield from roots and simultaneously higher concentration of 20-OH in CO_2 extract than in the conventional extract with ethanol could be achieved using higher ethanol concentrations in CO_2. than those applied in this work. The research will continue in this direction.

Table 2. Optimum results of SFE compared to extraction with ethanol (SE)

	Leaves		Roots	
Method	SFE	SE	SFE	SE
Y, mg/g dry mass	0.19	1.50	0.30	0.49
C, mg/g	5.2	7.1	28.0	17.4

Reference

Vokáč, K., Budešínský, M. and Harmatha, J., (2002) *Collection of Czechoslovak Chemical Communications*, 67,124-139.

Comparison of Predictive Models for Determination of Supercritical Fluids Solubility in Heavy Oils

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1. Summary

In this work a comparison between two predictive methods and cubic equations of state to calculate supercritical fluids solubility in heavy oils is presented. The first thermodynamic model is based on activity coefficient which is calculated by a group-contribution method (UNIFAC) and the second one is based on SAFT approach. Both predictive methods show better results than cubic EOS in comparison with experimental data for the systems containing supercritical fluids and oil fractions under investigation.

Keywords: supercritical fluids solubility, predictive models, UNIFAC model, SAFT approach, cubic equation of state

2. Extended Abstract

In the development of thermodynamic models to determine the phase equilibria of gas - oil systems, numerous works are presented in the literature. In the present work, the non ideality situation was considered only in the liquid phase (vapor phase – ideal behavior), incorporating this deviation in the activity coefficients calculus for the substances presented in this phase. To determine the vapor liquid equilibria, one starts from the chemical potential equality and from the classical thermodynamics, one obtains the equality for the fugacities of a component i presented in both phases.

Applying the expressions for the fugacities of the substances in each phase in the fugacity equality mentioned, one can do the sum of the partial pressures and obtains Equation (1) to represent the total pressure of the system in the vapor liquid equilibrium, where x denotes the substance molar fraction in the liquid phase, γ the activity coefficient of each substance and f^{ref} the fugacity reference.

$$P = x_{CO_2} \gamma_{CO_2} f_{CO_2}^{\,ref} + x_{oil} \gamma_{oil} f_{oil}^{\,ref} \tag{1}$$

The UNIFAC group contribution model modified by Hansen *et al* (1992) was chosen to represent the non ideality of the oleum phase due to that the interaction functional group parameters are available in the literature.

In general, a number of works use the reference state as being the fugacity of a pure liquid in the pressure and temperature of the system. For the oil, this approach was adopted and its fugacity calculated through the oil vapor pressure. However, in the usual conditions of reservoirs and in the operating conditions involving petroleum, carbon dioxide has a supercritical behavior and the correlation proposed by Prausnitz and Shair (1961) can be used to describe its hypothetical reference fugacity as shown in Equation (2), where P_c represents the critical pressure of the gas and T_r its reduced temperature.

$$\ln(f_{CO_2}^{ref} / P_c) = 7.81 - 8.06 / T_r - 2.94 \ln T_r \tag{2}$$

From preliminary results, it was possible to observe the existence of a constant deviation factor in the results obtained by the Prausnitz and Shair (1961) correlation. Multiplying the reference state fugacity by a unique factor, it was obtained a new equation for the fugacity reference for the gas as shown in Equation (3), where PA=26.5571, PB=-26.5434 and PC=-19.8052

$$\ln(f_{CO_2}^{ref} / P_c) = PA + PB / T_r + PC \ln T_r \tag{3}$$

Being thus, the developed model in this work was compared to the modified SAFT equation called Convex Body proposed by Pfohl O. and Brunner G. (1998) and some cubic equations of state. Both predictive methods, the proposed model and the SAFT equation, show better results than cubic EOS in comparison with experimental data for the systems containing supercritical fluids and oil fractions under investigation.

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Session T3-K: Theme-3 Keynote Lectures[*]

Abstract Number	Paper Title & Authors	Included
1562	Functionalized Microporous Membranes and Bimetallic Nanoparticle Synthesis for Environmental Applications Dibakar Bhattacharyya	Yes
4088	Integration of Chemical Engineering Science into Pharmaceutical Process Research and Development Neville LN Brewis	Yes
4159	Field Driven Assembly in Nanotechnology Juan J de Pablo	Yes
4175	Expediting Product and Process Development with Workflow Ka M Ng	Yes

* To be presented in different keynote sessions (see the technical program for details)

Functionalized Microporous Membranes and Bimetallic Nanoparticle Synthesis for Environmental Applications

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1. Summary

Membrane processes are finding wide applications ranging from water treatment to reactors to selective separations. The development of tunable (singe layer and multi-layer assembly in pores) membranes provide added opportunities in permeate flux and separation selectivity control. The attachment of selected types of polypeptides and the in-situ synthesis of nanoparticles in membranes allows highly effective separations at low pressures and toxic organic destruction at room temperature. The presentation will include the role of nano-domain interactions for selective separations, polypeptide assembly in membrane pores for environmental applications, synthesis of nano-structured metals (bimetallic systems) in membrane domain for dechlorination. The study of reductive dechlorination technology involved the synthesis of hybrid materials containing bimetallic (Fe/Ni, Fe/Pd) iron-based nanoparticles (<30 nm) using either functionalization and ion-exchange principles or phase-inversion membrane processing. In addition to the rapid degradation (by Fe/Ni) of TCE (trichloroethylene) to ethane, we were also able to achieve complete dechlorination of selected chloro-biphenyls (PCBs) using milligram quantities immobilized Fe/Pd nanoparticles in membrane domain.

Keywords: membrane functionalization, layer-by-layer assembly; catalysis, separation, nanoparticles, polymer

2. Extended Abstract

The development of new-generation materials that extend the industrial application of membrane processes will require a high level of control of both the characteristics of the base polymeric or inorganic support layer, as well as, its corresponding surface properties. Current research in membrane science is now focusing more on the modification of surface physical along with chemical properties using techniques like plasma or radiation-induced polymer grafting, immobilization of reactive ligands, layer-by –layer assembly, etc. Membranes functionalized with appropriate macromolecules (1-8) can indeed provide applications ranging from tunable flux and separations, toxic metal capture, to nanoparticle synthesis for toxic organic dechlorination. Microfiltration membranes (eg, cellulosics, silica, polysulfone, polycarbonate, PVDF) can be functionalized with a variety of reagents. Depending on the types of functionalized groups (such as, chain length, charge of groups, biomolecule, etc.) and number of layers, these microfiltration membranes could be used in applications ranging

from metal (or oxyanions) separation to biocatalysis. The dependence of conformation properties of polyelectrolytes on pH also provides tunable separation and flux control.

Layer-by-layer (LBL) assembly technique, most commonly conducted by intercalation of positive and negative polyelectrolytes, is a powerful, versatile and simple method for assembling supramolecular structures (9). Non-stoichiometric immobilization of charged polyelectrolyte assemblies within confined pore geometries leads to an enhanced volume density of ionizable groups in the membrane phase. This increase in the effective charge density allows for Donnan or charge-based exclusion of ionic species using porous materials characterized by hydraulic permeability values well beyond conventional membrane processes. For example (5), solute rejection (at only 3 bar) of $NaCl:Na_2SO_4:Na_2HAsO_4$ mixture solution using a gold-coated polycarbonate membrane containing PLGA/PLL (PLL = poly (L- Lysine), PLGA = poly (L-Glutamic acid)) layers in membrane pores showed SO_4^{2-} and $HAsO_4^{2-}$ show solute rejection values exceeding 90 %. Multilayer assemblies of polyelectrolytes can also be created within the membrane pore domain for enzyme immobilization and catalysis. This can be done by electrostatic incorporation of active enzymes (without covalent attachment) in the LBL assembly. Our work with glucose oxidase enzyme showed (8) showed excellent product formation rates and stability under convective flow operations. This LBL approach also allows membrane regeneration.

In the area of chloro-organic detoxification we synthesized Fe/Pd nanoparticles in a membrane domain by ion exchange and a post-reduction process. The use of nanostructured metals immobilized in membrane phase is expected to have significant positive impact on pollution remediation through compact and flexible dechlorination technology development with high reaction rates at room temperature, significant reduction of metals usage, and improvement in water quality (10,11). In this study, the membrane supported Fe/Pd nanoparticles were prepared in three steps: polymerization of acrylic acid (AA) in polyvinylidene fluoride (PVDF) microfiltration membrane pores, subsequent ion exchange of Fe^{2+}, and chemical reduction (by borohydride) of ferrous ions bound to the carboxylic acid groups. Fe/Pd bimetallic nanoparticles were formed by partial reduction of Pd^{2+} with Fe^0 nanoparticles (12). As shown in Figure 1, spherical shape Fe/Pd nanoparticles were homogeneously dispersed in membrane cross-section, indicating uniform PAA functionalization and Fe^0 nanoparticle formation over the entire membrane. A statistical analysis of the image yielded an average particle size of 30 nm in diameter, with a standard deviation of 5.7 nm. EDS analysis was also conducted to determine the elements present in the nanoparticles. The Pd content was determined to be 1.9 wt % By EDS quantification. Figure 2 shows the dechlorination of PCB 77 with the Fe/Pd nanoparticles immobilized inside PVDF/PAA polymer membrane matrix. Complete degradation of PCB77 by Fe/Pd in PAA/PVDF membrane was achieved within 2 hours. Biphenyl was formed as the main dechlorination product. The degradation of PCB77 by Fe/Pd nanoparticles occurred in a sequential reduction pathway, which is indicated by the detected less chlorine intermediates. The reactivity of the chlorine substituents decreases in the order para ≈ meta > ortho. The degradation for PCB77 showed all eight intermediates which can occur in theory by reductive pathway. All the intermediates appeared at very low concentration levels. This can be explained by the little difference of reactivity between para and meta chlorines substituents. It has been established that the PCBs dechlorination with Fe/Pd nanoparticles can be described by the following pseudo-first-order reaction kinetics:

$$-\frac{dC}{dt} = k_{obs}C = k_{SA}\rho_m a_S C$$

where C is the PCB77 concentration (mg L^{-1}) at time (h), a_S is the specific surface area of the nanoparticles (m^2 g^{-1}), ρ_m is the loading of the nanoparticles, k_{obs} is the observed rate constant (h^{-1}), and k_{SA} is the surface-area-normalized rate constant (L h^{-1} m^{-2}). Based on 30 nm average diameter for the nanoparticles, a_S was calculated to be 25 m^2 g^{-1}. Best linear fit to the experimental data ($R^2 = 0.97$), the k_{obs} and k_{SA} (PCB77) determined to be 2.82 h^{-1} and 0.141 L h^{-1} m^{-2}.
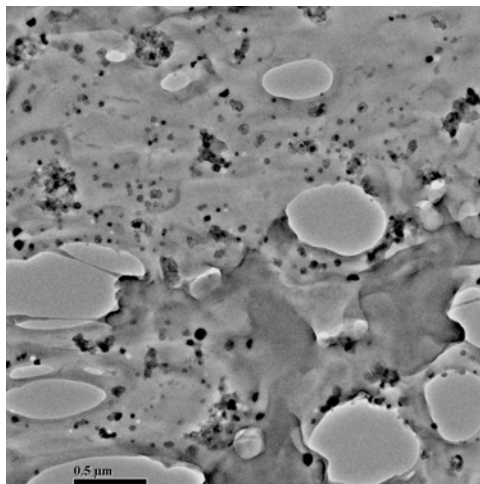
Figure 1. TEM image of PAA/PVDF membrane cross-section containing Fe/Pd nanoparticles
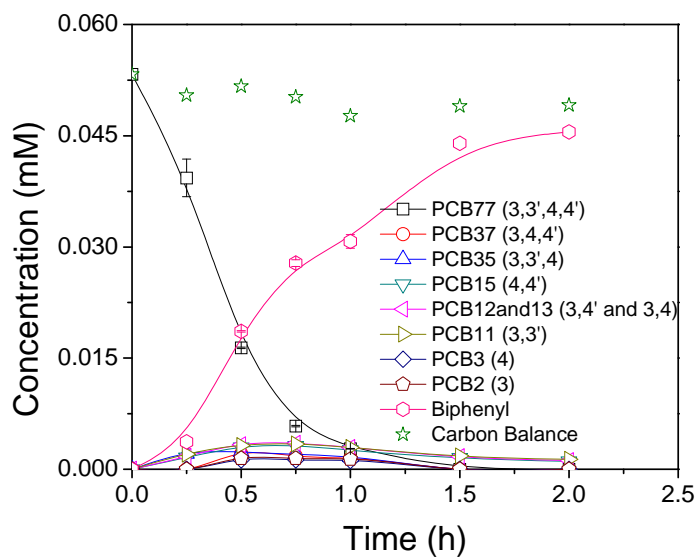
Figure 2. Batch reaction of PCB77 with Fe/Pd (Pd = 2.3 wt%) in PAA/PVDF membrane. Metal loading: 0.8 g L^{-1}. Initial PCB77 concentration: 15.6 mg L^{-1}.

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Acknowledgement

Integration of Chemical Engineering Science into Pharmaceutical Process Research and Development

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Introduction

Process development in the Pharmaceutical industry has been typically the domain of the process chemist with support provided by engineers only for asset development and modification. Increasingly however, process failures upon moving to commercial scale, the regulatory push for increased process understanding and increasing legislative constraints have demanded a different skill set to be brought into early development. Chemical engineering provides a blend of skills well suited to delivering the changes demanded by the industry, but working in rapidly changing environment of early process development brings a new set of challenges. Furthermore an understanding of the unit operations and the interaction of physical and chemical phenomena that occur within equipment is sufficient for the resolution of simple pilot plant related problems but potentially inadequate for process design. Bringing chemical engineers into early development is not straightforward but the rewards associated with successfully bringing chemical engineers and synthetic chemists together are high. What then must be done to mine the value at the chemistry – chemical engineering interface?

Role of Chemical Engineers in AstraZeneca Process Research and Development (PR&D) PR&D is responsible for delivering drug substance for development activity and a manufacturing process suitable for commercial material requirements. The latter is typically achieved through the solution of problems that arise during development using chemistry solutions and scale up heuristics. Rarely are the demands of the commercial process considered until initial drug substance demands are required. The chemical engineer working in process development is therefore responsible for the development of a robust and scaleable manufacturing process through the application of experimental and theoretical process engineering science. Through this a long term view is brought to the process development strategy that ensures SHE issues are raised and resolved, bulk drug capacity requirements are achieved and the most appropriate innovative technologies exploited.

The above applies to the later stages of the development pipeline, where time, although important is determined more through success in the clinic than success in the laboratory and pilot plant. Furthermore the route has often been selected and the chemistry is not changing as rapidly or as frequently as it does very early in development. Speed is critical at this time, and

during a very short period of time a final route may be selected and scaled up to deliver kilogram quantities of the desired product.

To deliver this, much of the work of the chemical engineers must be done at the interface between chemistry an chemical engineering and at the time solutions are required. The concept of unit operations is still appropriate though a more detailed molecular level understanding is required, particularly in key areas including crystallisation, mixing and transport phenomena, solvent selection and physical property prediction and reaction engineering. Other areas that require the integration of chemical engineers into process development concern the implementation of alternative and potentially novel technologies and engineering solutions and the development of a predictive capability. Brief examples of the role of chemical engineers in these key areas will be used to illustrate the progress that has been made with respect to the integration of chemical engineers into process research and development.

Chemical Engineering Science and Alternative Technologies

Given the time pressures in Pharmaceutical Process development and the regulatory need to freeze synthesis and process development, there is a tendency to run technology lean. It is often the case that equipment selection does not take place given the number of alternatives available to be low. There are a number of good reasons for this, but introducing chemical engineers to early development allows alternative technologies to be considered on a timescale relevant to the development project. Further work is necessary to respond rapidly enough to ensure technology solutions rather than sub-optimal chemistry fixes.

The approach being taken by AstraZeneca with respect to the implementation of microreactors and other alternative reactor technologies (e.g. microwave) during the development of processes for API production will be presented to exemplify the approach being taken. The importance of understanding the characteristics of both the chemical reaction and the reaction device will be explained using AZ experiences and case studies. In particular, the types of synthetic chemistry commonly encountered in process development, which work optimally in novel reactor technologies rather than in stirred tank reactors will be highlighted. A methodology used to characterise the devices will be described together with experience gained from investigating the switch from batch to continuous for a potentially high tonnage compound using microreactors and process intensification.

Predictive Capability

One very simple example of a predictive capability provided by chemical engineers in PR&D is an appreciation of process throughput. The throughput of a process defines the amount of material (in grams, kilos or tonnes) that can be manufactured per unit time (seconds, hours or years). Key variables that influence throughput of a process include (i) the chemical yield (ii) the capacity and number of processing vessels and their availability (iii) the "cycle time" (iv) limiting concentrations of the various stages and (v) number of unit operations (linked to the number of chemical steps).

Throughput issues may not be identified until late in development, potentially only upon transfer to manufacturing. This is due firstly to the implicit influence of commercial scale plant considerations on throughput calculations, but secondly because development drug substance is delivered in campaigns that can be planned off the critical path of the

development plan. However, consideration of throughput issues earlier than TT can benefit Process R&D in several ways. Increasing process throughput will potentially increase plant availability allowing more compounds to be processed. Identifying the volume or time limiting operations will allow optimisation work to be focused and directed to those operations that add most value. An understanding of throughput will improve the interaction and communication process at point of process transfer to manufacturing. Finally, the manufacture of the first GMP batch is typically on the critical path of the development process as no other work can start until material is available. Throughput will therefore critically affect delivery time and is therefore an important factor to consider.

An approach will be presented that allows throughput to be considered very early in development and then developed to determine the issues at commercial manufacturing scale. These issues and their resolution provide both focus and steer to the subsequent development.

Field Driven Assembly in Nanotechnology

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1. Summary

The preparation of advanced materials with nanometer structure and the assembly of devices with critical dimensions on the scale of nanometers require that nanoscale objects be positioned and manipulated in a reproducible manner, with exquisite control and, if at all possible, in a high throughput manner. Engineers are increasingly resorting to driven-assembly approaches that rely on external fields to conceive manufacturing processes that meet such constraints. Over the last several years, our group at the University of Wisconsin has been engaged in the development of multi-scale theoretical and computational techniques that seek to provide a faithful representation of field-driven assembly over multiple length and time scales. This presentation will provide an overview of some of these techniques, along with a discussion of their use for design of specific devices and processes.

Keywords: Molecular simulation, nanotechnology, sensors, liquid crystals, DNA, block copolymers

2. Extended Abstract

A wide variety of industries, ranging from the biomedical to the semiconductor, have continuously sought to decrease the critical dimensions of devices used for surgery, analysis, sensing, or data storage and computing. Such devices are generally assembled through elaborate multi-step processes that often involve out-of-equilibrium conditions. In an attempt to facilitate the design of such processes, our group at the University of Wisconsin has focused on the development of multi-scale theoretical and computational techniques aimed at providing a faithful description of the field-driven assembly of nanoscale objects over multiple length and time scales. These models and methods can be used to investigate the equilibrium structure and relaxation of a variety of fluids, including solutions of biological macromolecules. The usefulness and limitations of our proposed approaches will be discussed in the context of three applications for which enough experimental data are available to

provide an assessment of our theoretical efforts. The first application is concerned with the elongation and presentation of long DNA molecules in nanofluidic channels. A multiscale model, that includes fluctuating hydrodynamic interactions, has been used to design a gene mapping device and to interpret experimental data pertaining to the structure and dynamics of confined chromosome-length DNA. The validity of our results is established by comparison to results of detailed molecular dynamics simulations and results from coarse grain Lattice-Boltzmann simulations. The second application is concerned with the study of liquid-crystal based biosensors. A multiscale model has been used to design a liquid-crystal based device in which nanoscale particles suspended in a liquid crystal self assemble into highly regular structures, including chains, upon exposure to proteins or virions. As discussed in this presentation, the model can be used to explain the defects and transmission images that arise in laboratory experiments. The model is validated by comparison to results from atomistic simulations. The third application is concerned with the formation of ordered block copolymer structures on nanopatterned substrates. Results from mesoscopic multiple length and time scale simulations will be presented to explain the effects of surfaces and different types of confining walls on the free energy (and the concomitant stability) of a variety of morphologies. The results of these calculations will be compared to experimental observations, and to results of detailed atomistic simulations.

Expediting Product and Process Development with Workflow

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1. Summary

An engineer faces numerous challenges in product and process development in the chemical industry. For one, product/ process data tend to be unreliable, incomplete, or nonexistent. Experiments are generally required to secure the necessary information. To execute these experiments effectively, modeling as well as physical insights is indispensable. Also, it is important that the suitable instruments and modeling tools be deployed in a timely fashion so as to achieve the design objectives with the least amount of time, effort and money. To this end, workflow needs to be devised to integrate conceptual design, modeling and experimentation. We have to identify what is achievable based on the available time, technological limit, and both human and monetary resources. Such a workflow is the key to reduce time-to-market in today's competitive environment (Wibowo et al., 2003; Ng and Wibowo, 2003; Ng et al., 2005).

This presentation starts with workflow for product development in which the desirable product attributes are identified and realized. This is followed by a discussion of workflow for process development which integrates into a coherent whole systematic design and experimental procedures for reaction system synthesis, separation system synthesis, and solids processing. Selected examples including the manufacture of cosmetic creams, functional nanomaterials, dietary supplements, nanocomposites, etc. will be used throughout the presentation to illustrate the workflow strategy.

Ka M Ng

Session T3-1: Nanotechnology & Nanomanufacturing

Abstract Number	Paper Title & Authors	Included
164	Dynamics of speroidal particle in a leaky dielectric medium in the ac electric field Y Dolinsky, T Elperin	Yes
769	Nanopowders produced by electrical explosion of wires O Nazarenko	Yes
1232	Combining flame spray pyrolysis and high throughput experimentation for preparation and testing of multi-component noble metal catalysts S Hannemann, J-D Grunwaldt, S E Pratsinis, A Baiker	Yes
1781	Synthesis, characterization, and hydrogen storage capacity of magnesium hydrides on multi-walled carbon nanotubes K-S Lin, C-Y Pan, C-P Liu, W-R Chen, T P Perng	Yes
3548	Fractionation of metal and semiconductor nanoparticles and their deposition into wide area thin films and ordered arrays using CO2-expanded liquid solutions C B Roberts, M Anand, J Liu	Yes

Dynamics of a spheroidal particle in a leaky dielectric medium in the AC electric field

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1. Summary

We study a system comprising a spheroidal particle with permittivity e_2 and conductivity σ_2 immersed in a host medium with permittivity ε_1 and conductivity σ_1 in the AC external electric field with a strength $\dot{E}_0$ and frequency w. We determined conditions when orientation of a spheroidal particle with a finite electric conductivity at $t \to \infty$ coincides with the orientation of the ideal dielectric spheroid, when orientation of a spheroid at $t \to \infty$ is normal to the orientation of the ideal dielectric spheroid and when orientation of particle is not affected by the external electric field. We found the direct connection between the final orientation of the particle and the existence of two time intervals, $T_1(w)$ and $T_2(w)$, such that during time interval T_1 an equilibrium orientation of the particle is the same as the equilibrium orientation of an ideal dielectric particle while during time interval T_2 the direction of the stable equilibrium orientation is normal to the equilibrium orientation of an ideal dielectric particle. The values T_1 and T_2 depend on the frequency of the external field, ω, and $T = T_1(\omega) + T_2(\omega)$, where $T = 2\pi/\omega$.

Keywords: Nanoparticles, Biotecnology, Nanotechnology

2. Extended Abstract

The dynamics of solid or liquid particles in a host medium under the action of an external electric field is of theoretical and technological interest. Technological applications include manipulation of microparticles in biotechnology and genetic

engineering, nanotechnology, and non contact measurements of physical properties of particles.

In the present study using our previous results (for details see [1]) we investigate the dynamics of particle. In a general case the dynamics of particle, embedded in a leaky dielectric medium, is quite involved and can become chaotic under the sufficiently large amplitude of the external field as it was showed before.

In the present study we consider rotation of a particle around one of the axes of the spheroid that is not the axis of symmetry. The vector of the external field, $\vec{E}_0$, is in the plane normal the axis of rotation, and we consider also a time-dependent external field. In the general case, the behaviour of the particle is complicated. However, we have found the range of the parameters of the problem whereby the behaviour of the particle is determined only by the effect of alternating equilibrium orientation of the particle that was considered in our previous study. We found the direct connection between the final orientation of the particle and the existence of two time intervals, $T_1(\boldsymbol{w})$ and $T_2(\boldsymbol{w})$, such that during time interval T_1 an equilibrium orientation of the particle is the same as the equilibrium orientation of an ideal dielectric particle while during time interval T_2 the direction of the stable equilibrium orientation is normal to the equilibrium orientation of an ideal dielectric particle.

We also found the condition, when the final orientation of the particle at $t \rightarrow \infty$ is normal to the orientation of an ideal dielectric particle. If $T_2(\boldsymbol{w}) < T_1(\boldsymbol{w})$, then the final orientation of the particle coincides with that for the ideal dielectric particle and electric field does not affect the orientation of the particle. The obtained theoretical results are validated by analyzing the orientation spectra of particles which were overviewed in [2].

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Nanopowders produced by electrical explosion of wires

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1. Summary

The dispersed, phase and chemical compositions of nanopowders produced by electrical explosion of tungsten, titanium, aluminium wires in water and hydrocarbons depending on electrical parameters and environmental properties were investigated. The most significant factors determing the output of chemical compounds (carbides and oxides of metals) have been established: density or dynamic viscosity of working ambient, specific deposited energy, $?/?$ ratio in hydrocarbon molecules. The possibility of application of various nanopowders produced by electrical explosion of wires is discussed.

Keywords: nanopowder, electric explosion of wires, carbides, oxides

2. Extended Abstract

Nanosized powders, due to their specific properties, are more and more widely used as basic materials for production of ceramics and composites, filters, lubricant additives, for solution of ecological problems as catalysts, sorbents, etc.

One of the ways of nanopowder production is electrical explosion of wires (EEW). It is the process of explosive destruction of a metal wire under the action of great density current ($>10^6$ A/cm^2) [1]. This process accompanies by scattering products, shock waves and electromagnetic radiation. Material of the wire transmutes into particles of nanosized range (10–100 nm) in accordance with certain conditions. Extremely nonequilibrium conditions of EEW cause some unusual properties of nanopowders. Electroexplosive nanopowders have as a rule the spherical form of particles, they are steady against oxidation and sintering at room temperature and characterized with high diffusion activity at the heating.

EEW in inert gases or hydrogen is used to produce powders of metals, alloys, and intermetallic compounds. EEW in chemically active ambient is used to produce nanopowders of chemical compounds of metals: oxides, nitrides, carbides, etc. Phase and elemental compositions of nanopowders prepared by electrical explosion of

tungsten, titanium, aluminium wires in water and hydrocarbons were investigated. Control factors were electrical parameters, characteristics of wires, density of surrounding ambiences (hydrocarbons and water as gas, liquid, solid).

The increase of deposited energy e/e_s (rate of specific energy consumed by exploding wire e to sublimation energy of wire material e_s) leads to the rise of dispersity of electroexplosive powder. The velocity of energy input or power density, arc stage of electric discharge have the same effect on particles size.

The density of reactants is much higher during wire explosions in condensed media compared to explosions in gases that allows the chemical compounds output to be increased and their phase composition to be changed.

Phase compositions of nanopowders prepared by electrical explosion of tungsten, titanium and aluminium wires in liquid hydrocarbons (?$_6$?$_6$, ?$_6$?$_{14}$, ?$_6$?$_5$?$_3$, and ?$_{10}$?$_{22}$), multicomponent reactionary surroundings such as hexametilenetetramine-decane suspension, and solid paraffin were investigated. The output of carbon-saturated carbide (WC, WC_{1-x}) phases increases with increasing density of the working medium as well as deposited energy and elemental composition of hydrocarbons (?/? ratio in hydrocarbon molecules) [2]. The content of carbide phases depends on the values of the upper warm-up border of chemical compounds stability.

The tribological characteristics of industrial oil after treatment with electrical explosion of copper wires were studied. Copper nanopowder and carbon clusters (fullerenes) were obtained in result of EEW. Decrease of friction constant occurred to 40 %.

Nanopowders produced by electrical explosion of aluminium wires in water are different crystal modifications of aluminium oxides: Al(O?)$_3$, ?-Al_2O_3, a-Al_2O_3. The main product of EEW in liquid water is ?-Al_2O_3, content of that increases in case of increasing the deposited energy e/e_s. EEW in ice due to its bigger dynamic viscosity results in formation of high-temperature modification of aluminium oxide a-Al_2O_3.

Very active oxide-hydroxide phases can be used for water purification from ions of heavy and radioactive metals. Another perspective application of electric explosion of aluminium wires in water and aluminium nanopowder is production of hydrogen. The transformation ratio reaches 100 % without special additives.

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Combining flame spray pyrolysis and high throughput experimentation for preparation and testing of multi-component noble metal catalysts

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1. Summary

Alumina-supported mono- and multi-noble metal particles (Pt, Pd, Rh, Ru, Au) were prepared by one-step flame spray pyrolysis (FSP). This efficient preparation method was combined with high-throughput testing using an experimental setup consisting of eight parallel fixed-bed reactors for different reactions including catalytic partial oxidation of methane. The noble metal loading of the catalysts was close to the theoretical composition. The catalysts possessed a surface area > 100 m^2/g and were made up of alumina particles of ca. 10 nm with on which smaller 1-2 nm noble metal particles were discernible. The catalysts were investigated by means of STEM-EDX and EXAFS, particularly to address alloying in the noble metal particles. In bimetallic systems like Pt–Pd and Pt–Rh alloying close to the bulk alloys was observed, whereas Pt–Ru was only partially alloyed. *In situ* X-ray absorption spectroscopy on selected samples was used to gain further insight into the structure under reaction conditions.

Keywords: flame spray pyrolysis, nanoparticles high-throughput experimentation, noble metal catalysts, alloys, partial oxidation of methane

2. Introduction

High-throughput experimentation (HTE) techniques have received enormous attention in the past years and are applied in various fields, including pharmaceuticals, nanoparticle research and heterogeneous catalysis. Particularly, high-throughput preparation of solids, automated catalyst testing, and high-throughput characterization have been in the focus of recent studies[1,2]. High-throughput preparation comprises robot-controlled deposition-precipitation, impregnation, chemical vapor deposition, and sol–gel preparation methods[2]. The preparation routines become complex and the task more demanding if several components are present, e.g., in multicomponent nanomaterials or supported multimetallic catalysts. Flame spray pyrolysis (FSP) gives

the opportunity to prepare conveniently such multi-component nanomaterials in a single step[3]. The rapid quenching after the FSP process typically affords materials with high surface area, unique crystalline phases and tunable structural and chemical properties. Furthermore, the noble metal particle size can be kept relatively small[4].

3. Results and Discussion

Mono and multi-noble metal particles on Al_2O_3 were prepared by FSP of the corresponding precursors dissolved in methanol and acetic acid (v/v 1:1) or xylene[5]. The noble metal loading of the catalysts was close to the theoretical composition as determined by WD-XRF and LA-ICP-MS. The nanomaterials were further analysed using XPS, BET, STEM-EDXS and XANES/EXAFS. All catalysts exhibited a specific surface area of more than 100 m^2/g, and were made up of ca. 10 nm alumina particles on which the smaller noble metal particles (1–2 nm, partially oxidized state) were visible. The question of alloy formation was addressed by STEM-EDXS and EXAFS analysis. In some cases, particularly for Pt–Pd and Pt–Rh, alloying close to the bulk alloys was observed, in contrast to Pt–Ru being only partially alloyed.

Among other potential applications, the nanoparticles are interesting for partial oxidation of methane to CO and H_2, total combustion of hydrocarbons, and (selective) CO-oxidation. Therefore the preparation method was combined with high-throughput catalyst testing. Samples containing 0.1–5 wt% noble metals (Ru, Rh, Pt, Pd) on Al_2O_3 were investigated in the catalytic partial oxidation of methane. The ignition of the reaction towards CO and H_2 depended on the loading and the noble metal constituents. The selectivity of these noble metal catalysts towards CO and H_2 was similar under the conditions used ($CH_4 : O_2$ ratio 2:1, temperature from 300 to 500 °C) and exceeded significantly those of nickel, gold or silver containing catalysts. In situ XAS on selected samples was used to gain insight into the structure of the catalysts under reaction conditions[5]. Recently, also a strategy has been developed to record XAS spectra in parallel and thus to speed up the characterization process as well[6].

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Synthesis, Characterization, and Hydrogen Storage Capacity of Magnesium Hydrides on Multi-walled Carbon Nanotubes

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1. Summary

The microstructure or absorption/desorption characteristics of composite MgH_2 and 2-6 wt.% as-prepared multi-walled carbon nanotubes (MWCNTs) were investigated in the present work. The synthetic mechanisms, fine structures, surface properties of MgH_2/MWCNTs were also identified by FE-SEM/EDS, Raman or X-ray absorption near edge structure (XANES)/extended X-ray absorption fine structure (EXAFS) spectroscopy. Experimentally, MWCNTs were produced from the catalytic-assembly benzene-thermal routes by reduction of C_6Cl_6 with metallic K or Na in the presence of Co/Ni catalyst precursors at 503-623 K. MgH_2/MWCNTs were obtained by a mechanically well-mixing or grinding route. The H_2 storage capacity of MgH_2 and MgH_2/MWCNTs were conducted and measured by a TGA microbalance method. The experimental data indicate that the MgH_2/MWCNTs samples exhibits faster absorption kinetics and relatively lower desorption temperature than pure MgH_2 or MgH_2/MWCNTs (purified) nanocomposites. Hydrogen storage capacities of 1.3 wt.% for MgH_2/MWCNTs were achieved in 6h at 298 K and 1-30 atm. In addition, the different effects of MWCNTs and metallic nanocatalysts contained in the MWCNTs were studied. It is suggested that the metallic nanoparticles may be mainly responsible for the improvement of the H_2 absorption kinetics, and MWCNTs for the enhancement of H_2 absorption capacity of light MgH_2.

Keywords: magnesium hydride, carbon nanotube, hydrogen storage, nanocomposite

2. Extended Abstract

Magnesium hydride is one of the attractive and reversible hydrogen storage materials because it is directly formed from the reaction of bulk Mg with gaseous H_2 and reaches a high theoretical H_2 capacity of 7.6 wt.%. Such a storage system can store H_2 safely at an energy density equivalent to almost 100 g/L (Hanada et al., 2005). MgH_2 is also an abundant, low cost, easy to handle, and environmentally kindly light-metal hydrides. However, the practical application of Mg as a H_2 storage medium is greatly

hindered by its high desorption temperature and slow absorption/desorption kinetics. In addition, MWCNTs have been found to improve the H_2 storage capacity and absorption properties significantly of MgH_2. The results clearly show that the eradicated metal or alloy catalyst particles in MWCNTs contribute to the catalytic improvement of H-absorption of metallic magnesium (Wu et al., 2005).

Figures 1(a) and 1(b) showed that the Mg annealed with flowing H_2 at 573 K and then porous structure MgH_2 was observed. On the contrary, higher temperature of 673 K may cause the pore framework destroyed and the lower surface area of MgH_2 were found. TEM image (Figures 1(c)) indicated that irregular-shaped MWCNTs with inner and outer average diameters of 20 and 45 nm, respectively, the catalytic Co/Ni metal particles exist clearly, which may suggest that the Co/Ni particles are responsible for the nucleation of the MWCNTs. In addition, the MgH_2 particles were well dispersed in MWCNTs structures (Figure 1(d)). EXAFS data of Co/Ni precursor residues shown in Figure 2 revealed that the Co or Ni nanoparticles had a central Co (or Ni) atom of a coordination number of 2.92 ± 0.05 (or 5.96 ± 0.05) primarily Co-Co with a bond distance of 2.49 ± 0.05 Å (or 2.48 ± 0.05 Å). These results show how the yield and microstructure of MWCNTs formed by solvothermal route depend on the species of the Co/Ni metal catalysts. As shown in Figure 3, H_2 storage capacities of 1.3 wt.% for MgH_2/MWCNTs were achieved in 6h at 298 K. In addition, the different effects of MWCNTs and metallic nanocatalysts contained in the MWCNTs were studied and a hydrogenation mechanism was also postulated.
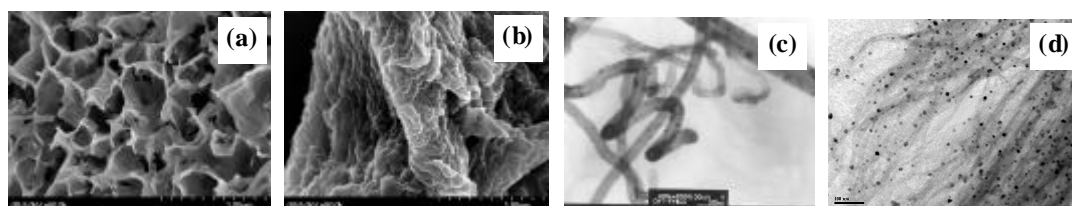
Figure 1: FE-SEM micrographs of Mg annealed with flowing H_2 at (a) 573 and (b) 673 K; TEM images of (c) MWCNTs synthesized by Co/Ni catalyzer precursors at T = 603 K and (d) MgH_2/MWCNTs mixtures.
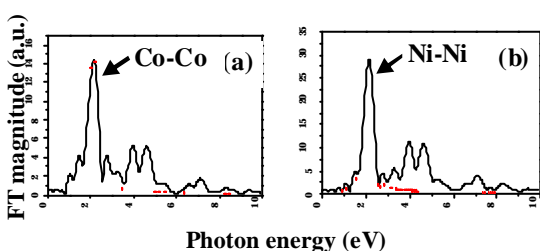
Figure 2: Fourier transform (FT) of the metallic (a) Co and (b) Ni K-edge EXAFS of the carbon nanotubes synthesized by Co/Ni catalyst precursors at T = 603 K for 8-12 h. The best fitting of EXAFS spectra are expressed by the dotted lines.
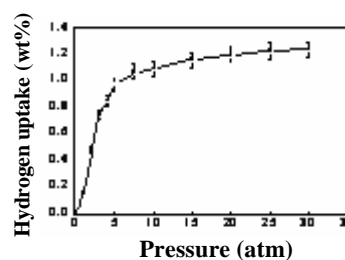
Figure 3: Hydrogen adsorption capacity of MgH_2/MWCNTs for 6h at 298 K and 1-30 atm.

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Fractionation of metal and semiconductor nanoparticles and their deposition into wide area thin films and ordered arrays using CO_2-expanded liquid solutions

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1. Summary

This paper demonstrates the rapid and precise size separation of nanoparticle populations using the pressure tunable solvent properties of CO_2-expanded liquids. Specifically, by pressurizing and expanding a single organic solution with carbon dioxide gas, ligand stabilized metal and semiconductor nanoparticles of desired mean size were size selectively precipitated at desired locations. Compared to current techniques, this CO_2-expanded liquid approach provides for faster and more efficient particle size separation, a reduction in organic solvent usage, and pressure tunable size selection. This paper also demonstrates the deposition of nanoparticles into low defect, wide area thin films using CO_2 as an antisolvent. Ligand stabilized metal particles are controllably precipitated from solvents by pressurizing and expanding the solution with CO_2. Subsequent addition of carbon dioxide as a dense supercritical fluid provides for removal of the organic solvent while avoiding the surface tensions common to evaporating solvents and detrimental to nanoscale structures.

Keywords: Nanoparticles, size-separation, CO_2 gas-expanded liquid, thin films

2. Extended Abstract

The size dependent properties of metallic and semi-conductor nanoscale materials allow them to be engineered for specific applications such as in catalysis and quantum dots in optoelectronic devices. Solution based nanoparticle synthesis techniques are among the most simple, but, they often result in particles with a wide size range. To address this limitation, post synthesis processing is required to further refine the size distribution. This paper presents an environmentally friendly and efficient process for size selective fractionation of polydisperse metal and semiconductor nanoparticle dispersions into multiple narrow size populations ($\pm$ 0.5 nm) using the pressure tunable physico-chemical properties of CO_2 gas expanded liquid solutions. Our work has shown that ligand stabilized nanoparticles can be size selectively precipitated by controlling the addition of CO_2 antisolvent (through pressurization) to an organic dispersion of nanoparticles. Compared to current liquid techniques, this CO_2-

expanded liquid approach provides for faster and more efficient size separation, a reduction in organic solvent usage, tunable size selection, and controllable deposition. In this CO_2-expanded liquid nanoparticle precipitation technique, ligand capped particles are first dispersed in solution where the interaction between the solvent and the ligand tails provides enough repulsive force to overcome the inherent van der Waals attraction between the particles that would otherwise result in agglomeration and precipitation. Through the addition of CO_2 antisolvent, the resultant poorer solvent mixture interacts less with the ligand tails than did the pure solvent, thereby reducing the ability of the solvent/antisolvent mixture to disperse the particles. Larger particles possess greater interparticle van der Waals attractions and therefore precipitate first upon worsening solvent conditions followed by subsequent precipitation of the smaller sized particles with further addition of antisolvent. To achieve these separations using CO_2 as an antisolvent, a novel high pressure apparatus has been designed that allows the controlled nanoparticle precipitations to occur from a liquid situated at a specific location on a surface by simply tuning the CO_2 pressure applied above the liquid dispersion. The efficiency of nanoparticle size fractionation was investigated on several types of metallic (Ag, Au) and semiconductor (CdSe/ZnS) nanoparticles to both illustrate the general applicability of the process and to provide fundamental information on the effects of processing parameters.

The general phenomenon of nanoparticle precipitation with CO_2 expanded liquids has been expanded to include an improved method for nanoparticle thin film deposition. Full exploitation of nanoparticles and their novel properties for application in areas such as catalysis, optical systems, electronic devices, and sensors requires the ability to effectively process and maneuver particles onto surfaces or support structures. This is often performed by simply evaporating a liquid solution containing ligand stabilized nanoparticles to leave behind dry nanoparticles coated on a surface. However, solvent dewetting and capillary forces at the liquid/vapor interfaces can lead to film defects such as nanoparticle islands, percolating networks, ring-like particle arrays, and uneven particle concentration. We have developed a novel nanoparticle deposition technique which utilizes CO_2 as an anti-solvent for low defect, wide area metallic nanoparticle film formation employing monodisperse nanoparticles. Ligand stabilized metallic particles are precipitated from organic solvents by controllably expanding the solution with carbon dioxide. Subsequent addition of carbon dioxide as a dense supercritical fluid then provides for removal of the organic solvent while avoiding the dewetting effects common to evaporating solvents. These dewetting effects and interfacial phenomena can be very detrimental to nanoscale structures. Controllable expansion of the liquid solution via CO_2 injection allows for control over the thermophysical properties that govern this deposition and assembly process. Ordered thin film arrays of metal nanoparticles were successfully produced using this CO_2-expanded liquid technique provided that the original dispersion of nanoparticles was fairly monodisperse.

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Session T3-2: Controlled Release of the Active Ingredient: Mechanisms, Devices & Analysis

Abstract Number	Paper Title & Authors	Included
2533	Analysis and modeling of radial water up-take in pure HPMC tablets S. Chirico, G Lamberti, V Nunziata, G Titomanlio	Yes
3354	Analysis and modeling of diclofenac sodium release kinetics from HPMC tablets A A Barba, M d'Amore, G Lamberti	Yes
3469	Microparticles formation of anti-inflammatory drug with bio-degradable polymer L Fele Zilnik, A Krzan, D Freitag	No
3656	Porous micro-cellular drug releasing foams as new implant material in post-surgical chemotherapy L Y Lee, J L Zheng, C-H Wang,	Yes

Analysis and modeling of radial water up-take in pure HPMC tablets

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1. Summary

This work deals with the analysis of transport phenomena involved in controlled drug delivery systems. In particular the attention is focused on the swelling and the erosion kinetics of pure hydroxypropylmethylcellulose (HPMC) tablets. The HPMC is commonly used in extended release formulation of systems for oral drug delivery.

The water up-take kinetics were investigated by means of a technique based on light intensity analysis and by means of a technique based on direct (gravimetric) measurement of water in tablet annuli. A satisfactory agreement was found between the light intensity analysis and the cut-and-weight technique.

Then, a model able to describe the transport phenomena (water diffusion, gel swelling and polymer erosion), taking place during drug release from swelling devices has been developed. Since the water up-take and the polymer erosion occurs only in the radial direction, the confined matrix has been treated as it was an infinite cylinder. The model prediction well agree with the evolution of radial water profiles determined experimentally.

Keywords: controlled release systems, swelling, erosion, HPMC

2. Extended Abstract

2.1. Material and methods

2.1.1. Material and tablets production
The hydrogel used in these experiments is HPMC K15M, kindly supplied by Colorcon. Tablets were made by compressing pure polymer powder with a tabletting machine having a 13 mm flat-faced punch, applying a force of 50 kN for 5 minutes. All tablets, shaped as discs, were 2.2 mm in thickness and they were made up of 350 mg of pure HPMC.

2.1.2. Image analysis technique
In order to study the swelling and erosion behavior of the HPMC tablets, they have been clamped between two square glass slabs, allowing the water up-take only by radial direction. These sandwiches were immersed in vessels filled with distilled and

stirred water kept at 37°C. By a video camera, programmed to capture one frame per minute, digital movie were collected. Subsequently several frames for each movie were analyzed providing the light intensity as function of tablet radius at different time of immersion. The analysis allows the identification of the erosion fronts. Furthermore, the light intensity profile was related to the water mass concentration profile.

2.1.3. Gravimetric technique

To confirm the data obtained by image analysis, a checking method was pointed out. Some swollen tablet, after a given immersion time, were cut by annular punches of different size, obtaining several annuli, and one core disc. The different amounts of partially hydrated polymer in different annuli were carefully weighted, dried, weighted once more. In this way it was possible to determine the mean concentration of water in each annulus, i.e. as function of tablet radius.

2.2. Results and discussion

Figure 1 shows, as open squares, the experimental results (normalized water mass fraction versus tablet radius) obtained by the image analysis of a snapshot taken after 1 day of immersion (reported itself in the Figure 1). Also the results of the gravimetric technique are reported as closed circles. The vertical bars represent the standard deviation data evaluated of triplicate measurements, the horizontal bars are the size of the annuli considered. The curve is the prediction of the model mentioned in the summary. It is worth noticing that the two experimental techniques are substantially in agreement, and the model is able to rightly reproduce the shape of the water mass profile. Since both the techniques and the model were found able to analyze this simple system (pure HPMC, only radial transport), they were applied in future to more complex systems (HPMC + drug, overall transport).
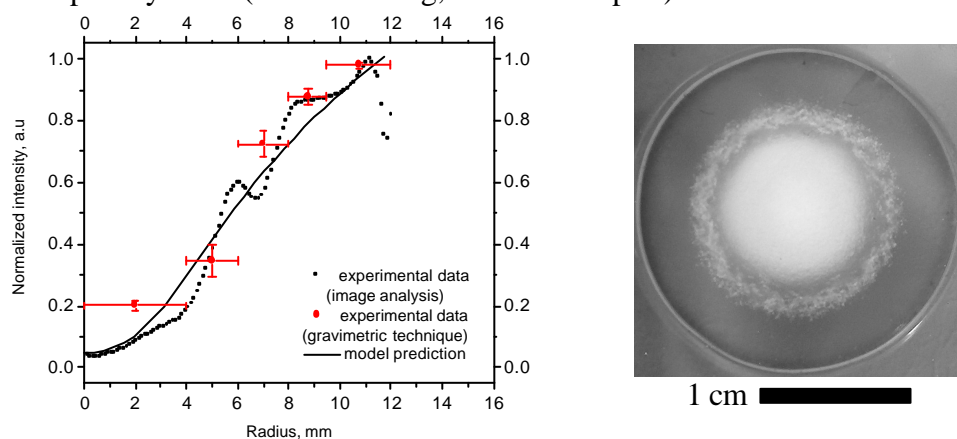
Fig. 1. (On the left) The radial profile of normalized water mass fraction after 1 day of immersion: □ experimental data from image analysis; ● experimental data from gravimetric technique; curve, model prediction; (on the right) the snapshot of the tablet after 1 day of immersion

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Analysis and modeling of Diclofenac Sodium release kinetics from HPMC tablets

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1. Summary

Controlled drug delivery from solid pharmaceutical systems is a key topic in pharmacology and many researchers all over the world are currently involved in related studies. The behaviors of pharmaceutical systems are dominated by mass transport phenomena, which can be described by methodologies typical of chemical and processes engineering. The proper description of these systems is very important in pharmaceutical systems design and drug delivery testing. In this work the release kinetics of DS (diclofenac sodium, a NSAID, non-steroidal anti-inflammatory drug) from tablets made of DS and of HPMC (hydroxy-propyl-methyl-cellulose, an hydrogel which swells in presence of water or physiological fluids) was investigated. Tablets were made by compressing HPMC and DS powders. Polymer matrix erosion and drug release phenomena are studied in a batch system where tablets are immersed for different residence times. Data of the masses evolutions (drug, polymer and absorbed water) are used as basis for the tuning of a physical model able to describe the water up-take by diffusion in the tablet, the swelling of the system, the drug diffusion toward the external medium (which causes the drug release) and the polymer erosion. The model is checked by comparison with the experimental release profile, showing a good agreement.

Keywords: controlled release, hydrogels, diclofenac sodium, swelling, diffusion

2. Extended Abstract

2.1. Materials and methods

Tablets of DS and HPMC are made by compressing their powders, previously weighted and mixed in the ratio 67% HPMC / 33% DS, with a tabletting machine having a 13 mm flat-faced punch, applying a force of 50 kN for 5 minutes. All tablets, shaped as discs, were 13 mm in diameter and up to 2 mm in thickness and are made up of 300 mg of HPMC/DS mixture. The tablets are dissolved in USP XXVIII apparatus 2, (AT7 Smart, Sotax). Each tablet is immersed in 900 mL of distilled water kept at 37°C, mixed by paddle rotating at 100 rpm. At given time intervals, the DS concentration in each vessel is assayed by an UV-visible spectrophotometer (Lambda

25, Perkin Elmer) working at a wavelength of 275 nm. The dissolution apparatus and the spectrophotometer were connected by a peristaltic pump, which avoids the need for periodic withdrawn/replacements of sample from the vessels. Furthermore, at a given time, tablets are extracted from the vessels, carefully weighed, dried, weighed once more and completely dissolved in distilled water to assay the unreleased drug. Thus, the traditional release profile is obtained in term of fractional release versus time, and also the polymer, the drug and the water mass in the swelling device are determined as functions of time.

2.2 Results and discussion

Experimental results of the described methods are reported in Figure 1, in terms of drug, polymer and mass evolutions (obtained by partial dissolution, weighting, drying, complete dissolution and drug assaying in dissolution medium), and in Figure 2, in terms of percentage of drug release (obtained by the method described before as well as by the use of USP type 2 apparatus). The data are reported as symbols (averaged from triplicate tests), with their standard deviations as vertical bars.
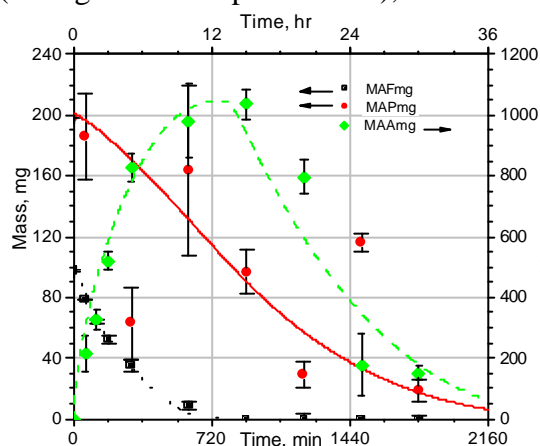
Fig. 1 Data of the masses evolutions, ■drug, ●polymer and ◆absorbed water, during dissolution tests. Experiments (symbols) and prediction (curves).
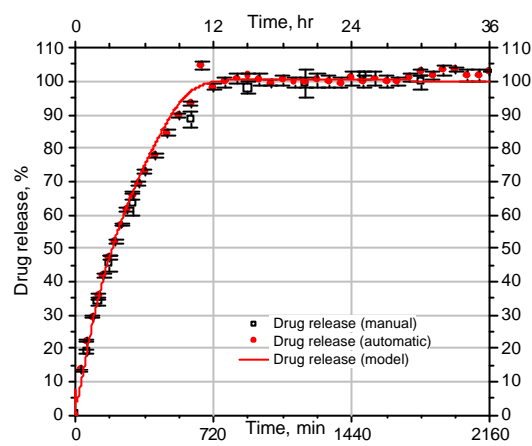
Fig. 2 Experimental (symbols) and predicted (curve) drug release evolution from Diclofenac Sodium tablets.

A model, developed after Siepmann and Peppas (2001) by our research group (Lamberti et al., 2005) has been used to describe the experimental data. The model consists in the transient mass balances of water and drug within the tablet, accounting for water diffusion in the tablet, polymer swelling and erosion, diffusivity increase due to the hydration and drug diffusion toward the dissolution medium. The model rightly predicts all the main characteristics of the system: the monotonic decrease of polymer and drug mass, as well as the increase of water content due to the hydration, followed by the decrease due to the tablet erosion. The model, tuned on the basis of the data in Figure 1, is predictive and thus the data in Figure 2 are rightly reproduced, and it will be applied in description of other, more complex, systems.

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Porous micro-cellular drug releasing foams as new implant material in post-surgical chemotherapy

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1. Summary

This study presents the encapsulation of paclitaxel, a promising chemotherapeutic agent, in Poly DL lactic-co-glycolic acid (PLGA) foams for controlled delivery in the surgical treatment of carcinomas as a potentially new type of surgical implant material. Using supercritical CO_2 as a foaming agent, the use of organic solvent may be minimized or even eliminated in the production of PLGA foams. Firstly, paclitaxel loaded microparticles were fabricated using conventional spray drying. Next, the microparticles were foamed directly to obtain the solid polymeric foams. Molecular dispersion of paclitaxel in PLGA polymer matrix was achieved in the foamed samples. The pore size and size distribution, thermal properties and *in vitro* swelling behavior of the foams were investigated. The in vitro release profile of paclitaxel from the foams show sustained release for more then 5 weeks with a close to linear release profile. As supercritical carbon dioxide has excellent miscibility with many organic solvents, the residual organic solvent content of the samples obtained in this study showed very low levels of residual dichloromethane which was used during the spray drying step.

Keywords: micro-porous foams, supercritical gas foaming, sustained release.

2. Extended Abstract

The fabrication of microporous foams from biodegradable polymers using supercritical CO_2 gas foaming technique have been applied for scaffold material in tissue regeneration studies, tissue engineering as well as protein encapsulation and delivery (Quirk et al. 2004; Nalawade et al. 2006; Singh et al. 2004; Hile and Pisko 2004). In this study, PLGA foams were fabricated for encapsulation and sustained delivery of paclitaxel. Pore size of the foams could be controlled by altering the saturation pressure and contact time used in the gas foaming process. Figure 2 shows PLGA foams with pore sizes as large as 500μm and as small as 20μm. In general, an increase in saturation pressure and contact time increase the concentration of dissolved CO_2 in the PLGA. Higher cell density with smaller cell sizes is achieved when concentration of dissolved CO_2 is high.
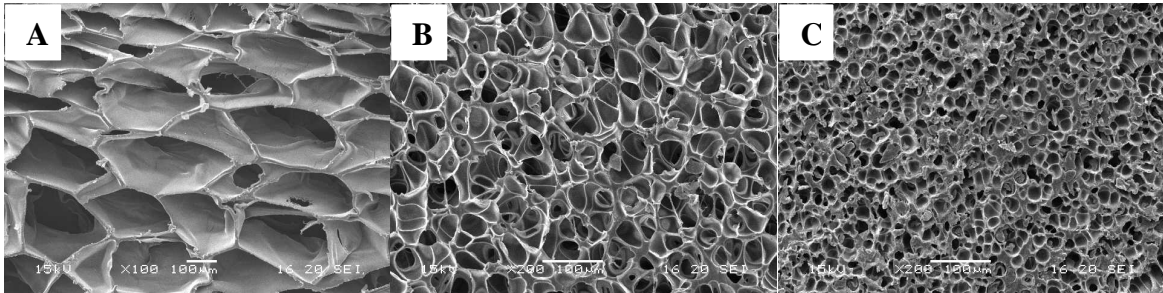
Figure 1. Scanning Electron micrographs of micro-porous PLGA (50:50) foams with mean pore sizes of approximately (A) 500μm; (B) 50μm and (C) 20μm, achieved by manipulating the saturation pressure and contact time used in the supercritical gas foaming process.

The paclitaxel-encapsulated foams were cut into discs of diameter 3mm and height 1mm. The *in vitro* release profiles from PLGA foams with 5% drug loading up to 5 weeks are shown in Figure 2.
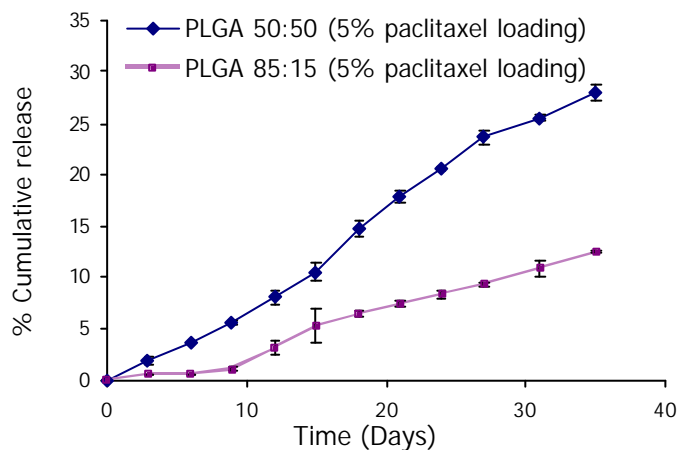
Figure 2. *In vitro* release profile of paclitaxel from discs of microporous PLGA foams. PLGA 50:50 is more hydrophilic than PLGA 85:15 due to its higher content of glycolic acid. Therefore, the overall release rate is faster from PLGA 50:50 foams.

A relatively linear release profile was achieved using the micro-porous foam discs which showed promising application as a post-surgical implant material for treatment of gliomas and other malignant tumors.

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Session T3-3a: Analysis of Energy Issues

Abstract Number	Paper Title & Authors	Included
745	Economic study of water steam production by biomass or domestic waste incineration R Rivera-Tinoco, C Bouallou, C Mansilla, F Werkoff	Yes
804	Sweet sorghum biomass fermentation: modeling of hydrogen and methane production based on ADM1 G Antonpoulou, H N Gavala, I V Skiadas, G Lyberatos	Yes
1894	Possibilities of microbial method of enhanced oil recovery Implementation in Danish chalk rocks S Rudyk, H Andersen, L W Jørgensen, I B Awasi, J Enas, A Jimoh	No
3360	On the modeling of metabolic products distribution during fermentative hydrogen production H N Gavala, I V Skiadas, G Lyberatos	Yes
4174	Bio-ethanol: is the world on the wrong track? H Wenzel	No

Economic study of water steam production by biomass or domestic waste incineration

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1. Summary

This work presents the study of water steam production, for the High Temperature Electrolysis process, by incineration of biomass and domestic waste. The estimated steam production cost seems competitive and its potentiality could lead to an annual hydrogen production up to 8.0 million tons, which could fuel around 72 million hydrogen vehicles per year.

Keywords: Biomass, domestic waste, incineration, steam, hydrogen production.

2. Extended abstract

In order to evaluate the use of non-fossil energy sources for hydrogen production, an economic and potential study of water steam production by incinerating biomass and domestic waste was carried out. Biomass presents non-negligible Heating Values (HV) for heat exchange in incineration units and emits green CO_2. Besides, domestic waste incineration reduces municipal waste discharges and contributes to high energy recovery. For both sources, water steam production would be coupled with a High Temperature Electrolysis (HTE) process for hydrogen production.

The economic study of steam generation is based on the incineration cost, which includes the investment cost and operation cost of the incineration units. Two different units are considered in this work. First, we considered the biomass incineration units, which investment is mainly dependent of the furnace cost estimated by considering the total steam production flow, the combustible LHV and mass rate. Secondly, we considered the domestic waste incineration units for which we retained the incineration cost presented in previous works.

In the case of the biomass incineration units, the outlet steam temperature is fixed between 350°C and 550°C at 4.0 MPa. For the domestic waste unit, the outlet steam temperature is fixed at 440°C at the same pressure.

The steam production cost is estimated by the following equation, where C_{inc} is the incineration cost, H_{vap} the steam enthalpy and η the unit efficiency.

$$C_{steam} = \frac{C_{inc}H_{vap}}{LHV_i \times h}$$

For the LHV references, two different kinds of biomass are retained, the wheat straw and pine tree wood at different moisture contents. The estimated steam production cost is found between 1.9 and 4.1 c€/kg. In figure 1, steam production costs are presented as a function of hydrogen demand at a steam conversion efficiency of 100%.
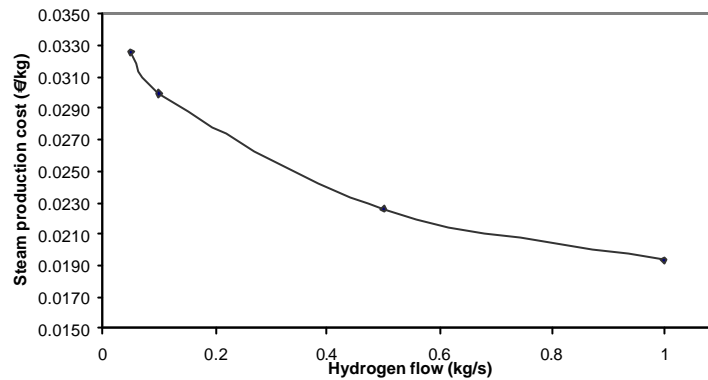
Fig 1. Steam production cost vs. hydrogen demand for biomass incineration units.

The steam production cost by the domestic waste incineration considers a unit efficiency of 80% and a value of 2600 W/kg as the waste LHV. The results for these units, as classed in [1], are presented in Table 1.

Table 1. Steam production cost by domestic waste incineration units.

Unit capacity kg/year	Steam cost €/kg
<20 000 000	0.057
20 000 000< x < 100 000 000	0.041
>100 000 000	0.033

In France, the steam generation by the incineration of the non-valorised biomass could produce enough hydrogen to supply the needs of almost 46 millions hydrogen automobiles, avoiding deforestation and reducing important changes in actual agriculture surfaces. Moreover, considering that, in France, 52% of waste was not valorised in 2002 and this percentage has remained constant, we estimate that the steam generation of the non-valorised domestic waste could produce enough hydrogen to supply the needs of almost 26 million hydrogen automobiles.

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On the modeling of metabolic products distribution during fermentative hydrogen production

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1. Summary

Biological fermentative hydrogen production, one of the several ways to produce hydrogen, has received special attention during the last decade. Carbohydrates are the main source of hydrogen and fermentation of sugars is accompanied also by the production of various metabolic products, mainly volatile fatty acids (acetic, propionic and butyric), lactic acid and ethanol. The hydrogen yield varies proportionally to the final metabolic products with hydrogen partial pressure, pH and substrate concentration being the main macroscopic factors influencing the distribution of metabolic products and consequently hydrogen yield. In the present theoretical study of the fermentative hydrogen production, a mathematical model able to predict the distribution of the various metabolic products as function of the operational parameters has been developed with the ratio of reduced to oxidized NAD being the key parameter. Glucose was chosen as sugars representative model compound and the products distribution among acetic, propionic, butyric and lactic acids and ethanol as well as hydrogen production was studied at different values of pH and loading rate. The novelty of the present study lies on the fact that the model allows the yield of metabolic products to vary depending on the microbial growth conditions and it was developed using the same platform as the Anaerobic Digestion Modeling No1 (ADM1).

Keywords: biofuels, biohydrogen, fermentation, products distribution

2. Extended Abstract

The present study is partly based on the study of Mosey (1983) who was the first to point out the role of NADH to NAD ratio as regulating factor of the distribution of volatile fatty acids during the anaerobic digestion process. The present modelling approach took into consideration the EMP pathway for sugars consumption and five main metabolic products: acetate, propionate, butyrate, lactate and ethanol. The ratio of reduced to oxidized NAD was the regulating factor for the production of the

different intermediates at the sites of pyruvic acid and acetyl-CoA, where distribution of the final products may take place. Moreover a "switch" function of the pH was added allowing the model to predict the distribution between ethanol and lactic acid despite the identical electron transfer potential of these two components. A representative carbon flow-chart for the glucose fermentation is presented in figure 1. Pairs of electrons transferred through NADH are denoted as "H_2".
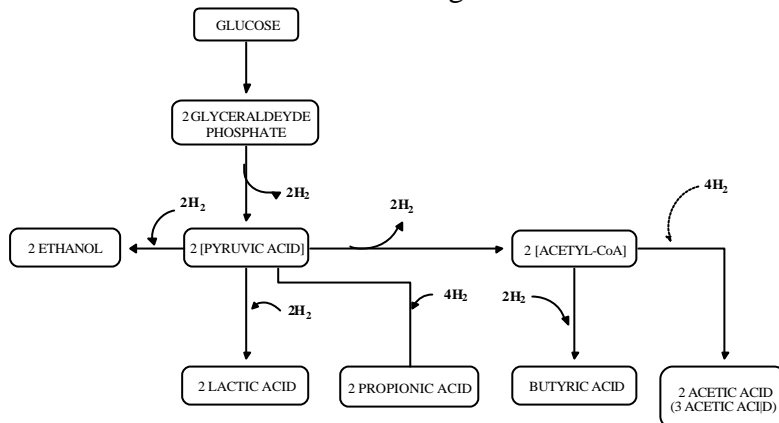
Figure 1. A representative carbon flow chart during fermentation of glucose

The carbon distribution among acetate, propionate, butyrate, lactate and ethanol as well as hydrogen production were predicted for different values of the pH and the loading rate. The model was build at the same platform as the Anaerobic Digestion Modelling No1 (ADM1). Figure 2 shows representative model predictions for the yield of butyric acid, ethanol and hydrogen during glucose fermentation and the respective ratio of the NADH to NAD with the pH of the growth medium.
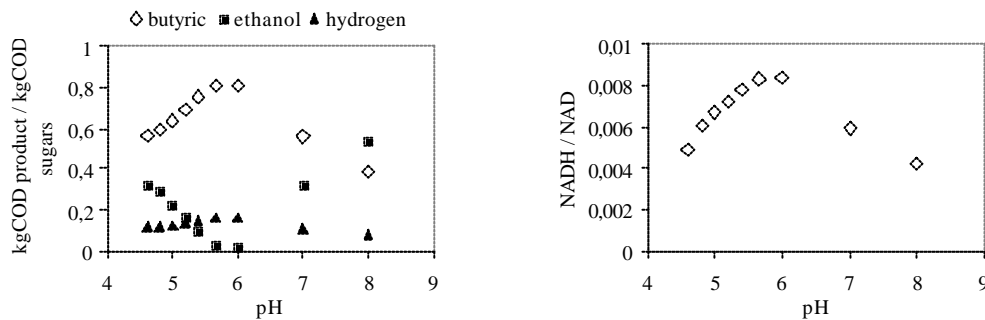
Figure 2. Butyric acid, ethanol and hydrogen yields as well as the ratio of the NADH to NAD with the pH

The modeling approach developed in the present study can be applied not only in fermentative hydrogen production area but also in other mixed fermentation processes used for solvents (including ethanol) production, lactic acid production etc.

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Sweet sorghum biomass fermentation: modeling of hydrogen and methane production based on ADM1

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1. Summary

?he Anaerobic digestion model 1 (ADM1) was used to simulate and predict the hydrogen and methane production from sweet sorghum biomass in a two stage anaerobic process. The ADM1 modeling framework simulated the anaerobic digestion of the effluent of the hydrogenogenic reactor quite well. The model was also modulated in order to describe the process of fermentative hydrogen production from the sugars of sorghum biomass. In order to improve the predictions for the bio-hydrogen production process, the structure of the model was modified. The modified ?DM1 simulated satisfactorily batch and continuous experiments for the production of hydrogen although more modifications could be included as well, in order to further improve the predictions for the hydrogenogenic process.

Keywords: ADM1, modeling, sweet sorghum, anaerobic digestion, hydrogen.

2. Extended Abstract

Experiments with sweet sorghum biomass

Sweet sorghum is an annual plant, characterized by high biomass yield. Its stalks are rich in readily fermentable sugars and thus sweet sorghum can be considered as an excellent raw material for biofuels generation (Gosse, 1996). Fermentative hydrogen production from the extractable sugars of sweet sorghum biomass was investigated in batch and continuous systems at mesophilic (35ºC) conditions. The continuous process took place in a CSTR-type bioreactor (H$_2$-CSTR) where an indigenous mixed microbial culture was established. Hydrogen production was studied at hydraulic retention times (HRTs) of 12, 8, 6 and 4 h (Antonopoulou et al., 2007). When a steady state was reached, batch experiments (H$_2$-batch) were carried out with H$_2$-CSTR effluent at the corresponding HRTs as inoculum and sweet sorghum extract as substrate, in order to validate the kinetic parameters extracted from continuous experiments. In parallel, the effluent of the continuous hydrogenogenic reactor was fed to a CSTR-type anaerobic methanogenic reactor (CH$_4$-CSTR) in order to reduce the organic content of the feed with simultaneous energy production. The continuous

methanogenic reactor was operated at hydraulic retention times of 20, 15 and 10 d. Batch experiments (CH$_4$-batch) were carried out with inoculum from the CH$_4$-CSTR and acetic, propionic and butyric acids and hydrogen as substrates.

Modeling

The IWA anaerobic digestion model (ADM1) developed by Batstone et al. (2002) was used to simulate and predict the hydrogen and methane production from sweet sorghum biomass in a two-stage anaerobic process. The software used for parameter estimation and simulation studies was Aquasim 2.1 (Reichert, 1998).

The ADM1 model includes the major processes that are involved in the bioconversion of complex organic substrates into methane, carbon dioxide and inert byproducts with the main metabolic intermediates being hydrogen, acetic, propionic and butyric acids. The model was used to simulate the anaerobic digestion process of the effluent of H$_2$-CSTR. The kinetic parameters for hydrogen and organic acids consumption were estimated through fitting of the model equations to the data obtained from the batch experiments (CH$_4$-batch). The estimated kinetic parameters were subsequently used to simulate the CH$_4$-CSTR performance at all HRTs.

The ADM1 model can be used as well to predict fermentative hydrogen production since the latter is directly related to the acidogenic stage of the anaerobic digestion process. Thus, the ADM1 model was modulated in order to describe the process of fermentative hydrogen production from the extractable sugars of sweet sorghum biomass. Kinetic parameters for sugars consumption and yield coefficients of acetic, propionic and butyric acid production were estimated using the experimental data obtained from the steady states of H$_2$-CSTR. The batch experiments (H$_2$-batch) were used for kinetic parameters validation. However, ADM1 does not take into account metabolic products such as lactic acid and ethanol that are crucial during hydrogen production process. Therefore, the structure of the model was modified to include lactate and ethanol among the metabolites in order to improve biohydrogen production predictions. The modified model simulated satisfactorily the production of hydrogen. Other essential modifications could be included as well in order to further improve the predictions for the hydrogenogenic process.

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Session T3-3b: Analysis of Environmental Issues

Abstract Number	Paper Title & Authors	Included
392	Gypsum crystal degradation in wet flue gas desulphurisation plants B B Hansen, S Kiil, J E Johnsson	Yes
462	Evaluation of the capacity of adsorption CO_2 in commercial zeolites on pilot plant Y Lima, P Guimarães, S Bello, L Carvallo, D Lisboa, R Carvalho, E Santos	Yes
844	Fly ash and adsorption of air-entraining agents in concrete: influence of combustion conditions K H Pedersen, A D Jensen, K Dam-Johansen	Yes
2017	Techno-economic evaluation of a PVAm CO_2-selective membrane in an IGCC power plant with CO_2 capture D Grainger, M-B Hägg	Yes
3381	Zero emission hydrocarbon-fueled vehicle transportation with fuel re-synthesis from on-board sequestrated CO_2 M Musadi	No

Gypsum crystal degradation in wet Flue Gas Desulphurisation (FGD) Plants

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1. Summary

The extent of crystal degradation taking place in the wet flue gas desulphurisation (FGD) process has been investigated in a pilot plant. Samples of gypsum slurry were subjected to the mechanical stresses caused by stirring, recirculation and air injection for up to 600 hrs. The experiments showed that gypsum particles above approximately 25 µm were broken into a wide range of smaller pieces. Conventional breakage models, assuming a breakage mechanism that yields equal-sized pieces, has been unable to describe the observed changes in particle size distribution (PSD). A new model based on multiple breakage mechanisms has been verified against experimental data.

Keywords: FGD, particle technology, population balance modeling, particle breakage.

2. Extended Abstract

2.1 Introduction

The combustion of fossil fuels such as coal, oil and gas covers a significant amount of the worlds present energy demand and is expected to do so for the coming years [1]. Due to the sulphur content of coals and oils, acidic compounds such as sulphur dioxide (SO_2) and to a lesser extent sulphur trioxide (SO_3), will be released during combustion. Various Flue Gas Desulphurisation (FGD) technologies may be used to limit the release of these compounds. The majority of the worldwide installed FGD capacity consists of the wet scrubber FGD technology using forced oxidation to produce gypsum [2].

$$CaCO_3 \text{ (s)} + SO_2 \text{ (g)} + 2\,H_2O \text{ (l)} + \tfrac{1}{2}O_2 \rightarrow CaSO_4 \cdot 2H_2O \text{ (s)} + CO_2 \text{ (g)} \qquad (1)$$
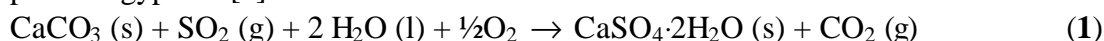
The sales potential of the produced gypsum depends on parameters such as the particle size distribution (PSD), the moisture content and the content of impurities such as residual limestone. This study consists of experimental as well as theoretical

investigations of the gypsum crystallisation (crystal formation and growth) in a wet FGD plant. Experiments performed on a wet FGD pilot plant will be supplemented by measurements from FGD units at full-scale power plants. Based on the experimental results it is the aim of this study to develop population balance equations for the prediction of gypsum PSD based on operating conditions. Initial experiments have been focused on the mechanical degradation of gypsum crystals in a wet FGD pilot plant.

2.2 Crystal degradation in a wet FGD pilot plant

The extent of crystal degradation has been investigated by subjecting samples of gypsum slurry to the mechanical stresses caused by stirring, recirculation and air injection for up to 600 hrs in a wet FGD pilot plant. The development in PSD as a function of time was monitored by analysing slurry samples with a Malvern Mastersizer S (laser diffraction measurements). A decrease in the volume fraction of particles above a size of approximately 25 µm was observed during the experiments. The degradation produced pieces of sizes ranging from the submicron range up to 25 µm. The increased fraction of small particles may cause a reduced dewatering potential of the gypsum. Conventional models, assuming a single multiple piece breakage mechanism, have been unable to describe the experimentally observed changes in PSD. A new model based on multiple breakage mechanisms has been verified against experimental data.

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Evaluation of the Capacity of Adsorption of CO_2 in Commercial Zeolites on a PSA Pilot-Plant

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1. Summary

This study is concerned with the capacity of CO_2 adsorption on commercial zeolites in a Pressure Swing Adsorption (PSA) pilot-plant. The determination of the equilibrium CO_2 adsorption capacity of these adsorbents has been carried out through gravimetry. The isotherms obtained for both zeolites were adjusted to the models proposed by Langmuir, Freundlich and Tóth and have shown a particularly good agreement to the Langmuir model. The equilibrium isotherm for zeolite 13X has then been used to determine the optimum operating conditions for the PSA pilot-plant, with regard to temperature and adsorbent moisture content, so as to maximize CO_2 adsorption.

The breakthrough experiments in the PSA pilot-plant, using zeolite 13X as adsorbent, have been undertaken at 300 K and flow rate of 3.0 mL/min , for a gaseous mixture containing 11,5 % CO_2, 87,5 % N_2 and 1.0 % O_2, and resulted in an adsorption capacity of 10.38 g of CO_2 / 100 g of adsorbent. This is in agreement with the equilibrium adsorption isotherms obtained through gravimetry (10.4 g of CO_2 / 100 g of adsorbent), and shows that, at these operating conditions, the adsorption of CO_2 in the PSA pilot-plant is very close to equilibrium.

Keywords: zeolite, adsorption, PSA.

2. Extended Abstract

The experimental evaluation of the CO_2 adsorption capacity of zeolites 13X and 5A involved the physicochemical characterisation of these adsorbents, followed by determination of equilibrium data through gravimetry and finally, breakthrough runs on a PSA pilot-plant. The results indicate a very good agreement with other data already reported in scientific literature.

The characterisation of the zeolites involved techniques such as X-Ray diffraction (DRX), electronic scanning microscopy (MEV) and BET. The adsorption equilibrium data were obtained through gravimetry for several CO_2/Argon mixtures, using an

apparatus composed of mass flow meters, an adapted muffle, a high precision micro scale and a gas chromatograph. For these tests the zeolites have been previously treated at 403 K and 673 K for moisture removal.

The breakthrough runs were performed on a custom designed PSA pilot-plant, and were undertaken on zeolite 13X only, since this adsorbent gave better results on the equilibrium adsorption tests, as shown in Figure 1. It can also be observed that the experimental data for both zeolites are well represented by the isotherm models of Langmuir, Tóth and Freundlich, with a better adjustment for the first two, as indicated by the respective correlation coefficients (R^2)

Fig. 1. Adsorption isotherms at 298 K for CO_2 on zeolites 5A (a) and 13X (b), treated at 673 K, for the Langmuir, Tóth and Freundlich models.

Following activation, the adsorbent has been submitted to a continuous flow of a gas mixture composed of 11.5% de CO_2, 87.5% N_2 e 1.0% O_2, supplied by Air Products, at 523 K, 150 kPa and a 3.0 cm3/s flow rate, for 98.1 min. These runs resulted in the breakthrough curve shown in Figure 2.

Fig. 2. Breakthrough curve for zeolite 13X at 298 K.

The adsorption capacity of the 13X fixed-bed, determined through Ruthven's equation (Equation 1), was 10.71 g/100 g_{ads}, which is in agreement with equilibrium adsorption previously determined through gravimetry (10.41 g/100 g_{ads}).

$$t' = \frac{L}{V}\left[1 + \left(\frac{1-e}{e}\right)\left(\frac{q'}{Co}\right)\right] = \int_0^{t'}\left(1 - \frac{C}{Co}\right)dT \tag{1}$$

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Fly ash and adsorption of air-entraining agents in concrete: Influence of fuel type and combustion conditions

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1. Summary

Utilization of fly ash from solid fuel combustion plays an important role in environmentally clean and cost effective power generation. The primary market for fly ash utilization is in the production of concrete, but fly ash is known to have a negative effect on the air entrainment, a property important for the workability and resistance toward freezing and thawing conditions of the concrete. The problem has increased, by the installation of low-NO_x combustion technologies. This presentation presents the results of solid fuel combustion experiments carried out on an entrained flow reactor with the aim of obtaining knowledge of how fly ash quality is affected by fuel type and combustion conditions, the latter including oxy-fuel combustion.

Keywords: Fly ash, concrete, air-entraining agents

2. Extended Abstract

Fly ash, a by-product from combustion of pulverized coal or biomass, is utilized in the concrete manufacture as pozzolanic additive, but the residual carbon in the fly ash is known to adsorb air-entraining agents (AEAs) added to the concrete. A problem that has increased by the introduction of low-NO_x combustion technologies, which causes elevated carbon content in the fly ash and higher AEA adsorptivity per gram of carbon. In future design and operation of new combustion technologies, it is important to understand the mechanisms in the combustion process causing the problem.

In the present work, fly ash has been produced from combustion of pulverized bituminous coal in an entrained flow reactor (EFR). The collected fly ashes have been analyzed for carbon content (loss-on-ignition, LOI) and adsorption capacity of AEAs, the latter using the foam index test (FI). The values have been compared with total excess air, the ratio between the air introduced through the solid feed probe and the total combustion air, and the obtained NO_x emissions.

The carbon content of the fly ashes is found to decrease with increasing feed/total air ratio (Fig. 1), presumably due to an improved mixing between coal and air caused by increasing jet velocity at higher feed/total air ratio leading to an increased oxygen concentration in the early stage of combustion and thereby higher conversion of the coal particles. The elevated oxygen concentration in the reactor, at higher excess air, has a positive effect on the burnout as well. The determined FI values of the coal ashes (Fig. 1) follows the tendency of the carbon content; increasing excess air and feed/total air ratio result in ashes

with lower FI values. However, the decrease in FI is not solely caused by a decrease in the carbon content as shown in Fig. 2,
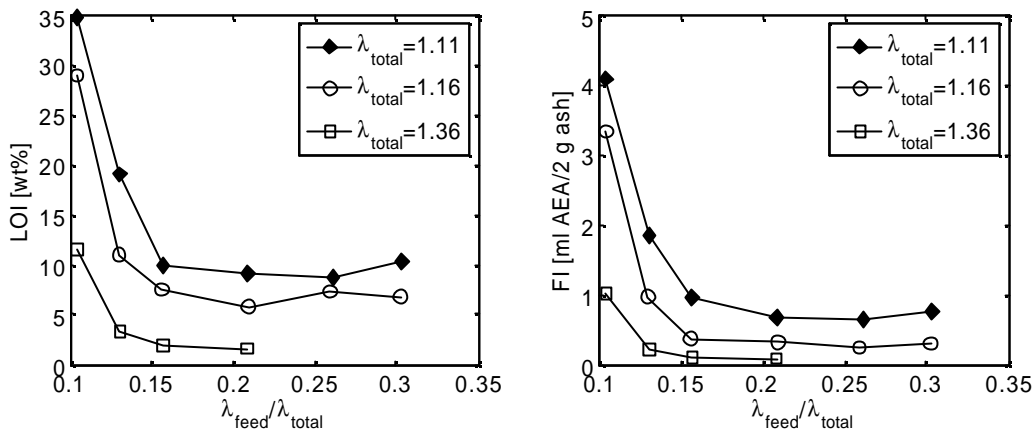
Figure 1 Relationship between LOI (left) and FI (right) and feed/total air ratio at different total excess air.

where the measured FI values are normalized to the carbon content (spec. FI). Lower AEA adsorptivity of the carbon is found at increasing feed/total air ratio and at higher excess air. It has been suggested [1] that more fuel rich conditions, here presented as lower total excess air and feed/total air ratio, may increase the AEA adsorption capacity of the residual carbon. A linear relationship was found between the NO_x emission and the feed/total air ratio, while the major change in FI of the fly ash occurred at lower ratios or NO_x emissions, the latter presented in Fig. 2. Thus, small variations in the oxidizing conditions appear to affect the fly ash quality at lower NO_x emissions, while enhanced oxidizing conditions result in higher NO_x emissions, but
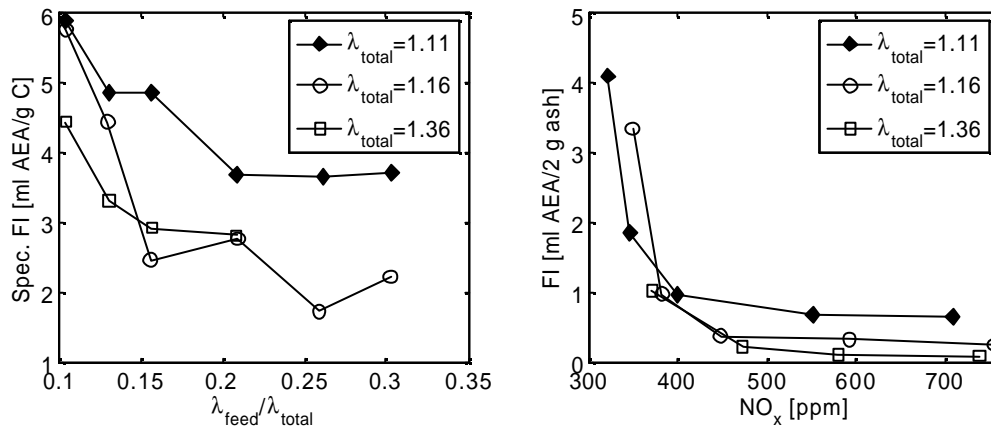
Figure 2: Relationship between spec. FI and feed/total air ratio (left) and FI and NO_x at 10 % O_2 (right).

have no affect on the fly ash quality. Determination of the optimal combustion conditions, where high fly ash quality and low NO_x emission are achieved, will be beneficial in operation and future design of combustion technologies.

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Techno-economic evaluation of a PVAm CO_2-selective membrane in an IGCC power plant with CO_2 capture

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1. Summary

The high partial pressure of CO_2 in a water-gas-shifted syngas stream in an Integrated Gasification Combined Cycle offers an excellent driving force for membrane separation. A study has been performed where CO_2 capture using a fixed-site-carrier polyvinyl amine membrane, developed at NTNU, was simulated in Aspen Hysys®. It appears that the modified process, using a sour shift catalyst prior to sulphur removal, could achieve greater than 85% CO_2 recovery at 95 vol% purity. The efficiency penalty for such a process would be approximately 10 percentage points, including CO_2 compression.

Keywords: IGCC, FSC membrane, CO2 capture

2. Extended Abstract

The high partial pressure of CO_2 in a water-gas-shifted syngas stream in an Integrated Gasification Combined Cycle offers an excellent driving force for membrane separation. The challenge has been to find an inexpensive membrane that has a high enough selectivity to separate CO_2 without losing a significant fraction of hydrogen to the CO_2 stream. A polyvinyl amine membrane is under development at the Norwegian University of Science and Technology that permeates CO_2 by a fixed-site-carrier mechanism, which allows both a high selectivity over hydrogen (approximately 100) and a reasonable permeance (0.05-0.1 $m^3(STP)/m^2.bar.h$).The polymeric membrane can be supported on polysulfone hollow fibres and may therefore be produced in bulk without drastic modification of current membrane spinning techniques.

Published data for an operating power plant, the ELCOGAS 315 MWe Puertollano plant, was used as a basis for the simulation of an integrated gasification combined cycle process with CO_2 capture (see Figure 1). This incorporated the fixed site carrier PVAm membrane to separate the CO_2 from a CO-shifted syngas stream.
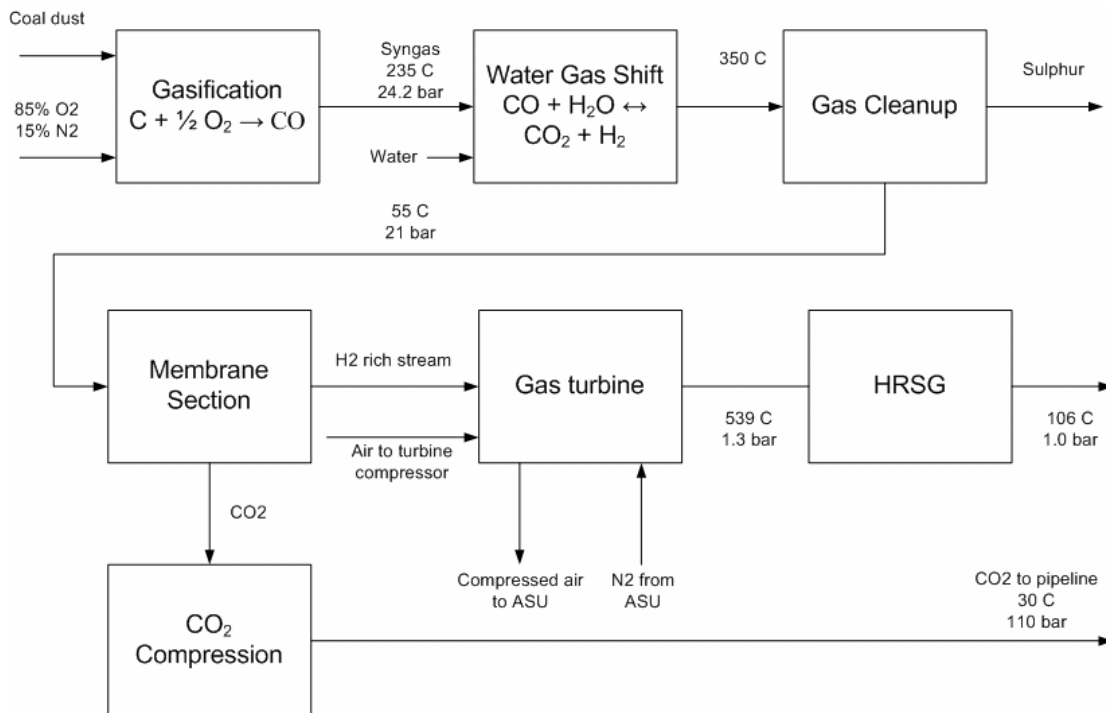
Figure 2: Process block diagram for an IGCC process with CO_2 capture with a fixed-site carrier membrane

Continuous-rig laboratory permeance data was used in an in-house membrane model integrated with Aspen Hysys®. The study included the effect of membrane selectivity, CO_2 recovery, membrane configuration and the position of the shift reaction in the process route on the plant efficiency and cost. It was found that the selectivity of the membrane and the degree of CO_2 recovery has a significant effect on the overall efficiency of the power plant, because they affect the amount of hydrogen lost to the CO_2 product stream.

It appears that the modified process, using a sour shift catalyst prior to sulphur removal, could achieve greater than 85% CO_2 recovery at 95 vol% purity. The efficiency penalty for such a process, including CO shift and CO_2 compression, would be approximately 10 percentage points. The membrane section compared favourably with respect to the energy consumption of physical solvent CO_2 capture and was similar in capital cost.

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Session T3-4a: CFD & Chemical Engineering- I

Abstract Number	Paper Title & Authors	Included
712	CFD modelling of HVPE reactor for gallium nitride deposition L Sytniewski, A Lapkin, W N Wang	Yes
1102	High-fidelity CFD modeling of particle-to-fluid heat transfer in packed bed reactors M Kuroki, S Ookawara, D Street, K Ogawa	Yes
2185	Macroscopic and CFD modelling of droplet formation during cross–flow membrane emulsification G De Luca, A Di Renzo, F P Di Maio, E Drioli	Yes
2940	Multi-scale modelling of the anode and cathode compartments and the IIR unit within a MCFC M Pfafferodt, P Heidebrecht, K Sundmacher	Yes

CFD modelling of HVPE reactor for gallium nitride deposition

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1. Summary

An up-flow hot wall hydride vapour phase epitaxy (HVPE) reactor with a single stationary substrate was designed for growth of thick free-standing GaN substrates. The influences of (*i*) reactor chamber geometry and aspect ratio, (*ii*) orientation of the reaction chamber along the gravity field, (*iii*) reactants composition, (*iv*) total flow through reactor, and (*v*) pressure were systematically investigated using a computational fluid dynamics (CFD) model. Reactor optimisation was performed against specific design objectives of high growth rate, high uniformity of reactants concentrations near substrate and efficiency of utilisation of the metal precursor. The results show that it is possible to achieve good uniformity (less than 2.5 % difference in molar concentration across substrate) for both ammonia and gallium chloride, with the V/III molar ratio near substrate around 10 at the reactor chamber pressure 1 bar. GaN growth rate was estimated to be 400 $\mu m \cdot h^{-1}$ assuming 100 % conversion of molecules reaching substrate. These performance criteria allow practical realisation of an efficient reactor system.

Keywords: hydride vapour phase epitaxy, nitrides, computer simulation, semiconducting gallium compounds

2. Extended Abstract

Gallium nitride (GaN) is an excellent candidate for high temperature and high power optoelectronic devices such as blue-violet light emitting diodes (LED's) or lasers, with a major application in high-density DVD data storage technology [1]. However, in the heteroepitaxy process, the most common technique for the growth of freestanding GaN, the dislocation density is still a critical issue which limits the lifetime of devices and availability of low-cost high quality materials for mass market [2]. The homoepitaxy growth process can reduce the defects dislocation density by two or even three orders of magnitude [3]. Only the hydride vapor phase epitaxy

process (HVPE) seems to be a suitable and economically justified technique to grow thick freestanding gallium nitride crystals on hetero-substrates, which can then be used in the homoepitaxy process [4]. To reduce the overall cost of experimental procedure and facilitate process development, computational fluid dynamics has been used in the project to optimize the reactor design affecting required species concentration on the substrate, the correct N:Ga species ratio and optimal flow conditions.

Figure 1 shows concentration profiles across of the half of 2 inch substrate for GaCl and NH_3 for different orientations of reactor chamber along gravity field.
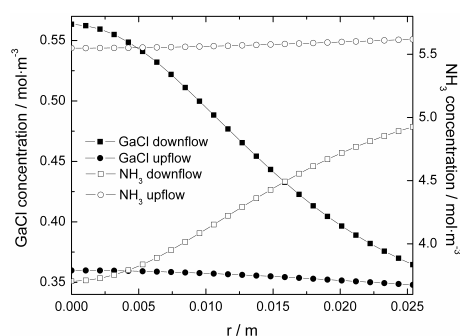
Figure 1. Concentration profiles across the half of the substrate for GaCl and NH_3 for down and upflow case.

Upflow case provides much better species concentration uniformity across the substrate with the differences smaller than 2.5%. Simulation results showed that geometry of the reaction chamber have little effect on the uniformity of reactants concentrations and the substrate. An increase in GaCl inlet flow concentration results in an increase in concentration of both reacting species at the substrate. An increase in the total inlet flow results in the decrease in uniformity and the deposition rate. Shorter reactor chamber length reduces length of laminar mixing zone inside the reactor, resulting in worse uniformity profile for both species and a lower V/III ratio of reactants on the substrate surface. The optimal operating conditions for maximum growth rate and maximum utilisation of reactants corresponds to 1 bar total pressure. Simulation results show that it is possible to achieve good uniformity and a desired V/III ratio of reactants near the stationary substrate for the upflow HVPE reactor with high growth rate which is similar to experimental growth rate achieved by AIXTRON for HVPE upflow system [5].

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High-fidelity CFD modeling of particle-to-fluid heat transfer in packed bed reactors

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1. Summary

A novel high-fidelity CFD model for packed bed reactors was validated in terms of Nu regarding particle-to-fluid heat transfer. The predicted Nu for 220 particles well agreed with a correlation, experiments and model predictions in the literature in the Re range of less than 700. Meshing strategy for increasing particle/Re was rationally given by means of boundary layer theory.

Keywords: high-fidelity CFD model, packed bed reactors, heat transfer, DEM

2. Extended Abstract

A better understanding of packed beds can be gained by developing high-fidelity models that take into consideration the flow of heat, mass and momentum through and around the particles that constitute the packed bed. The recent hi-fi models treated tens of spheres in contact packed either regularly or randomly in a tube (Guardo et al., 2004; 2006). This is because the previous studies eliminated contact points by making the particles larger and then overlapped. The approach limited the packing structure and the number of particles. In the present approach, packed beds are modelled by allowing spherical particles to fall randomly under gravity into a cylinder by a commercial code EDEM (DEM Solutions Ltd). Cylindrical shaped solid geometries are used to bridge particles in (nearly) contact assuming the regions are stagnant. The bridges reduce the requirement for very small or skewed elements by eliminating narrow gaps between particles thus enable treating hundreds of particles in the model.

220 of spherical particles are randomly packed in a cylindrical tube whose diameter and length are 4 and 50 times larger than the particle diameter. The inlet velocity of air with 300 K is varied in the particle Re ($=\rho U d_\mathrm{p}/\mu$) range of 0.1 to 1000. The temperatures of tube and particles are specified as 300 K and 400 K ($=T_\mathrm{s}$) respectively. The Nu ($=hd_\mathrm{p}/k$) is evaluated from Eq. (1) based on heat flux q through

the particle surface and bulk-averaged temperature T_b in the bed region shown in Fig.1.

$$q = h(T_s - T_b) \tag{1}$$

Examined each coarse, medium and fine mesh covers a particle surface with about 300, 1000 and 1500 of triangular surface cells respectively. All the CFD processes are performed by a commercial code FLUENT6 (Fluent Inc.).

Fig.2 shows the predicted Nu in comparison with the literature (Wakao et al., 1979). In the Re range less than 10, the Nu converges to about 10 regardless of mesh density. It should be mentioned that the model predictions at small Re also fell into the range of 3.9 to 18 in the literature. The Nu starts deviating higher from the correlation at Re of 100 and it approaches to 10 with a decrease of Re. The predicted trend is apparently similar with the experimental results. In the higher Re range, the applicable Re within 15 % deviation from the correlation varies from 200 to 700 depending on the mesh density. A thickness of momentum boundary layer around the spheres is hypothetically determined from Nu and Pr applying boundary layer theory. The thickness agrees with the cell height on the particle surface at a particular Re where the predicted Nu starts deviating lower from the correlation for each mesh density. The present hypothetical approach could rationally give an appropriate mesh density at any Re rather than searching mesh-independent solution step by step as usual in the literature. The method is useful both to increase Re with a necessary fine mesh and to increase the number of particles with a minimum mesh density.
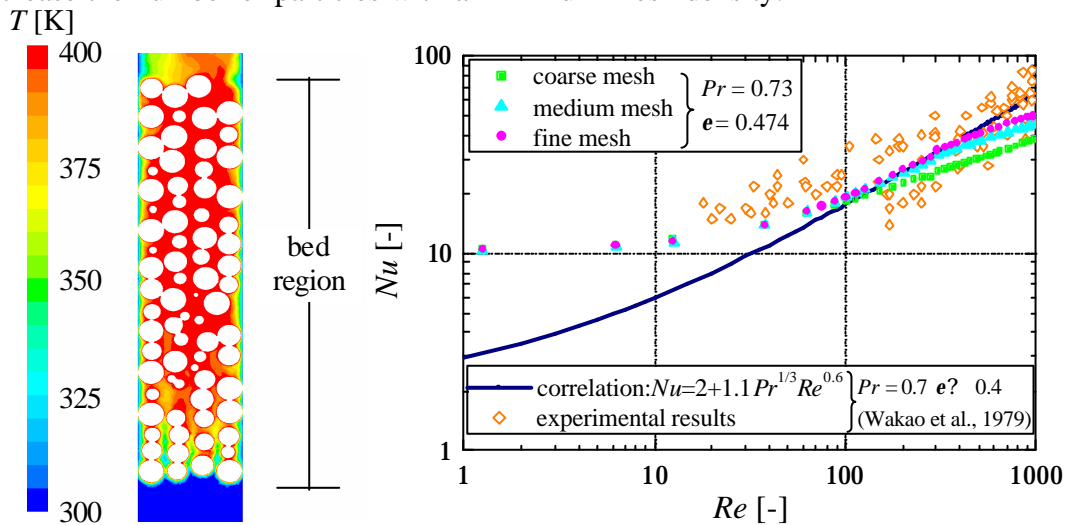
Fig.1 Temperature distribution in the packed bed region ($Re = 200$)

Fig.2 Comparison of predicted Nu with a correlation and experimental results

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Developments in modelling droplet formation during cross-flow membrane emulsification

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1. Summary

We illustrate a macroscopic force balance model and CFD simulations to describe the growth and detachment of droplets on a membrane pore in emulsification processes. The analysis of the simplifying assumptions on which force balance are based is carried out with the aim to increase the model predictive capabilities.

Keywords: membrane emulsification, droplet formation mechanisms, modelling

2. Extended Abstract

Emulsions play an important role in the formulation of foods, cosmetics, pharmaceuticals, lubricants, dyes and take part in many industrial processes such as polymeric capsule production. Accurate predictions of the droplet size as a function of the experimental conditions and apparatuses are crucial to optimise emulsions production. Compared to traditional methods, Direct Cross-flow Membrane Emulsification (DCME) shows considerable advantages in terms of better control of droplet diameters and size distribution as well as lower energy density requirement.
A macroscopic approach (FBE) based on overall balance of forces acting on the droplet is shown to allow expressing the final droplet diameter as function of the DCME unit geometry and process conditions with satisfactory prediction capabilities [1,2]. The model equations, considering the droplet stuck on the pore as a result of contact angles (advancing and receding contact angles) and without neck, are integrated in a number of cases. Also, microscopic modelling of droplet formation has been attempted through the solution of the two-phase flow field by means of a CFD commercial code. The Navier-Stokes equations are coupled with the VOF method and the system integrated to trace the evolution of the moving interface as the droplet grows on the membrane pore. The three-dimensional CFD simulations have been carried out in order to assess the conditions by means of which droplet detaches with negligible neck formation. It is possible, in fact, to suppose that the droplet, during its growth, reaches a volume such that the global force balance is broken (*critical*

volume); larger droplets are unable to stick on the pore and detachment begins with a neck. If the neck size is negligible then the critical volume can be considered as a good estimate of the produced droplet diameter.

Figure 1 shows the relationship between actual [3] and predicted droplet sizes *vs.* cross-flow velocities. Under high cross-flow velocity conditions, good agreement of the FBE values with experimental data is observed. Utilizing data from the same work [3] and using the FBE model the correlation between pore and droplet sizes is reported in Figure 2.

In order to gain more insight into the process, two important theoretical issues can be analysed: the definition of the process conditions leading to the formation of negligible necks or tails and the development of improvements of the macroscopic FBE approach aiming at enhancing the model predictions by relaxing simplifying assumptions. This type of study can be carried out in the framework of CFD simulations of the two-phase flow field. To this purpose a computational model of a droplet forming on a membrane pore has been developed. Simulation results of a test case with data taken from Abrahamse et al. [4] are shown in Figure 3. Comprehensive campaigns of simulations are expected to produce interesting results valuable for validating and/or improving the FBE macroscopic approach.
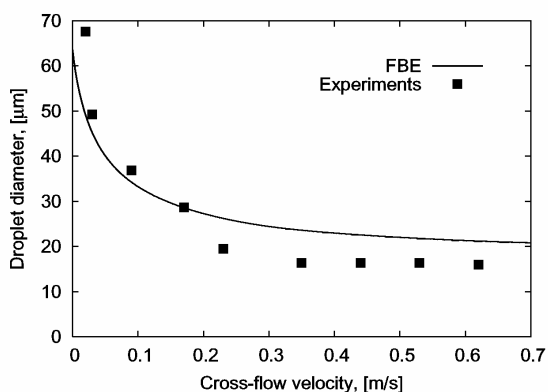
Figure 1. Experimental data [3] and model predictions of droplet size *vs.* cross-flow velocity.
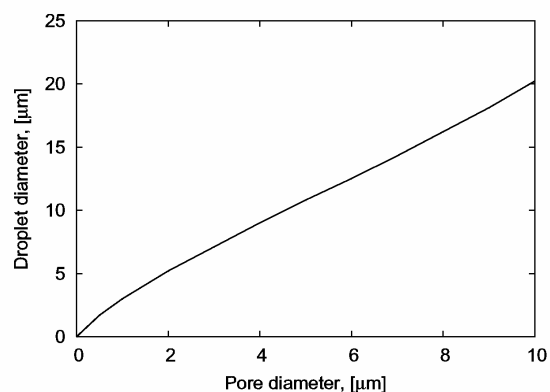
Figure 2. Model predictions of the droplet *vs.* pore diameter.

Figure 3. Droplet formation in the symmetry plane as calculated using 3D CFD simulations (VOF method).

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Multi-scale modeling of the anode and cathode compartments and the IIR unit within a MCFC

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1. Summary

The coupled heat and mass transfer as well as the chemical reactions within the anode compartment, the cathode compartment and the Indirect Internal Reformer (IIR) of a Molten Carbonate Fuel Cell (MCFC) are modelled. Using a multi-scale approach, both models of the detailed structure and simplified models of the entire units are analysed. The aim is to identify the dominating processes within the fuel cell and to understand and predict the (spatial) temperature distribution.

Keywords: MCFC, reaction engineering, multi-scale simulation, CFD

2. Extended Abstract

Fuel cells allow the efficient conversion of chemically bound primary energy into electrical energy. A stationary fuel cell power plant based on a MCFC is developed by the CFC Solution GmbH, in Germany.

The life time and efficiency of an MCFC mainly depends on the spatial temperature profile within the fuel cell stack. The temperature itself is determined by the interaction of the endothermal methane reforming process and the heat releasing electrochemical reactions. The electrochemical reactions take place at the fuel cells' electrodes whereas the reforming reaction takes place inside the anode channels and in special units within the fuel cell stack – the Indirect Internal Reformer (IIR) units. An improvement of the efficiency and the life time can be achieved by a better adjustment of these heat sources and sinks. Detailed multi-scale modelling of the specific parts of the MCFC – the anode (Fig. 1) and cathode compartment as well as the IIR unit – can help in this task.

In a first step, small sections of each (anode, cathode and IIR unit) are simulated using the commercial CFD software CFX (version 11.0). In each of these detailed

models, the coupled heat and mass transport is considered. Additionally, the methane reforming and the water gas shift reaction are considered within the IIR unit and the anode compartment. The electrochemical reactions at the anode and at the cathode electrodes are implemented as simple wall reactions.
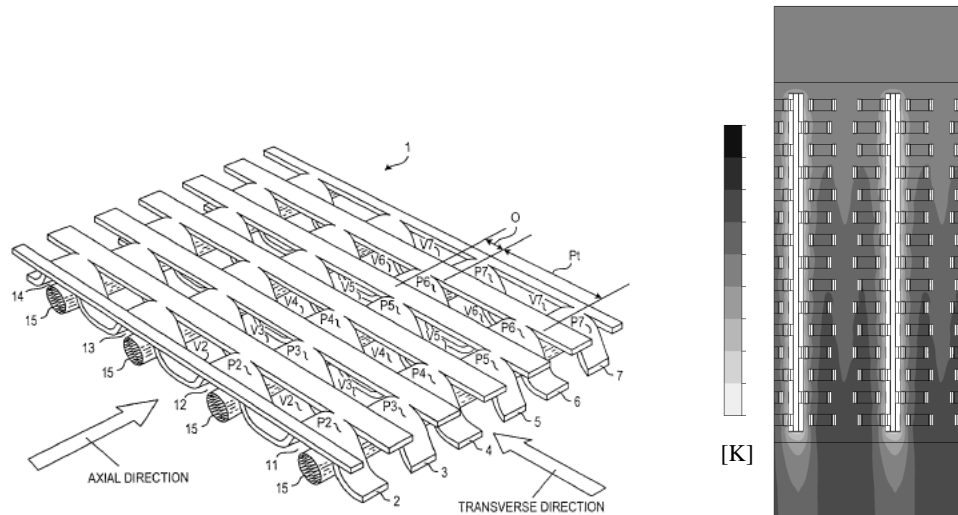
Figure 1: Detailed model for the anode compartment of the MCFC. Left: structure of the detailed anode model with the corrugated sheet and the catalyst (US Patent No. 6492045 B1). Right: contour plot of the temperature within the detailed anode model. The endothermal reforming reactions take place at the catalyst surface whereas the electrochemical reaction takes place at the boundary layer between the gas domain and the anode electrode.

In a second step, models of the entire compartments are created. For these simulations, the geometry is simplified and quasi-homogenous models are used. An anisotropic permeability as well as a locally distributed catalyst activity incorporate the results of the detailed models.

Major assumptions as well as the structure of the models are discussed and simulation results are presented. Subsequently, possible improvements of the models are proposed and first conclusions for an optimal design and further modelling approaches are drawn.

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Session T3-4b: CFD & Chemical Engineering- II

Abstract Number	Paper Title & Authors	Included
238	Numerical and experimental investigation of flow patterns in scraped surface heat exchangers M Yataghene, F Fayolle, J Legrand	Yes
815	Transport phenomena inside liquid chromatographic columns and CFD modelling based on X-ray CT measurements F Lottes, D-U Astrath, W Arlt, E Stenby	Yes
858	A study of hydrodynamics in cylindrical bubble column by CFD M R Kamali, A Laari, I Turunen	Yes
864	Simulation of drop formation in a single hole in solvent extraction using VOF method A Soleymani, A Laari, I Turunen	Yes
1132	CFD Modeling of Solid-Liquid Suspension Flow in a Horizontal Pipe G Yang, Y Enqvist, H Qu, M Louhi-Kultanen, J Kallas, J Wang	Yes
1863	Simulation of laminar reactive mixing in micro-flows A Vikhansky	Yes
3483	Steady-state riser simulations using filtered gas-solid flow models J De Wilde, A Habibi	Yes

Numerical and experimental investigation of flow patterns in scraped surface heat exchangers

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1. Summary

A numerical investigation of a scraped surface heat exchanger was undertaken using the commercial CFD code FLUENT in order to characterize the flow patterns for Newtonian and Non-Newtonian fluids where experimental measurements are difficult to obtain. Simulation results were validated with experimental shear rates measured using electrochemical method (Mabit et al., 2003). Two different flow configurations were treated separately: first, the inlet bowl not reached by the scraping blades, and second the exchanger itself, with two scraping blades. In the inlet bowl, velocity profiles calculated show a dead zone where clogging can occur. In the exchange part itself, the zone localized between the tip of the blades and the stator has to be studied more carefully. Laminar isothermal steady-state flow was studied in a 2D cross section of the exchanger. Comparison between predictions and experimental measurements gave good agreement.

2. Extended Abstract

Introduction:

Scraped surface heat exchangers (SSHE) are often used in the food industry to process highly viscous fluids. However, they are known for their high shearing properties, which can influence the product texture at the outlet. Experimental investigations on SSHEs have been done extensively (Dumont et al, 2000a, b, Mabit et al., 2003, Fayolle et al. 2005). However, because of the complexity on their geometry, it is not possible to go further with experiments. Thus, a numerical investigation of SSHE was undertaken using the commercial CFD code FLUENT in order to characterize the flow patterns for Newtonian and Non-Newtonian fluids. The aim of this study is to understand the flow pattern in SSHEs, which is responsible for thermal treatment heterogeneities, and help industrials in choosing the more appropriate operating conditions for their product fabrication.

Simulations were carried out in standard geometries of SSHE. Two different flow configurations were treated separately: first, the inlet bowl which is not reached by the scraping blades, and second the exchanger itself, with two scraping blades.

3D simulation of the inlet bowl:

Simulation results were validated with experimental shear rates measured using electrochemical method and conducted on the exchange surface as well as in the inlet bowl (Mabit et al., 2003), for rotating velocities from 0.5 to 4 rps (Q = 35 l/h). Figure 1 shows shear rates measured for Newtonian HV45 on the bowl surface and on the rotor and compared with CFD simulations, both in very good agreement. Velocity fields in the bowl (fig. 2) shows that the flow is mainly due to the shaft rotation, even for high flowrate (150 l/h).At the top of the bowl and at the junction between the bowl and the inlet pipe, the flow rate is very low, creating a dead zone, where there is a high probability for the product to stay longer than in the rest of the bowl. For shear thinning fluids, as temperature and shear rates are low in the bowl, viscosity will stay high, and clogging may occur in this part.
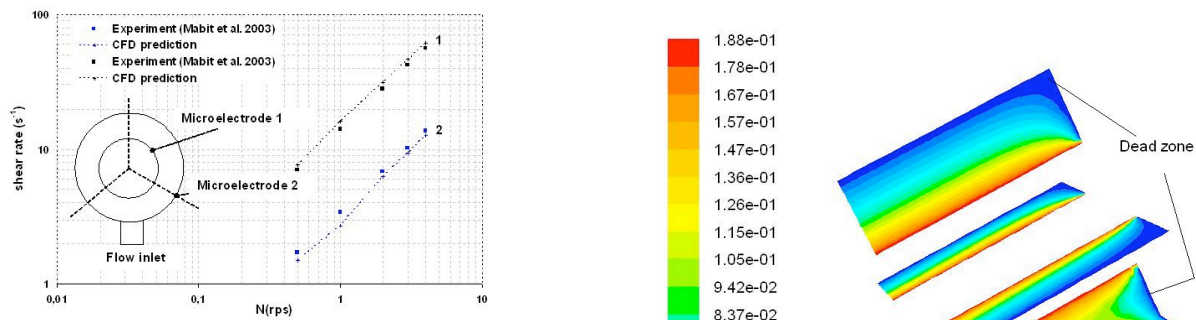
Figure 1: shear rates in the inlet bowl for HV45
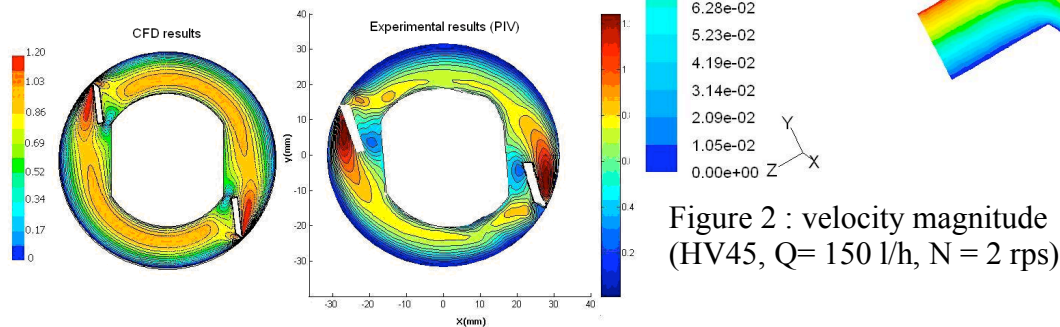
Figure 2 : velocity magnitude (HV45, Q= 150 l/h, N = 2 rps)

Figure 3: velocity profiles for glycerol (m/s)

2D Simulation of the scraped part:

Simulations where done for different Newtonian (HV45, Glycerol) and none Newtonian fluids (CMC). Figure 3 shows the results obtained for glycerol (no axial flow, rotating velocity: N = 5 rps, viscosity: η=1.2Pa.s , density: ρ=1240 kg/m^3), also in good agreement. The main interest of the simulation is that it can give more precise information of what occurs near the tip of the blade. Because of the thin gap identified between the exchange surface and the tip of the blade (around 100 μm), shear rates increase drastically in this zone, which induce the viscosity decrease identified before.

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Transport phenomena inside liquid chromatographic columns and CFD modelling based on X-ray CT measurements

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1. Summary

It is well known that the efficiency of liquid chromatographic (LC) columns strongly depends on the homogeneity of the packed bed inside. As the separation takes place in closed columns, the measurement of local system parameters related to the column efficiency cannot be achieved without deterioration of the flow field. X-ray CT provides an opportunity to measure local packing properties in a non invasive way. The results show a clear existence of a homogeneous core region and an inhomogeneous wall region with different packing properties. In this wall region the interstitial porosity decreases compared to the core and additionally the fluid velocity drops due to a smaller permeability. These effects lead to a considerably decreased efficiency in these parts of the column. The influence of applying different pressures during the packing procedure and using differently shaped stationary phases on the overall and local column efficiency were intensively studied.

Keywords: Chromatography, X-Ray Computed Tomography, CFD

2. Extended Abstract

Chromatographic glass columns of ID 26 mm and packed with different porous stationary phases were investigated with a medical CT device. Based on the attenuation of the X-rays, which are passing through the column, a two dimensional image of the column cross section was reconstructed. The degree of attenuation, which is material-dependent, is expressed by means of the so-called CT-number. By using potassium iodide as a contrast medium the measurement of intra-column breakthrough curves was possible. Iodide was used in these frontal analysis experiments due to its high atomic mass and thus a high attenuation for X-rays, leading to a qualitatively good contrast within the images. The columns were scanned at four axial positions, which were evenly distributed along the column length. To get

radial resolved parameters an additional subdivision of the images into ten concentric annuli was necessary. From these images the information about the local column properties, like porosity or flow velocity can be extracted. Additionally the visualization of locally resolved column efficiency was possible through calculation of local axial Dispersion coefficients.

Subsequently the results of the CT experiments, e.g. permeability and Dispersion coefficients were implemented into a more dimensional CFD model. The CFD results show better agreement with experimental data than commonly used one dimensional models, e.g. the Equilibrium-Dispersive-Model of Chromatography.

These results show that it is worth to take local resolved parameters into account. This work gives clear evidence that connecting X-ray CT and CFD is a good approach in order to get a more precise performance prediction of LC-columns. Work in progress covers the modelling of the specific zones, like the near-wall region using different numerical methods and finding the reasons for the formation of an inhomogenous bed plus appropriate methods to avoid the latter.

A study of hydrodynamics in cylindrical bubble column by CFD

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1. Summary

Flow fields and bubble size distribution are two critical issues in the determination of reaction rate and mass transfer in bubble columns. In this work the hydrodynamics of a laboratory scale cylindrical bubble column with a diameter of 0.19 m and height of 1.7 m was studied. Air is evenly fed to the column from the bottom and with different flow rates. The calculated flow fields were verified by the experimental results gained from PIV measurements.

Keywords: bubble column, hydrodynamics, CFD, Interfacial momentum exchange, MUSIG.

2. Extended Abstract

In order to predict the flow behaviour in the column the Eulerian-Eulerian approach was used as multiphase model. Liquid turbulence was considered by the k-epsilon model. Bubble sources in Eulerian-Eulerian continuity equations come from solution of discretized population balances using MUSIG model. According to experimental data, 5 different bubble size groups with the size between 3-8 mm were considered. The Prince&Blanch and Luo&Svendsen models were selected as the coalescence and breakage models, respectively.

The interfacial momentum exchange terms in equations were examined by different drag and non-drag force models. In the non-drag forces the effect of lift, turbulent dispersion, virtual mass and wall lubrication forces on time averaged liquid, slip and bubble velocity and gas hold up were studied. The validated simulation results by PIV measurements show that the drag, lift and turbulent dispersion forces are the most important momentum transfer terms in the model. However, effect of the wall lubrication force is also considerable. Slightly more accurate results can be obtained by including the virtual mass force in the calculation. However, the inclusion of virtual mass force causes some convergence problems increasing the computation time remarkably. The study shows that the appropriate drag model has crucial effect on the hydrodynamics of the domain. Moreover, the effect of the bubble size on the lift force should be considered. This behaviour can affect the radial gas hold up distribution and also water velocity vectors in the column. Different interfacial exchange closures were investigated. As shown in Fig. 1, closures A and B with the following formulas (Table1), had better prediction of flow domain compared to PIV results. Closure C is based on experimental models proposed by Ishi Zuber (1979).

Table 1: two sample interfacial force closures which were used

Closure A	Closure B (based on Tomiyama 2004)
$C_D = 0.2 + \dfrac{(d_{32} - 0.0015)^2}{0.42(d_{32} - 0.0015)^2 + 2.7 \times 10^{-6}}$ Jacobsen et al. , 1997 $C_L = \begin{cases} 0.06 & Eo < 4 \quad \textit{Krepper et al.,2005} \\ -0.1 & Eo \geq 4 \quad \textit{Sokolichin et al.,2004} \end{cases}$	$C_D = \dfrac{8 Eo(1 - E^2)}{3 g(E)^2 E^{2/3} Eo + 16(1 - E^2) E^{4/3}}$ $E = \dfrac{1}{1 + 0.163 Eo^{0.757}}, \quad Eo = \dfrac{g(\rho_l - \rho_g) d_b^2}{\sigma}, Eo_h = \dfrac{Eo}{E^{2/3}}$ $g(E) = \dfrac{\sin^{-1}\sqrt{1 - E^2} - E\sqrt{1 - E^2}}{1 - E^2}$ $C_L = \begin{cases} \min[0.288\tanh(0.121\text{Re}), f(Eo_h)] & Eo_h \prec 4 \\ f(Eo_h) & 4 \leq Eo_h \leq 10 \\ -0.29 & Eo_h \succ 10 \end{cases}$ $f(Eo_h) = 0.0010\, Eo_h^3 - 0.0159 Eo_h^2 - 0.0204 Eo_h + 0.474$

$C_{VM} = 0.3$

Wall Lubrication Force: Antal et al. 1991, Krepper et al. 2005   ($C_{w1} = -0.0064$, $C_{w2} = 0.016$)

Turbulence Dispersion Force: Lopez de Bertodano, 1991   ($C_{TD} = 0.1$)

Turbulence Transfer model: Sato Enhanced model
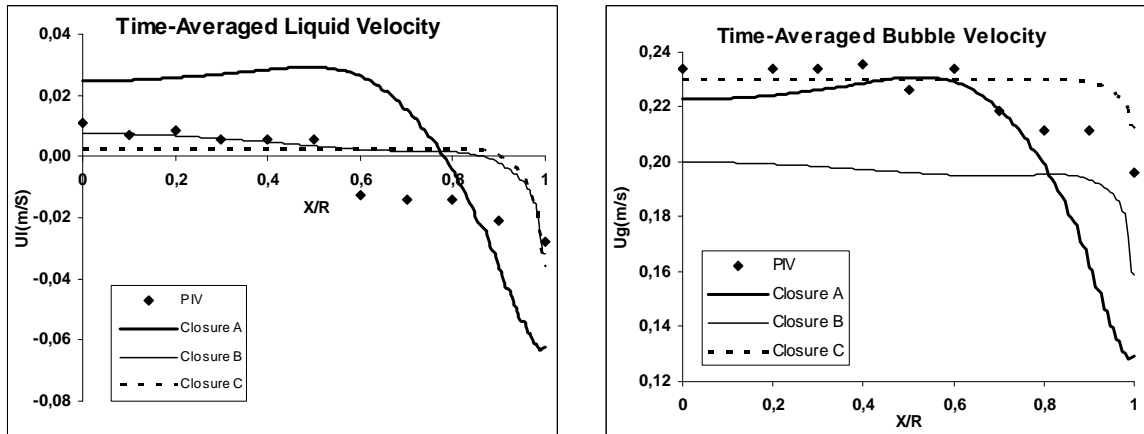
Figure1: Comparison of experimental Time-Averaged Liquid and Gas velocities obtained by PIV with simulation results gained by three different closures.(Z/H =0.7, Inlet Superficial Gas Velocity=0.36 cm/sec)

Moreover, the valid models were used to find the effect of the inlet superficial gas velocity for the same column. The simulated time averaged liquid, slip and bubble velocity vectors accompanied by turbulent kinetic energy distribution in the column were verified by the PIV measurements in the same experimental conditions. Gas hold up, bubble size and interfacial area are some important variables which were predicted by the validated models.

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Simulation of drop formation in a single hole in solvent extraction using VOF method

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1. Summary

Drop formation in solvent extraction was studied numerically by CFD simulations using the VOF method available in commercial CFD codes (ANSYS CFX 10, Fluent 6.0). The effect of the material properties of the solid, such as the wetting properties and surface roughness, were tested together with different hole sizes and structures to optimize the flow conditions in the hole. It was found that the VOF method is well capable of solving this kind of flow situations including interfacial phenomenon such as drop breakage and coalescence. A reasonable agreement with experimentally observed drop formation was found to exist.

Keywords: drop formation, single hole, wetting, contact angle, VOF

2. Extended Abstract

Formation of solvent drops in sieve plates is a very important phenomenon in solvent extraction. Small droplets are usually desired to increase the interfacial area available for mass transfer and to maximize the process efficiency. Formation of very small satellite drops is, however, a common problem, which is frequently met in industrial extraction equipment. Very small droplets are difficult to separate from the continuous phase and their presence can adversely affect the extraction efficiency. Formation of satellite drops can be affected by changes in flow conditions and in the mechanical structure of the sieve plates. Drop formation in sieve plates is a complex phenomenon, which depends on the flow velocity in the holes, physical properties of the liquid phases, like surface tension and density difference between the phases, material properties of the sieve plate, like the wetting properties and surface roughness, hole size and structure, distance between the holes and alignment of holes on the sieve plate.

The motivation of this study is the need to find optimal structure for the holes, optimal construction material for the sieve plates and optimal flow conditions in the

holes to minimize the production of small satellite drops. At the same time, high mass transfer efficiency is required.

Drop formation in single holes is studied by using Computational Fluid Dynamics simulations. Simulations were carried out by using ANSYS CFX 10. The VOF method was implemented for the calculation of the location of the interface between the phases.

The simulated results were verified by comparison to experimental observations obtained by high-speed video recordings. Experiments and simulations were carried out for different hole sizes, ranging from 2 to 4 mm, and for different flow velocities ranging from 0.1 to 0.4 m/s. The material of the plate was stainless steel. The surface of the steel was polished and cleaned with acetone to remove any contaminants. The shape of the hole was also varied including a shape of conical opening and a shape of conical contraction above the base level (volcano shape). The purpose of the different shapes was to produce different contact angles around the hole. A reasonable agreement between the measured and calculated drop formation was observed in each case.
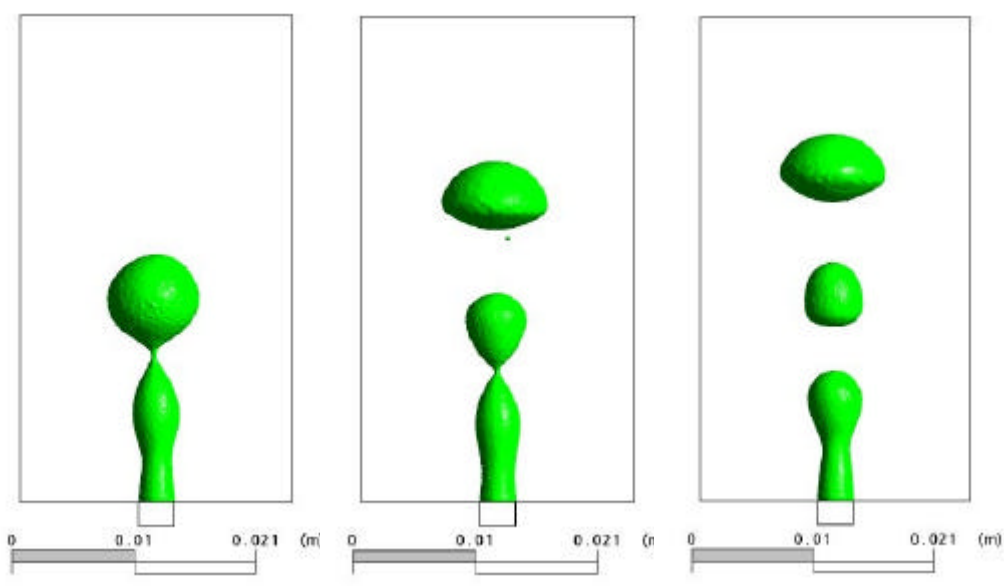
Figure 1. Simulated results for solvent drop formation in water in a 3 mm hole at times 0.24 s, 0.295 s and 0.31 s with solvent feed velocity 0.21 m/s. Contact angle between solvent and solid is 67°.

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CFD Modeling of Solid-Liquid Suspension Flow in a Horizontal Pipe

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1. Summary

The present work focuses on the three-dimensional modeling of the solid-liquid suspension flow based on the Eulerian-Eulerian multiphase flow model. The k-ε turbulence model and particle-induced turbulence model were used to simulate the solid-liquid suspension flow. The momentum transfer between the solid and liquid phases including drag force, shear-induced lift force and virtual mass force, together with buoyancy force, were considered in the model. The simulation geometry focuses on a horizontal pipe, where an imaging probe was installed for in-line analyzing the size distribution of solid particles. The simulation results clearly show that the representative particle size distribution can be captured with the critical flow rate when the in-line probe is installed at the low vertical position in the pipe.

Keywords: solid-liquid suspension, horizontal pipe, in-line measurement, CFD modeling

2. Extended Abstract

In the industry, a horizontal pipe was often used to transport the solid-liquid suspension flow. In some cases, in-line measurement of the particle size distribution in the pipe is needed, such as for establishing the feed back control scheme. Therefore, it is important to investigate the optimum condition for in-line probe to obtain the representative particle size distribution. In this work, computational flow dynamics (cfx5.7) was used to simulate the solid-liquid multiphase flow. In the simulation, the particle size distribution of solids was described with the seven sizes of classes and each size class was regarded as a separate phase. The suspension density of solution used in the simulation was 0.1% and the particles were assumed to have the spherical shape and the solid density was 1450 kg/m^3. The fluid was water at room temperature. The simulation geometry used was a horizontal pipe with the length of 1.5 m and the diameter of 0.1 m. The in-line probe was installed with the different vertical positions in the pipe, as shown in Fig. 1. The transient simulation was used for modeling the

process to reach the final steady state. First, particle size distribution was measured experimentally with in-line probe in the well-mixed tank, which was marked with measured PSD in Fig. 2. The simulated particle size distributions at the different probe locations with the different flow rates are also presented in Fig. 2. It is clearly shown that the location of in-line probe and flow rate of suspension should be carefully selected in order to capture the representative particle size distribution. Besides the studied case, the developed CFD model can be used more widely to simulate solid-liquid flow in a horizontal tube.
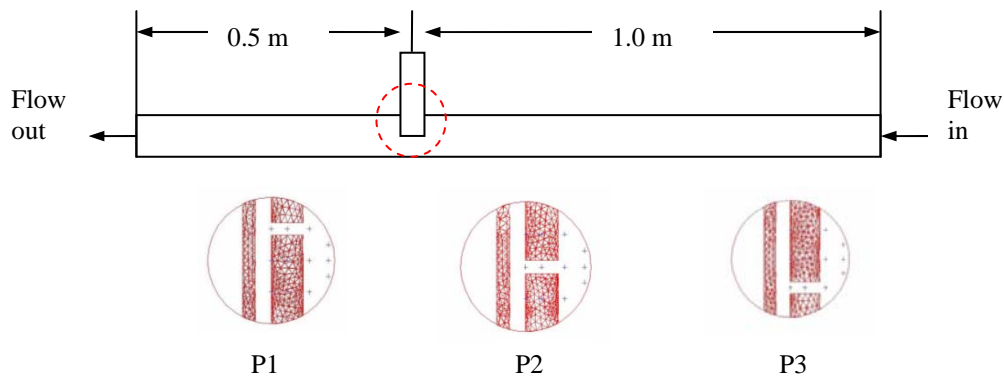
Fig. 1 The simulation geometry and the different locations of the in-line probe
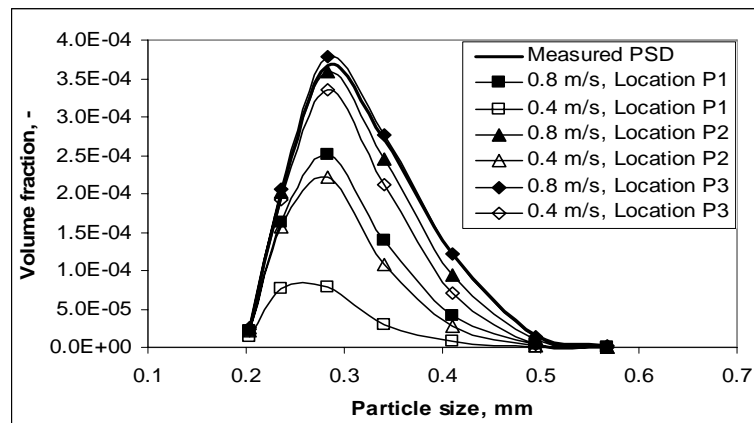
Fig.2 The volume fraction of solid particles obtained at the different conditions

Simulation of laminar reactive mixing in micro-flows

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1. Summary

In the present investigation we discuss reliable and computationally non-expensive numerical methods for simulation of laminar reactive mixing in micro-flows. The numerical solution of advection-diffusion-reaction equations with high Péclet numbers is almost as time-consuming as a direct numerical simulation of turbulent flows with high Reynolds numbers. We discuss two main approaches which provide a solution to the above-mentioned difficulty, namely, coarse-grained modelling and Monte Carlo stochastic simulations, which can be combined with conditional moment closure (CMC) method.

Keywords: laminar mixing, numerical methods, Monte Carlo

2. Numerical methods for laminar reactive mixing

Many micro-reactors are operated at low Reynolds numbers, but at high Péclet numbers, and this combination of parameters poses particular difficulties for efficient chemical reaction from a segregated initial state, because the low Reynolds numbers make turbulence impossible, and the high Péclet numbers limit the efficiency of molecular diffusion. Fortunately, it is now well established that effective mixing can be achieved in the necessarily laminar flows that are realized at low Reynolds numbers, provided the Lagrangian particle paths are made chaotic. Such chaotic flows rapidly generate, from an initially segregated distribution of reactants, an intertwined pattern of highly complicated morphology. In three dimensions, sheet-like ''lamellar'' structures are formed in some regions; reduced models for reaction in the .flow are then commonly based on ''straightening out'' the lamellae into a one-dimensional array, leading to so-called lamellar models. Although admittedly limited in scope, a recent evaluation of some simple lamellar models has revealed shortcomings in the quantitative predictive power of such models [Vikhansky and Cox, 2006]. It is, therefore, appropriate to seek more accurate reduced models.

Note that the advection-diffusion is a linear equation (while the Navier-Stokes equations are nonlinear) and we can use the similarity between the advection-

diffusion equation and Fokker-Plank equation of a diffusive process. Then linear functionals of the solution of the advection-diffusion equation can be estimated by a Monte Carlo method and the required computational resources do not depend on Péclet number [MacInnes et al., 2007].

In the coarse-grained simulations [Vikhansky, 2006] the large scales of the concentration field are resolved by a finite-volume method. A closure assumption is used to account for the sub-grid scales. The proposed model captures the two main features of the chaotic mixing, namely, lamellar structure of the concentration field and exponential decay of the variations of the scalar.

We implement CMC for simulation of chemical reactions in laminar chaotic flows [Vikhansky and Cox, 2007]. The CMC approach predicts the expected concentration of reactive species, conditional upon the concentration of a corresponding non-reactive scalar. We first use a Monte Carlo method to calculate the evolution of the moments of a conserved scalar; we then reconstruct the corresponding probability density function and dissipation rate. Finally, the concentrations of the reactive scalars are determined. The results are compared (and show excellent agreement) with full numerical simulations of the reaction processes in a chaotic laminar flow.

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STEADY-STATE RISER SIMULATIONS USING FILTERED GAS-SOLID FLOW MODELS

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1. Summary

To account for sub-grid-scale phenomena in coarse grid simulations, correlation terms appearing in the filtered gas-solid flow equations have to be modeled. Filtered models for the gas-solid momentum transfer are focused on and possible approaches are presented and evaluated. The evaluation supports the combination of an apparent distribution of the filtered gas phase pressure gradient over the phases and an apparent drag force to describe filtered gas-solid momentum transfer. As the filter frequency decreases, the contribution of the apparent distribution of the filtered gas phase pressure gradient over the phases to the filtered description of gas-solid momentum transfer gradually grows in importance up to a mass fraction based distribution, whereas the contribution of the apparent drag gradually vanishes, the mesoscopic description of gas-solid momentum transfer gradually being replaced by a more macroscopic description.
Three-dimensional steady-state simulations of developing flow in the bottom section of a riser are presented that illustrate the importance of using filtered gas-solid flow models for coarse grid simulations.

Keywords: gas-solid flow, filtered models, apparent added mass, apparent drag force, Computational Fluid Dynamics

2. Extended Abstract

Real fluidized beds contain structures of different length and time scales or different spatial and temporal frequencies ω. The smallest structures that can be calculated using a continuum approach are meso-scale structures, like clusters (Agrawal et al., 2001). Their calculation requires, however, the use of very fine and computationally too expensive grids. Due to the finite spatial and temporal grid dimensions used for solving the continuum gas-solid flow models, a filter frequency ω_f is introduced. The filter frequency ω_f is defined as the frequency up to which phenomena can be accurately resolved and can be spatially or temporally determined. Unresolved sub-grid-scale phenomena ($\omega > \omega_f$) should be accounted for by using so-called filtered models and including sub-grid models (Agrawal et al., 2001; Zhang and

VanderHeyden, 2002). In particular, meso-scale structures affect the crucial gas-solids momentum transfer and its filtered description.

Descriptions of the filtered gas-solid momentum transfer based on an effective or apparent drag coefficient closure model for the filtered drag force (Agrawal et al., 2001) and a generalized or apparent added mass closure model for the correlation between the solid volume fraction and the gas phase pressure gradient (Zhang and VanderHeyden, 2002) are evaluated via a linear wave propagation speed test. Whereas an unacceptable behavior for the effective drag coefficient approach is observed, an acceptable behavior for the generalized added mass approach is revealed. The generalized added mass can be reformulated in terms of an apparent distribution of the filtered gas phase pressure gradient over the phases and an apparent drag force. The reformulation of the generalized added mass and the evaluation of the linear wave propagation speed test then suggest a generalized added mass type closure approach to completely describe filtered gas-solid momentum transfer, that is including both the filtered drag force and the correlation between the solid volume fraction and the gas phase pressure gradient. For large values of the generalized added mass coefficient, the distribution of the gas phase pressure gradient over the phases becomes mass fraction based, whereas the apparent drag force vanishes. The linear wave propagation speed test shows that large values of the generalized added mass coefficient are allowed if the filter frequency is sufficiently low, i.e. if the mesh is spatially or temporally sufficiently coarse, as e.g. in the limit of steady-state simulations.

3D Steady-state simulations of the acceleration zone of a riser using a non-filtered model and a filtered generalized added mass based model illustrate the effects and the importance of using filtered models. The main difference between the non-filtered and the filtered model is in the gas-solid slip behavior calculated. With the non-filtered model, the gas phase is immediately decelerated upon contact with the slower moving solids. Hence, the slip is in general small and gas and solids accelerate jointly. With the filtered model, however, the gas phase is hardly decelerated upon contact with the solids, resulting in a much larger contact slip velocity. As the solids accelerate, the slip velocity decreases.

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Session T3-5: Multiscale Modeling

Abstract Number	Paper Title & Authors	Included
584	Development of a multi-scale dynamic model for the prediction of polymer distributed properties in catalytic olefin polymerization slurry loop reactors V Touloupides, V Kanellopoulos, G Dompazis, C Kiparissides	Yes
1145	Lattice Boltzmann 3d flow simulations in a metallic foam, on a computing grid D Beugre, M Crine, G Dethier, A Léonard, D Toye, P Marchot	Yes
1227	Solving complex problems in formulation processing by building a pragmatic multi-scale model P S Chua, P Sharratt, A Kowalski	No
2695	Multi-scale modelling of bio-energy networks: a complex systems approach R Kempener, J Beck, J Petrie	Yes
3229	Rapid scale-up of pharmaceutical processes- Finding the trees in the forest S Lawton	Yes
3633	Cyclization effects in continuum / dynamic Monte Carlo model of drying and curing in sol-gel silica films S E Rankin, X Li	Yes

Development of a Multi-scale Dynamic Model for the Prediction of Polymer Distributed Properties in Catalytic Olefin Polymerization Slurry Loop Reactors

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1. Summary

In the present study, a comprehensive multi-scale mathematical model is developed to predict the dynamic evolution of morphological (i.e., particle size distribution (PSD)) and molecular (i.e., molecular weight distribution (MWD)) distributed polymer properties in catalytic Ziegler-Natta (Z-N) slurry phase olefin polymerization reactors. The multi-scale description of the continuous olefin polymerization reactors utilizes models at three different levels, namely, a kinetic model, a single particle model and a population balance model.

Keywords: polymerization, processes, reactor modelling, slurry, polyolefins

2. Extended Abstract

Because of their simple construction and operation as well as their well defined mixing and dispersing effects with relatively low power requirements continuous slurry polymerization with heterogeneous Ziegler–Natta catalysts is one of the most employed processes for the production of polyolefins (Warnecke, et al., 1985).

In the present study, a comprehensive multi-scale mathematical model is developed to predict the dynamic evolution of morphological (i.e., particle size distribution (PSD)) and molecular (i.e., molecular weight distribution (MWD)) distributed polymer properties in catalytic Ziegler-Natta (Z-N) slurry phase olefin polymerization reactors. The multi-scale description of the continuous olefin polymerization reactors utilizes models at three different levels, namely, a kinetic model, a single particle model and a population balance model.

To calculate the monomer(s) consumption rate(s) and molecular weight developments of polyolefins produced over a heterogeneous Z-N catalyst, a generalized two-site kinetic model is employed. The kinetic mechanism comprises a series of elementary reactions, including site activation, propagation, site deactivation and site transfer reactions.

To simulate the growth of a single polymer particle, the random pore polymeric flow model (RPPFM) of (Kanellopoulos, et al., 2004) was employed. Heat and mass transfer resistances as well as thermodynamic phenomena are what define monomer(s) concentration and temperature in the catalytic sites where the polymerization takes place, determining growth rate, particle overheating and the molecular properties of the particle.

To calculate the dynamic evolution of PSD in a catalytic slurry phase reactor a dynamic population balance model needs to be solved together with the system of differential equations describing the radial monomer(s) concentration and temperature profiles in a single particle (Kanellopoulos, et al., 2004). According to the developments of (Dompazis, et al., 2005) the following dynamic population balance equation, accounting for particle growth and particle agglomeration can be derived:

$$\frac{\partial n_p(D,t)}{\partial t} + \frac{\partial \left[G(D) n_p(D,t) \right]}{\partial D} = B(D,t) - D(D,t) + \frac{1}{W} \left[F_c n_c(D,t) - F_p n_p(D,t) \right] \tag{1}$$

In Figures 1 and 2, the effect of the external mass transfer limitations on the polymerization rate in a growing catalyst/polymer particle and on MWD in a slurry phase reactor is depicted. It is apparent that the transport of gaseous monomer (e.g., ethylene) in the diluent significantly affects the rate of monomer transfer from the bulk liquid phase to the active catalyst sites, especially during the first few seconds of the polymerization.
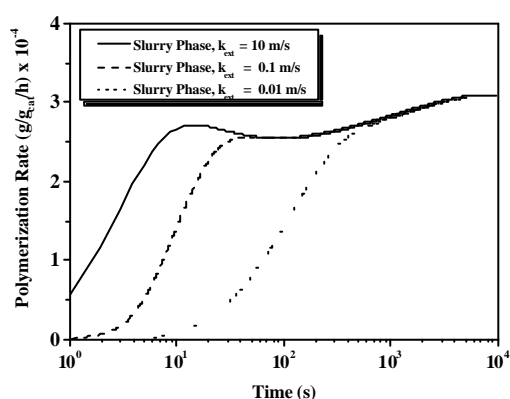
Fig. 1. Effect of the external mass transfer limitations on the particle polymerization rate.
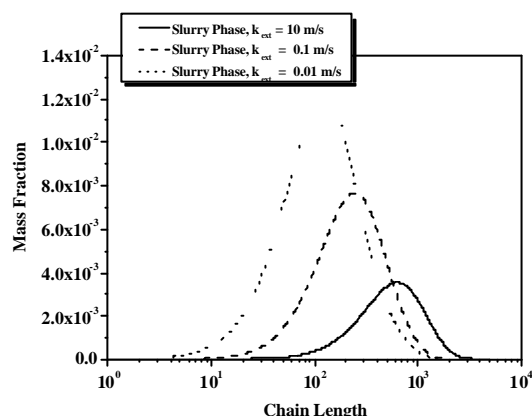
Fig. 2. Effect of the external mass transfer limitations on the MWD, at the particle level ($t_{process}$ = 5 min).

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Lattice Boltzmann 3D flow simulations in a metallic foam, on a computing grid.

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1. Summary

The use of Lattice Boltzmann methods is extremely appealing to describe flows through complex geometries encountered in Chemical Engineering (porous media, packed beds, multi phase flows). Results concerning flow simulations in a metallic foam, the structure of which is obtained by micro tomography, performed on a computing grid are presented showing the interest of this computing solution.

Keywords: lattice Boltzmann, X-ray tomography, grid computing

2. Extended Abstract

Recent progresses in the macro and micro X-ray computed tomography allow access to complex geometries encountered in various fields of chemical engineering. In the unit operations domain, high energy setup (400 kV) may be operated on columns of 0.5 m diameter and several meters height with resolution ranging around 0.5 mm. In the materials domain, X-ray micro tomographic devices are commonly available at 100 kV energy for samples of around 5 cm with resolutions ranging around 5 microns.

More accurate descriptions of phenomena occurring in packed beds, fibrous media, metallic foams, etc leading to better design, efficiency and selectivity of related chemical engineering processes become possible. The use of efficient computational fluid dynamic tools should help to reach these goals. However, the problem of incorporating these intricate geometries is challenging. Indeed, the numerical reconstruction of the 3D images from these tomographic measurements leads to large matrix of voxels which are boundaries for the flows. Lattice Boltzmann methods can easily accommodate directly these matrices, but require large computing powers, only available on very expensive computers with shared memory.

Progress in production of CPU's allows to consider grid computing as a pragmatic solution to this computing power problem, trying to get the most out of the inherently parallel structure of Lattice Boltzmann algorithms.

We use different grids composed of up to 54 common PC and also a small grid of 3 powerful machines (4 CPU's of 2,1Ghz with 16GB RAM each). We consider the deployment of a in house "gridified" 3D lattice Boltzmann ULGLBGrid code to simulate a single phase flow through a metallic foam RCM-NCX-1116, a Ni-Cr manufactured by Recemat International B.V. (The Netherlands).

The geometric structure of the foam used in the simulations is obtained with a Skyscan 1172 microtomograph as 351^3 voxel matrix corresponding to a volume of 19^3 mm^3. A single relaxation time lattice Boltzmann algorithm (SRTLB) is used to simulate a laminar flow through the metallic foam. The lattice chosen is a D3Q19. Periodic boundary conditions are assumed on faces parallel to the flow direction, a pressure gradient is applied between the entrance and exit faces. On the solid, full bounce back conditions are used. The equilibrium distribution corresponds to a slightly compressible fluid.

The LBSRT algorithm is optimised. The data are organized in memory to take advantage of the CPU caching. The translation step works "in place" so there is no need to copy the data in a new structure during the translation step. In a parallel environment, each thread or process receives a piece of the initial lattice, a sub-lattice. The algorithm run by each thread is almost identical to a non-parallel LB. To adapt the method to the grid environment, we distribute the process on several CPU's which may be on different machines. To achieve this, we must know the number of CPU's on each machine of the grid to distribute the sub-lattices on each CPU. Each machine receives, in the simplest case, as many sub-lattices as CPUs. In the current system, this is automatically done without special parameter setting. The time required for 1000 iterations of the algorithm are listed in Table I. Five grids build with different CPU's are considered. G1 is composed of 12 Xeon dual-core, 2.0 Ghz, 4 Mo cache, each with 16 GB of RAM residing in 3 Hewlett Packard machines. G2 is composed of only one machine of G1 (4 Xeon). G3 is composed of 27 P4, 3.06 Ghz, 1 Mo cache, each with 1 GB of RAM, residing in 27 PC, G4 is composed of 27 Celeron, 2.40 Ghz, 128 ko cache, each with 512 MB of RAM, residing in 27 PC and G5 is composed of the 27 Celeron of G4 with the 27 P4 of G3.

GRID	Time 1000 iterations
G1 12 Xeon	69 min
G2 4 Xeon	192 min
G3 27 P4	77 min
G4 27 Celeron	88 min
G5 27 P4 +27 Celeron	78 min

Table 1: Comparison of total computation times

G1 and G2 show a quasi linearity in the performances. In this case the communications between the CPU's are kept to a minimum, this represents the ideal situation. Presently, in the ULGLBGrid software, the slowest CPU determines the progress of the computation processes. So, G5 may be considered as being composed of 54 Celeron. The gain in performances between G4 and G5 is only 12% whereas the number of CPU is doubled. This result is due to the fact that each CPU receives a smaller sub-lattice to process, then the network transfer time supplants the computing time.

Multi-scale modelling of bio-energy networks: a complex adaptive systems approach

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1. Summary

Bio-energy networks are an attractive option for a transition towards a CO_2-neutral energy system, although the introduction and management of large-scale bio-energy infrastructures presents several technical and organisational challenges. Firstly, the development of a bio-energy network is a function of the complex interaction between technology development, market players and their behaviour, stakeholder preferences and governmental interventions. Secondly, these evolutionary forces are dynamic depending on the specific interaction and interrelation between each other. A multi-scale modelling tool is proposed to analyse bio-energy network evolution and in order to develop and explore government instruments and/or business strategies that promote the most sustainable bio-energy network configuration.

Keywords: bio-energy, multi-scale modelling, complex systems, networks, infrastructure, sustainability

2. Extended Abstract

With diminishing fossil fuel resources, biomass derived energy is an attractive option for a transition towards a CO_2-neutral energy system. Such a transition would require new energy infrastructures for the large scale production of electricity and biofuels with biomass as feedstock.

The introduction and management of large-scale bio-energy infrastructures present several challenges due to the intrinsic differences between fossil fuels and biomass as energy sources. Biomass cannot be stored without pre-treatment, it has a low energy density and variability in quality is much higher than for fossil fuels. Furthermore, the availability of biomass is seasonal, and the opportunity for small-scale local production of electricity allows for different system operation. These and other differences pose several new questions and challenges for the introduction and management of bio-energy networks. Is it preferable to convert biomass into biofuels

or into green electricity? Which technologies are preferable? What are the impacts of pre-treatment of biomass? What are the implications of any of these choices on the sustainability of the bio-energy network? Furthermore, the complexity of this problem is amplified by the multitude and diversity of stakeholders displaying conflicting or competing interests in the infrastructure development.

The questions posed can only be answered from a systems perspective, whereby the dynamics, interaction and co-evolution between technology development, the agent's behaviour and the social embeddedness of the industrial network are analysed explicitly and simultaneously. Since technology development, agent decisions and institutionalisation take place on different length and time scales, from operational to evolutional, a multi-scale modelling approach is required to model the full complexity of the system. Specifically, a multi-scale modelling approach is developed that entails the following scales:

- operational performance of agents;
- strategic decision making;
- institutionalisation through social embeddedness;
- technology development through learning.

The multi-scale model is implemented as a hybrid model of agent-based modelling and system dynamics, and applied to a case-study of a biomass energy network in South Africa. In the context of the case-study, the following features and dynamics are considered:

- different conversion technologies, such as combustion, gasification, pyrolysis, enzymatic hydrolysis, electricity distribution via transmission lines, biofueled engines for local electricity production in mini-grids, the distribution of biofuels, centralised versus decentralised production of electricity and/or biofuels;
- agent behaviour, such as goal setting, investment decisions, suppliers/customers choice and the development of policy instruments;
- institutional effects, such as imitation and the generation of social norms and routines;
- technological learning curves.

The results of this study provide an opportunity to analyse the sustainability of any possible bio-energy network configuration over time. Subsequently, these results can be used to develop and evaluate government instruments and/or business strategies that promote the most sustainable configuration.

Rapid scale-up of pharmaceutical processes – Finding the Trees in the Forest

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1. Summary

The scale-up of pharmaceutical syntheses can often lead to wasted effort when projects are fail during their development. An approach to risk-manage the resource expended on process development whilst providing a means of tackling common issues is presented.

Keywords: pharmaceutical synthesis, scale-up, knowledge management,

2. Extended Abstract

The development of chemical processes for the manufacture of pharmaceuticals in early development is fraught with challenge for the practicing chemical engineer, particularly given the attrition rate of projects typical of the industry.

Scale-up is further hindered by the small quantities of material available for investigating such problems that may or that do arise.

AstraZeneca has developed a knowledge base for the scale-up of frequently used batch processing operations (e.g. hydrogenations, mixing, filtration, drying). These are designed in specifically to ensure that knowledge of processing characteristics increases in-line with increasing maturity of a product (and thus an increasing likelihood of success). A knowledge base is known within AstraZeneca as a "**Toolbox**".

Using the toolbox, gains in both efficiency and effectiveness are made by matching the investment in investigator resource to the extent of project risk.

The toolbox incorporates basic education on an operation's principles as applied within the company, combined with common laboratory equipment and experimental methodologies. Finally, there are sets of pre-constructed mathematical models that provide a common language for the communication of information, removing the unnecessary duplication of effort when predicting performance at plant scale. Another

advantage of the use of Toolboxes is that it provides all geographical locations with a common capability, and a *lingua franca* easing communications across international boundaries.

The Toolbox approach will be introduced; along with a case study to illustrate it's use.

Cyclization Effects in Coupled Continuum / Dynamic Monte Carlo Model of Drying and Curing in Sol-gel Silica Films

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1. Summary

We describe a multiscale model in which dynamic Monte Carlo (DMC) simulations are coupled to a continuum model of drying for sol-gel silica films. The DMC approach is needed to simulate nonideal polymerization effects including first-shell substitution effects (FSSE) and, most importantly, cyclization. The simulation tracks the populations of differently connected sites and bond blocks to derive the rates of bimolecular reactions and cyclization reactions, respectively. Unlike statistical methods, DMC simulations track the entire molecular structure distribution to allow the calculation not only of molecular weight but also of topological indices related to molecular size and shape. These topological indices can be used for improved correlations of transport coefficients in polymers with different degrees of branching and cyclization. The entire DMC simulation (containing $\sim 10^6$ monomers) is treated as a particle of sol whose position and composition are tracked using a diffusion/evaporation finite difference calculation. By simulating a swarm of particles starting from different positions in the film and using variable parameters, we observe the effect of drying parameters on the gelation regime, predict different drying/gelation phenomena, and predict the occurrence of gradients of concentration, gelation, and structure in the films. In this contribution, we will focus on the modeling of cyclization and its effects on the evolution of the films.

Keywords: polycondensation, multiscale, modelling, gelation, coating

2. Extended Abstract

Cairncross et al. [1996] published a comprehensive study of silica sol-gel film formation based on a finite element approach and a kinetic-recursive model for gelation. This model is capable of describing the counterplay between the polycondensation process and drying in a film, and the occurrence of qualitatively different phenomena: gelation before drying, drying before gelation, and literal "skinning" in which a thin layer of gel would be expected to form at the free surface of the coating prior to gelation in the sublayers. Skinning is an important

phenomenon in coating, because it is expected to give rise to defects such as wrinkling of a coating surface, and may initiate other defects such as cracks.

Here, we discuss coupling a dynamic Monte Carlo (DMC) model of polycondensation that is better able to describe highly nonideal polycondensation processes such as silica sol-gel coating to a continuum-based, finite difference description of drying in a thin film. The DMC model adds one bond at a time to a large but finite population of monomers (10^5-10^6) in a manner consistent with the rates of all possible reactions. Reactions include bimolecular polycondensation reactions between sites on different polymers, and unimolecular cyclization reactions, as detailed in a previous publication of Rankin et al. [2000] This DMC model is able to model both the connectivity of individual sites and the gelation point of these systems.[Šefcík 2003]

A 1D model of solvent and solute concentrations in a drying film based on Fickian diffusion and vapour-phase mass transport limited evaporation is written in a form similar to that of Cairncross et al. [1996] and is solved using the centered finite difference method. The innovation here is coupling the two types of models. This is accomplished in two ways. First, the concentration of a specific particle of fluid in the film is tracked by using a mass balance on that particle to develop an equation for its position:

$$\frac{dH_p(t)}{dt} = D_1 \frac{\partial C_1}{\partial z} \hat{V}_1$$

where $H_p(t)$ is the particle position relative to the base of the film, t is the time, D_1 is the solvent diffusion coefficient, C_1 is the solvent concentration, z is the height in the film and $\hat{V}_1$ is the solvent molar volume. It is assumed that the concentration within the particle of fluid is uniform, and is the concentration used in a DMC simulation. The second way of coupling the two models is through the time intervals used for the two models. In the DMC model, the time interval for a single reaction is defined using Gillespie's method [1974], and this time interval is then used in the finite difference method. Thus, the two methods evolve according to consistent time scales.

The effects of cyclization on the rates of drying vs. gelation, the severity of gelation time gradients (which give rise to skinning) and the appearance of structural gradients are predicted using this approach. For example, Figure 1 shows the dependence of gelation conversion on position in a film for a particular set of conditions, indicating a gradient in gelation conversion, which implies a gradient in gel structure.
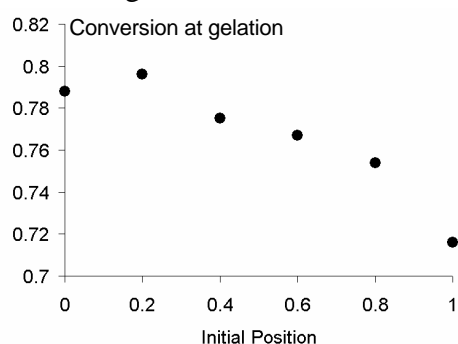
Figure 1. Dependence of conversion at gelation on initial particle position in the film showing a structural gradient.

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Session T3-6: Nanotechnology: New Developments

Abstract Number	Paper Title & Authors	Included
3859	Nanoscale simulations from the semiconductor industry to the life science T H Rod, L D'Anterroches, K Stokbro	Yes
2655	Aerogels as carriers for immediate and controlled drug release I Smirnova, S Suttiruengwong, M Alnaief, W Arlt	Yes
2659	Width variations of hydrodynamically focused streams in low to moderate Reynolds number P M Domagalskia, M Dziubinskia, P Budzynskia, M M Mielnikb, L R Saetranc	Yes
3581	A Dynamic model for in vivo glucose-insulin metabolism V Hrafnkelsson, J B Jørgensena	Yes

Nanoscale simulations from the semiconductor industry to the life science

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1. Summary

This talk discusses some of the challenges we are facing when electronic device are approaching the atomic scale and when the functional properties of molecules are structure dependent and cannot be explained from a macro level point of view. At this scale, we need to take into account the quantum nature of electrons.

Keywords: electron transport, ab initio calculations, nanoelectronics, molecular modeling

2. Extended Abstract

In the first part we will give an introduction to the field of quantum transport, and describe how the quantum nature of electrons changes the properties of nanoscale devices and the challenges we face. The modelling of quantum transport is particularly difficult since the small scale requires that the quantum nature and the atomic details of the system are accurately described, while the size of the system often comprises millions of atoms.

Some years ago we introduced the important notion of dividing a nanoscale device into an active device region and a passive electrode region.[1] In this way the simulation can often be limited to describing a few hundred atoms and it is possible to calculate the current-voltage characteristics of the device with ab initio electronic structure techniques.[1] This theoretical development has laid the foundation for the company Atomistix, in 2003.

In the second part of the talk, we will tell the story behind Atomistix, the theory behind their software products, and some insight gained on using their software to model the electrical properties of nanoscale devices like carbon nanotubes[1], 1-D graphene sheets, molecular electronic devices,[2] atomic wires,[3] spintronics

components or interfaces between different materials.[4] To conclude, the use of atomic-scale simulations to problems in chemistry, catalysis, and life science will be discussed together with a discussion of current and future challenges in the chemical industry.
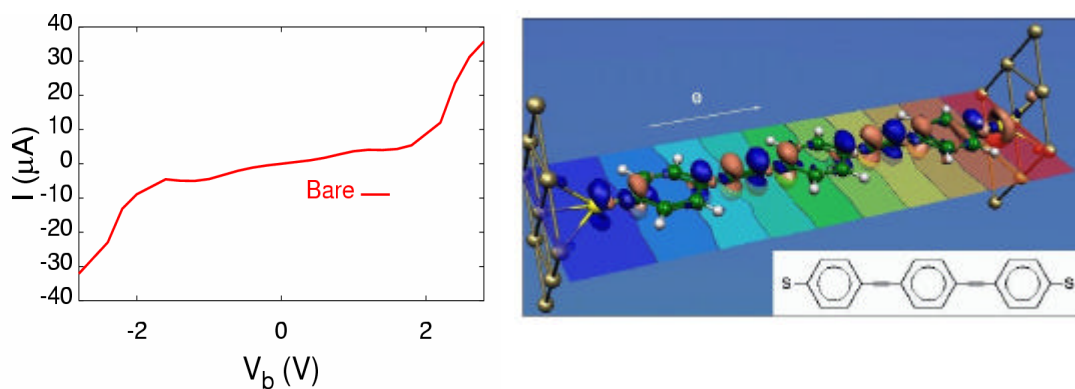
Figure 1: I-V characteristic of a molecular wire sandwiched between two gold electrodes (right hand picture). The I-V curve is computed from first principle.[5]

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Aerogels as carriers for immediate and controlled drug release

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1. Summary

In this paper the potential of silica aerogels as tailor-made drug delivery systems is discussed. The possibility to tailor the release kinetics of drugs by changing of aerogel`s properties (hydrophobicity, density, surface area, pore size) and surface functionalization is demonstrated. The dependence between the nature and amount of the functional groups on the aerogel surface and the adsorption and release properties of aerogels is established In case of hydrophilic aerogels extremely fast release of drugs is achieved, which is especially advantageous for poorly water soluble drugs. This effect bases on the collapse of the structure of hydrophilic aerogels in aqueous solutions due to the surface tension inside the pores.

Keywords: aerogels, drug delivery, functionalization

2. Extended Abstract

Introduction

Aerogels are low-density nanoporous solids with a fine, open-pore structure. Their unique properties include open mesopores (5 to 100 nm), very high surface areas (500 – 1000 m^2/g) and low densities (0.003 – 0.15 g/cm3). The chemistry of aerogel materials is rather flexible: their pore size and surface area can be tailored; furthermore different functional groups can be implemented in order to provide effective drug-aerogel interactions (depending on the nature of the drug) and so to influence the release kinetics. The aim of this work is to show the dependence between the nature and amount of the functional groups on the aerogel surface and the adsorption and release properties of aerogels.

Methods

Silica aerogels were produced using a two-step sol-gel process and dried with supercritical CO_2. The density of the resulting monolith silica aerogels was calculated by weighing a sample and measuring of its volume. The surface area and pore size of the samples were determined by nitrogen adsorption (BET method). The aerogels produced in this way were initially hydrophilic. Functionaliztaion of aerogels was realized by exchanging of OH groups to (a) ester groups (b) amino groups.

To deposit a drug on silica aerogel a weighed amount of the drug and an aerogel sample (0.1-0.2g) was placed in an autoclave and pressurized with carbon dioxide for 24 hours. Than CO_2 was vented and the loaded aerogel samples were weighed and powdered in a porcelain mortar.

To determine the drug concentration in the sample, a part of the aerogel powder was dispersed in acetonitrile and analized using UV-spectrometry (UV-Vis spectrometer Specord 200, Analytic Jena). The results were additionally verified by CHN elemental analysis. Additionally all samples were characterized by IR spectroscopy and X-ray diffraction spectrometry.

The assembly for drug-release measurements was designed according to the recommendation for the dissolution test [FIP 1996]. The amount of the drug was chosen so that the final concentration was equal to 10% of the maximal solubility of this drug in 0.1N HCl (sink conditions).

Results

The loading procedure (adsorption from supercritical gas) allows the homogeneous distribution of the drugs inside the aerogel matrix on the molecular level. The resulted formulations are stable and no chemical degradation of drugs is observed. The drug concentration in the aerogel is explicit determined by the temperature, bulk concentration of the drug in the supercritical phase and the properties of the aerogel. For a given drug the loading increases with the increasing surface area and with the volume of the mesopores of the aerogel, whereas esterified samples have higher loading as hydrophobic ones in all cases (figure 1). In case of aminomodified aerogels, adsorption of several drugs could be significantly increased in comparison to both hydrophilic and esterified aerogels.

The release rate of the drug from the drug-aerogel formulations is significantly influenced by the hydrophobicity and pore size of the aerogels. In case of hydrophilic aerogels an extremely fast release –even compared to nanocrystals- of drugs is achieved, which is especially advantageous for poorly water soluble drugs. This effect bases on the collapse of the structure of hydrophilic aerogels in aqueous solutions due to the surface tension inside the pores. Hydrophobic aerogels exhibit slower release, which is governed by diffusion, since they are more stable in water (figure 2). Release from aminomodified aerogels is closed to esterified ones.
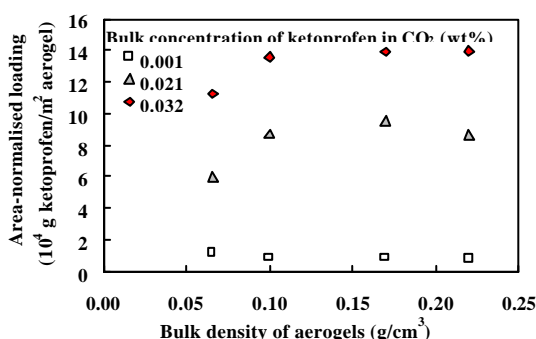
Figure 1: Adsorption of ketoprofen as a function of aerogels structural properties (40°C, 180 bar)
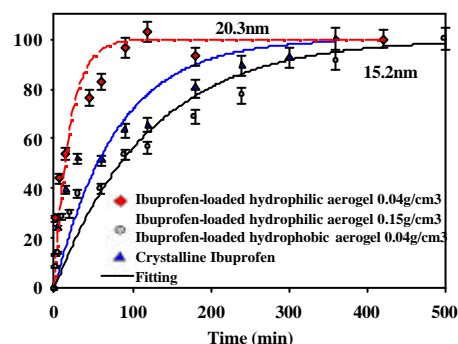
Figure 2: Release of ibuprofen as a function of aerogels structural properties (37°C, 0.1 N HCl)

Width variations of hydrodynamically focused streams in low to moderate Reynolds number

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1. Summary

Hydrodynamic focusing is a widely used technique in the microfluidic world. Our research shows a new, complicated three-dimensional aspect of this phenomenon indicating novel, promising possibilities of future applications and development.

Keywords: microfluidics, hydrodynamic focusing

2. Extended Abstract

Hydrodynamic focusing is a technique used to introduce the sample streak into the capillary axis, by reshaping and squeezing the initial stream by side, inert streams. It is a well established technique in the microfluidic world. Due to specific features it has been successfully involved in several applications ranging from ultra fast mixers [Knight 1998] and reactors [Jahn 2004], via flow addressing in Lab-on-a-chip applications [Lee 2001] and cytometry [Huh 2004], to two-phase systems generators [Anna 2003], rheometry [Wong 2003], flow visualization [Mielnik 2006] and microfabrication [Kenis 1999].
The hydrodynamical focusing phenomenon is however quite complex [Domagalski 2007] where the focused sheet leaving the system shows significant width variations across its span, which in many circumstances does not allow treating this phenomenon as two dimensional. Detailed investigation of the three dimensional flow pattern of the hydrodynamically focused stream, performed by means of CLSM (Confocal Laser Scanning Microscopy) in PMMA channels of 1040x800 and 260x200 μm^2 cross-sections reveals the focused sheet deformation problem (Fig 1).
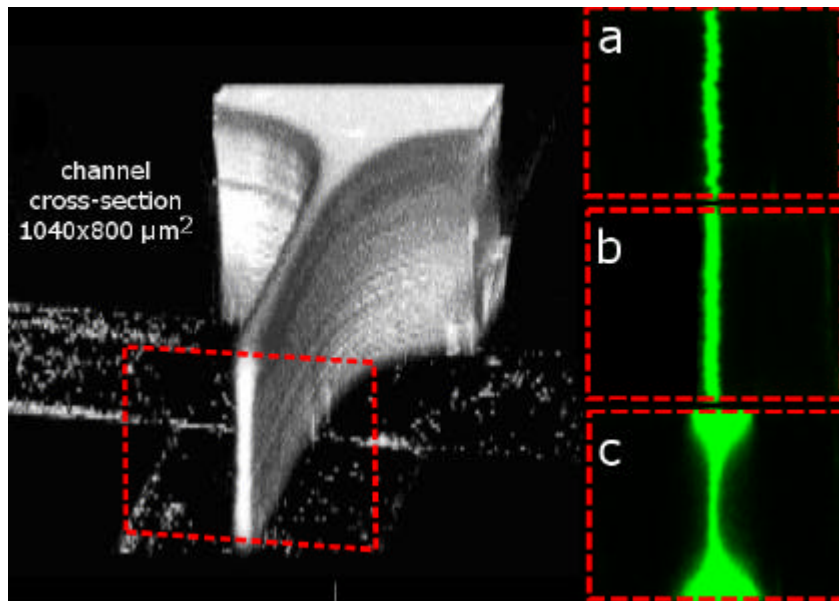
Fig. 1. The 3D projection of confocal microscope image with corresponding cross-sections; velocities in the outlet channel: a) 1,66 cm/s; b) 3,32 cm/s; c) 6,65 cm/s.

The investigation revealed three, dependant on overall flow velocity, possible 'regimes' of focused streak shape: the barrel like shape, characterized by decrease of width towards the top and bottom walls (Fig 1a), the flat – uniform shape (Fig 1b), and the hour-glass like shape, where the focused stream has double-concaved shape (Fig 1c).

Our research clearly indicates the hydrodynamic focusing future development directions. The observed three-dimensional effects are prone to bring the novel applications and to improve the existing ones, by giving the additional tools for design and control the process parameters.

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A Dynamic Model for *in vivo* Glucose-Insulin Metabolism

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1. Summary

We present a mathematical model describing the dynamics of glucose and insulin metabolism in man. The model can be used to evaluate the effect of insulin therapies for people with diabetes as well as aiding in the development of an artificial pancreas. We present the model as well as simulation results obtained using the model.

Keywords: Drug delivery, physiological modelling, dynamic simulation

2. Extended Abstract

We present a mathematical model that describes glucose and insulin metabolism in man. The model describes the effect of meals and physical exercise. Meals and physical exercise are the main disturbances to the blood glucose level in man. Additionally, the model describes diffusion of subcutaneously injected insulin to the blood vessels as well as diffusion of glucose from the blood vessels to subcutis. The model can be used to simulate healthy people as well as people with Type I diabetes. The model allows computer-aided evaluation of various insulin therapies including evaluation of a fully closed-loop insulin therapy. The latter therapy is often referred to as an artificial pancreas.

The model is a compartment model. Like the models by Sorensen (1985) and Pucketts (1990), the compartments are the major organs of the body: Brain, heart & lungs, kidney, liver, gut and periphery. The interconnection of these compartments is dictated by the topology of the flow of blood in man through arteries and veins. Each compartment contains a mass balance for glucose and insulin. The main structure of the compartmental model is illustrated in Figure 1. The compartments for the gut, brain and heart & lungs are modeled to have constant glucose uptake. The peripheral tissue and hepatic glucose uptake is regulated by local changes in the glucose and insulin level. Glucose enters the system through hepatic glucose production and through meals. Hepatic glucose production is influenced by changes in the hepatic glucose, glucagon and insulin levels. The meal glucose uptake enters the gut and the rate of adsorption is based on a 2nd order adsorption model.
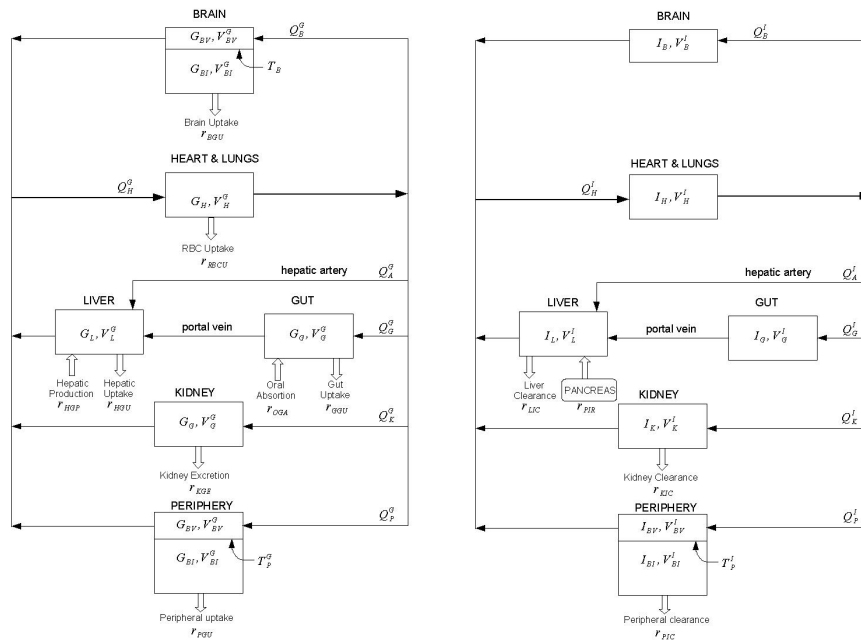
Figure 1. Schematic representation of the glucose and insulin mass-balances.

Insulin present in the kidney, liver and peripheral tissues is cleared at constant rates. Insulin is synthesized in the pancreas and stored in labile form that can be released in response to stimulatory factors, mainly glucose levels. Due to the anatomical position of the pancreas in the circulation, pancreatic released insulin enters the portal vein and thus traverses the liver prior to entering the system circulation.

The effects of exercise are modeled by accounting for increase and redistribution of blood flow, the increase of glucose uptake and the increased glucose production by the liver (Lenart and Parker, 2002). The glucose flow to peripheral issues increases while the glucose flow to the liver and the kidneys decrease. Glucose flow to the brain remains constant with respect to its basal value, as its energy needs remain fixed.

The validity of the model is tested by comparing simulations with clinical experiments. The model is population based and therefore applicable to people of all weights. In addition it is constructed such that it can be used in the simulation of both healthy and diabetic individuals.

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Session T3-7: Integrated Methodologies for Process Development

Abstract Number	Paper Title & Authors	Included
1552	Design of sustainable chemical processes: Systematic retrofit analysis and generation & evaluation of alternatives A Carvalho, C Vázquez, R Gani, H Matos	Yes
2370	Life cycle assessment technique coupled with simulation for enhanced sustainability of phosphoric acid production A D Bojarski, L Gimenez Esteller, A Espuña, L Puigjaner	Yes
2715	A semi-batch (on-line) method for biokinetics determination in an enhanced biological phosphorus removal system E Vaiopoulou, Alexander Aivasidis	Yes
3334	Optimal biorefinery resource utilization by combining process and economic modeling N Sammons Jr., W Yuan, M R Eden, B Aksoy, H T Cullinan	Yes
3646	Designing waste minimization alternatives for batch processes using an intelligent simulation-optimization framework I Halim, R Srinivasan	Yes

Design of Sustainable Processes: Systematic generation and evaluation of alternatives

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1. Summary

The objective of this paper is to present a new generic and systematic methodology for identifying and evaluating the potential design (retrofit) alternatives of chemical processes operating in continuous and/or batch modes. This methodology uses three general indices to measure parameters in a specific chemical process that allow the identification of operational difficulties, process sensitivities and/or unused resources, and, through their analysis, identifies opportunities for targeted process/operation improvements. These indices (or indicators) give us general information about the costs, benefits and accumulation problems present across the process. In addition; a set of sustainability metrics are employed to evaluate the impact of the process on its surroundings (environmental, social and economic impact); and a set of safety indices are employed to measure the inherent safety of the process. Assigned values for the indicators are used as improvement targets, while the sustainability and safety indices are used as performance criteria to identify the best alternative.

Keywords: Process design, Sustainability metrics, Mass and energy indicators, Safety index, indicator sensitivity algorithm

2. Extended Abstract

Nowadays the concerns about the future of humanity are growing due to an increase of environmental problems, the depleting of natural resources as well as the social effects generated because of industrial activity. Consequently, one issue that has gained importance is Sustainability. It is possible to define sustainability as a development strategy that meets the needs of the present without compromising the ability of future generations to meet their own needs. One way to apply this strategy to industry is to retrofit their processes by generating new process/operation alternatives. These alternatives will integrate the economic, the environmental and the social aspects into industry production. The methodology presented in this work has

being developed in order to generate and evaluate process alternatives for improved sustainability. This methodology involves the calculation of parameters such as the indicators, the sustainability metrics and the safety index. A software (*Sustain Pro*) has been developed to calculate these parameters for a given process. Using data from plant or from results of a simulation of the process at a reference design, it is possible to calculate a set of indicators and analyze them to generate process alternatives. The critical points of the process are identified through the indicators and the impact of the process to its surroundings is highlighted by the sustainability metrics and the safety indices. *Sustain Pro* decreases the time spent in generating and evaluating alternatives by concentrating on the calculations that lead to identifying the most promising alternatives. Also *Sustain Pro* integrates different computer aided tools by providing efficient data transfer between them and can handle complex processes with multiple reactors, and large and/or complex flowsheets.

The main features of the indicator based methodology has been highlighted through different case studies, for example, the well known HDA process the production of Methyl Tertiary Butyl Ether (MTBE) [6]. With the *Sustain Pro s*oftware it was also possible to apply this methodology to more complex processes such as Vinyl Chloride Monomer (VCM) production and Ammonia production. Through these case studies the main features of the algorithm, such as the determination of the indicators and the generation of targeted retrofit alternatives, will be illustrated. This revamping action will improve the process performance making these processes also more competitive and sustainable.

Another important feature of this methodology is its applicability in real plants. To highlight this feature, a case study based on a real industrial process will be presented and the results discussed. This case study was jointly developed as a trial of the methodology and the *Sustain Pro* software.

Finally, the main features and developments of an extension of this methodology has being developed for batch processes. The new methodology adopted is an analogy with the one used for continuous processes.

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Life Cycle Assessment technique coupled with simulation for enhanced sustainability of phosphoric acid production

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1. Summary

Phosphoric acid is the second largest mineral acid produced worldwide considering its volume and value. The production process is based on sulphuric acid lixiviation of fluoroapatite, followed by filtration of the formed phosphogypsum (PG) and the subsequent concentration of the solution, yielding phosphoric acid (PA), (EFMA, 2000). To study the environmental effects associated to the PA related industry it is useful to adopt a Life Cycle Assessment (LCA) approach. A main limitation in the application of the LCA is the availability of reliable data, so a combination of LCA and process simulation is proposed. This approach also allows assessing the model uncertainty arising from industrial data and simulation hypothesis. Towards this end, a Monte Carlo (MC) scheme is adopted.

Keywords: wet process phosphoric acid, life cycle assessment, process simulation.

2. Case study

The production facility is situated in Greece so electricity use is based on industrial data and Greek network. No integration of steam produced in H_2SO_4 plant is considered. The duty required for PA concentration is supposed to be obtained from natural gas combustion. System's boundary for PA production lies just after the production of concentrated PA, making this LCA fit a cradle to gate approach. Transportation of chemicals from and to the process plant is excluded from the model. Regarding PG, no production of usable byproduct is analyzed. It is considered to be stockpiled on land, considering that lixiviate of trace components is 1% of total trace species present (Seijdel R.R., 1999). A partition coefficient based on (van der Loo J.H.W et al, 2000) was considered for the split of trace species between PG and filter liquor. Allocation of remaining trace species between filter liquor and product PA was based on simulation mass flows.

Different scenarios were set according on the treatment of the liquid effluents from scrubbing units and gypsum filter unit: (a) waste water (WW) is dumped into the ocean; (b) WW is neutralized and then dumped as groundwater and finally (c) WW is treated to recover H_2SiF_6 (22%), neutralized at a second step and then disposed as

groundwater. Fluorine air emissions from vapor effluents were calculated considering a scrubbing efficiency of 99% (Wiesenberger H, 2002). H_2SiF_6 byproduct recovery from scrubbing liquors was calculated considering a F recovery of 90% mole basis and an outlet concentration of 22% (EFMA, 2000). This recovery unit was modeled using a black box model, given that no industrial data was available. Avoided environmental impact resulting from the production of HF was considered. Throughout this paper LCA calculations are done using SimaPro®, while process simulation is performed with Aspen Plus®. MC scenarios were generated using Matlab®.
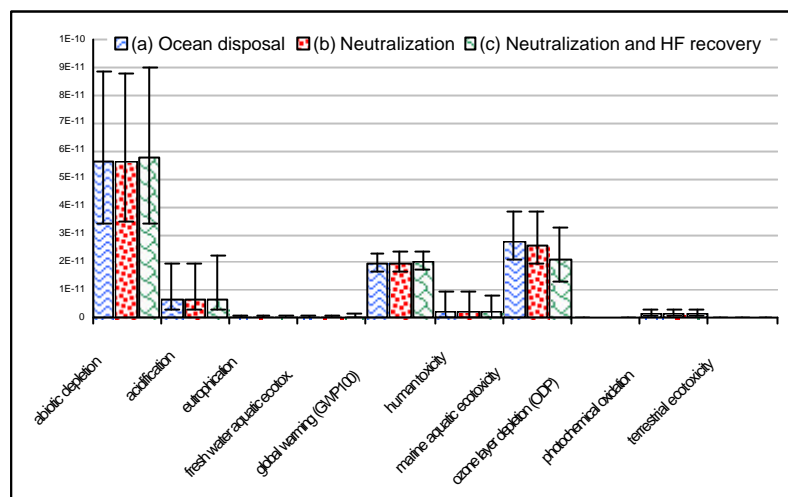
Figure 1. Environmental scores for the process alternatives, method CML 2 baseline 2000 V2.03 normalization and weighting for West Europe, 1995.

Abiotic depletion and marine aquatic ecotoxicity are the most important impacts for all waste treatment options. Other important impacts are GWP100 and acidification. Eutrophication scored low, even when the process emits phosphate. High uncertainty is associated to impacts where the variables had more uncertain ranges as can be seen in ecotoxicity and acidification. This issue is an inherent problem of all LCA analysis. Nevertheless from the results we can derive that neither option scores best in all categories, and therefore multicriteria techniques must be used in order to assess the "best" alternative, as the relative importance of the impacts had to be balanced.

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A Semi-Batch (On-line) Method for Biokinetics Determination in an Enhanced Biological Phosphorus Removal System

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1. Summary

Kinetics of nitrification, denitrification and dephosphatation were studied in the aerobic, anoxic and anaerobic stages of a pilot scale Biological Nutrient Removal plant treating municipal wastewater. In order to study the process kinetics and to obtain actual values for the investigated kinetic parameters semi-batch experiments were performed. Continuous feeding of the treating system was interrupted and instantly the pilot plant was turned into a batch mode operation. Thereafter, substrate was added and its consumption was monitored. The nitrification process was found to follow Monod type kinetics. In general, nitrification activity is enhanced along the treatment train, whereas the low values of the half saturation constant show that nitrifiers with high affinity to the influent substrate grow in the system. Denitrification experimental results indicated zero order kinetics. Two specific denitrification rates, an initial high one, $q_{DN,1}$ and a following low one, $q_{DN,2}$, until complete substrate consumption were determined in the anoxic tanks. In any case, maximum denitrification activity is recorded in the first anoxic tank of the cascade. During denitrification phosphate concentration was fluctuating, whereas phosphorus was instantly released in nitrate absence. Denitrifying phosphate accumulating organisms are estimated at 25 %. By testing the anaerobic sludge of the BNR unit, specific anaerobic phosphorus release rate and specific aerobic uptake rate was low. On-line biokinetics determination using the proposed semi-batch method results to real time data acquisition and thus, to actual unit monitoring under operating conditions.

Keywords: biokinetics, nitrification, denitrification, biological phosphorus removal

2. Extended Abstract

Kinetics of nitrification, denitrification and dephosphatation were studied in the aerobic, anoxic and anaerobic stages of a pilot scale Biological Nutrient Removal (BNR) plant treating municipal wastewater. The configuration of the plant's design is based on the combination of the UCT (University of Cape Town) process and the step feeding in a three-stage denitrification cascade.

In order to study the process kinetics and to obtain actual values for the investigated kinetic parameters semi-batch experiments were performed. For this purpose, continuous feeding of the treating system was interrupted and instantly the pilot plant was turned into a batch mode

operation. No sludge was extracted and experiments were conducted in the actual environment of bacteria life cycle. Thereafter, addition of NO_3^- and NH_4^+ into the anoxic and aerobic compartments of the treatment plant respectively, took place, whereas adequate initial concentration of a carbon source (municipal wastewater or acetate) was added in the mixed liquor. Aeration was implemented in the anaerobic tank to reach maximum phosphorus release. At this point and after transition to anaerobic conditions acetic acid was added to provide a readily biodegradable carbon source for phosphorus uptake.

The nitrification process was found to follow Monod type kinetics. The maximum specific nitrification rate, $q_{N,max}$, was determined to vary between 1.71 and 2.95 g NH_4^+-N/(g VSS_{aut}·d) for synthetic wastewater addition. The half saturation constant for the nitrification process, $K_{m,N}$, was estimated graphically at 2.2 – 6.4 g NH_4^+-N/L. When the substrate was real wastewater, $q_{N,max}$ averaged at 1.14 g NH_4^+-Nr/(g VSS_{aut}·d) and $K_{m,N}$ at 1 g NH_4^+-N/L. In general, nitrification activity is enhanced along the treatment train, whereas the low values of the half saturation constant show that nitrifiers with high affinity to the influent substrate grow in the system.

Denitrification experimental results indicated zero order kinetics. Two specific denitrification rates, an initial high one, $q_{DN,1}$ and a following low one, $q_{DN,2}$, until complete substrate consumption were determined in the anoxic tanks. Using synthetic wastewater $q_{DN,1}$ and $q_{DN,2}$ were found to obtain mean values of 0.12 and 0.06 g NO_3^--N/(g VSShet·d) respectively. In any case, maximum denitrification activity is recorded in the first anoxic tank of the cascade. Since real municipal wastewater lacks of readily biodegradable organics, values of the specific denitrification rates are lower. During denitrification phosphate concentration was fluctuating, whereas phosphorus was instantly released in nitrate absence. Specific phosphate release rates, phosphate profiles and maximum phosphate release were quite similar in all anoxic tanks. Denitrifying phosphate accumulating organisms (DPAOS) are estimated at 25 %.

By testing the anaerobic sludge of the BNR unit, specific anaerobic phosphorus release rate was determined averagely at 0.03 g PO_4^{3-}-P/(g VSS_{het}·d), whereas specific aerobic phosphorus uptake rate was estimated averagely at 0.05 g PO_4^{3-}-P/(g VSS_{het}·d). These values are considered low.

The determination of kinetic parameters can be considered as a useful tool for the process design, operation and improvement of wastewater treatment plants. Furthermore, the study of the biological process kinetics contributes to the better understanding and outline of the complicated biological processes that contemporarily take place within the various stages of BNR wastewater treatment plants. On-line biokinetics determination using the proposed semi-batch method results to real time data acquisition and thus, to actual unit monitoring under operating conditions.

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Optimal Biorefinery Resource Utilization by Combining Process and Economic Modeling

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1. Summary

The integrated biorefinery uses renewable feedstocks from the forest-based industries in order to provide a sustainable alternative for the production of energy and chemicals. Changing market conditions may dictate a dynamic optimum for the allocation of resources and production capacity, resulting in a myriad of possible long-term product portfolios. Consequently, there is a need for systematic, reliable methods capable of incorporating different levels of process detail in the decision making framework. By constructing simulation models for various biorefining processes, determining variable and fixed cost components of these processes, and combining this cost data with information on expected return and market conditions, firms interested in biorefining will be able to determine the effects of changes in shareholder value as a result of deciding which products to pursue among the many biorefinery possibilities. Collaboration with key stakeholders in industry, academia and government has been established enabling access to proprietary process specifics and business models. In this way, experimental and theoretical efforts can supplement each other in a synergistic manner, by providing direction and data for continued work. The proposed framework is flexible enough to be modified upon discovery of scientific breakthroughs to determine if these technological changes alter the optimal product portfolio. By incorporating optimization under uncertainty and financial options theory, the framework may be a powerful tool in forecasting production decisions in the face of an unpredictable financial landscape.

Keywords: Biorefining, process economics, process integration, bioenergy

2. Extended Abstract

The process of separating biomass constituents and converting them to high value products is known as biorefining, and the integrated biorefinery provides a unique opportunity for reinvigorating an entire manufacturing sector by creating new product streams (Bridgwater, 2003). These products range from bulk and fine chemicals,

polymers, fiber composites, pharmaceuticals to energy, liquid fuels and hydrogen. Economic and environmental sustainability are achieved through the optimal use of renewable feedstocks, and a need exists for a process systems engineering (PSE) approach to ensure maximum economic and societal benefit through minimizing the usage of raw material and energy resources as well as the cost involved in supply chain operations intrinsic to biorefining.

With such a wide range of processing steps and possible products, it is obvious that identification of the optimum process structure can not be done based on heuristics or rules of thumb. Depending on market prices and trends, the optimum allocation of resources and production capacity may switch between the different products. Economic market analysis, predictive financial modeling, and optimization under uncertainty are tools that can be used to determine the sensitivity of a decision-making framework to market fluctuations. Thus there is a need for systematic, reliable methods capable of incorporating different levels of process detail in the decision making framework in order to determine environmental metrics, financial profitability, and other techno-economic metrics that correspond to product portfolio combinations.

In this work a mathematical optimization based framework is being developed, which enables the inclusion of profitability measures and other techno-economic metrics along with process insights and performance characteristics obtained from experimental and modeling studies (Sammons et al., 2006). By utilizing process integration methods, the processing steps can be optimized to ensure efficient use of energy and materials resources while assuring an acceptable, minimal level of environmental impact through the use of EPA's WAR algorithm (Young and Cabezas, 1999). A novel feature of the proposed framework is the decoupling of the complex models from the selection step, which enables adaptation to new developments within any of the processing steps and thus can incorporate novel innovative production processes in the decision-making framework. This decoupling enables more efficient solution of the production optimization/allocation problem as the non-linearities embedded in the process models have been removed.

Collaboration with key stakeholders in industry, academia and government has been established enabling access to proprietary process specifics and business models. In this way, experimental and theoretical efforts can supplement each other in a synergistic manner, by providing direction and data for continued work. This contribution will illustrate the strategy for developing the decision making framework as well as highlighting the flexibility of the framework to utilize data from technological breakthroughs in the field of biorefining.

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Designing Waste Minimization Alternatives for Batch Processes Using an Intelligent Simulation-Optimization Framework

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1. Summary

The issue of environmental sustainability has prompted the batch chemical industries to switch from end-of-pipe treatment to waste minimization as top priority in tackling the pollution problem. In this paper, we introduce a novel simulation-optimization framework that integrates different process systems engineering (PSE) methodologies such as process graph (P-graph) scheme, Douglas' hierarchical design approach, WAR algorithm and multi-objective optimization algorithm to solve the waste synthesis problem for the batch process plants.

Keywords: sustainable development, intelligent system, process synthesis, multi-objective decision making, simulated annealing

2. Extended Abstract

Given the complex and multidisciplinary nature of waste minimization analysis, a systematic way of identifying and evaluating suitable design alternatives is thus essential. Previously, we have developed a framework (Batch-ENVOP*Expert*) that can automatically identify, diagnose and analyze waste minimization alternatives in any batch process (Halim and Srinivasan, 2006). In this paper, we extend the framework by integrating an expert system with process simulator and mathematical optimization technique to derive more comprehensive and cost-effective waste minimization solutions. We illustrate the framework by solving a case study involving reaction and distillation (von Watzdorf *et al.*, 1994). The process starts with reaction between chemical A and B in a jacketed vessel to produce product C and byproduct D. As the reaction is exothermic, once the temperature reaches a certain level, cooling of the reactor is started to maintain a constant temperature till maximum yield of C is achieved. At that point, the reactor is cooled rapidly to bring the temperature to the ambient level. The reaction mixture are transferred to an intermediate storage tank

and the reactor vessel washed with cleaning liquid. From the storage, the mixture is batch distilled to produce two main cuts of high purity A and C. The final residue from distillation is byproduct D. In this process, two waste streams are generated: spent cleaning liquid and waste-byproduct D. Our objective here is to derive waste minimization alternatives pertinent to these waste streams.

The first step in our waste minimization analysis is to diagnose the sources of wastes in the process. For this, we have implemented a P-graph approach to trace through the process operations and identify the ones that contribute to the presence of the different material components in the waste stream. The subsequent step after diagnosing the waste sources is to derive heuristic solutions to the sources. These include such as "optimize the reaction condition to reduce byproduct D", "use further separation at the end of distillation to reduce material A and C in the waste stream", and "reuse (recycle) of cleaning liquid".

While heuristic suggestions provide potential solutions, their analysis results are not capable of specifically determining "which" variables should be manipulated and "how much" waste would be reduced as a result. Thus, the next step in our waste minimization procedure is to perform detailed analysis at the level of process variable. This is done through process simulator combined with environmental and cost impact calculations. In this way, the effects of changes to the design and operating condition on the amount and composition of the generated wastes and economic implications can be assessed. However, like many other design problems, the environmental impacts and economic aspects of the proposed alternatives may conflict one another. Thus the next step is to perform multi-objective optimization and resolve the environmental and the economic impact trade-offs. This is done using simulated annealing to obtain the Pareto optimal set.

The following lists some of the Pareto optimal solutions obtained from modifying the process set points. Here, the objective functions are maximum amount of C, and minimum production time and waste byproduct D. As seen, the table shows improvement from the base operation. At the same time, reuse of cleaning liquid from the first reaction cycle to the subsequent second and third operation reduces the amount of spent cleaning liquid from 3200 to 1200 kg.

	C production (kmol)	Production time (s)	D production (kmol)
Base case	2,830	12,937	1,238
Pareto set	3,026	12,858	1,201
	3,044	12,869	1,195

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Session T3-8: Novel Separation Techniques

Abstract Number	Paper Title & Authors	Included
1820	Ultra purification of ionic liquids by melt crystallisation A König, M Stepanski, A Kuszlik, P Kei I, C Weller	No
1842	FricDiff: A novel and innovative separation process B Breure, E A J F Peters, P J A M Kerkhof	Yes
2833	Development of a photocontrollable aqueous two-phase system for a novel separation method J-I Edahiro, K Sumaru, T Takagi, T Shinbo, T Kanamori	Yes
3869	Prediction and verification of the solubility of flavonoids in ionic liquids--A priori design of the green routes for efficient enzymatic synthesis of lipophilic flavonoid derivatives Z Guo, B-M Lue, X Xu	No

FricDiff: a novel and innovative separation process

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1. Summary

FricDiff is a novel and energy efficient separation process based on a difference in transport velocities of the components of a gas or vapour mixture in an enhancer or sweep gas. The separation process takes place inside the pores of a non-selective barrier, whose only function is to prevent mixing of the feed mixture with the sweep gas. In this research, FricDiff is applied for the separation of azeotropic mixtures of alcohol and water. Two numerical models are developed with which results are generated and compared with data obtained with lab-scale experiments. The influence of process conditions and the geometry and characteristics of the porous barrier on the separation process are studied.

Keywords: FricDiff, novel separation process, azeotropic alcohol-water mixtures, sweep gas, macro porous membrane

2. Extended Abstract

One of the major disadvantages of the separation processes that are currently used in the (petro-)chemical industry is their high energy-consumption. This is particular the case for distillation, the most widely applied industrial separation technology. In addition, hazardous chemicals are often required to facilitate the separation. Over the past years, the interest for membrane separation processes, like pervaporation, vapor permeation and gas permeation has grown tremendously. The relatively low energy consumption and the fact that no additional chemicals are required, makes these processes interesting candidates to replace distillation. In spite of major efforts in universities and research institutes, membrane processes are still not suitable to replace distillation. The fluxes through the membranes are still too low, requiring large membrane areas. Furthermore, the ceramic membranes that are used are very fragile and expensive, whereas polymeric membranes have a low chemical and thermal stability. In order to find a solution for these drawbacks, an alternative separation technology called "FricDiff" was developed at Eindhoven University of Technology.

FricDiff [1] is a novel and energy-efficient separation process that can be used for the separation of both gas and liquid mixtures. With this technology, a gas or vapor mixture (the liquid mixture is first evaporated to bring it in the vapor phase) is separated by letting it diffuse against an additional component. This additional component, which is called the enhancer, is a permanent gas (in case one wants to separate a vapor mixture) or a condensable vapor (when the mixture we want to separate is a gas mixture) that will show more friction with one component in the mixture. This component will, while interdiffusing, be more retained by the enhancer, leading to an enrichment of this component in the retentate. The separation process takes place inside a non-selective porous barrier (macro porous membrane) with the feed mixture and enhancer flowing at opposite sides of it. The advantage of using a macro porous barrier instead of a selective micro porous membrane, is that the fluxes through the barrier are much higher. Furthermore, the barrier can be made of a robust and relatively cheap material, like stainless steel.
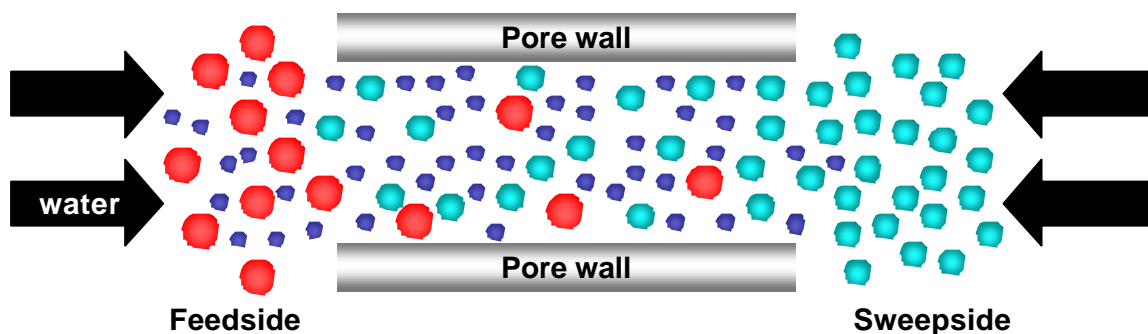
Figure 1: Schematic overview of the FricDiff-process for the separation of an alcohol-water mixture

In this project, the applicability of FricDiff for the separation of azeotropic mixtures of alcohols and water is studied. Experiments are performed with a lab scale experimental set-up and compared with results obtained with two computer models developed in the program Aspen Custom Modeler. The first model describes the mass transport in the tubes (at opposite sides of the porous barrier) with a plug flow and assumes that the mixtures are perfectly mixed in the radial direction. The second model is a more detailed model, which takes into account axial velocity profiles and radial concentration gradients and velocities. In this case, the effect of concentration polarization on the separation can be examined. In both models, the mass transport through the porous barrier is described with the Binary Friction Model. The influence of process conditions (e.g. absolute pressure, ratio of flow rates of feed mixture to enhancer) and the geometry and characteristics of the porous barrier (e.g. pore size, thickness of the porous barrier) on the separation are studied. In this way, the FricDiff-process can be optimized for the separation of a specific mixture.

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Development of a photocontrollable aqueous two-phase system for a novel separation method

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1. Summary

In order to develop a novel separation method, an aqueous two-phase system, which shows a reversible photo-induced phase separation, has been developed with the photochromic dextran modified with a photochromic chromophore, 6-nitrospiropyran. For mixed aqueous solution of the photochromic dextran and poly(ethylene glycol), it was observed that the solution, which had been uniform in the dark at 25 ℃, quickly separated into two phases through blue light irradiation within 1 min and returned to the former uniform state spontaneously after heating at 50 ℃ for 1 h.

Keywords: Aqueous two phase system, Photoresponsive phase separation, Photochromic polymer, Poly(ethylene glycol), Spiropyran

2. Extended Abstract

An aqueous two-phase system essentially consists of two immiscible aqueous solutions of different polymers. Due to the minimal invasive nature, an aqueous two-phase system has been employed to separate a mixture of naturally derived substances. However there are technical problems in the aqueous two-phase separation method: long separation time, and low selectivity. As a possible solution of these problems, we suggest a novel separation method based on the aqueous two-phase system of which phase separation can be switched by light
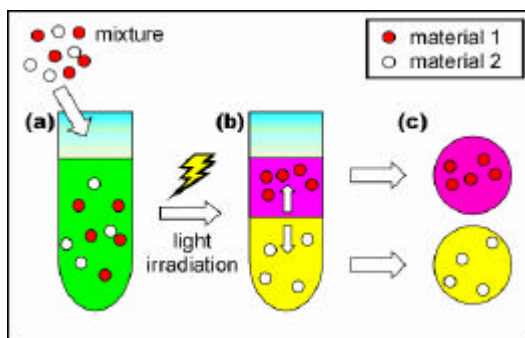
Figure 1 Scheme of separation method based on photoresponsive aqueous two-phase system: (a) introduction of mixture (b) photo-induced phase separation (c) separation of introduced mixture based on difference in affinity for the two phase system.

irradiation (Fig.1).

We synthesized the photochromic dextran (NSp-DXT, Fig.2) by substituting 0.3 mol% of hydroxyl groups with the photochromic chromophore, 6-nitrospiropyran (NSp). For an aqueous mixed solution of 0.5 wt% of the NSp-DXT, 7.0 wt% of poly(ethylene glycol) (Mw: 6000) and 3.0 mM HCl, it was observed that the solution, which had been clear yellow in the dark at 25 ℃ (Fig. 3(a)), changed to colorless and cloudy within 1 min through irradiation of blue light with a wavelength of 436 nm (Fig. 3(b)). Since the solution was stirred vigorously, the change in turbidity shows that uniform single phase was separated into two phases. Subsequently, the cloudy solution (Fig. 3(b)) became clear yellow spontaneously after heating at 50 ℃ for 1 hr

(Fig.3 (c)). In acidic aqueous solution of NSp-DXT, yellow and relatively hydrophilic open-ring NSp can be changed into colorless and hydrophobic closed-ring NSp by photoisomerization and it reverts back to former open-ring NSp spontaneously by heating (Fig. 2). These results suggest that closed-ring NSp generated through the photoisomerization serves as a trigger in inducing phase separation of the NSp-DXT/PEG aqueous two-phase system since hydrophobicity of the polymer affect the phase separation in the aqueous two-phase system.

Figure 2 Chemical structure of the NSp-DXT.

In the photoresponsive aqueous two-phase system, unlimited interfacial area can be obtained instantaneously while phase separation is induced from a single uniform phase by light irradiation. In the situation, it is anticipated that an ideal separation operation can be achieved in which all substances in the solution are in contact with the interface. We expect that this novel separation mechanism is promising for a high-throughput separation method of biological substances.

Figure 3 Phase separation behavior of mixed aqueous solution of NSp-DXT and PEG in acidic condition: (a) at 25℃ in the dark (b) 1 min after light irradiation (c) after heating for 1 hr at 50℃.

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Session T3-9: Evaluation-Analysis of Bio-Fuels

Abstract Number	Paper Title & Authors	Included
1036	Study on stability of ethanol/diesel fuel emulsion G Nagy, G Marsi, J Hancsók	Yes
1223	Development of multifunctional additives based on vegetal oils for high quality diesel and biodiesel fuels J Hancsók, M Bubálik, A Beck	Yes
3275	Evaluation of liquid bio-fuels using the analytic hierarchy process M Papalexandrou, P A Pilavachi, A I Chatzimouratidis	Yes
3772	Biofuels: Myths and Reality (Keynote) M N Karim, R Khare, S Peri	Yes

Study on Stability of Ethanol/Diesel Fuel Blend

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1. Summary

The effect of temperature, bioethanol concentration, application of biodiesel (RME: repeased-oil-methyl-ester) in various concentration and preparation conditions on the stability of bioethanol/diesel fuel and/or /biodiesel blends and analytical and performance characteristics was studied in the paper. The following changes were observed when blends containing 5% bioethanol were prepared form the base gas oil: density decreased; kinematical viscosity decreased; flash point decreased (from 75°C to 15°C); CFPP remained unchanged; Reid vapour pressure increased (from 0.65 kPa to 13.4 kPa), cetane number decreased (from 54 to 50). The stability of bioethanol/diesel fuel blends without additive was improved in case of RME in various concentrations.

Keywords: bioethanol, bioethanol/gas oil fuel blend, biodiesel, emulsion, stability

2. Extended Abstract

2.1. Introduction

The use of biomass-derived fuels has been considerably increasing in the European Union in the last years and this tendency is expected to grow in the near future [Lü Xing, 2004] according to Directive 2003/30/EC. Out of the biomass-based engine fuels, which are suitable to operate diesel engines, biodiesel (vegetable oil fatty acid methyl esters) become the most wide-spread in the European Union. However, the investigation of bioethanol-diesel fuel and/or biodiesel blends or emulsions as possible fuels to be applied in Diesel engines is also of increasing importance [Weber de Menezes, 2006]. This is constrained by the stability of these emulsions, which is highly dependent on temperature, water content, presence of biodiesel in the mixture, type and concentration of and of stabilizing additive and hydrocarbon composition of the base diesel fuel [Fredriksson H., 2006].

2.2. Experimental

Preparation of the blends was carried out with magnetic agitator equipment at medium speed (600-700 rpm) The duration of agitation was 10 minutes in case of all samples. After the agitation, the samples were left alone at room temperature for 3x24 hours in a measuring tube of 100 cm³ closed with a glass stopper.

2.3. Results and discussion

The products prepared in the experiments were solutions, which were studied for stability. The concentration of the additive strongly affected the volume of bioethanol kept dissolved. The base gas oil alone without any additive was only able to keep maximum 3 v/v% bioethanol in the solution. The decrease of temperature had a negative effect on the amount of dissolved bioethanol. The biodiesel co-solvent significantly enhanced the stability of the blend, ie. a defined amount of base gas oil was able to dissolve a higher amount of bioethanol. This is caused by the unlimited solvency of bioetanol and biodiesel. The reduction of temperature had a negative effect on the amount of dissolved ethanol even in the presence of biodiesel. Without the use of additive, bioethanol did not dissolve into the base gas oil at a temperature of 1°C but the presence of 5% biodiesel facilitated the admixture at low temperature. This finding is important, because the diesel fuels containing at least 4.4 v/v% biodiesel can be marketed with tax incentives in Hungary beginning with January 1, 2008. Biodiesel acts as a co-solvent and can improve the stability of bioethanol/diesel fuel blend meaning that the low temperature might occurring during the storage or transportation will not cause phase separation. Density of the base gas oil used for the blending was 0.8372 g/cm³ at 15°C-on. Density of the blends was lower due to the addition of ethanol having a lower density. Density of the blends containing up to 10 v/v% bioethanol has met the specification (0.820-0.845). Viscosity of the base gas oil measured at 40°C was 2.60 mm²/s, which dropped to 2.18 mm²/s after blending 10 v/v% bioethanol. Flash point (as of Pensky-Martens) of the base gas oil was 64°C, which decreased to an average of around 14°C (± 1°C) as a result of adding 5% bioethanol. Among cold properties the CFPP values decreased only slightly, pour point also decreased greatly and cloud point greatly increased as a result of bioethanol blending. Reid vapour pressure of the base feedstock was 0.6 kPa, while those of the blends containing 5% bioethanol were about 13.2 kPa in average. The anti-friction effect of the fuel mixture also worsened, but the loss of lubricity effect can be compensated to a certain level by adding biodiesel into the mixture. The distillation properties of base gas oil greatly changed due to the lower boiling point of bioethanol. Cetane number is an important property of diesel fuels. Due to the blending of bioethanol with gas oil the cetane number decreased by 5-6 units. Due to the loss in cetane number use of cetane boosters (ethyl-hexyl-nitrate) is needed.

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Development of multifunctional additives based on vegetal oils for high quality diesel and biodiesel fuels

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1. Summary

The increasing qualitative requirements of the fuels of modern Diesel engines can be satisfied by applying environmental friendly blending components of high energy content and additive-packages having high performance level.

The aim of our experimental work was to produce vegetable oil-based multifunctional additives which have not only lubricity improving effect applying in fuels but other necessary properties can be achieved, too. Beside, our object was to use raw materials originated from partly renewable source meeting the biodegradability requirements. These synthesized additives showed same or even better detergent-dispersant properties compared to the traditional PIB-succinimides and also provided other functional effects such as corrosion inhibiting and antifriction effects.

Keywords: multifunctional additives, vegetable oil, lubricity, detergent-dispersant

2. Extended Abstract

Experimental methods

The analytical and performance test of the intermediates and the final products were carried out according to international and local standards and proprietary methods.

Results and discussion

The synthesis of the additives containing rapeseed oil methyl ester components was carried out in two steps. First polyisobuthylene-succinic anhydride containing rapeseed-oil methyl ester were prepared by the reaction of polyisobuthylene (PIB, Glissopal 1000; $\overline{M}$: 1000; BASF Chemical Company), maleic anhydride and rapeseed-oil methyl ester (RME, prepared by us). The reaction was carried out at atmospheric pressure and different temperatures in aromatic solvent, with radical

initiation using reactants in various molar ratios. The solvent and the unreacted materials were removed at 200 °C by vacuum distillation.

The effect of temperature, the change of molar ratio of the raw materials, the amount of the solvent and the initiator on the properties of the polyisobuthylene-succinic anhydrides containing rape-oil methyl ester was investigated.

The selected intermediates were used to acylate polyethylene polyamines. The additives were prepared under inert N_2 atmosphere in a five-neck flask equipped with a stirrer, reflux cooler, thermometer and N_2 feeder. The polyethylene polyamines (PEPA) were added to the intermediate containing base oil (SN-150/A) at continuous stirring. The acylating reactions were carried out at 165-185 °C under mild vacuum and the reaction time was 4-6 hours (the well known methods by synthesis of polyalkylene succinics). The unreacted polyamines were removed at 200 °C by vacuum distillation.

The potential DD effect and Peugeot XUD-9 tests showed that efficiency of traditional succinics could be achieved.

Based on the copper strip corrosion test it was found that the additives had excellent corrosion inhibiting properties, too. The results of the stricter rust prevention test performed with ferrous parts confirmed the previous effects gained by the copper strip test.

The lubricity improving efficiency of the additives was investigated in the range of 50-200 ppm in gas oil. According to the HFRR and Fourball performance tests, the lubricity of all gas oils was enhanced significantly. These results showed that the additives based on vegetable oil had significant lubricity improving effect, too.

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Evaluation of liquid bio-fuels using the Analytic Hierarchy Process

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1. Summary

Biomass derived liquid bio-fuels are being promoted as a major feasible fuel alternative in the European Union, in order to reduce Europe's transport dependency on crude oil. There are numerous pathways dealing with the production and use of liquid bio-fuels, depending on biomass feedstock, production technology, by-product usage and final bio-fuel consumption in vehicle power trains. This paper evaluates different bio-fuel pathways, which can be used to substitute conventional fuels in the European transport sector for 2010 and beyond, using the Analytic Hierarchy Process. The assessment includes a synthesis of evaluation criteria and a sensitivity analysis. The evaluation led to useful results, ranking the bio-fuel pathways from the best to the worst according to the priority of the criteria weights.

Keywords: Liquid bio-fuel evaluation; Well to Wheels pathways; Analytic Hierarchy Process

2. Extended Abstract

The evaluation of liquid bio-fuel pathways was based on data taken from the *Well to Wheels analysis of future automotive fuels and power trains in the European context* [1]. The bio-fuels that were assessed include conventional bio-ethanol and bio-diesel, which derive from agricultural crops as well as second-generation bio-ethanol and syn-diesel which derive from lignocellulosic biomass.

In particular, conventional bio-ethanol can be produced from sugar beet or wheat and the by-products can either be used as animal feed or as fuel for the production process. In the case of wheat the heat needed can be supplied from natural gas, lignite or straw in a CHP scheme or by a conventional natural gas boiler. Conventional bio-diesel can be produced from rapeseed or sunflower and the glycerine produced from the process can either be used as chemical or as animal feed. Second generation bio-ethanol can be produced from farmed wood, waste wood or straw, while syn-diesel can be produced from farmed wood, waste wood or waste wood via the black liquor process.

The methodology used in the Analytic Hierarchy Process (AHP) [2] for the evaluation is based on structuring a simple decision hierarchy problem, as shown in Figure 1.

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The criteria that were analyzed throughout the complete bio-fuel chain include bio-fuel substitution cost over conventional fuels (economic criterion), potential of substitution of conventional fuels by domestic EU sources (potential), total cycle GHG emissions (environmental) and total cycle energy consumed (resource). The AHP process is based on simple pair wise comparison judgments throughout each level of the hierarchy to arrive at overall priorities for the alternatives. This is achieved by comparing elements with respect to their parent element. Finally, the AHP synthesizes all the evaluations into a unified whole in which alternatives are clearly classified from best to worst.
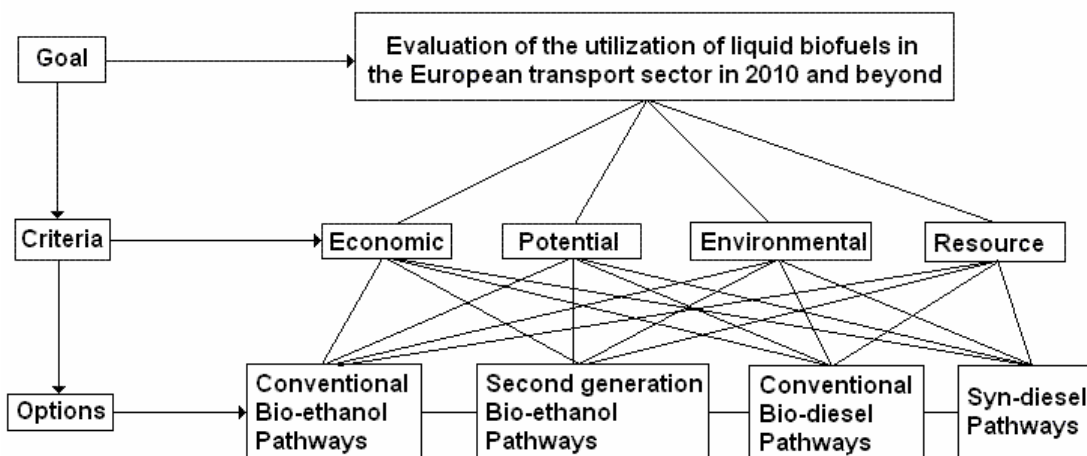
Figure 1. Evaluation structure

A sensitivity analysis was carried out by changing the priority of the criteria weights and led to useful results. It was established that the best bio-fuel pathways using EU domestic sources include bio-ethanol produced from wheat straw, syn-diesel produced from waste wood via black liquor and bio-ethanol produced from wheat with process heat supplied from a natural gas fired turbine with a CHP scheme.

It should be mentioned that in real life, the development of the most attractive bio-fuel pathways, apart from policy measures, will result due to the cost competitiveness of the primary biomass resources delivered to the processing plants. Thus, in the case of conventional bio-fuels the development of the most attractive specific pathway will depend upon the competitiveness of the agricultural crop for bio-fuel and food use, while in the case of second generation bio-fuels, the use of lignocellulosic biomass has to be compared between bio-fuel use and CHP or other uses.

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Biofuels: Myths and Reality

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1. Summary

This presentation highlights the problems and opportunities in ethanol production from renewable resources. Typically ethanol from lignocellulosic biomass can be made either through "thermo-chemical" or "enzymatic" route. This presentation will focus on "enzymatic route." Ethanol from corn or grains is a well-established technology, though advances have been made in new generation enzymes, and high yielding yeasts. Process automation and optimization is still lacking typical chemical industries. There is room for productivity improvement. Lignocellulosic ethanol production has remained mainly in the domain of research over the last twenty five years. Currently, only one ethanol plant from lignocellulosic biomass is in production in North America. Though many companies have established fast track commercialization plans. The bottlenecks are in pretreatment, high solids saccharification and fermentation, designing appropriate enzyme systems, developing microbial strains, which can tolerate harsh environmental conditions and can metabolize both pentose and hexose. Effective utilization of byproducts and minimization of water usage may be important issues for community acceptance and commercialization of these processes. This talk highlights some of the technical barriers and progresses made in our labs in different research labs in the world.

2. Extended Abstract

One of the bottlenecks in the production of bio-fuels using the biochemical platform is the recalcitrance of the cell wall of the lignocellulosic biomass (Himmel *et al.,Science,* **315**, 804**,** 2007). A key step in this process is the enzymatic hydrolysis. As cellulose –cellulase reaction is heterogeneous, there is a limitation on the activity of the cellulase enzyme on this insoluble substrate. Cellulose is an unbranched polymer containing cellobiose as the repeating unit. Cellulose in nature is organized into micro fibrils where these chains are oriented and arranged in parallel arrays. The top and bottom of the cellulose chains contain the hydrophobic faces which allow the internal hydrogen bonding in the chains. The sides of the cellulose chains are free to form hydrogen bonds with water. Even though, a number of hydrogen bonds are formed with water, this structure is highly insoluble in water. Enzymatic depolymerization of this insoluble cellulose involves the action of cellulases in the

removal of the glucose chains from the surface of the crystal structure. In the past, molecular simulation studies on the cellulose-water described the solvent structuring around the cellulose and the free monosaccharide molecules (Brady, *J. Am. Chem Soc*., **111,** 5155, 1988). This study revealed that the solvent structure extends up to two or three solvation layers away from the solute. This kind of solvent structuring affects the rate of the diffusion and slows down the hydrolysis process. Research on the monomer simulations were carried for the last two decades. It is understood from the literature, that the glucose molecule exhibits considerable flexibility to undergo a variety of conformational fluctuations and transitions in vacuum as well as in water. The gauche trans (GT) conformation changes to trans gauche (TG) conformation which allows intra molecular hydrogen bonding (Brady, 1988). A recent report on molecular dynamic simulations on small micro crystallites of cellulose in aqueous solution characterized the behavior of these crystals, and the solvent structures both inside the crystal and at the interfaces (Matthews, *et al. Carbohydrate Research,* **341** 138, 2005). They have concluded that these hydration layers act as the main barriers for the free diffusion of the enzyme onto the substrate. Process of moving cellulose chain from the surface of the cellulose crystal into the binding cleft of the enzyme is highly favourable, energetically. The energy drop was determined to be nearly 80 kcal/mol. These simulations did not account for the presence of water molecules (Skopec *et al.,Protein Engineering*, 16 1005,2003). Free energy changes are helpful in understanding the types of binding between the molecules. Umbrella sampling calculations which give the free energy changes were performed on a sample enzyme-substrate system (Glucose and Benzene). The potential of mean force (pmf) for the binding of glucose and benzene in aqueous solutions was shown to have an oscillatory profile where the peak positions corresponded to the water layers.

The present work in cellulose degradation deals with the fundamental studies to investigate the "non-reaction" factors, which affect the enzymatic hydrolysis. Some of the non-reaction factors include: interfacial area; diffusion of enzyme, substrate and product; and adsorption of enzyme onto non-cellulosic components. The sensitivity analysis performed on kinetic parameters derived from our previous experiments on enzymatic hydrolysis of crystalline and non-crystalline celluloses showed the effect of different compositions of the enzymes on the maximum glucose yield (Peri *et al., Biotechnol. Prog*., **23**, 626, 2007). As the available enzyme compositions are almost at optimal condition, there is a need to understand the behaviour of the substrate – enzyme – water systems. Some results are elucidated in the presentation.

Session T3-10: Innovative Process Equipment-Operation Design

Abstract Number	Paper Title & Authors	Included
1475	Gas dispersion in highly viscous liquids using a SMX static mixer T Lang, J Hepperle, M Piesche	Yes
2019	Liquid-liquid mass transfer in square micro-channels N Di Miceli, L Prat, P Cogneta	Yes
3019	Homogeneous particle suspension in an agitated reactor: A comparison between the pitched blade turbine and the Maxblend Impeller K Takenaka, R Yatomi, S Morinaga, P A Tanguyb	Yes

Gas dispersion in highly viscous liquids using a SMX static mixer

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1. Summary

In the presented study, SMX static mixers were used to disperse gas into highly viscous liquids. Because the investigated gases show a noticeable solubility in the liquid phase, the break-up of the bubbles is associated with the absorption of the gas into the liquid. The effects of the operating conditions such as energy input and gas phase mass fraction as well as the length of the mixers and the rheology of the liquid phase were investigated. The results are presented in terms of the bubble size distribution and the mass fraction of the gas dissolved in the liquid.

Keywords: Gas dispersion, mass transfer, laminar flow, static mixer, dynamic mixer

2. Extended Abstract

The dispersion of gas into liquids is a common unit operation in the chemical industry. However, in cases where the liquids have a high viscosity, e.g. the processing of foods like dairy products or the production of foams made from polymers, gas dispersion is a difficult mixing task due to the high viscosity ratio of the continuous and dispersed phase and the small diffusion coefficients of the gas dissolved in the liquid. The SMX mixer is a suitable device for this difficult mixing task due to its internal structure, which consists of crossed blades resulting in a uniform energy dissipation and a flow field with extensional components favorable for bubble break-up.

In the presented study, SMX static mixers were used to disperse gas into highly viscous liquids. The flow was kept laminar in all experiments. Different silicone oils with varying viscosities and a polymer melt were used as the liquid phase, helium and nitrogen as the gas phase. Because the two gases show a noticeable solubility in the liquid phase, the break-up of the bubbles is associated with the absorption of the gas into the liquid.

The results are presented in terms of the bubble size distribution and the mass fraction of the gas dissolved in the liquid. The measurement of the bubble size distribution was based on photographs of the bubbly flow that were taken through a transparent section after the static mixer. The mass fraction of gas in the liquid phase was determined by a mass balance of the gas.

Using an average difference $?w_m$ of the gas mass fraction before and after mixing, the mass transfer coefficient $k_L a$ can be calculated as

$$k_L a = \frac{\dot{M}_{abs}}{V ?_c ?w_m}$$

with the mass flux $\dot{M}_{abs}$ of the absorbed gas, the density $?_c$ of the continuous phase and the volume V of the static mixer. In Figure 1 the mass transfer coefficients for the absorption of helium and nitrogen in a silicon oil (Baysilone® M 10000) are shown as a function of the volumetric power input P/V for a constant pressure p_2 after the static mixer. The length and diameter of the static mixer are constant. Despite the different solubilities of helium and nitrogen in the silicon oil, the mass transfer coefficients in Figure 1 can be represented by a single curve with

$$k_L a \sim \left(P/V \right)^{0,45}.$$

The mass transfer coefficients for the SMX static mixer range atop of those of agitated vessels with various impellers found in the literature (Henzler, 1998; Himmelsbach, 1985), which are given by the hatched area. Compared to these dynamic mixers, the energy input into the static mixer is transformed more efficiently into liquid phase mixing and the growth of the interfacial area due to bubble break-up.
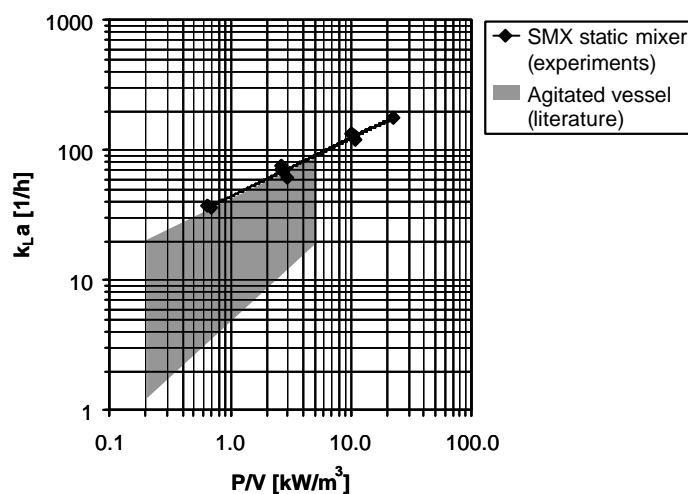
Figure 1: Mass transfer coefficients $k_L a$ as a function of the volumetric power input P/V.

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Liquid-liquid mass transfer in square microchannels

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1. Summary

Microreactors are of great interest to carry out extraction processes since they offer high exchange area. Furthermore, the containment imposed to droplets increases significantly the velocity gradient inside the droplet. This leads to an enhancement of mass transfer between two phases compared to common device (macro scale). This work focuses on acetone transfer from toluene to water. A square microchannel of 100 µm is used so as to obtain a better understanding of the transfer process at such scale. Slug flow is generated in a T-shape junction. The first results show that more than 80% of the extraction can be achieved in roughly 0.5 seconds. Moreover, it seems that the mass transfer coefficient is not strongly dependent with the droplets velocity for the operating conditions studied (from 0.015 to 0.030 m/s).

Keywords: mass transfer, microchannel, slug flow

2. Extended Abstract

Mass transfer is a key phenomenon in many chemical engineering operations such as extractions or two-phase reactions. Its prediction is therefore fundamental to design two-phase units. Numerous models have been proposed to explain the transfer of a solute across liquid-liquid interfaces at a macro scale [Kessler et al. (1999)]. The more common model is the boundary layer theory since it allows the estimation of the mass transfer coefficient using empirical correlations that depend on the hydrodynamic of the system. However, microfluidic hydrodynamic is too complex to use this model.

Mass transfer is studied according to the slug flow characteristics in view of determining a model to estimate the mass transfer coefficient in micro scale. The two phases considered are water and toluene. The solute is acetone and is initially introduced in the toluene. The micro-device used is made of silicium and glass. Square microchannels of 100 µm are engraved in the silicium part by photolithography. Then the two parts are stuck together by anodic bonding. Droplets of toluene are generated in a T-shape junction.

The microreactor is made of one main channel in which the mass transfer proceeds, and a secondary microchannel for the partial and selective extraction of the continuous phase [Prat et al. (2006)]. The water enriched in acetone coming from the secondary channel is analysed thanks to a UV probe connected to a UV-Vis spectrophotometer. The peak absorbance value, measured between 265 nm and 300 nm, is directly related to the acetone concentration through Beer-Lambert's law.

Experiments show that mass transfer is very fast since more than 80% of the extraction can occur in roughly 0.5 seconds. This is particularly due to the high interfacial area offers by the slug flow in microchannels (around 12000 m^2/m^3) which is approximately ten times higher than in common device. An experimental global mass transfer coefficient k_L is estimated using Equation 1, where a represents the interfacial area, t_r the residence time, C^* the equilibrium concentration, C_{in} and C_{out} the inlet and outlet concentrations in acetone. "d" stands for the dispersed phase.

$$k_L a = \frac{1}{t_r} \ln\left(\frac{C_d^* - \overline{C_{d,out}}}{C_d^* - \overline{C_{d,in}}}\right)$$

Equation 1

The first results show that the mass transfer coefficient is not strongly affected by the change of velocity in the studied domain of droplets velocity (from 0.015 to 0.030 m/s). Vandu et al. model mass transfer in circular microchannel for gas-liquid system as the result of two contributions: from the caps at both ends of the bubble, and from the liquid film surrounding the bubble [Vandu et al. (2005)]. In the considered case, assuming that the film thickness is such that it is quickly saturated, the mass transfer coefficient can be written in terms of Equation 2, with C a constant, D the diffusion coefficient of acetone, U_d the droplets velocity, d_c the characteristic diameter of the channel and L_{UC} the unit cell length. The experiments were carried out for a constant dispersed phase flow rate while the continuous phase flow rate was increased: therefore, both U_d and L_{UC} increased in the experiments which may explain the weak influence of the velocity on the mass transfer coefficient.

$$k_L a = k_{L,cap} a_{cap} + k_{L,film} a_{film} \approx k_{L,cap} a_{cap} = C\sqrt{\frac{DU_d}{d_c L_{UC}^2}}$$

Equation 2

In conclusion, this work confirms that microreactors are highly effective in terms of mass transfer since they can generate high interfacial area between two immiscible fluids. Droplets velocity in the studied range does not seem to influence mainly the mass transfer coefficient, but it of course affects the yield of the extraction since it plays a key role on the residence time.

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Homogeneous Particle Suspension in an Agitated Reactor: a Comparison between the Pitched Blade Turbine and the Maxblend Impeller

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1. Summary

Particle suspension is used in many polymerization and fine chemical synthesis applications. The quest for higher productivity makes that the concentration in solids and the particle size trend to an increase, which creates difficulties to maintain homogeneous suspension. In this work, the performance of two impeller technologies has been characterized and compared in terms of their ability to ensure good suspension for a wide variety of operating conditions. The effect of the vessel size has also been studied in the context of process scale-up.

Keywords: Impeller configuration, suspension polymerization, high concentration of solid, homogeneous suspension

2. Extended Abstract

Mixing at high solid concentration is fairly common in processing engineering. In order to improve productivity, chemical industries tend to increase the particle concentration and the particle size in their processes. Under those conditions, as highlighted by previous investigators (Kraume 1992, Hicks et al. 1997, Bittorf et al. 2003), a clear layer may form at the liquid surface above the cloud suspension layer separated by a sharp interface, resulting in extremely long mixing times. The presence of this interface yields loss of productivity due to fouling, product adhesion and insufficient property of the end product. An essential characteristic of the reactor to avoid adhesion on the wall and the generation of by-products is to have a homogeneous suspension.

The general objective of this presentation is to show the effect of particle size, concentration, and tank size on suspension and give hints for reactor selection and operating conditions.

In this work, the performance of two types of mixers, namely a traditional pitched turbine and the Maxblend impeller is compared for glass beads suspension (75-1200micron, ~50wt%) at high particle concentration, in two vessels having diameters of 0.31m and 0.60m.

The pitched blade turbine is the classical choice for particle suspension. It is an open impeller with a relatively small surface area and it is usually operated with a large bottom clearance. The Maxblend impeller is a relatively new technology. It consists of a flat impeller based on a combination of a large paddle and an upper grid installed close to the vessel bottom. The suspension behaviour induced by each impeller is different due to the effect of the bottom clearance and the flow patterns generated by the impeller/bottom and impeller/wall interactions.

In the presentation, the suspension mechanisms will be discussed for both types of impeller. The mixing time with and without clear liquid layer above the suspension layer will also be analyzed. It will be shown that the mixing time increases drastically in the presence of a clear liquid layer, as compared to the situation without a clear layer for which the mixing time value is very similar to that obtained with a pure liquid. Finally, the influence of the tank size will be explored.

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Session T3-P: Theme-3 Poster Session

1. Session T3-P: Nanotechnology & Nanomanufacturing (T3-1P)

Abstract Number	Paper Title & Authors	Included
108	DNA nanobiosensor based on silicon chip A M Karbassian, B M Vosuoghi	Yes
291	Preparation of nanoparticles using a membrane contactor: influence of process parameters C Charcosset, H Fessi	Yes
1448	Application of magnetic nanostructures in biotechnological processes: Biodiesel production using lipase immobilized on magnetic carriers K J Dussán, O H Giraldo, C A Cardona	Yes
2691	Assembly and electric double-layer capacitive behavior of three-dimensional carbon nanocluster electrodes C-T Hsieh, K-S Lin	No
2698	Attachment of nickel nanoparticles on carbon nanotube electrodes for enhancement of electrochemical capacitance C-T Hsieh, K-S Lin	No
2781	Micro- and submicrocrystalline structure of cooper: processing and low temperature mehanical behaviour V V Pustovalov, Y Estrin, L S Fomenko, V S Fomenko, N V Isaev, M Janecek, S V Lubenets, S V Malyhin, A T Pugachov, E N Reshetnyak, S E Shumilin, R Hellmig	Yes
3364	Stabilization of enzymes by surrounding them with thin, porous polymer layer I Hegedüs, E Nagya	Yes
3649	Environmentally Friendly Pathways for Synthesis of Titanium Dioxide Nano-particles S Sunol, H Li, A Sunol	Yes

2. Session T3-P: Controlled Release of the Active Ingredient: Mechanisms, Devices & Analysis (T3-2P)

Abstract Number	Paper Title & Authors	Included
693	Solid lipid nanoparticles for controlled release prepared using a membrane contactor C Charcosset, A A El-Harati, H Fessi	Yes

2111	Production of particle powder for inhalation process and controlled release of drugs K Kula, T Ciach, K W Szewczyk	Yes
2419	Protein-based drugs encapsulation in biodegradable microparticles by co-axial electrospray J Xie, W J Ng, L Y Lee, C-H Wang	Yes
2535	Modeling the pharmacokinetics of Extended Release pharmaceutical systems G Lamberti, M Di Muria, G Titomanlio	Yes
3197	Modified sulfur coating of urea with polymers addition in spouted bed M Nasrollahzadeh, N Ashrafizadeh	No

3. Session T3-P: Analysis of Energy-Environmental Issues (T3-3P)

Abstract Number	Paper Title & Authors	Included
996	A kinetic study of gaseous potassium capture by coal minerals in a high temperature fixed bed reactor Y Zheng, P A Jensen, A D Jensen	Yes
1219	Hidden issues when installing heat pumps into buildings with existing heating systems C-G Berg, N-C Berg	Yes
1951	Evaluation of Gum Formation in Automotive Gasoline Under the Action of Multiple Metals (Fe, Ni and Cu) Using Factorial Planning L S de Carvalhoa, L S G Teixeiraa, R V Lopeza, A S Novaesa, E G dos Santosa, P R B Guimarãesa	Yes
2133	Application of carbon molecular sieve membranes in a mixed hydrogen-natural gas distribution network J A Lie, D Grainger, M-B Hägg	Yes

4. Session T3-P: CFD & Multiscale Modelling in Chemical Engineering (T3-4P)

Abstract Number	Paper Title & Authors	Included
494	Dynamic neural network model and parameter estimator for hydrochloric acid recovery process P Thitiyasooka, P Kittisupakorna, W Daosuda	Yes
519	Characterization of flow pattern in a rotor stator mixer A Pacek, M Baker, A T Utomoa	Yes
662	Effect of the yield stress on the characteristics of the laminar flow of a Bingham fluid in a circular pipe maintained at uniform temperature A K Boutra, N Labsi, Y K Benkahla	Yes
855	Simulation of entrained air separation from paper	See T2-5P

	machine circulation water using CFD A Laari, A Haapala, T Stoor, I Turunen	
862	Prediction of bubble size and interfacial area in bubble column CFD simulations through solution of population balance equations M R Kamali, A Laari, Z Sha, I Turunen	See T2-5P
662	Effect of the yield stress on the characteristics of the laminar flow of a Bingham fluid in a circular pipe maintained at uniform temperature A K Boutra, N Labsi, Y K Benkahla	Yes
1158	Enhancing the RIM process with pulsation technology: CFD study E Erkoça, R J Santosa, M M Dias, J C B Lopesa	Yes
3214	Simulation of a bubble column reactor using CFD approach. Application: ferrous biooxidation S M Mousavia, A Jafari, S Yaghmaei, M Vossoughi, I Turunen	No
1613	Computer-Aided multiscale product-centric process modelling R Morales-Rodríguez, R Gani	Yes
2045	Seeking the optimum solution for the design of a typical PHE A G Kanaris, S V Paras	Yes
2459	CFD Simulation of Methane Steam Reforming Furnace M Molaei, M T Sadeghi	Yes
3104	Model of the partial oxidation of methane to methanol in a gas-solid-solid reactor C G Dallos, V Kafarov	Yes
3565	CFD simulation of heat transfer in ferrofluids A Jafari, T Tynjälä, S M Mousavi, P Sarkomaa	No

DNA Nanobiosensor Based on Silicon Chip

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1. Summary

The electrochemical properties of DNA immobilized to Au Nanoparticle deposited onto suitable surfaces have been analyzed to detect hybridization processes of specific DNA sequences as possible alternatives to fluorescent labeling methods. In this project we support the preparation of gold nanoparticles directly deposited onto the surface of silicon (Si) substrate by a physical methodology, consisting in the thermal evaporation of a thin Au film and its successive annealing. In the next step self-assembly of thiolated DNA, as well as the DNA hybridization have been sensed by the redox signals of base residues in DNA immobilized at the surface of gold nanoparticles. We show that the changes of electrochemical signals before and after DNA functionalization and subsequent hybridization of Au nanoparticles immobilized onto Si substrate can be exploited to fabricate specific nanobiosensors devices in solid phase.

2. Extended Abstract

The immobilization of DNA on solid supports is a crucial step for any application in the field of DNA microarrays. It determines the efficacy of the hybridization and detection signals. For the best result in the immobilization of DNA, Au nanoparticles heavily functionalized with oligonucleotides have been used.[1,2] Most widely used methods for synthesizing Au nanoparticles are based on solution chemical reactions, yielding nanoparticle colloids.[3,4] Despite of more advantages, in this field physical methods are less considered. In the field of detection, electrochemical DNA biosensors have proved to be excellent tools for investigating the effects of various endogenous and exogenous sources of hazard on the genomic material [5, 6, and 11]. Most electrochemical DNA biosensors are based on the determination of purine oxidation peaks, principally the guanine peak, to monitor the degree of oxidative damage caused to DNA [7–8]. This is due to the fact that guanine has the lowest oxidation potential of all DNA bases [9, 10] and that its principal oxidation product, 8-oxo-7,8-dihydroguanine (8-oxoGua),1 is considered a useful biomarker of DNA damage by oxidative stress [11–12] and can be easily quantified by voltammetry [13,14]. This paper reports on the preparation of Au nanoparticles directly onto the surface of silicon (Si) substrate by a physical methodology, consisting of the thermal evaporation of a thin Au film and its successive annealing. The method guarantees the preparation of monomodal Au nanoparticles with Atomic Force Microscopy (AFM) pictures. In next steps, hybridization of DNA to the Au nanoparticles immobilized onto the silicon surface as well as the electrochemical detection of

DNA will be considered. We show that the changes of CV diagram before and after functionalization and subsequent hybridization of Au nanoparticles immobilized onto Si substrate can be exploited to fabricate specific biosensor in solid phase.

Figure1- plan view AFM micrograph of a 4nm thin Au film on Si before annealing
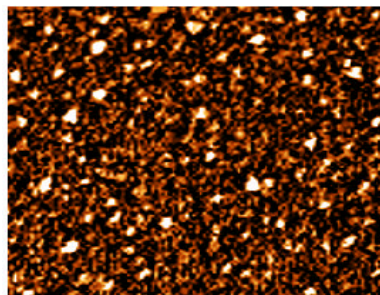
Figure2- plan view AFM micrograph of a 4nm thin Au film on Si after annealing
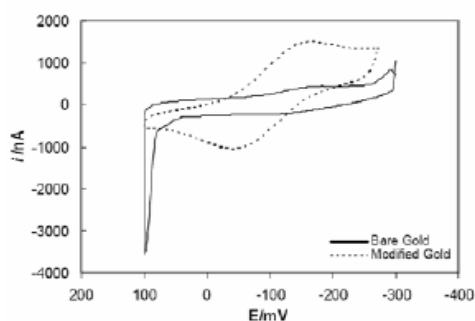
Figure3- Cyclic Voltammogram for bare Au nanoparticle & DNA functionalized Au nanoparticle
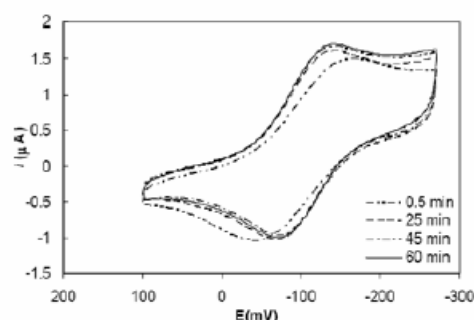
Figure4- Cyclic Voltammogram of Different incubation time of Ru(Hex)$^{+3}$

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Preparation of nanoparticles using a membrane contactor: influence of process parameters

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1. Summary

Nanoparticles have known recently an increasing interest because of their potential use as drug carriers. In this paper, we describe a membrane contactor for the preparation of nanoparticles. The organic phase is pressed through the membrane pores via the filtrate side. The aqueous phase circulates inside the membrane module, and sweeps away the nanoparticles forming at the pore outlets. Two methods for the formation of nanoparticles are investigated: the nanoprecipitation and the interfacial polymerization methods. The influence of process parameters (membrane pore size, flowrate and organic phase pressure) on the organic phase flux and on the nanoparticles size is investigated. It is shown that nanoparticles as small as 260 nm are obtained with the 1000 daltons nanofiltration membrane, a transmembrane pressure of 3 bar and a crossflow rate of 1.7 m.s^{-1}. Very high fluxes are obtained with the 0.1 μm pore size microfiltration membrane (1.6 m^3/h.m^2), leading to the preparation of 1.8 10^{-3} m^3 nanoparticles, with an average diameter of 360 nm, in 4 min. The advantages of this membrane contactor compared to other processes for nanoparticles preparation are its scale-up ability, and the possibility to control nanoparticles size by an appropriate choice of the membrane.

Keywords: Membrane reactor, Membrane contactor, Nanospheres, Nanocapsules, Nanoparticles.

2. Extended Abstract

Colloidal delivery systems such as oil-in-water emulsions, liposomes, microparticles and nanoparticles, show great potential as a means of delivering a drug to its site of action efficiently, thereby minimizing any unwanted toxic effects. Among these colloidal systems, nanoparticles (nanospheres and nanocapsules) are ranging in size from about 10 to 1000 nm [Allémann et al., 1993]. Nanoparticles have been investigated for the entrapment of a wide variety of drugs, for applications ranging from ophthalmic delivery to carriers in chemotherapy. The present study investigates the preparation of nanoparticles with a membrane contactor to allow large scale

production of nanoparticles. The principle is the following [Charcosset and Fessi, 2005a, 2005b]. The organic phase (Phase **A**) is pressed through the membrane pores allowing the formation of small droplets. The reaction occurs between the droplets of the organic phase and the aqueous phase (Phase **B**) flowing tangentially to the membrane surface. Two methods of nanoparticles preparation are investigated: the nanoprecipitation (dispersion of preformed polymers) and the interfacial polymerization methods (polymerization of dispersed monomers).

Lumen side

Tangential flow of Phase **A**

Nanoparticles

Membrane

Shell side

Phase **B**
permeation under applied pressure
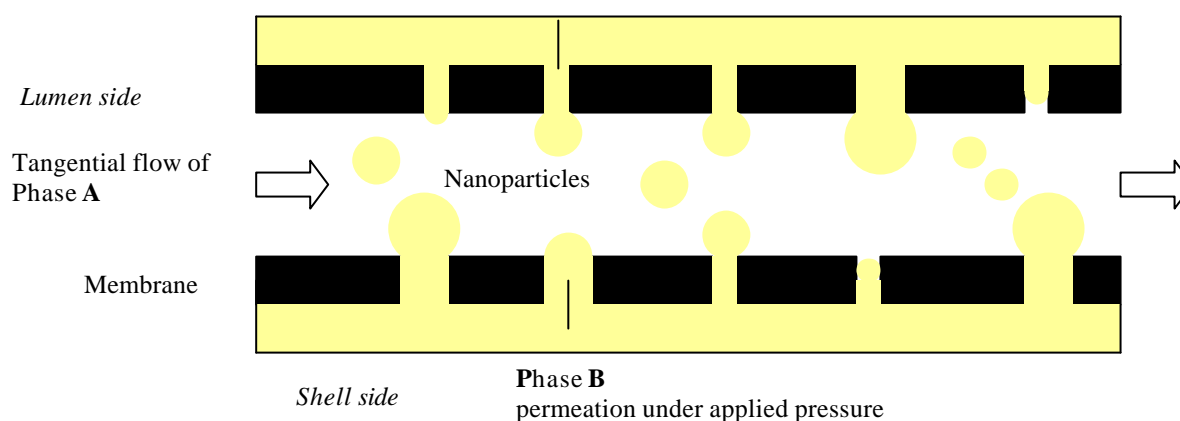
Figure 1: Schematic principle of the membrane contactor process.

The influence of process parameters (membrane pore size, flowrate and organic phase pressure) on the organic phase flux and on nanoparticles size is investigated for the nanoprecipitation method and the interfacial polymerization method. Very high fluxes are obtained with the 0.1 µm pore size microfiltration membrane (1.6 $m^3/h.m^2$), leading to the preparation of 1.8 10^{-3} m^3 nanoparticles, with an average diameter of 360 nm, in 4 min.

The main advantage of this membrane contactor is the high flux obtained with microfiltration membranes, making possible scaling-up for industrial applications. Other advantages are its versatility for the preparation of either nanocapsules or nanospheres, by methods involving a polymerization of dispersed monomers or a dispersion of preformed polymers, and the control of the average nanoparticles size by an appropriate choice of the membrane.

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Charcosset, C. and Fessi, H., (2005b) « Novel method for preparing particles whereof at least the peripheral surface is polymeric, using a membrane reactor » Patent N° PCTFR2005003144, N° WO 2006/067307.

Application of magnetic nanostructures in biotechnological processes: Biodiesel production using lipase immobilized on magnetic carriers

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1. Summary

The lipase-catalyzed synthesis of alkyl esters from palm oil using *Candida Rugosa* lipase immobilized on a magnetic particle was investigated. The effects of the alcohol concentration and the amount of enzyme used were studied. The lipase immobilized on a magnetic particle was easily recovered and could be reused. Therefore, the magnetic particle of immobilized *Candida Rugosa* lipase is potentially useful for the production of biodiesel.

Keywords: Biodiesel, reaction-extraction process, magnetic nanostructure, lipase.

2. Extended Abstract

Magnetic nanostructures have gained a remarkable interest in the last years both for basic research and applied studies. The use of magnetic nanostructures has been applied in biochemistry, biomedicine, and waste treatment among other fields (Tartaj *et al.*, 2005; Korecká *et al.*, 2005). This broad range of applications is based on the fact that magnetic particles have very large magnetic momentum, which allow them to be transported and driven by external magnetic fields.

The magnetic nanostructures have also a great potential in biotechnological processes taking into account that they can be utilized as a carrier for enzymes during different biocatalytic transformations. In this way, the biocatalyst can be easily manipulated by a controlled magnetic field allowing it to be located permanently in the zone where the maximum concentration of reagents is present.

The research for efficient methods of immobilizing lipases also has emerged as an important field of interest. Recently, we used a modification of the method purposed by Zeng *et al.*, 2006 for enzymes immobilization on magnetic particles using a cross-linked reagent. In this work, according to this method, for the preparation of magnetic

carriers, a mixture of FeCl₂ and FeCl₃ aqueous solution was added to a flask that containing stearic acid. Then the mixture was stirred vigorously for a while, and NaOH aqueous solution was dropped into the flask. A black precipitate was obtained. The precipitate was filtrated, washed and dried. For the preparation of composite magnetic carrier, certain amount of Fe_3O_4 (particle magnetic) was suspended in distilled water. A mixture of [3-(2-aminoethylamino)propyl]trimethoxysilane, methanol and NaF aqueous solution was stirring for 24 hours. Then tetraethyl orthosilicate was dropped slowly into the flask and stirred vigorously at room temperature. The precipitate was collected, washed and dried. For the immobilization of the enzyme, glutaraldehyde was added to certain amount of particles, and stirred at room temperature. Then, certain amount of lipase *Candida Rugosa* was added to phosphate buffer solution and stirred until all the lipase was dissolved. To this solution was added the solution prepared previously, and stirred for several minutes at room temperature. The immobilized lipase was separated by centrifugation and washed with phosphate buffer and dried. The figure 1 showed the FTIR spectra of these particles. This immobilization technique was applied only to lipases, which enhanced their esterification activity and improved their stability and reusability. This system composed of an immobilized lipase on a magnetic nanostructure for biodiesel production is analyzed. Finally, this technology can offer innovative configurations allowing the intensification of enzymatic processes and the reduction of their costs.
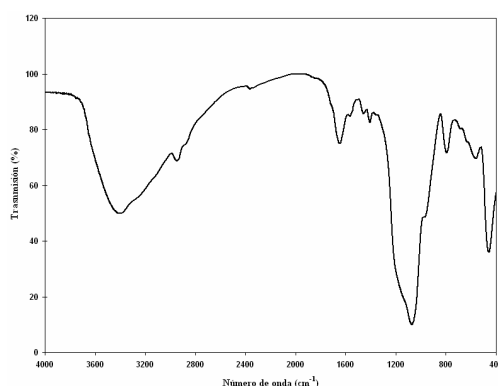
Figure 1. FTIR spectra of the lipase immobilized on magnetic particles

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Micro- and submicrocrystalline structure of cooper: processing and low temperature mechanical behaviour

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1. Summary

A study of the mechanical properties of microcrystalline (MC) and submicrocrystalline (SMC) Cu specimens with different microstructures produced by severe plastic deformation with subsequent natural ageing was carried out at low to extremely low homologous temperatures.

Keywords: cooper, structure, low temperature plasticity

2. Extended Abstract

TEM and X-ray analysis were used to study the microstructure of commercially available copper with purity of 99.95% that underwent severe plastic deformation by ECAP for grain refinement. From the grain structure viewpoint, samples may be divided into three groups covering a range of states from SMC to coarse-grained (CG).

Tensile tests were performed at four temperatures: 0.5, 4.2, 77 and 295 K and microhardness measurements were carried out in the temperature range of 77– 295 K. It was shown that the yield stress obeys a Hall– Petch relation, although adjustments of the data points to match the literature data were needed for room temperature deformation. Further analysis of microstructure details and their effect on the mechanical behaviour is desirable, however. In particular, a more precise determination of the volume fraction of different constituents of the structure needs to be made.

The following features of the plastic flow of polycrystalline copper under tensile deformation were uncovered: a) a significant increase of tensile ductility with decreasing temperature; b) an enhanced grain size dependence of the yield stress at

cryogenic temperatures, as manifested in the values of the Hall–Petch coefficient; c) a low-temperature anomaly of the temperature dependence of the yield stress at cryogenic temperatures, which becomes more pronounced with grain refinement; d) discontinuous plastic flow at 4.2 and 0.5 K, the stress drop amplitude increasing with decreasing grain size.

Microhardness measurements revealed strong inhomogeneity of the microstructure of all specimens investigated. This observation suggests that strength and ductility of the ultrafine-grained Cu studied are not determined by a single characteristic structure element.

The temperature dependence of the microhardness increases with decreasing grain size. A low-temperature plateau in the dependence, $H_V(T)$, was found for some specimens. A conversion of microhardness values to yield strength on the basis of a common relation using a coeffcient of 3 is possible only for the SMC and nanocrystalline (NC) states.

This study has demonstrated that – apart from enhanced discontinuous plastic flow – severe plastic deformation does not have any detrimental effect on the mechanical properties of copper at cryogenic temperatures, and it does improve its strength in accordance with the Hall-Petch law without compromising ductility.

Stabilization of enzymes by surrounding them with thin, porous polymer layer

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1. Summary

By covering each enzyme molecules with porous, very thin, a few nanometer thick polymer layer, thus, separating them from its microenvironment could essentially improve the enzyme stability. Following the preparation method recommended by Kim et al. [1] using alpha-chymotrypsin as enzyme, the activity change of the modified and the native enzymes could significantly differ from each other as a function of time and temperature.

Keywords: stability of enzyme, single enzyme nanoparticles, biocatalyst activity.

2. Extended Abstract

Single enzyme nanoparticles (SENs) represent a new approach in industrial and medical enzyme research [1-3]. The form of SEN means, that each enzyme molecule is surrounded with a nanometer scale polymer matrix layer, resulting in stabilization of enzyme activity without any serious limitation for the substrate transfer from solution to the active site. The synthesis of SEN particles is available via more or less simple laboratorial technique. We would like to apply this technique for industrial enzymes in order to improve the biomass utilization. Our prepared enzymes surrounded by polymer network can be more stable under extreme conditions.
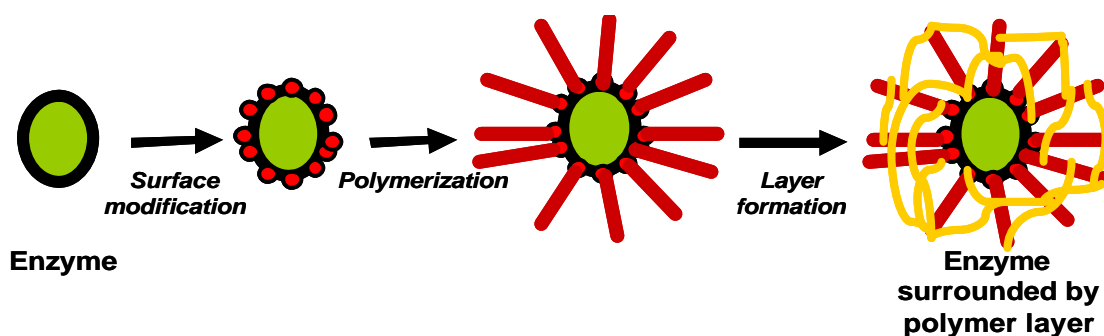
Figure 1. a) Synthesis steps and of single enzyme nanoparticles.

The synthesis of SEN chymotrypsin (SEN-CT) consists of three-step process (Figure 1). Few parts of the synthesis have been changed for available application under our laboratorial conditions. The first step is the enzyme modification on the surface. Terminal primer amino groups on the surface of the enzyme have been modified with microliter amount of acryloyl chloride at zero temperature. Vinyl group polymerization reaction at room temperature in hexane phase between methacryloxypropyltrimethoxysilane and acryloylated chymotrypsin was initiated by UV light (365 nm) in the presence of the free radical initiator 2,2'-azobis-(2,4-dimethylvaleronitrile). The polymerization starts from the surfaces of the enzyme molecules. It leads to single enzyme molecules with short linear polymers that are covalently bound to the enzyme surface (see Figure 1). The two-phase system was vortexed and shaken at 22 °C and 300 rpm for 5 min. The buffer phase was removed and filtered by the syringe filter unit (with pore size 0.1 µm), and produced a transparent solution that turned into a turbid solution within 10–30 min. The extracted buffer solution, containing modified CT enzymes, was aged in the refrigerator. The pendant trimethoxysilyl groups are hydrolyzed and condensed to each other, yielding a cross-linked composite network around each separate enzyme molecule.
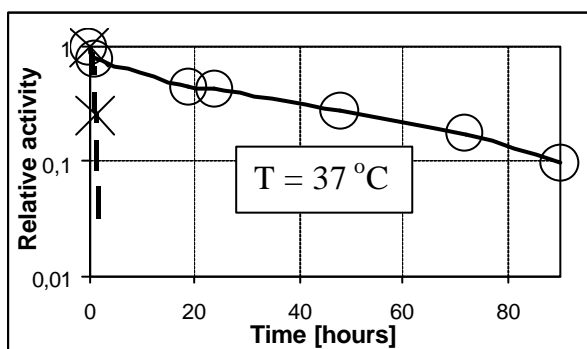
Figure 2. The stability of SEN (O) and native (X) CT at 27 °C and 250 rpm.

The activity of SEN chymotrypsin was detected by the method of Garrel and Cuchillo witch means the measurement of UV-absorbance of modified substrate of chymotrypsin enzyme as a function of time. The activity of the SEN enzyme was measured to be between about 50-70 percent of the natural chymotrypsin. The stability of natural CT enzymes was compared with the SEN enzyme samples in aqueous buffer (10 mM phosphate, pH = 7.8) by the measurement of the residual activity of both (natural and SEN) enzyme samples as a function of time during incubation at 37 °C and shaking (250 rpm). It was founded that SEN chymotrypsin molecules are really more stable - about one or two order of magnitude - than natural ones even if under most extreme conditions (37 °C, 250 rpm, Figure 2).

The investigations are extended for other types of enzymes for example lipase and esterase and the stability of SEN enzymes in other conditions of pH, ion strange and temperature. In the other side the biocompatibility of SEN enzymes in biological systems required more investigations.

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Environmentally Friendly Pathways for Synthesis of Titanium Dioxide Nano-particles

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1. Summary

Titanium dioxide nano-particles were synthesized via the sol-gel method using titanium butoxide as the precursor. Acid catalyzed and aged gels were dried under air to produce xerogels and under supercritical conditions to produce aerogels. Obtained porous nano-particles were characterized using X-ray diffraction, SEM and BET analysis. Aerogel powder was found to have more favorable properties compared to xerogel powder. Aerogel particles were more porous with more profound anatase crystal structure.

Keywords: supercritical carbon dioxide, aerogel, nanostructures, sol-gel, titanium dioxide

2. Extended Abstract

Titanium dioxide is the most widely used photo-catalyst. It is preferred due to its non-toxicity, availability and relatively high activity. The catalytic properties of titanium dioxide that dictate its activity as photo-catalyst are its surface area, pore size, particle size, and crystallographic structure.

In heterogeneous catalysis, reaction takes place at the active surface of the solid catalyst. For effective use of the catalyst, the solid catalyst needs to provide high active area. Sol-gel process ensures production of high surface area gels. Also, pore size and its distribution are critical in effective use of the solid catalysts. Large pores may be essential for some applications. In other cases, smaller pores may be more desirable because they provide higher surface area. Sol-gel process also provides narrow distribution of pore size. However, during drying of the gel, pores shrink due to capillary action and as a result, pore size of the larger pores decreases and smaller pores collapse resulting also in loss of surface area. In order to prevent the destruction in the pore structure during drying, the solvent can be removed from the wet gel under supercritical conditions.

Aerogels are prepared through sol-gel process followed by supercritical drying. Supercritical drying eliminates capillary forces exerted on the walls of the pores and results in highly porous materials. Consequently, aerogel catalysts have desired properties of catalysts such as high surface area. Altough sol-gel derived titanium dioxide is amorphous, when calcined at relatively low temperatures, it can be transformed into the desired crystalline form.

Titanium dioxide particles were synthesized through sol-gel process. They were dried under air or supercritical conditions to produce xerogel and aerogel samples respectively. Preparation of the titanium dioxide particles is summarized in Figure 1. After drying they were calcined, xerogel and aerogel samples were characterized in order to compare their porous and crystallographic structures.
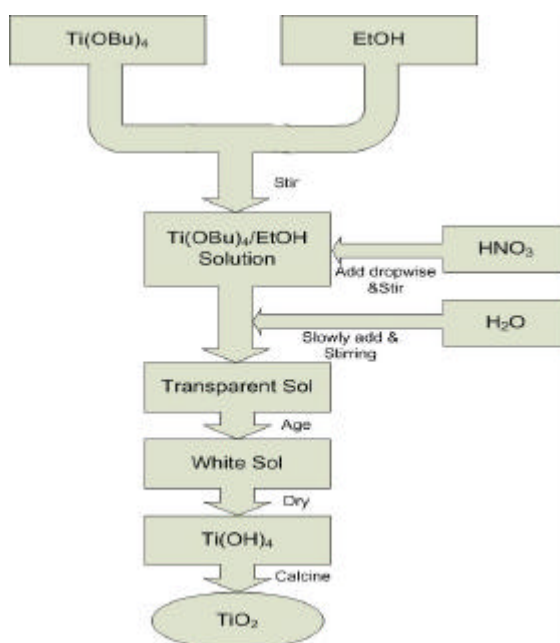
Figure 1: Preparation of titanium dioxide

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Solid lipid nanoparticles for controlled release prepared using a membrane contactor

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1. Summary

Solid lipid nanoparticles (SLN) were introduced in the 90's as an alternative to microemulsions, polymeric nanoparticles and liposomes. SLN are reported to have several advantages, i.e. their biocompatibility, and their controlled and targeted drug release. In this paper, we present a new process for the preparation of SLN using a membrane contactor to allow large scale production. The lipid phase is pressed, at a temperature above the melting point of the lipid, through the membrane pores allowing the formation of small droplets. The lipid droplets are then detached from the membrane pores by the aqueous phase flowing tangentially to the membrane surface. SLN are formed by the following cooling of the preparation below the lipid melting point. The influence of the aqueous phase and lipid phase formulations on the lipid phase flux and on the SLN size are studied. It is shown that SLN are obtained with a lipid phase flux between 0.21 and 0.27 $m^3/h.m^2$, SLN size between 175 and 260 nm. The advantages of this new process are demonstrated to be its facility of use and its scaling-up ability.

Keywords: Membrane, Membrane reactor, Membrane contactor, Nanoparticles, Solid lipid nanoparticles.

2. Extended Abstract

Solid lipid nanoparticles (SLN) were introduced at the beginning of the 1990s, as an alternative to solid nanoparticles, emulsions and liposomes in cosmetic and pharmaceutical preparations [Mehnert and Mäder, K. 2001]. The SLN were realised by exchanging the liquid lipid (oil) of the emulsions by a solid lipid, which means lipids being solid at room temperature but also at body temperature. The present study investigates a new process for the preparation of SLN using a membrane contactor, to allow large scale production [Charcosset et al. 2005, Charcosset and Fessi, 2006]. The lipid phase is pressed, at a temperature above the melting point of the lipid, through the membrane pores allowing the formation of small droplets. The aqueous phase

circulates inside the membrane module, and sweeps away the droplets forming at the pore outlets. SLN are formed by the following cooling of the preparation to room temperature.

The influence of process parameters (aqueous phase and lipid phase temperatures, aqueous phase cross-flow velocity and lipid phase pressure, membrane pore size) on the SLN size and on the lipid phase flux is investigated. It is shown that the membrane contactor allows the preparation of SLN with a lipid phase flux between 0.15 and 0.35 m^3/h.m^2, and a mean SLN size between 70 and 215 nm.

Tangential flow of the aqueous phase

SLN

Membrane

Lipid phase
permeation under applied pressure
(Temperature > lipid melting point temperature)
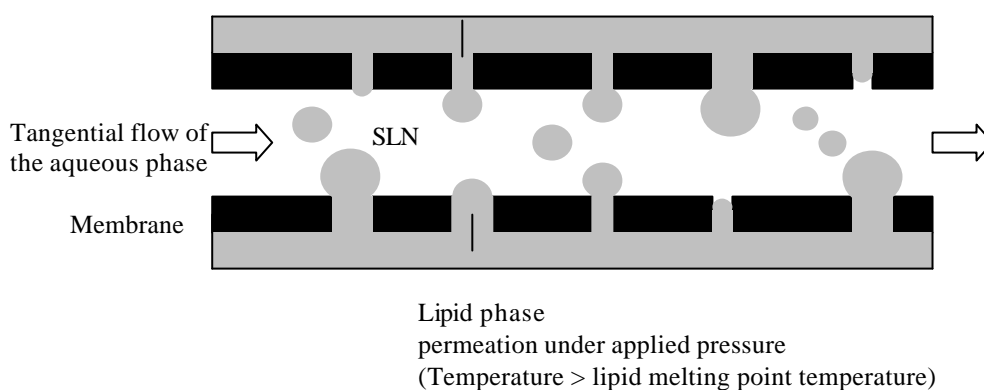
Figure 1: Principle of the membrane contactor for the preparation of solid lipid nanoparticles

As an example, vitamin E loaded SLN are prepared with the membrane contactor, and a 0.2 μm Kerasep membrane (Orelis, France). The lipid phase contained 300 g lipid and 3 g vitamin E at 65°C, and the aqueous phase 1.2 l water and 2.04 g Tween 20 at 60°C. The preparation is successfully obtained with a mean lipid flux equal to 0.26 $m^3.h^{-1}.m^{-2}$ and leads to the preparation of SLN with a mean diameter of 175 nm. The drug loading capacity was calculated as the amount of vitamin E present in the SLN divided by the total amount of vitamin E in the preparation. The drug loading capacity was found equal to 100 %. This high drug loading capacity is explained by the oily nature of vitamin E.

The advantages of this new process for the preparation of SLN are shown to be its facility of use, the control of the SLN size by an appropriate choice of process parameters and its scaling-up abilities.

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Production of particle powder for inhalation process and controlled release of drugs

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1. Summary

Particle powder for controlled release has been produced of drugs through atomization processes – EHDA and spray drying. Polymer and paracetamol solutions in organic solvents have been used. The influence of solvent type, polymer additives on particle morphology, as well as drug release rate have been investigated.

Keywords: EHDA, spray drying, controlled release, paracetamol, polycaprolactone

2. Extended Abstract

A controlled delivery and release of drugs has recently become an intensively developing field of pharmaceutical activity. The advantages of using controlled delivery systems can include the maintenance of drug levels within a desired range, the concentration monitoring, the accidental effects decrease, and optimal use of the drug. The inclusion of therapeutic active molecules in polymer-based microparticulate delivery systems is one of the methods to protect and transport the medication to the exactly right place

Two atomization processes have been used to produce particle powders used for controlled release of drugs – electro hydro dynamic atomization (EHDA) and spray drying process (SDP). Both methods allow to produce small monodisperse particles of complex, porous or hollow structures. Polymer and paracetamol solutions in organic solvents have been sprayed and obtained particles have been collected.

In electrostatic atomization atomized liquid was supplied to a nozzle connected to the high voltage power supply, whereas in case of spray drying the power supply was replaced by the high pressure supply. In both methods the particles could be dried also by hot air. The obtained particles have been collected in a different way, on a smooth plate connected to the opposite voltage power supply or in a cyclone, respectively (Fig. 1).

Paracetamol (Acetaminophen) was used as an active agent. This is an easily accessible drug with analgesic and antipyretic properties. It was purchased from Fluka. Polymer – polycaprolacton, medical grade 20kDa, was a gift from Solvay. Solvents applied in the experimental work were purchased from POCH distributor. They were of analytical grade. All the chemical substances were used without further purification or other processing. In the experiments different mass fraction solutions of paracetamol and polymer/paracetamol mix in organic solvents were used.
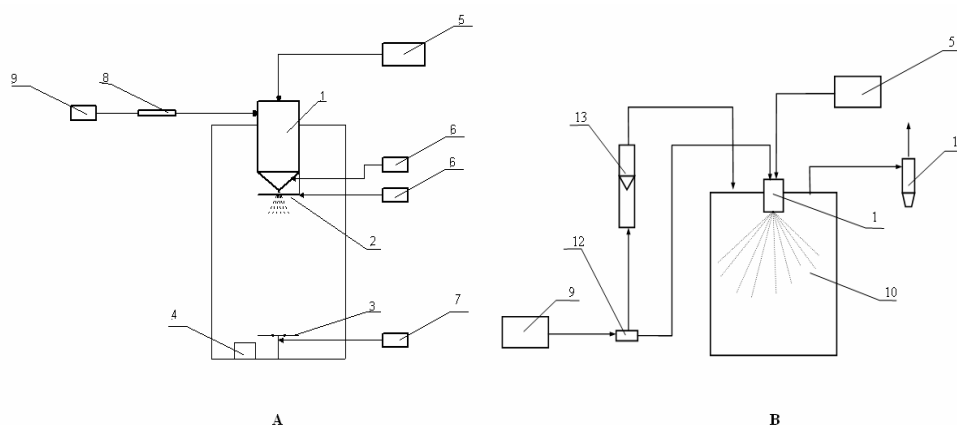
Fig. 1. A scheme of set – up: a – EHDA; b – SPD.

1 – a nozzle, 2 – a stabilizing ring, 3 – grounded collecting plate with a scrapper a discharge electrode, 4 – collecting box, 5 – a syringe pump 6 – high voltage (+) power supplier, 7 – high voltage (-) power supplier, 8 – an air heater, 9 – an air supplier, 10 – a drying chamber, 11 – cyclone, 12 - T -connection, 13 – rotameter.

The size and morphology of collected particles were analyzed using electron microscopes. A drug release rate was analyzed as well. The particles from 3% and 7% paracetamol solutions in organic solvents, as well from polycaprolacton with paracetamol solutions, have been collected. The structure of obtained particles was different. If the paracetamol solution has been sprayed, the particles were porous and consisted of nanocrystals of paracetamol on the particles surface. If polymer with a drug were dissolved, the particles obtained from such solution were solid. EHDA gives a narrow distribution of a particle diameter, whereas SDP gives more wide. Both methods give particles of diameter below 10 µm. The drug release rate from the particles is shown in Fig. 2 The constant rate of paracetamol release from produced particles has been observed. The addition of polymer results in deceleration of release rate.
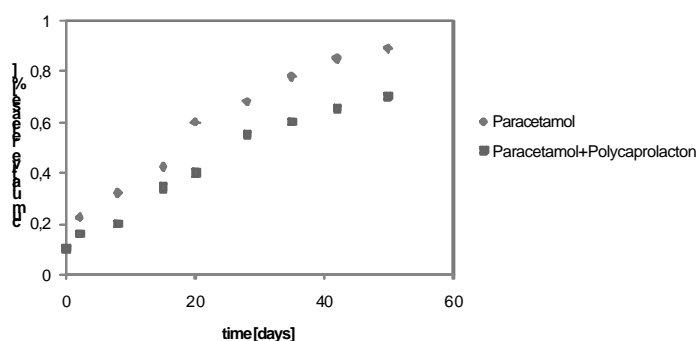
Fig. 2. Drug release from the particles.

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Protein-based drugs encapsulation in biodegradable microparticles by co-axial electrospray

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1. Summary

A co-axial electrospray process was developed to encapsulate protein-based drugs in biodegradable polymeric microparticles eliminating the key problem faced by other conventional methods of protein encapsulation – the primary emulsion being a major cause for protein denaturation and aggregation. Bovine serum albumin (BSA) and lysozyme were chosen as model protein drugs for this study. Scanning electron microscopy observation of the morphology of particles showed spherical microparticles of several microns could be achieved. The in vitro release profiles measured using Micro BCA assay suggested that sustained release of proteins could be attained for more than 30 days. The results of circular dichroism suggest that the secondary structure of released BSA can be retained. The bioactivity of released lysozyme was found to be more than 90% which is higher than the values reported from most of literatures. Therefore, co-axial electrospray could be a very promising approach to encapsulate biomacromolecules such as proteins, enzymes, DNA plasmids or living cells inside microparticles for the controlled release drug delivery applications.

2. Extended Abstract

Microparticle fabrication

A schematic of the basic experimental setup is shown in Figure 1(a). In the co-axial electrospray, an aqueous protein solution was introduced in the core needle and the organic solution containing the polymer was introduced in the annulus flow. To set up an electric field for electrospray, a high voltage generator was connected to the core needle, with the help of a crocodile clip. The applied voltage difference would be varied depending on the type of formulations and flow rates used to achieve a stable Taylor cone-jet mode as shown in Figure 1 (b) during the coaxial electrospray to control the monodispersity of the particles fabricated. Representative particle morphology was shown in Figure 1 (c). The particle size for formulation A and B are 10.0±1.5μm and 8.0±1.2μm which can be tailored by adjusting operating parameters and physical properties of solutions (Xie et al., 2006).

Drug loading and in vitro release

Drug loadings for the formulation A and B were 0.28% and 0.50%, respectively. The drug loading could be increased by increasing inner protein aqueous solution flow rate or

increasing inner protein concentration. In vitro release profiles for formulations A and B shown in Figure 1(d) suggested that BSA release profiles could be tailored under different fabrication conditions. The release profiles indicated typical protein bi-phased release characteristics and an initial burst release followed by a slow release was observed. The sustained release can last more than 30 days with low initial burst.
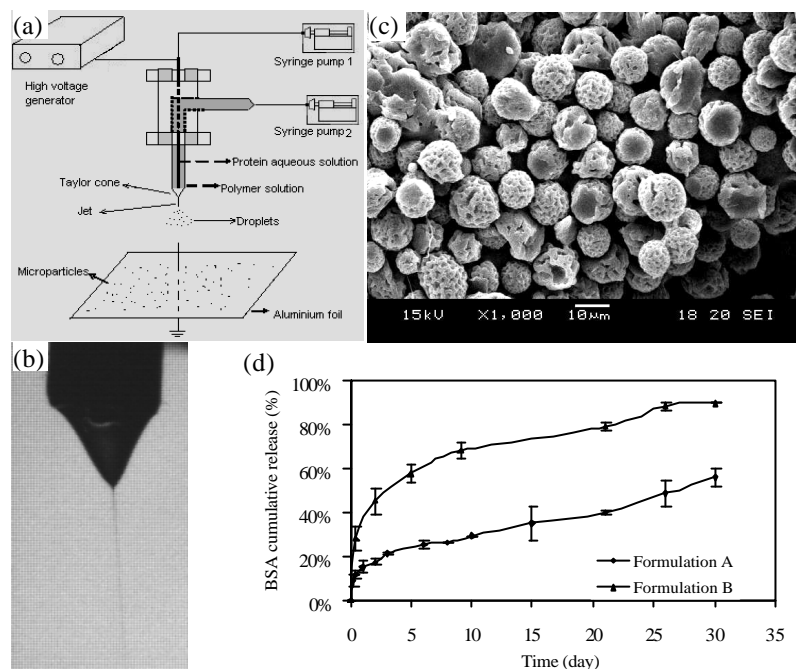
Figure 1. (a): Schematic of the co-axial electrospray apparatus for microencapsulation.; (b): Taylor cone-jet mode; (c): SEM images of BSA-loaded PLGA microparticles (formulation A); (d): BSA in vitro release profiles of formulations A and B.

Lysozyme bioactivity test

The lysozyme bioactivity test showed that using co-axial electrospray to encapsulate lysozyme in PLGA microparticles, around 94.6% of the bioactivity of lysozyme after in vitro release was maintained, which is higher than most of the values reported (Kang et al., 2002; Weert et al., 2000).

We have demonstrated that BSA and lysozyme were successfully encapsulated in biodegradable microparticles using co-axial electrospray. This approach could be very promising to encapsulate biomacromolecules such as proteins, enzymes, DNA plasmids or even living cells inside polymeric microparticles.

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Modeling the pharmacokinetics of Extended Release pharmaceutical systems

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1. Summary

In this work a conventional method to model the drug hematic concentration after a pharmaceutical system oral administration was improved by adding the ability of modeling the lag time typical of the extended release formulations.
The improved model was applied to describe cases, taken from literature, for which both the In Vitro (% of drug release versus time, in a vessel) and the In Vivo (concentration of drug in blood versus time, in humans) data are available.
Proposed approach is really simple and requires the availability of a limited set of data (at least one couple of In Vitro and In Vivo data). Therefore, it can be of aid for rational development, optimization, and evaluation of controlled-release dosage forms and manufacturing process.

Keywords: extended release pharmaceutical systems, pharmacokinetics, compartmental modeling

2. Extended Abstract

2.1. Introduction

Usually, the (human) body was modeled as a single or as a couple of compartments, i.e. one or two ensembles of blood and tissue more or less perfused (rich in blood) (Fournier, 1999). The transient mass balances within these compartments (which from a chemical engineers' point of view could be taken as reactors) constitute the model equations whose solution is the desired drug concentration profile in blood. However, the traditional approach is based on the full availability of the drug at the site of absorption at the same instant of the administration. For a number of systems this is a good approximation (fast release tablet, highly soluble drugs), but this is incorrect for several systems (extended release tablet, scarcely soluble drugs). Usually, the prediction of the drug concentration profile in blood, starting from the release kinetic data measured In Vitro, i.e. in laboratory, for system which exhibit a lag time, was performed by means of purely statistic tools (various level of IVIVC, In Vitro-In Vivo

Correlations, ranging from the worst, level C, to the best, level A), or on the basis of non-compartmental models which require cumbersome calculations.

2.2. Results and discussion

Here we propose a very simple model which relates the availability of the drug in the blood to the release kinetics as measured by In Vitro tests. The model accounts for the in-vitro kinetics by introducing in the drug balance equation an input term, time-dependent, which was proportional to the in-vitro kinetics.

The predictive nature of our innovative approach has been tested on the *in-vitro/in-vivo* data which are available from literature for several formulations of oral tablets containing Divalproex Sodium (an anticonvulsant, used also against epilepsy). Dutta et al. (2005) produced several tablets which, depending from hydroxy-propyl-methylcellulose content (HPMC, a hydrogel commonly used in extended release preparations), obtaining different release kinetics, ranging from very fast to very slow. For each formulation, they studied the *in-vitro* release kinetics (by standard USP dissolution apparatus) and the *in-vivo* plasma levels observed in a number of healthy volunteers (these experimental data are reported in Figure 1). Our model was tuned on the basis of the data for one formulation (medium release), and then it was proved to be predictive (the same of a Level A IVIVC, Prediction Error less than 10% in prediction of maximum plasma concentration and of total Area Under Curve) for the fast and the slow release formulations (Di Muria, 2006).
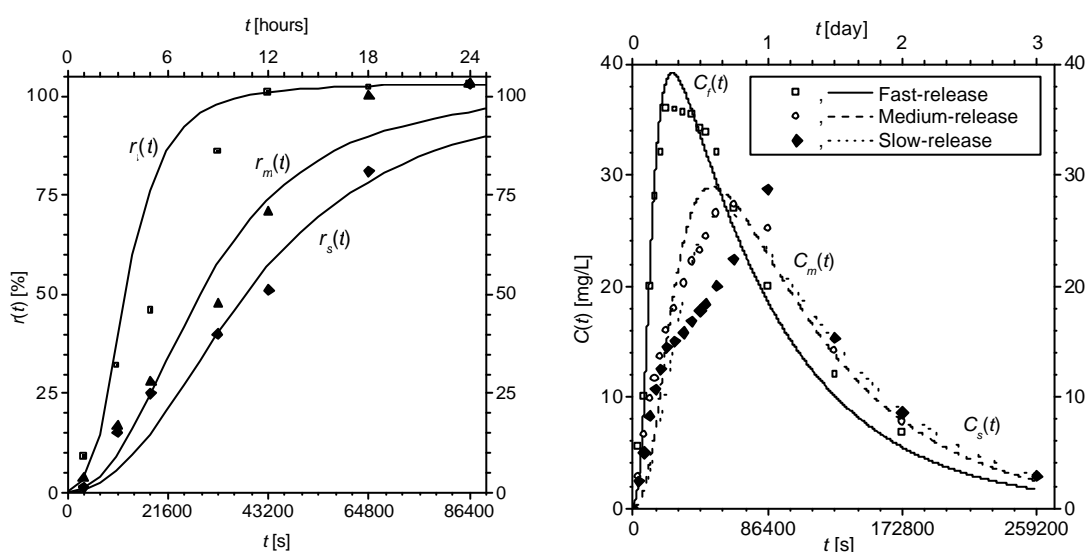
Fig. 1. (On the left) The *in-vitro* release kinetics of the three pharmaceutical systems (symbols: experimental data, curves: fitting). (On the right) The *in-vivo* pharmacokinetics of the three pharmaceutical systems (symbols: experimental data, curves: predictions of the model)

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A kinetic study of gaseous potassium capture by coal minerals in a high temperature fixed bed reactor

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1. Summary

The reactions between gaseous potassium compounds and coal minerals were investigated in a lab-scale high temperature fixed bed reactor under well-defined conditions. The applied coal minerals included kaolin, silica, alumina, bituminous, lignite coal ash and were formed into cylindrical pellets. Alumina pellets saturated with potassium salts were used as alkali source and the applied reaction temperatures were 900-1500°C. Experimental results show that capture of potassium by kaolin is independent of oxygen content in the gas and is a first-order reaction concerning bulk KCl concentration when excess water vapor is available. Metakaolin conversion decreases with increasing temperature in the range of 900-1300°C and increases again with further increasing temperature up to 1500°C. Metakaolin can be converted to mullite by high temperature treatment. The results show that no reaction of mullite with KCl was observed at temperatures below 1300°C indicating that formation of mullite may be an important deactivation mechanism of the kaolin pellet. A simple model was developed for the gas-solid reaction between potassium vapor and metakaolin pellet below 900°C assuming no deactivation of the pellet and that external mass transfer can be neglected

Keywords: potassium vapor capture, coal minerals, kinetics, co-firing, straw and coal

2. Extended Abstract

Co-firing of biomass and coal in suspension fired power plant boilers is an attractive option for utilizing a CO_2 neutral fuel and obtaining a high electrical efficiency. The high content of Cl and K in the straw fuel ash may lead to problems regarding fly ash utilization, deposit formation, corrosion and SCR catalyst deactivation. The interactions of the inherent coal ash and potassium from straw have a strong influence on ash deposits formation and corrosion, and fly ash quality. Therefore, it is important to get a better understanding of the interactions between the potassium vapour and coal minerals at temperatures relevant to pulverized fuel combustion.

Kaolin and COPRIB ash that have both significant amount of Si and Al show superior potassium capture characteristics compared to other coal minerals applied in this work. Potassium capture by different minerals as function of temperature is illustrated in figure 1. The initial decrease of the potassium capture by kaolin is probably attributed to the sintering of the kaolin pellet that could cause a gradual replacement of fast gas diffusion by slow condensed-state diffusion. At temperatures above 1300°C molten or molten-like phases will be formed inside the pellet, as a result the liquid diffusion will improve the transport properties. Furthermore the high rate constant at high temperatures can also explain the re-increase of the potassium capture.

SEM-EDX analyses were conducted to study the element distribution inside the exposed pellets and the pore structure evolution during heating and reaction. Significant amount of Cl was detected in alumina pellet exposed to 1000 ppmv KCl at 900°C indicating that capture of potassium by alumina at 900°C is partly through physical adsorption. Almost no Cl was detected in all the others samples. This implies that capture of potassium by coal minerals applied in this work except alumina is obtained mainly by chemical reaction. The observed potassium profiles inside the exposed pellets indicate that there is significant transport resistance inside the pellet. Mullite formation was observed by SEM image of kaolin fired at 1500°C (figure 2).

A Computer model that simulates the capture of potassium by kaolin at temperatures below 900°C was developed. The model considers diffusion and reaction of KCl(g) in the porous pellet, while the solid product is accumulated over time. The KCl concentration profile inside the pellet is solved numerically using the finite difference method. The model can reasonably predict the pellet conversion as function of potassium vapor pressure, exposure time and the distribution of captured potassium in the pellet. The model can be used to obtain a better understanding of the complex interactions between chemical reactions and mass transport phenomena for potassium vapor capture by coal minerals in a limited temperature range.
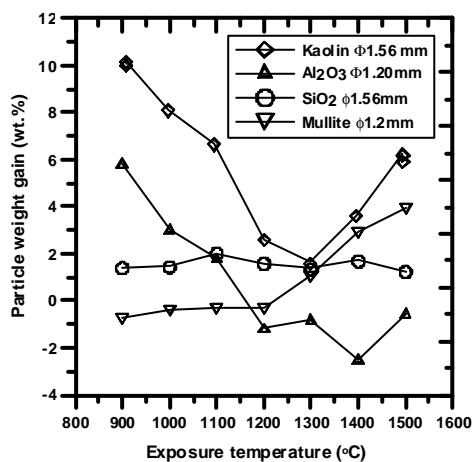
Figure 1. *Particle weight gain as function of temperature, exposed to 1000 ppmv KCl for 1 h.*
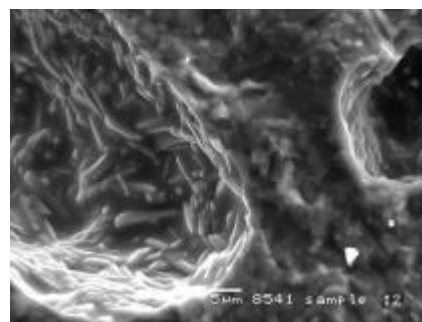
Figure 2. *SEM image of mullite pellet (kaolin heated at 1500°C for 12 h) exposed at 1300°C to 1000 ppmv KCl for 1 h.*

Hidden issues when installing heat pumps into buildings with existing heating systems

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1. Summary

Fluctuations in energy prices and new technology, raises new issues of how to renew heating systems in old buildings or how to build new ones. If electricity is the source of heat, novel heat pumps are easily motivated in most climates, as it is easy to convince consumers that total use of electricity may be cut by 50%. This has initiated market forces and heat pumps are today manufactured, sold and installed more than ever under lacking supervision. This in turn actualizes, once more, the question what is likely to happen when installing ad hoc heating or cooling (air conditioning) parallel to existing heating and ventilation systems? Are we as consumers actually without our knowledge, in a desperate need of more in detail knowledge/legislation to rule out unsuccessful installations? Can unsuccessful usage or installation cause new problems or even threat to our health! This is the issue that will be penetrated further in our extended abstract/poster where surprising problems of an ad hoc heat pump installation (air conditioning unit) is exposed and exemplified. The example shows that even small heat pumps may have a surprising effect on local changes of temperature and relative humidity. The effect of the heat pump installation, which has been used for both heating as cooling, is illustrated by color pictures showing findings of mildew stains, see figure 1. The article includes calculations on how to avoid mould or mildew stains, and factors that enforce conditions for local mould, mildew or fungi growth.

Keywords: electric heating, hygroscopic, moist air ventilation, mildew growth, cooling

2. Extended Abstract

Heating of buildings is big business and a vast field of individual solutions. For example may simple electric resistance heat be supplied by centralized forced-air furnaces or by heaters that are specific for each room. Room heaters can consist of baseboard, wall, space and radiant heaters. It is also possible to use thermal storage systems to avoid heating during times of peak power demand but ventilation is needed all around the clock to have fresh air. Ventilation increases the complexity of the issue, whilst ventilation affects the heat balance as well as partial mass balances of for example oxygen, carbon dioxide or partial pressure of water vapor and even dust particles. Traditional board heaters are usually installed underneath windows. There,

the heater's rising warm air counteracts with cool air falling from the cold window glass. Baseboard heaters are seldom located on interior walls because standard heating practice is to supply heat at the home's perimeter, where the greatest heat loss occurs. Board heaters should sit at least three-quarters of an inch (1.9 centimeters) above the floor or carpet. This is to allow the cooler air on the floor to flow under and through the radiator fins so that it can be heated. The heater should also fit tightly to the wall to prevent the warm air from convecting behind it and streaking the wall with dust particles (creating grey strikes). These detailed rules are the outcome of many decades of practical experience from heating of buildings.

We declare the following heat and mass balance for the mildew stain, in figure 1:

$$\underbrace{\boldsymbol{a}(t-t_{wb})dA}_{\substack{\text{heat by}\\\text{convection}}}+\underbrace{\boldsymbol{a}_R(T^4-T_{wb}^4)dA}_{\substack{\text{heat by}\\\text{radiation}}}+\underbrace{\boldsymbol{a}_C(t_C-t_{wb})dA}_{\substack{\text{heat by}\\\text{conduction}}}=(\boldsymbol{l}_f+C_vt-C_wt_{wb})d\dot{m}_v \tag{1}$$

Equation (1) needs an expression for the mass transfer that couples the heat and mass transfer and that is valid for both low as high humidity. In this work mass transfer is described with the Lewis equation referring to Berg et al [1]. Our calculations will show the critical factors that enforce conditions for local mildew growth [1, 2]. The effect of the heat pump installation, which has been used for both heating as cooling, is illustrated by color pictures showing findings of mildew stains, see figure 1 and 2.

Fig 1. Photo of the corner having mildew stains.   Fig 2. Same corner, no mildew under the baseboard!

Figures 1 and 2 make us wonder, if we as consumers just should continue to buy heat pumps, or are we in a need of more knowledge of the possible impact of ad hoc air conditioning and heating!
We believe that the results of this work will increase knowledge of how heat pumps have to be used or installed in old or new buildings. Increased knowledge and constructive criticism is needed to reduce the number of unsuccessful installations. Gained trust from successful installations, is clearly needed, to ensure that this mature and environmentally friendly technology, after decades of development, gets consumers full approval!

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Evaluation of Gum Formation in Automotive Gasoline Under the Action of Multiple Metals (Fe, Ni and Cu) Using Factorial Planning

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1. Summary

Gum formation in car engines causes serious problems to systems such as the fuel pump, fuel injection, and engine valves. A number of metals, such as iron, copper and nickel, may accelerate gum formation, and since these are usually found in fuel tanks, this research work is concerned with undertaking a thorough investigation on the influence of the simultaneous presence of these metals on gum formation.

Keywords: Gasoline, Gum, Metals, Factorial Planning.

2. Extended Abstract

Among the metals most commonly found in carbon steel fuel tanks are iron, copper and nickel. Some of these are particularly important when a high proportion of ethanol is added to conventional petrol, such as in Brazil, where commercial gasoline contains 20 to 25 %v/v of ethanol.

The experimental tests involved a factorial planning, of the 2^4 type with 05 experiments at the central point. The input variables under study were metal concentrations, 25, 150, 275, 400 and 525 µg/L, and storage time, 1, 31, 46 and 61 days. The response variable, gum content, has been determined through ASTM D381. A variance analysis (ANOVA) of the experimental results has been carried out and the results are shown in Table 1. It can be observed that the % explained variance is rather low, 73.59%, which can be attributed to experimental errors inherent to the gravimetric measures required by the experimental technique employed.

Table 1. Variance analysis (ANOVA) for the gum formation.

% of variance explained	73.59
Correlation Coefficient	0.85
F Test calculated	56.17
F tabulated at 95 % confidence	3.01
$F_{calculated} / F_{tabulated}$	18.66

A higher precision would require the use of a 5 digit precision scale, instead of the 4 digit scale used in this research work.

The F test has been used to investigate how well the 2^4 model describes the experimental results. The $F_{calculated}/F_{tabulated}$ ratio of 18.66 demonstrates that the proposed model describes very well a significant number of the experimental data, since a ratio above 3 means that the empirical model is highly predictive, in accordance with the findings of Barros Neto (1995).

Figure 1(a) shows that the interactions between iron and copper are highly favourable to gum formation. On the other hand, Figures 1(b) and 1(c) show that interactions of these metals with nickel are less favourable to gum formation. In both cases, however, as either iron or copper contents increase, so does gum formation. This demonstrates that iron and copper have, on their own, a marked influence on gum formation, let alone together.
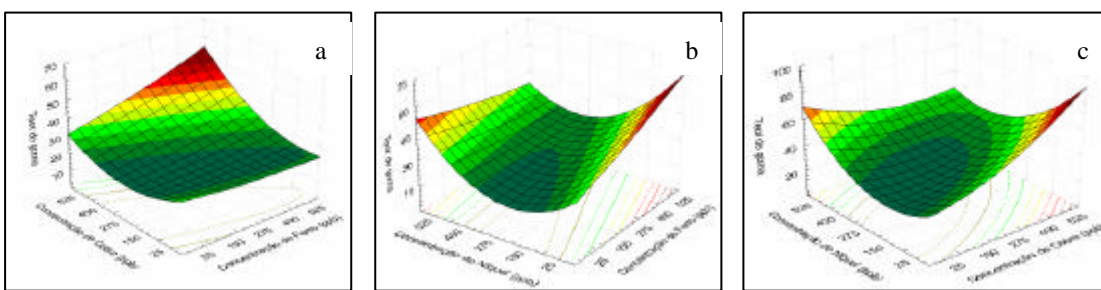
Figure 1. (a) Concentrations of Iron and Cooper; (b) Concentrations of Iron and Nickel; (c) Concentrations of Copper and Nickel.

The results obtained in this research work demonstrate that the presence of some metals, in particular iron and copper, in high concentrations, associated with long storage periods, are highly favourable to the catalytic oxidation of the olefins usually present in gasoline, thus resulting in gum formation. These results are in accordance with other data previously reported scientific literature, showing that both iron and copper individually favour intense catalytic activity, thus allowing for the oxidation reaction that will result in gum formation.

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Application of carbon molecular sieve membranes in a mixed hydrogen-natural gas distribution network

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1. Summary

Carbon membranes have been identified as a promising technology for separation of hydrogen from natural gas. These are produced by carbonization of cellulose in vacuum or in an inert gas atmosphere. Mixed gas tests show a hydrogen selectivity over methane greater than 1000 and a pressure-normalised flux greater than 0.2 m^3(STP)/m^2.bar.h. Carbon membranes may experience a loss of permeability when exposed to strongly adsorbing gases at ambient to moderate temperatures. Electrothermal treatment is presented as a possible solution to this aging issue. A procedure for making hollow carbon fibres is also presented.

Keywords: H_2, membranes, carbon, natural, gas

2. Extended Abstract

The transition to a full hydrogen distribution system may be a lengthy and costly exercise; hence a transitional approach using existing natural gas (NG) networks to transmit mixtures of hydrogen and NG is being investigated. NaturalHy, a 6th Framework Programme EU project, in which the NTNU is a participant, aims to test all critical components in a mixed network by adding hydrogen to existing natural gas networks.

Membranes have been identified as a promising technology for recovering hydrogen for end-use. One promising membrane material, under development at the Membrane Research Group (MEMFO) at NTNU, is the carbon molecular sieve. This is produced by the carbonisation of cellulose at temperatures of 550-750°C to produce a nanoporous carbon film, capable of discriminating between the smaller hydrogen molecules and the remaining molecules in a NG stream. The starting material, cellulose, is also cheap and abundant.

Carbon membranes at MEMFO are at the bench scale testing stage. Performance has been shown to depend on the temperature, pressure and composition of the feed. Mixed gas feed tests show that carbon membranes can achieve a hydrogen selectivity over methane greater than 1000 and a pressure-normalised flux greater than 0.2 m^3(STP)/m^2.bar.h.

An obstacle for a breakthrough of carbon membranes has been the loss of permeability when exposed to strongly adsorbing gases at ambient to moderate temperatures. This paper addresses a possible solution to this aging issue. When a low voltage direct current is applied to the metal doped carbon during a permeation test, the permeability increases instantaneously and remains stable. The relative permeability increase depends among other factors on the gas type and on the amount of current applied. Carbon membranes containing different metals will be compared with respect to the effect of electrothermal treatment. Possible explanations of the phenomenon will also be given. A great advantage of this regeneration technique is the on-stream operation, avoiding shutdown or switching to an extra set of membranes.

To be commercially attractive, the packing of the membrane inside a module has to be efficient. Hollow fibres provide a configuration with a packing density up to 30 000 m^2 membrane per m^3 module. A procedure for making such fibres from cellulosic materials will be presented.

Membranes placed at various end-user sites on the distribution network must cope with varying hydrogen concentrations in, and pressures of, the feed. However, process simulations show that 80% of the hydrogen can be recovered from the pipeline or a slipstream thereof at a purity greater than 90 vol%, in a single separation stage. The volume and footprint of these membranes would be small and they could conveniently be placed at commercial and residential sites.

Dynamic Neural Network Model and Parameter Estimator for Hydrochloric Acid Recovery Process

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1. Summary

This paper describes the development of neural network models and a parameter estimator of a hydrochloric acid recovery process, consisting of double fixed-bed ion exchange columns, which is used to remove Fe2+ and Fe3+ ions from pickling liquor of a pickling bath. Due to the complexity and highly nonlinearity of the process, the modeling of the process based on the first principle is rather difficult and involves many unknown parameters. Therefore, neural network modeling has been applied to model this system and estimate unknown/uncertain process parameters such as Biot and Peclet numbers based on process data sets gathered from a real hydrochloric acid recovery plant. Then, the first principle models of the process coupled with the estimates of the Biot and Peclet numbers are employed to carry out simulation study. The data generated from the simulation study are then verified with those of experimental study and are utilized to train and validate neural network models for the process. The simulation results have shown that the developed neural network models with one hidden layers provide sufficiently accurate prediction of the concentration profile of the process.

Keywords: Neural network modeling, Neural network parameter estimator, Pickling process, Hydrochloric acid recovery process, Ion exchange resin

2. Extended Abstract

Hydrochloric Acid Recovery System by Ion Exchange

The acid recovery system is applied to recover unreacted acid in the wastewater by separating free acid out of steel (Fe^{2+}/Fe^{3+}) ions. An adsorption fixed-bed consists of a vertical cylindrical pipe packed with an ion exchange resin (Fig 1). Macroscopic conservation equations of the column are complex and highly nonlinear.

Neural network parameter Estimator

Based on the MSE method, 4-6-1 and 4-4-1 structures appear the best to be applied respectively for the cation and anion resin column models. Fig. 2 and 3 show the

results of concentration profile prediction with the flow rate of 140 liters per hour of the pickling liquor in the cation column and that with the flow rate of 110 liters per hour in the anion column respectively. Hence, the obtained NN models give good prediction of Fe ion concentration compared with experimental data.
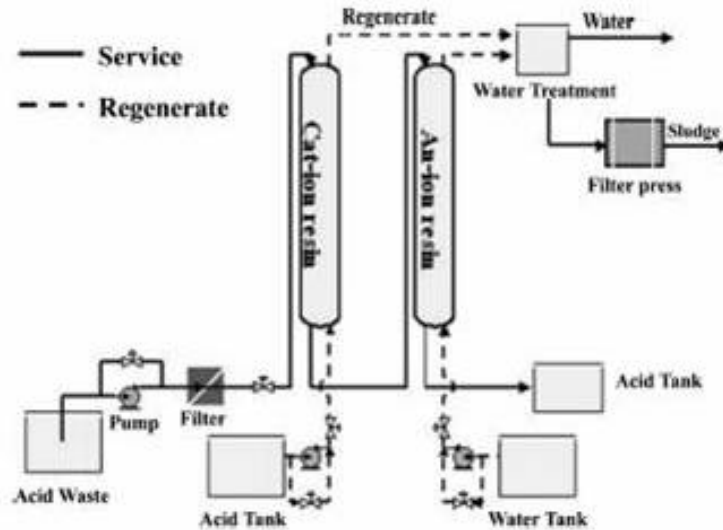
Fig. 1. Double fixed bed ion exchange resin column (Kittisupakorn, 2005)
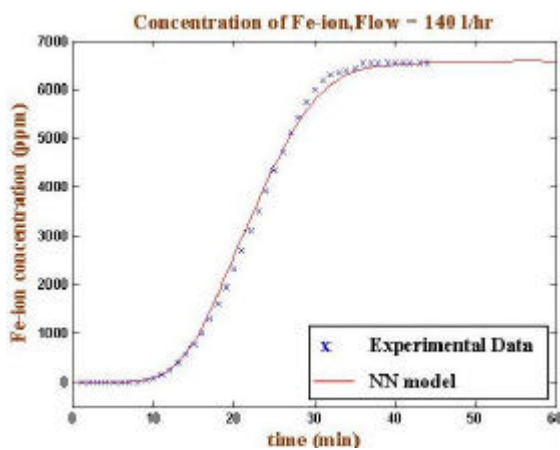
Fig. 2 Concentration profile of cation resin column
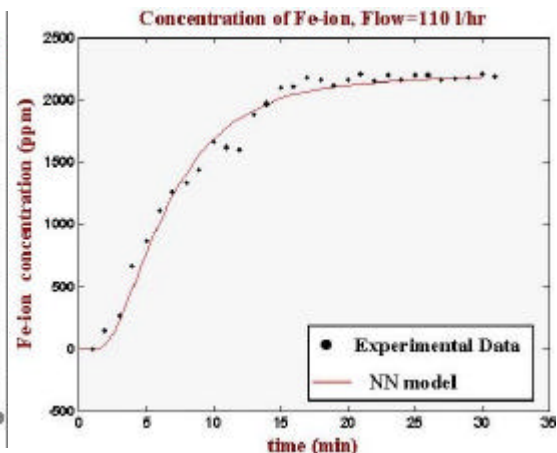
Fig. 3 Concentration profile of anion resin column

Conclusion

A hydrochloric acid recovery process is a complex and highly nonlinear system. Here, a neural network has been used to provide the prediction of Fe ions concentration profiles in the hydrochloric acid recovery process. It was observed that the obtained optimal structure neural networks can successfully predict the effluent concentration profile of Fe ions.

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Characterization of Flow Pattern in a Rotor Stator Mixer

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1. Summary

The flow in a rotor-stator high shear mixer (Silverson) at different rotor speeds have been simulated in Fluent using sliding mesh method with standard k-ε turbulence models and verified using LDA. The flow rate through the stator was directly proportional to rotor speed and the maximum energy dissipation rates occurred in the stagnation points at the edge of the stator holes. The agreement between measurements and simulation was generally very good, but the maximum velocity of the jets emerging from stator holes was underpredicted and the flow number calculated from numerical simulations were lower than flow number obtained from LDA measurements. The energy balance based on LDA measurements indicated that 70% of the energy is dissipated in close proximity to the mixer head whereas the k-ε model predicted that 50% of the energy is dissipated in the rotor swept volume, 5% in the gap between rotor and stator, 8% in the walls of the holes and 16% in the jets.

Keywords: rotor stator mixer, flow field, energy dissipation, CFD, LDA

2. Extended Abstract

In this work the velocity field around high shear rotor stator mixer (D=28.2 mm, gap width 0.175 mm) fitted with standard disintegrating head (6 holes of diameter 8 mm) placed in the centre of a cylindrical vessel (T =150 mm) was investigated. The liquid height was equal to the tank diameter and the clearance was half of liquid height. The working fluid was water and the rotor speed was varied from 2000 – 4000 rpm.

A CFD simulation was carried out in a full tank geometry which was divided into a stationary bulk region (meshed into 500,000 hybrid cells) and moving rotor stator region (meshed into approximately 400,000 cells). The gap between rotor and stator was meshed with 5 hexahedral cells. The simulation started using steady state multiple reference frames with standard k-ε model and continued with transient sliding mesh simulation with time step 1/30 of rotor speed. The transient simulation was carried out for 20 impeller revolutions.

The normalized (to the tip velocity) radial velocity distributions across the hole at three rotational velocities are shown in Figure 1 (a) which also illustrates the proportionality of radial velocity to the rotor speed as the normalized velocity falls into one line. The vector plot of radial/tangential velocity component clearly shows that the liquid is flowing into the rotor/stator assembly through the holes in the stator. The contours of normalized energy dissipation rate (with respect to N^3D^2) around the rotor/stator at 2000 and 4000 rpm are shown in Figure 2. The magnitude of energy dissipation per unit mass (ε) in the impeller swept volume is in the same order as that in the jets. The high ε in the regions close to the holes occurs due to the impingement of liquid on the stator and the sudden expansion.

(a)

(b)
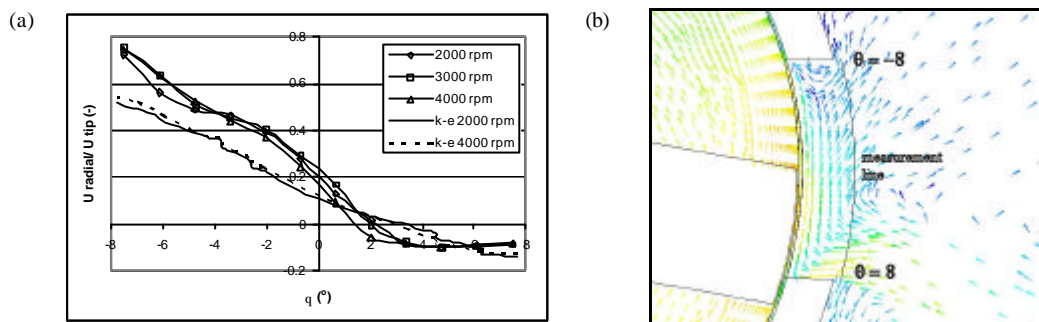
Figure 1 : (a) comparison of normalized radial velocity at the centre of the hole (positive direction is out of stator); (b) velocity vectors of the jet.
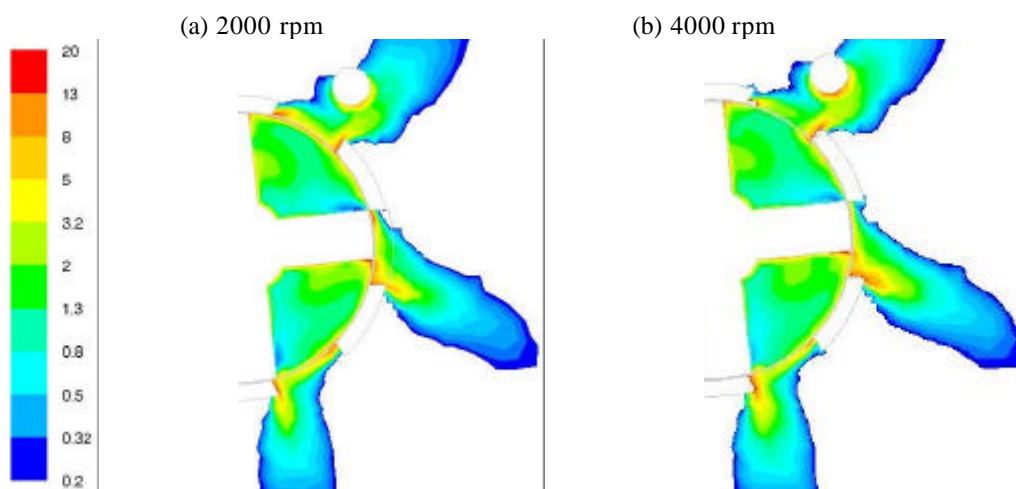
(a) 2000 rpm   (b) 4000 rpm

Figure 2 : Normalized contours of the energy dissipation rate (ε/N^3D^2) predicted by k-ε model at (a) 2000 rpm and (b) 4000 rpm.

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Effect of the yield stress on the characteristics of the laminar flow of a Bingham fluid in a circular pipe maintained at uniform temperature.

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1. Summary

The Bingham fluid is a viscoplastic medium characterized by a yield stress from which the fluid moves. This model describes the rheological behaviour of many materials (paints, drilling mud, etc.). The present study is directed towards the numerical analysis, by means of a finite volume method, of the influence exerted by the yield stress represented by the Bingham number on the velocity field as well as on the Nusselt number of a steady laminar flow in forced convection of an incompressible Bingham fluid in a circular pipe maintained at uniform temperature without variation in rheological and physical properties of the fluid. To be able to describe the behaviour of the fluid in the low shear region and to avoid numerical instabilities, a constitutive equation proposed by Papanastasiou was used. The comparison between the obtained results and those of Min et al. as well as those of Vradis et al. proves to be satisfactory.

Keywords: Bingham fluid, yield stress, forced convection, finite volume method

2. Extended Abstract

Many investigations were done in order to study the behaviour of the Bingham fluid such as those of Vradis et al. (1993) then Min et al. (1997), who studied numerically the problem of simultaneous development of hydrodynamic and thermal fields in the entrance region of a circular pipe for a laminar flow of a Bingham fluid. The governing equations are the usual ones, i.e. continuity, momentum and energy equations without taking viscous dissipation into account. The constitutive equation is that proposed by Papanastasiou:

$$\eta_{\text{eff}} = 1 + \frac{\text{Bn}}{\dot{\gamma}} \left[1 - \exp\left(-m\ \dot{\gamma} \right) \right]$$

Where η_{eff}, m, $\dot{\gamma}$ and Bn represent the effective viscosity, the exponential growth term, the shear rate and the Bingham number, respectively.

The computing program was validated by comparing the present numerical results with those obtained by Min et al. (1997). Figure 1 shows good agreements between these results since the maximum error does not exceed 3%.
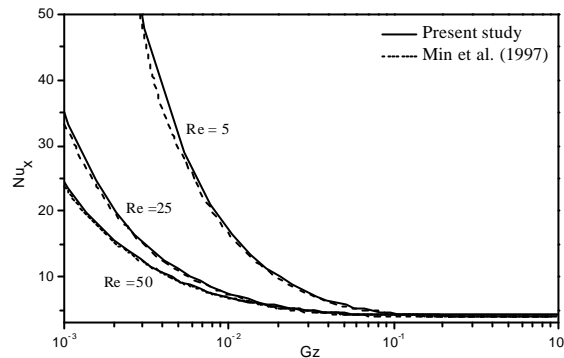
Figure 1. Validation of the computing program. Pr = 1, Bn = 1.99

The effect of the Bingham number on the evolution of the local Nusselt number, presented in figure 2, show an increase in the value of the Nusselt number for the higher value of Bingham number, located at the fully developed region. This can be explained by the fact that the wall velocity gradients are higher when the Bingham number is increased since the centreline velocity decrease when the Bingham number increase as it is shown in figure 3. In addition, increasing the Bingham number leads to short both hydrodynamic and thermal entrance lengths. These observations were also made by Min et al. (1997) and Vradis et al. (1993).
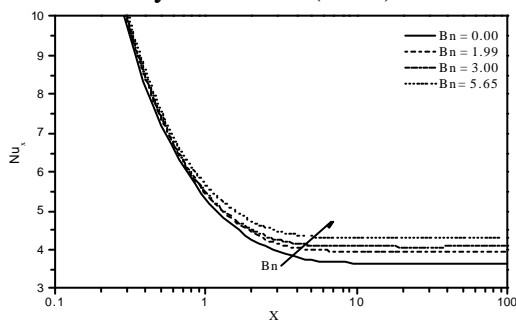
Figure 2. Axial evolution of the local Nusselt number for several values of the Bingham number. Re = 25, Pr = 1
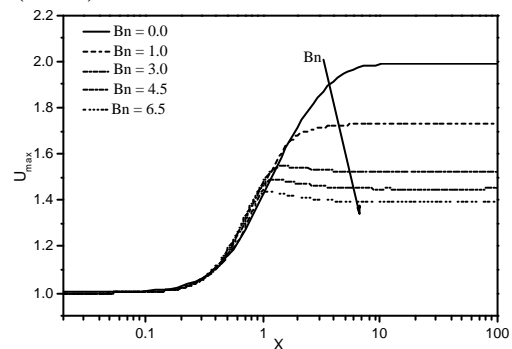
Figure 3. Evolution of the axial velocity for several values of the Bingham number. Re = 25, Pr = 1

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Enhancing the RIM process with pulsation technology: CFD study

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1. Summary

In the production of polyurethanes in Reaction Injection Moulding machines, the quality of the final product strongly depends on the quality of mixing in t-jet mixers. In this study, to increase the quality of the product and control mixing, the effect of pulsation and oscillation on the flow regime and structure in t-jet mixers was studied using CFD methods.

Keywords: RIM, chaotic mixing, T-jet mixers, oscillation and pulsation

2. Extended Abstract

T-jet mixers, where two opposed jet streams impinge each other in a confined mixing chamber have a wide range of applications, mainly for the production of polyurethanes in Reaction Injection Moulding, RIM, as well as in micro-mixers applications. The flow regime inside the chamber can be oscillatory or self-sustainable chaotic. In self-sustainable chaotic flow regimes, the jet streams engulf each other in evolving vortices throughout the mixing chamber; in oscillatory flow regimes both streams flow segregated throughout the mixing chamber due to the low amplitude of flow oscillation, which is not sufficient to break the segregation plane between the streams. In self-sustainable chaotic flow regimes the vortices formation is associated with strong jets oscillations that present frequencies around typical values, while the oscillatory flow regimes present low amplitude oscillations with very well defined frequency.

The flow field structures occurring for self-sustainable chaotic flow regimes are the main mixing mechanisms in the RIM process, as shown in Santos et al. (2005). On the other hand, the efficiency of mixing in such type of processes is crucial for the quality of the product as shown from the polymerization works of Kolodziej et al. (1982 and 1986), and thus the importance of maintaining a self sustainable chaotic

flow regime in the mixing chamber. Erkoç et. al. (2007) showed that the continuous operation of RIM at self-sustainable chaotic regime is not assured, since even for the same conditions, both oscillatory and self sustainable chaotic regime can always be observed.

The use of forced pulsations of the feeding streams can enhance mixing and promote robust operation of T-jets. If the natural/non-forced frequencies of oscillation of the flow are known, the process of forcing mixing can be enhanced in various ways: by increasing the amplitude of the natural frequency; by inducing multiple frequencies, which break the typical flow field structures; or at least by aid/forcing the natural system oscillations through pulsation in order to prevent transient situations where convective mixing patterns may not occur under short periods. To evaluate the effect of pulsation on mixing in T-jet mixers, CFD simulations were performed under different pulsation strategies where the jets are oscillated only from one side, from both sides as out-phase mode and finally from both sides as in-phase mode.
 Figure 1 shows the streamlines for four cases where Re =300 and: (a) the jets are not pulsated and the flow is parallel, (b) the flow was oscillated by only one of the injectors, (c) the flow was oscillated from both of the injectors as in-phase mode and (d) the flow was oscillated from both of the injectors as out-phase mode. While the mixing quality is low and derived by molecular diffusion in Fig.1a, chaotic mixing and formation of small vortices downstream the jets can be observed in Fig 1b and 1c. Application of the out phase oscillation with a given frequency and amplitude to the system yields well defined vortices and control of the mixing as shown in Fig 1d. These results show that complete different flow fields can be induced from pulsation strategies.
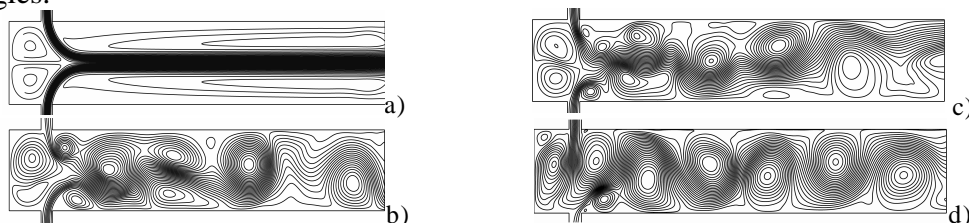
Figure 1 Simulation results of flow fields without pulsation (a) and with different pulsation strategies (b,c,d)

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Computer-Aided Multiscale Product-Centric Process Modelling

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1. Summary

The use of multiscale modelling has been increased for many engineering disciplines to extend their modelling capabilities to achieve higher levels of detail and accuracy. Integration of different software for the design/analysis/solution embedding multiscale modelling will allow the development and application of model-based embedding multiscale modelling approach. Direct methanol fuel cell model will be show as a case study to highlight the advantages the use of multiscale modelling as well as the software integration.

Keywords: Multiscale modelling, MoT, computer-aided

2. Extended Abstract

Many engineering disciplines are turning to extend the range of their modelling capabilities, such as the modelling of chemical processes which are generally modeled through monoscale approaches while not adequate, they satisfy a useful role in product-process design. Use of a multi-dimension and multi-scale model-based approach is, however, beneficial and necessary in product process development of special materials and/or chemical products. Higher levels of details and accuracy involving a wide spectrum of partial and temporal scales can be achieved in this way. A flexible computed-aided framework for model generation, analysis, solution and implementation will allow the development and application of the desired model-based approach for product-centric process design/analysis. This can be achieved through the integration of a modelling tool (Mot) for model translation, analysis and solution and some external software.

MoT (Sales-Cruz, M. and Gani, R., 2003) is a computer-aided tool able to make the translation, analysis and solution of the generated model equations. Moreover, MoT is able to generate model objects that could be used in other computational tools such as external software (i.e. EXCEL), simulation engines (Icassim and Dynsim available in

ICAS software) or even external simulators (ProSim, etc). The combination of MoT and ICAS (or any other simulators) permits that different models and/or process configurations can be simulated very easily and quickly, reducing time and human resources for model development and solution. But, *why do we need to use MoT together with other external software as a new modelling framework?* Because through their interaction, model equations for a specific equipment, process or operation would be developed, translated, analyzed and solved through MoT with almost zero programming effort with the multiscale modelling approach embedded in the final model equation.

The objective of this paper is to present the modelling framework, and through it, the synergy between MoT; together with new modelling features such as multiscale modelling and models needed for specific product-centric process design that are usually not found in commercial simulators. Application of these modelling tools will be highlighted through one case study involving a fuel cell model. The multiscale issues handled by the modelling tools will be illustrated.
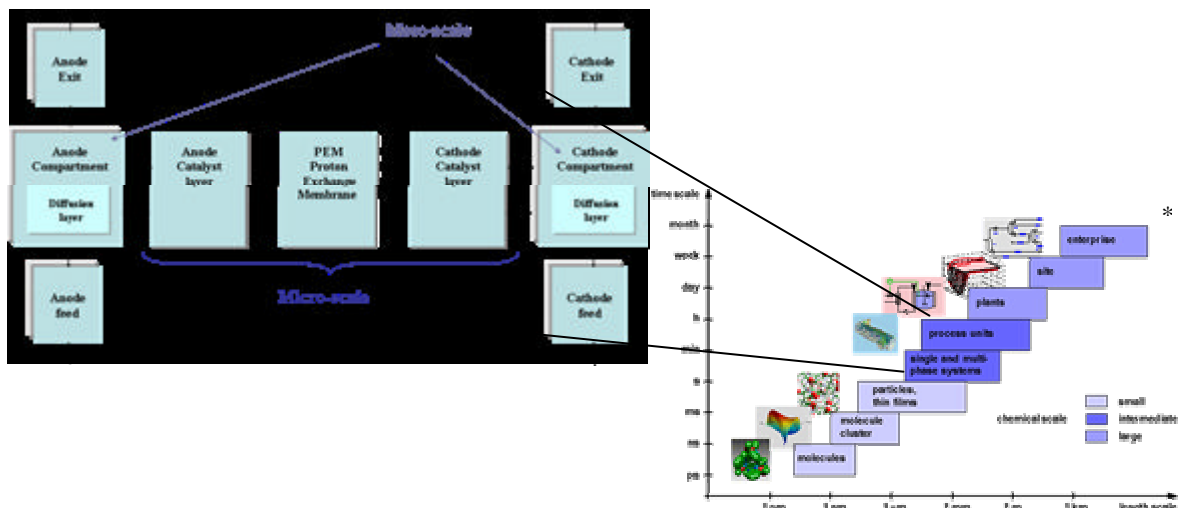
Figure 1. Multiscale scheme for a direct methanol fuel cell and multiscale classification ([*]Grossman, I.E., 2004)

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Seeking the optimum solution for the design of a typical PHE

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1. Summary

This study aims to contribute to the optimal design of plate heat exchangers (*PHE*) with corrugations following a herringbone pattern. A commercial *CFD* code, known to produce valid results for this type of equipment, is used to simulate the performance of a series of simplified *PHE* models, by varying four design variables, namely the blockage ratio, the corrugation aspect ratio, the channel aspect ratio and the chevron angle. This work, currently in progress, will use the results of the simulations to provide the optimal design parameter values for this type of *PHE* by compromising between heat transfer augmentation and friction losses.

Keywords: plate heat exchanger, *CFD*, optimization

2. Extended Abstract

In the last decades, the need for compact yet efficient heat exchange equipment led to innovations in the design of plate heat exchangers (*PHE*) with corrugated walls. The type of flow inside *PHE* channels augments heat transfer, due to flow separation and reattachment, while the complexity induced by the corrugations significantly increases the friction losses. The limited available experimental data that deal with the effect of various geometrical parameters on the heat transfer coefficient, the friction factor and the flow field in general (e.g., Taslim & Kercher, 1996; Heavner & Kumar, 1993; Sparrow & Comb, 1983) concern plate configurations with specific geometrical characteristics. In our Laboratory, by studying a typical commercial *PHE* both experimentally and numerically (Kanaris et al., 2005; Kanaris et al., 2006), it is proved that *CFD* is a reliable tool to predict flow characteristics and to estimate heat transfer rates and pressure losses in this type of equipment. Thus, the geometrical design parameters that influence the thermohydraulic features of the flow can be numerically studied and their effect on the overall performance of a *PHE* can be estimated.

Among the most important design parameters are the "chevron angle" (f), the interwall spacing (blockage ratio, d/H) and the channel as well as the corrugation aspect ratios (H/W and d/z). W and H are the channel height and width, while d and z are the corrugation height and width, respectively (***Fig. 1***). The above parameters are used for

creating a great number of computational domains. The computational model is an orthogonal channel with one corrugated plate following a herringbone design.

Figure 1. The geometrical parameters used for the design of the simulation models.

The aforementioned design variables cover a wide range of values. The chevron angle *f* ranges from 30° to 75°, while the blockage ratio varies from 0.1 to 0.6. Corrugation and channel aspect ratios vary from 0.05 to 0.15 and from 0.025 to 0.075, respectively. Typical results for *Re*=1000 concerning the dependence of two of the design variables on *Nusselt* number (*Nu*) and friction factor (*f*) are presented in ***Fig. 2***. More simulation runs are currently in progress covering a range of Reynolds numbers. Dimensional analysis led to the formulation of generalized correlations on *Nu* and *f* that incorporate the relative effect of all the above parameters. These correlations, along with a weighting factor accounting for the relative significance of friction losses over thermal energy, will allow the formulation of an objective function that would optimize the energy economy of the *PHE*. As the underlying phenomena are highly non-linear, the objective function is also non-linear, thus necessitating the use of global optimization techniques for identifying a true optimal solution.
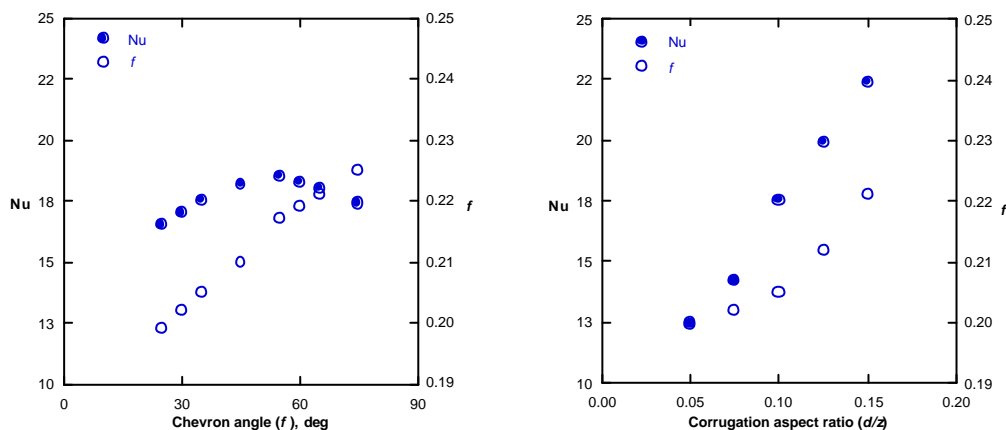
Figure 2. The effect of geometrical configuration of a simplified *PHE* on *Nu* and *f* (*Re*=1000).

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CFD Simulation of Methane Steam Reforming Furnace

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1. Summary

Steam reforming is a widely used method in industry for the production of synthesis gas. Synthesis gas is a mixture of hydrogen gas and carbon monoxide, which is used in many processes. An industrial size steam reforming furnace generally has some tubular fixed-bed reactors. Due to the highly endothermic reaction taking place in the catalyst filled tubes, some series of burners are needed to supply the required energy to the tubes. Excess air in hydrogen furnaces is a major problem in steam reforming plants in oil refineries. It strongly affects production of combustion polluted gases, inefficient temperature distribution on tubular reactors and hydrocarbon conversion of reforming process. A three-dimensional computational fluid dynamics (CFD) simulation of the steam reforming furnace is performed in this work. An industrial size furnace including burners, inside ambient of the furnace as well as tubular fixed bed reactors was modeled. More than 4 million nodes which were used for finite volume discretization of the furnace structure comprise the generated mesh. The influence of excess air on the burner combustion reactions and skin temperature of reforming reactors are investigated.

Keywords: CFD, Simulation, Steam Reforming Furnace, Excess Air.

2. Extended Abstract

In this paper the governing system equations of the process were Discretized and solved in a large number of finite volumes. Numerical solutions of the balances were obtained by applying boundary conditions and initial values. All of the equations are based on the Navier Stokes equations for conservation of continuity and momentum.

In order to predict the local mass fraction of each species, the mass conservation equations should be applied for the chemical species i as follows:

$$\frac{\partial}{\partial t}\left(rY_i\right) + \nabla.\left(r\,\vec{u}\,Y_i\right) = -\nabla.\vec{J}_i + R_i + S_i \qquad \text{Where} \qquad R_i = M_i \sum_{k=1}^{N} R_{i,k}$$

The eddy-dissipation concept considers the influence of turbulent flow on the reaction rate. In this model, the rate of reaction $R_{i,k}$ is given by two expressions as:

$$R_{i,k} = EFr\frac{e}{k}\mathbf{n}'_{i,k}M_i\frac{\sum_p m_R}{\sum_{j=1}^{N}\mathbf{n}''_{j,k}M_R}$$

Operating conditions and overall view of geometry are shown in table 1 and figure 1:

Table 1: Specifications and operating condition

Total number of burners	96
Number of burners used for simulation	4
Excess air (%)	25
Fuel mole flow rate for each burner (kmole/h)	1.05
Fuel temperature (k)	300
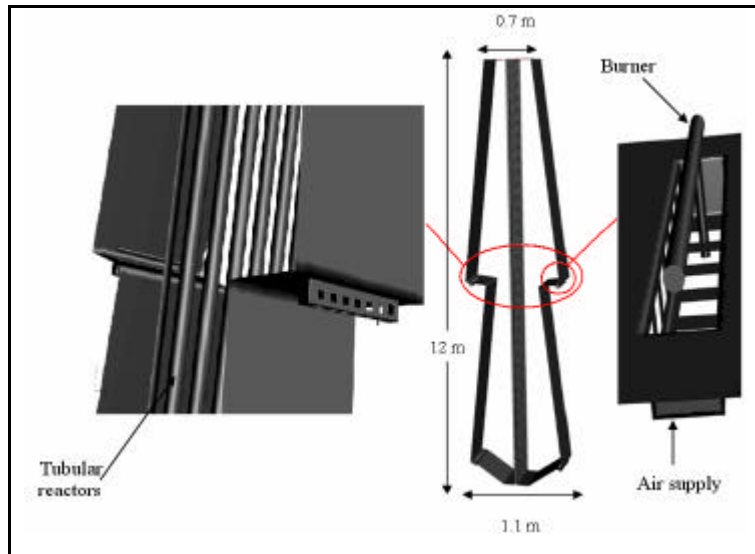
Figure 1: Overall views of simulated slice of the furnace.

Results

Figure 2 shows that more increasing in excess air reduces the furnace temperature. On the other hand, using a low excess air ratio causes increase of polluted gases (figure 3). Furthermore, figure 2 shows that the optimum amount of excess air is about 20% which leads to highest temperature and reasonable CO production.
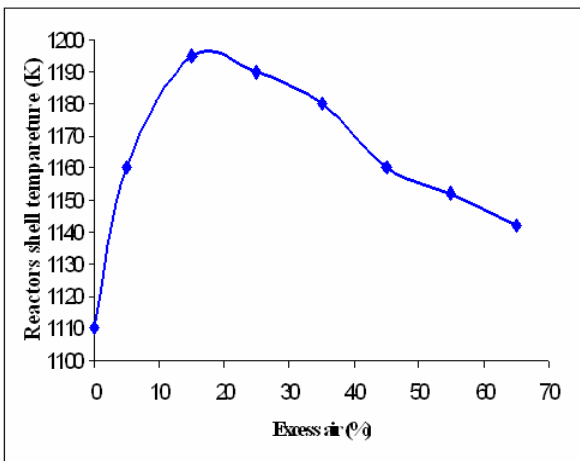
Figure 2: Effects of excess air on reactors shell temperature.
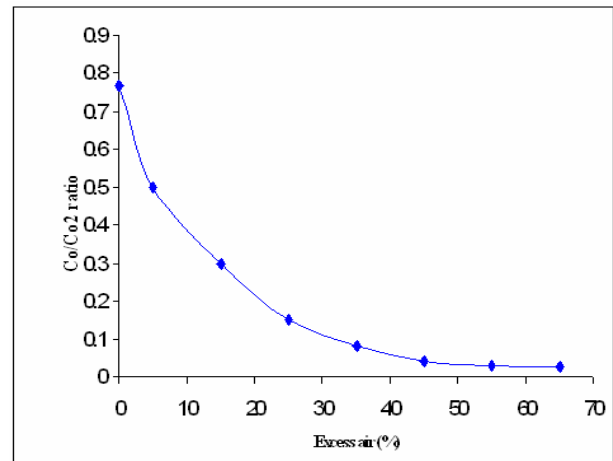
Figure 3: Effects of excess air on polluted gases

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Model of the partial oxidation of methane to methanol in a gas-solid-solid reactor

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1. Summary

This work presents the modeling and the selection of best topology for the gas-solid-solid system for direct synthesis of methanol from methane. The system proposed consisting of a catalytic fixed bed and a solid adsorbent that flow in parallel or in counter-current with the flowing gas. We apply our model to the case of methanol synthesis from methane over a ferric molybdate catalyst, using a silica-alumina adsorbent to remove the methanol from the reaction zone.

Keywords: methanol, gas-solid-solid reactor, cfd

2. Extended Abstract

The partial oxidation of methane to methanol has considerable potential for the utilization of vast natural gas fields in remote areas of the world. This process would not only be easier to of transport, but also increases the range of subsequent applications for further processing. The number of recent publications in this area reflects renewed interest in this reaction as an alternative to the two-stage steam reforming route to methanol [1-4]. The partial oxidation reaction is, potentially, a simpler and more energy-efficient process than the steam-reforming route, but in spite of the effort of investigators, no catalyst has been obtained to achieve desired levels of selectivity and conversion to take this process at industrial practice.

Bearing this in mind, this work focuses in the way to increase the conversion of reversible reactions in a special kind of multifunctional reactors [5-7]: the gas-solid-solid reactors. In this reactor, a mixture of gaseous reactants is fed at the bottom of the packed column. The solid packing contains catalyst pellets. Another solid material, a selective product adsorbent, is fed at the top of the column and trickles down over the packing. The solids stream adsorbs the product immediately after it has been released from the catalyst surface. The reaction product therefore leaves the reactor in the adsorbed state at the lower end of the reactor. The unconverted reactants leave the

reactor at the top, together with the non-adsorbed fraction of the product formed. With such design the reaction rates are not hampered by a reversed reaction and remain high. In this way, higher conversions and reaction rates can be expected. It may be possible even to find out operation conditions so that almost complete conversion can be achieved, so that the recycling is no longer necessary. This necessarily will result in considerable investment and operating costs savings.

In this work this concept of reactor design is explored. A two dimensional steady-state model for the reactor is developed based on the mass and energy balance. The model was solved numerically through the finite difference method with software written in FORTRAN 90 with the NAG routines. The influence of the process parameters on the behaviour of the reactor is discussed. The model was applied to the case of methanol synthesis directly from methane over ferric molybdate [8-9], with an amorphous silica-alumina powder as the methanol adsorbent. The concentration of the adsorbed methanol was optimized at the exit of the reactor using as decision variables the feed relationship CH_4/O_2 and the supply rate of adsorbent. The results show that this reactor, in principle, must be able to lead to high conversions of the feed gas to product in spite of unfavourable equilibrium.

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Session T4-K: Theme-4 Keynote Lectures[*]

Abstract Number	Paper Title & Authors	Included
225	Process Performance Monitoring – Towards Model Based Approaches Julian Morris	Yes
4043	Industrial Process Systems Engineering: Identification and Realization of Economic Potentials A Bode, E Uerdingen, T Wisniewski	Yes
4076	Knowledge engineering in CAPE systems -Can chemical engineers finally get around programming ? L von Wedel	Yes
4092	Energy Systems Engineering – an integrated approach for the energy systems of the future E N Pistikopoulos	Yes
4093	Drinking from a Fire Hose: Cyberinfrastructure Methods and Tools for Managing Information Overload and Complex Decision-Making in Molecular Products Design and Engineering V Venkatasubramanian	Yes

* To be presented in different keynote sessions (see the technical program for details)

Process Performance Monitoring – Towards Model Based Approaches

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1. Summary

In today's process manufacturing environment, a number of issues arise which can challenge the application of standard MSPC based process performance monitoring. Most methodologies are based on static PCA or PLS approaches with only a few addressing the impact of process dynamics and auto-correlated data. The impact that process dynamics can have on the assured detection, diagnosis and sensitivity of the performance monitoring charts is becoming important. Earlier work has been provided by, for example Negiz & Cinar, 1997, Russell *et al*, 2000, Simoglou *et a*l, 2002, McPherson *et al*, 2002, and Fletcher *et al*, 2002. This paper presents the use of Canonical Variate Analysis (CVA) and Autoregressive (AR) time series models for multivariate statistical process control based process performance monitoring systems which are discussed alongside two benchmark process simulation studies.

Keywords: Multivariate Statistical Process Control; Process Dynamics

2. Extended Abstract

Two case studies are presented; one based on a benchmark semi-batch styrene-butadiene rubber (SBR) emulsion polymerization (Nomikos and MacGregor, 1994) and one on a free radical batch polymerization of methyl methacrylate (MMA), (Kiparissides *et al*, 2002). The Autoregressive time series dynamic performance monitoring approach is compared with the standard multiway PCA (MPCA) batch unfolding approaches of Wold et al (1998) and Nomikos and MacGregor, (1994). Three batches were used for performance monitoring validation. The first batch exhibited normal behaviour, whilst the second batch was run with an initial organic impurity that resulted in the contamination of the butadiene feed from the start of the batch. The third batch exhibited the same set of conditions as for batch 2 but with additional contamination occurring halfway through the batch. In this study, the first

and third batches were considered. In the second case study three non-conforming batches were used to validate and compare the monitoring performance of the different batch process monitoring methods presented - a decrease in the overall heat transfer coefficient, the onset of an impurity problem, and a control valve failure.

Normal probability and autocorrelation plots of the residuals allow any non-normal and serial correlation to be identified in the removal of unwanted structure in the residuals to allow for appropriate statistical monitoring (McPherson *et al*, 2002). For on-line monitoring, a number of different monitoring statistics are considered alongside variable contribution plots for each monitoring statistic for fault diagnosis. The studies indicated that the model-based monitoring method not only reduces the time to fault detection while keeping the false alarm constant but also detects very small faults rapidly. In other words, the proposed batch monitoring approach yields superior results to the other methods in terms of sensitivity and speed to fault detection. In this study, one dynamic model is utilized for describing the dynamic behaviour of the deviation from the desired trajectory and thus it is assumed that the dynamics are not significantly different throughout the batch. This appears to be a reasonable assumption for the case studies considered. If, however, the dynamics change as the batch proceeds, multiple AR models, or an adaptive scheme, would be required to be considered (Choi *et al*, 2006). Nevertheless, the concept and potential of using a time series batch modelling approach, in this case using one AR model, has been demonstrated and opens the way for more studies. Drs Sang Wook Choi and Ahmed Alawi are gratefully acknowledged for their contributions.

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Industrial Process Systems Engineering: Identification and Realization of Economic Potentials

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1. Summary

Methods and tools currently used for process analysis and visualization are presented. The whole chemical process is addressed and special focus is directed to the modeling, calculation and visualization of processes and process systems. Not only material and energy flows can be modeled, but also cost flows for single-product, multi-product and coupled-product systems.

Keywords: chemical process, cost allocation, system analysis, visualization

2. Extended Abstract

Highly integrated production networks in the modern chemical industry require methods and tools for process analysis and visualization. Technical feasibility, production cost, as well as safety and environmental issues have to be tackled when process improvement ideas are generated. Industrial Process Systems Engineering is assessing the whole chemical process and provides an interface between technical expertise and process economics during different stages of process improvement.

The method presented here is a consequent approach starting from the circle of problem definition, evaluation of potential cost savings and generation of ideas. After, usually multiple, iterations within this circle, measures, cost and risks of the ideas have to be identified for potential investment projects (Figure 1).

Tools to support the generation of ideas are used for
- Analysis of the basic cost structure of the process
- Identification of maximum cost saving potentials and
- Detailed analysis of mass-, energy-, and cost flows.
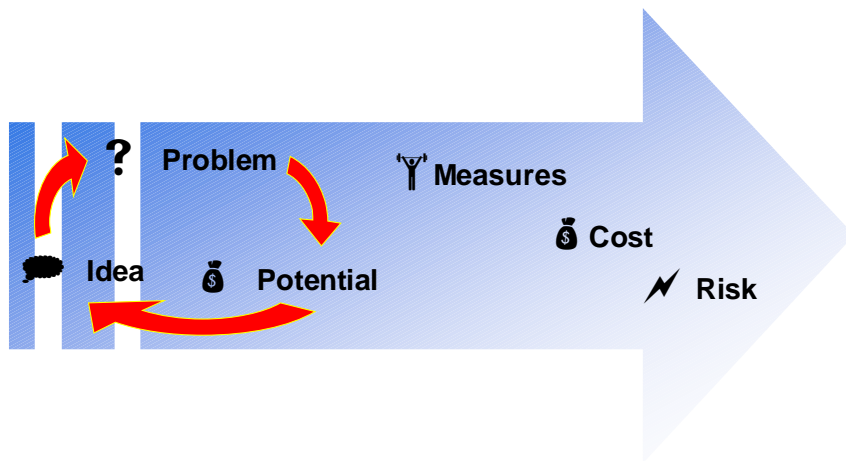
Figure 1: Identification of economic potentials in Industrial Process Systems Engineering

The detailed analysis of mass-, energy-, and cost flows is based on a software tool for modeling, calculation and visualization of process systems. Figure 2 displays an example for the visualization of material flows as a Sankey diagram for a production process. Material and energy flow analysis provide the basis for subsequent cost flow analysis. The cost flow analysis reveals production cost not only for single product processes but also for multi-product as well as coupled-product systems.
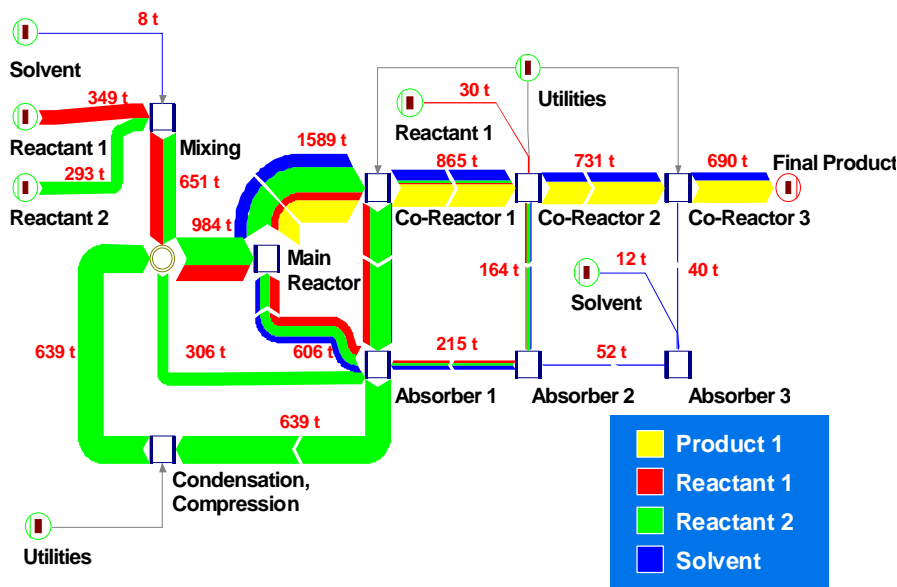
Figure 2: Example for Sankey-visualization based on a material flow analysis for a production process

Thermodynamic modeling is not possible within this environment for the sake of other advantages due to the special calculation algorithm based on Petri-networks: Vertical model integration is possible by incorporation of different levels of detail within one model. For horizontally integrated modeling, process models along the value chain can be coupled.

Model-driven development of CAPE systems –
Can chemicaI engineers finally get around programming ?

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1. Summary

The subject of computer-aided process engineering is inherently linked to the task of programming computers, i.e. telling machines what to do in order to solve problems in the chemical engineering domain. Although the software industry is constantly proposing new programming languages, the overall task of software development does not seem to become easier. As a consequence, the overall process of software construction is an active area of research, but its results seem to penetrate the area of CAPE systems development rather slowly. This contribution looks at methods that have emerged more recently and tries to motivate where future developments in the CAPE community should head towards.

Keywords: CAPE, software development, knowledge representation, languages

2. Extended Abstract

CAPE tools and solutions are actively developed in areas such as research, industry, or commercial software development and range from ad-hoc developments for single problems up to software environments that last over several decades, These development tasks typically require engineers who combine expertise from the field of chemical engineering as well as software engineering. A major reason is that the software developed is expressed in program code that mixes aspects of the chemical engineering and software engineering domains. The actual knowledge, how the problem is expressed in the code has been buried implicitly in the process of constructing the software and is neither accessible nor reusable afterwards.

A better approach is to consider the development of CAPE tools from two separate aspects: On the one hand, we need domain-specific problem specifications which are posed in concepts and languages familiar to the domain expert. On the other hand, we need applications which rely on problem solving knowledge and consume such a problem description from our domain and are able to compute desired results from it.

Hence, the focus should be on a specification of problems in a language that is independent of the actual solution of the problem on e.g. some digital computer. Such a language is based on an explicit representation of concepts and their relations in a certain domain and is declarative by nature. The property of being declarative, i.e. describing the actual problem instead of an approach to its solution, improves the understanding and reusability of the problem specification as well as the components for its solution.

Mathematical modelling environments are a good example where this approach is partially applied: Engineers nowadays develop models in systems modelling languages and use modelling environments which contain the necessary problem solving knowledge. This representation of a model is reusable apart from changes or improvements to the underlying solution machinery and easy to understand by noncomputer scientists. This is contrasted by the approach to code low-level subroutines for numerical solvers in FORTRAN as it was performed not too long ago, Here, changes to e.g. libraries incurred corresponding adaptation of the model code, something that was impossible to do without detailed process modeling knowledge.

Research in software engineering has recently adressed the issue whether the use of models and metamodels can simplify the overall development process, Interesting areas to leam from are e.g. knowledge systems engineering, model-driven development, or generative programming which have evolved from active fields of research into standard technologies that can be applied in software development. These techniques aim at explicitly modeling knowledge about a domain (such as chemical engineering in this case) by means of domain specific languages or ontologies. Due to the formal and precise nature of these representations, the computer is able to exploit this knowledge and make use of it in (at least) partially generating application code, automatically choosing relevant components, or even employing this knowledge immediately for problem solving,

Applications of these techniques have the potential to tremendously change the way CAPE systems are being developed. Focus can shift away from code and move towards explicit modeling of domain knowledge and the development of more granular, but reusable components that provide specific problem solving approaches, This will ease tasks like construction, validation, maintenance, extension, or integration of CAPE systems. Further, transferring research results into engineering practice and commercial solutions is simplified because the reusable knowledge is available explicitly and does not have to be reengineered from prototypical code. Individuals may better focus on required skills and the lifecycle of CAPE systems from research towards commercialization may undergo a radical change. This contribution presents some of these approaches and discusses how to achieve a new generation of CAPE systems that would be impossible to construct using traditional programming.

Energy Systems Engineering – an integrated approach for the energy systems of the future

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1. Summary

Energy systems engineering provides a methodological scientific framework to arrive at realistic integrated solutions to the complex energy problems, by adopting a holistic, systems-based approach. In this presentation, we will demonstrate the potential of energy systems engineering to systematically quantify different options at different levels of complexity (technology, plant, mega-system) through a number of real-life applications. Applications include (i) hydrogen infrastructure planning problems, where the potential for using hydrogen as a clean sustainable fuel is assessed in some detail, (ii) poly-generation energy systems, where a variety of fuel stocks, such as coal, natural gas and biomass, can be converted into a variety of products, such as electricity, transport fuels and chemicals, and (iii) urban energy systems, where a process integration approach to the flow of energy and materials through an urban environment is applied to analyse and significantly improve the very low efficiency of urban energy systems.

Keywords: energy systems, hydrogen infrastructure, poly-generation, urban systems

2. Extended Abstract

Energy is one of the most critical international issues at the moment and most likely to be so for the years to come. As part of the energy debate, it is becoming gradually accepted that current energy systems, networks encompassing everything from primary energy sources to final energy services, are becoming unsustainable. Driven primarily by concerns over urban air quality, global warming caused by greenhouse gas emissions and dependence on depleting fossil fuel reserves, a transition to alternative energy systems is receiving serious attention. Such a tradition will certainly involve meeting the growing energy demand of the future with greater efficiency as well as using more renewable energy sources (such as wind, solar, biomass, etc). While many technical options exist for developing a future sustainable

and less environmentally damaging energy supply, they are often treated separately driven by their own technical communities and political groups.

Energy systems engineering provides a methodological scientific framework to arrive at realistic integrated solutions to the complex energy problems, by adopting a holistic, systems-based approach. In this paper, we will demonstrate the potential of energy systems engineering to systematically quantify different options at different levels of complexity through a number of real-life applications.

Hydrogen Infrastructure Planning

Despite the growing awareness, remarkably little quantitative support has been provided to assist the supply chain design, technology selection and infrastructure investment decisions. This is partly due to the difficulty in establishing what the best pathway is for delivering hydrogen, given that a large number of technological options exist for its manufacturing, storage, distribution and dispensing. Here, we describe a systems-based approach to model the hydrogen infrastructure (Hugo, 2005).

The development of a generic mathematical model of the future hydrogen supply chain that can assist the capital investment decision-making process is first presented. The model assesses the performance of different infrastructure scenarios involving various production and distribution technologies, and raw material feedstock. Realizing that multiple performance criteria are of interest, a quantitative assessment is conducted in terms of both investment and environmental criteria, with the ultimate goal being to identify optimal infrastructure pathways. Such a multi-criteria decision-making model provides a comprehensive basis for investigating the trade-offs between increasing financial returns and decreasing environmental damage.

Poly-generation Energy Systems

The forecasted shortage of fossil fuels and the ever-increasing effect of greenhouse gas (GHG) emissions on global warming and environmental stability are two international problems with major technical, economic and political implications in the 21st century. Therefore, it is urgent to restructure present energy production and utilization systems in order to ensure that fossil fuels are used with high efficiency and low to zero emissions.

Poly-generation energy systems combine power generation and chemical fuel synthesis in a single plant (producing both electricity and fuels) and thus provide a promising alternative pathway towards achieving sustainable and flexible economic development. Mixed-integer programming (MIP) is useful in constructing long-term decision models that are suitable for investment planning and design of poly-generation infrastructure systems. Here we present a model for the investment planning of a poly-generation energy system, and use the model for a case study addressing a system for production of methanol and electricity (Liu, 2006)

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Drinking from a Fire Hose: Cyberinfrastructure Methods and Tools for Managing Information Overload and Complex Decision-Making in Molecular Products Design and Engineering

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1. Summary

Designing new materials and formulations with desired properties is an important and difficult problem, encompassing a wide variety of products in the specialty chemicals and pharmaceuticals industries. In going from discovery to delivery in the market via several intermediate stages, a *staggering* amount of information of *different types, ranging from raw data to lab reports to sophisticated math models,* is shared and revised by humans with the aid of computational tools in each stage. Traditional trial-and-error design approaches are laborious and expensive, and cause delays time-to-market as well as miss some potential solutions. A new paradigm is needed that increases the idea flow, broadens the search horizon, and archives the knowledge from today's successes to accelerate those of tomorrow. With the onset of information and knowledge explosion, it is clear that we need intelligent software systems to effectively manage and access information for efficient decision making. Cyberinfrastructure will play a crucial role in product design, process development and commercial scale manufacturing by streamlining information gathering, data integration, model development, and managing all these for easy and timely access and reuse. In this talk, I will discuss a novel cyberinfrastructure framework called *Ontological Discovery Informatics*. The foundation of such an infrastructure is the explicitly and formally modeled information, called an Ontology. This framework enables the management of complexity, accumulation of knowledge, systematic hypotheses testing by interaction with experiments, and optimal decision-making. I will discuss the application of this paradigm for industrial molecular products design problems in the specialty chemical and pharmaceutical industries.

Keywords: pharmaceutical informatics, cyberinfrastructure, ontology, molecular systems engineering, product design

2. Extended Abstract

Information management systems have been developed for product development and they may be considered to fall into two broad classes; experimental information management systems and process information management systems. The former includes LIMS and e-Lab Notebook. LIMS are database applications whose functionalities include data entry, sample tracking and data transfer. An e-Lab Notebook can provide functionalities like browsing information, managing data, publishing information (Zall, 2001). The later includes efforts such as PROART/CE, which is a tool integration environment based on a definition of representation of data and specification of the physical structure (Jarke and Marquardt, 1996) and the CAPE-OPEN effort for process modeling software integration.

The Purdue Ontology for Pharmaceutical Engineering (POPE) was developed for the product development domain in response to these challenges [Zhao et al, Venkatasubramanian et al.]. A central concept is the *material*, which represents substances and mixtures (which are characterized by pure substances and their compositions). A *material* has several physical and chemical *properties* (e.g. specific heat capacity), and can be involved in several *experiments* (e.g. Compression Tests). Conversely, each material property value is obtained from a *source of value,* which includes *experiments*, *literature* or *mathematical models*. An *experiment* is described through its *specifications* (equipments, settings), *procedure*, *context* (environmental conditions), *setup*, *data analysis method* and raw data. Such an information structure allows the preformulator to store the data with appropriate semantics while allowing the formulator to access the same data with a more complete description. In addition several queries, which are difficult or impossible to do with current query techniques like SQL e.g. finding all materials whose tapped density exceeds bulk density while measured under conditions that make relative humidity important, may be made in such an information management system. In addition, through description of the mathematical model, one may make use of customized tools for property computation through export of the model in an appropriate format.

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Session T4-1a: Process Synthesis & Design - I

Abstract Number	Paper Title & Authors	Included
649	Development of process alternatives for separation and purification of natural products C Wibowo, B Harjo, K M Ng	Yes
1953	Process synthesis and optimization of a supercritical methanol biodiesel production plant S Espinosa, S Diaz, E Brignole	Yes
3049	Towards the integration of chemistry and chemical engineering for innovative process and materials synthesis P Linke, D Linke	Yes
3317	A property based design approach for simultaneous optimization of product and process needs F T Eljack, C C Solvason, N Chemmangattuvalappil, M R Eden	Yes

Development of Process Alternatives for Separation and Purification of Natural Products

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1. Summary

An approach for designing natural product crystallization process based on thermodynamic solid-liquid equilibrium (SLE) phase behavior is demonstrated using two examples. In this approach, the design engineer first sketches the relevant phase behavior based on all the information on hand. Then, an experimental plan is designed to determine the minimum amount of data necessary for process synthesis. Bench-scale experiments proceed alongside conceptual design to provide the missing information in a practical and systematic manner, resulting in technically feasible process alternatives.

Keywords: natural products, crystallization, process design, process development

2. Extended Abstract

One of the major challenges in process development is the conceptualization of a realistic process that is viable for commercial manufacturing. This is particularly true for natural product processes, for which basic information such as thermodynamic and physical properties of the key components involved are seldom available (Harjo et al., 2004). The major issues in designing a separation or purification process for such products, which normally involves crystallization, often include the selection of a suitable solvent or optimization of operating conditions (temperature, concentration, pH, and so on). In these cases, it is inevitable that conceptual design must proceed alongside bench-scale experiments, which provide the missing information in a practical and systematic manner. This exercise results in technically feasible process alternatives that can be further evaluated via material balance calculations.

Two examples are presented to demonstrate an approach for designing natural product crystallization process based on thermodynamic solid-liquid equilibrium (SLE) phase

behavior. The first is separation of soybean isoflavones daidzein and genistein, both of which have been reported to play a role in preventing and treating cancers and cardiovascular diseases (Harjo et al., 2007a). The second is production of L-glutamic acid and its monosodium salt, which involves crystallization from a mixture containing other acids and bases that have to be added to control pH (Harjo et al., 2007b). In both examples, key solubility experiments are performed to obtain relevant SLE phase diagrams featuring different regions of temperature and composition in which various products can be crystallized. With such an understanding of the underlying thermodynamic behavior, feasible process alternatives can be generated in a much more efficient manner compared to a trial-and-error method.

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Process synthesis and optimization of a supercritical methanol biodiesel production plant

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1. Summary

In this work, we address the process synthesis, simulation and optimization of the supercritical transesterification of vegetable oils with supercritical methanol. A rigorous process simulation is performed based on a group contribution equation of state with association for the prediction of the phase equilibria. The nonlinear problem is solved with a successive quadratic programming algorithm.

Keywords: biodiesel, supercritical, transesterification, optimization.

2. Extended Abstract

Recent experimental studies (Saka and Kusdiana, 2001; Kusdiana and Saka, 2001; Cao *et al*., 2005) on non-catalytic transesterification, have shown that high reaction rates, that justifies the process commercial application, can be obtained if the operating conditions are above the critical pressure and temperature of methanol. Even though it is generally agreed that temperatures above 550 K and high methanol/oil ratios are required to obtain high conversions and high reaction rates in non catalytic transesterification of vegetable oils, there is disagreement among the different authors regarding the operating pressure, assumed phase conditions, the use of cosolvents and the justification of the sudden increase of rate of reaction with temperature. In a recent work (Hegel *et al.*, 2007) the reaction process and its phase equilibrium engineering characteristics, were directly observed in a double window cylindrical reactor and the conversion in methyl esters was measured. These results indicated that high conversion to biodiesel can be obtained even at moderate pressures (10-12 MPa) if the reactants residence time is higher than 20 minutes. In the present work it is discussed the process synthesis, simulation and optimization for the supercritical transesterification of vegetable oils with supercritical methanol. The rigorous process simulation is based on a group contribution model with association

for the prediction of the phase equilibria and the modeling of the separation processes. The process optimization variables are: methanol/oil ratio, reactor temperature and pressure, methanol recycle pressure. A sensitivity study of the process optimization is made regarding the reactor volume and the raw material costs, for a plant producing 100000 tons/year of biodiesel.

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Towards the integration of chemistry and chemical engineering for innovative process and materials synthesis

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1. Summary

We present ongoing research towards the development of a technology platform for the integrated development of catalysts and chemical processes. The research is structured into complementary themes in kinetic modelling, multi-scale reaction systems modelling for decision-support from high-level to detailed design, integrated framework development for process concept screening and evolution into innovative but practical chemical processing schemes, and large-scale distributed computing environments in the form of computational Grids.

Keywords: process synthesis, catalysis, High Throughput Experimentaion, modelling

2. Extended Abstract

The current approach to the development and design of a chemical process is largely sequential. Specific issues such as the evaluation of catalyst performance, the design of reactors or the design of separation systems are addressed as separate steps one at a time. The overall success of the design activity is hampered by the lack of systematic support tools to assist the scientists and engineers involved in the design processes to identify innovative solutions reliably and quickly in the context of the overall design goal, i.e. to identify the best possible process system that is comprised of these subsystems. Methodological shortcomings are exemplified by the lack of coordination of kinetic model development, reactor design and process synthesis. More often than not, kinetic models are developed for operating regions that do not correspond to the optimal values identified later on in process synthesis when the experimental studies have long been concluded. The result is either a compromise design dominated by kinetic model reliability issues or a project delay caused by additional experimental investigations of the kinetics. Technological shortcomings are exemplified by current conceptual process synthesis tools: the available tools for the generation of innovative design candidates are limited to systems of very moderate complexity and quickly fail as complexity increases. Although successes of process synthesis methods have been significant even for simple systems, most industrially relevant systems are considerably more complex and cannot be addressed with existing technology. However, if reliable methods to address such systems can be developed, step changes in innovation are to be expected.

Our work aims at the development of methods that will allow systematic capitalisation on synergies across the chemical process development cycle. Initially,

we have focused our interests on the basic research and development issues required to realise an integrated approach in which the key process design issues can be addressed in parallel to the investigation of the chemistry through High Throughput Experimentation from the earliest stage to arrive at the most economically viable and sustainable design via the shortest possible route. We will report on technology developments for the integrated conceptual design and evolution of processes with heterogeneously catalysed gas-phase reactions on the basis of available kinetic information. Building upon previous efforts in process synthesis (Ashley and Linke, 2004; Linke and Kokossis, 2003; Rigopoulos and Linke, 2002), we have developed a multi-scale approach, which starts from conceptual design to screen vast numbers of processing alternatives for optimal designs. This conceptual stage employs superstructure models embedding combinations of ideal reactor models with practical constraints on heat exchange and explosion limits that can be realized in practice and exploits trade-offs between the reaction and separation systems to identify promising process candidates and operating conditions. As practical processes for heterogeneously catalysed systems can never achieve ideal behaviour, subsequent synthesis stages enrich the reaction models to incorporate nonideal behaviour so that the process designs can be evolved into optimal schemes that can easily be reached in practice. Throughout the multiscale design cycle, information on the optimal operating envelopes is generated and can be fed back to the kinetics development team to guide additional experiments so as to ensure that kinetic models match the optimal process in which the catalyst is to be used. We will discuss the important role of advanced computing technologies in the form of Grids in enabling rapid integrated development. Our approach is conceptually presented in Figure 1.
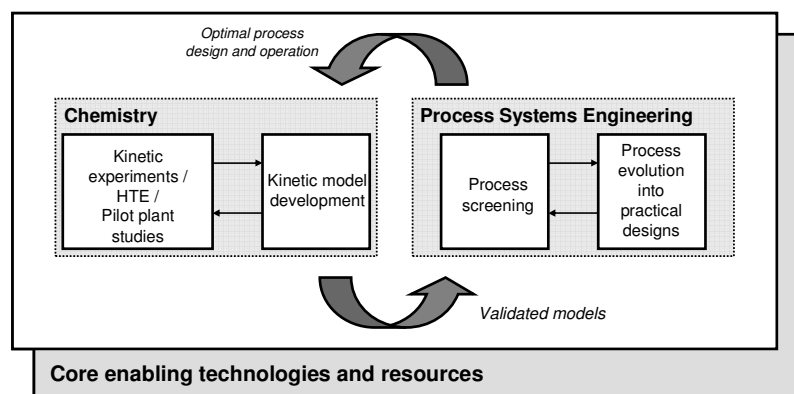
Fig 1. Integration and coordination of design activities

We will demonstrate the technology developments with industrially relevant applications including the production of acetic acid (Linke et al., 2001). The systems have been chosen as their highly complex reaction networks are representative for the complexities of many heterogeneously catalysed gas-phase systems. With our approach we have identified novel processing schemes with significantly improved performances as compared to conventional process designs.

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A Property Based Design Approach for Simultaneous Optimization of Product and Process Needs

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1. Summary

In this work the property clustering technique has been combined with first-order Group Contribution Methods (GCM) to produce a systematic methodology capable of handling property design targets and synthesizing molecular options to satisfy them. The method is capable of simultaneously considering both process and molecular design needs. In that sense it is a truly integrated approach. Visualization aids in deciding which groups to include in the synthesis and which to omit as they will not help in achieving the performance requirements. For cases that require more than three properties, this paper presents an algebraic molecular clustering approach that enables lowering the dimensionality to a simple linear program (LP).

Keywords: Property clusters, molecular design, algebraic approach

2. Extended Abstract

The terms product synthesis and design designate problems involving identification and selection of compounds or mixtures that are capable of performing certain tasks or possess certain physical properties. Since the properties of the compound or mixture dictate whether or not the design is useful, the basis for solution approaches in this area should be based on the properties themselves. However, the performance requirements for a solvent are usually dictated by the process and thus the identification of the desired solvent properties should be driven by the desired process performance. Traditionally process design and molecular design have been treated as two separate problems, with little or no feedback between the two approaches. When considering conventional process design methodologies, the selected species are chosen from among a list of pre-defined candidate components, therefore, limiting performance to the listed components. On the other hand, with molecular design techniques, the desired target properties are required input to the solution algorithm. Once again these decisions are made ahead of design and are usually based on qualitative process knowledge and/or experience and thus possibly yield a sub-optimal design. Introduction of the property integration framework allows for

representation of process and products from a properties perspective (Shelley and El-Halwagi, 2000). Utilizing this methodology enables identification of the desired solvent properties by targeting the optimum process performance without committing to any components during the solution step (Eljack et al., 2006). The identified property targets can then be used as inputs for solving a molecular design problem, which returns the corresponding components (Eljack et al., 2007).

The presented property framework combines property clustering techniques and group contribution methods (GCM) to facilitate simultaneous consideration of the property performance requirements as well as process and molecular constraints. For visualization purposes only three properties can be used to characterize the system. The process requirements along with the molecular fragments can be represented on a ternary cluster diagram. The basis for the property clustering technique is the use of property operators, which are tailored to exhibit linear mixing rules. The mixing rules are functionally different for molecular groups and process streams; however since they represent the same property, they can still be visualized on the same diagram. Once visualized it is possible to solve the process design problem by identifying the solvent properties corresponding to the desired process performance. On the ternary diagram the target solvent properties are represented as a region. The structure and identity of candidate solvents are then identified visually by combining molecular fragments until the resulting properties match the targets.

The ability to synthesize molecules within the clustering domain is key to bridging the gap between process and molecular design, however utilizing the visualization approach limits the application range to cases that can be expressed using three properties. It is recognized that not all design problems can be described by just three properties. For property integration through componentless design of processes, Qin et. al (2004) introduced an algebraic approach to overcome this bottleneck, by taking advantage of the mathematical structure of the property clusters. Presented here is an analogous algebraic method that will expand the application range of the molecular property clustering technique. This method further exploits the advantages of the linear additive rules of the molecular operators to setup the design problem as a set of linear algebraic equations.

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Session T4-1b: Process Synthesis & Design – II

Abstract Number	Paper Title & Authors	Included
774	Simultaneous optimization of different strategies for co-production of sugar and ethanol D Krajnc, P Glavic	Yes
1149	Towards synthesis of an optimal thermal cracking reactor M W M van Goethem, S Barendregt, J Grievink, J A Moulijn, P J T Verheijen	Yes
1245	Optimisation-based design of reactive distillation columns S Barkmann, G Sand, S Engell	Yes
1584	Multicriteria optimization under uncertainty – considering insufficient process data at the operation stage L E K Achenie, I Datskov, G Ostrovsky	Yes
1977	Decision suport system for unsteady-state reactors design using case-based reasoning approach B-J C Cristiana, Y Avramenkob, A Kraslawski, P S Agachi	Yes
3393	Uncertainty analysis during the multi-criteria evaluation of wastewater treatment plant design alternatives X Flores, J Comas, M Poch, I Rodríguez-Roda, R Bañares-Alcantára, K V Gernaey	Yes

Simultaneous optimization of different strategies for co-production of sugar and ethanol

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1. Summary

Due to the EU sugar reform, a restructuring of European sugar industry sector by innovative approaches is inevitable, in order to achieve sustainable development. This contribution deals with co-production strategies of beet sugar and bioethanol production, in order to gain an advantage and flexibility in producing varied quantities of beet sugar and bioethanol depending on prevailing market conditions.

Keywords: beet sugar production, bioethanol, sugar industry, optimization

2. Extended Abstract

Owing to the surplus of sugar on the World Market, the European Union (EU) is reducing economic support for refined sugar by about a third. The aim is to reduce the mass of sugar produced, so that the excess is not exported to non-EU markets. Because of these new market conditions, it may be advantageous to assess alternative profitable usages for sugar beet which may assist in reducing environmental impact while improving the overall economy of sugar production. Due to reduced price support from the EU, it is obvious that only the most advanced sugar plants will survive these keen market conditions. Thus, a restructuring of sugar production by applying alternative production processes is inevitable for the sugar plants, in order to achieve sustainable development.

Efforts to improve production efficiency and economic viability in the sugar industry have traditionally focused on maximizing sugar yield per hectare of agricultural land and sugar produced per tone of sugar beet grown. Although some co-products of sugar production such as beet pulp and molasses are utilized in other industrial processes, priority is accorded to sugar production. The traditional focus on sugar has made the industry vulnerable to changing market prices and weather patterns, and prone to financial instability. There have been few attempts by sugar plants to

consider all sugar beet resources as a bundle of potential products and services whose value could be maximized simultaneously.

Sugar plant that wishes to stay competitive must attain flexibility and diversity in adapting to changing markets. Co-production strategies present attractive options because key co-products of one process, such as molasses from sugar production, are available onsite for use as raw materials for the additional processes, for example bioethanol production. Sugar plants could be redesigned by annexing the distillery with the sugar plant, in order to gain a spatial advantage and flexibility in producing varied quantities of sugar, ethanol and electricity depending on prevailing market conditions.

The objective of our work was to economically evaluate investment needed for the co-production of sugar and ethanol. The aim was to optimize combined sugar–ethanol production and simultaneously improve the economic and environmental performances of the sugar and ethanol plant. A conceptual design for an integrated sugar and ethanol production was used. Both processes were simulated using computer simulator and results served as the basis for the optimization of the integrated sugar–ethanol process. The objective of optimization was to find economically and environmentally optimal strategy for co-producing sugar and ethanol. The decision was made on the production in fixed or flexible quantities. Production in fixed quantity has reserved all of the economically extractable sugars for sugar production by using "C" molasses or "final" molasses for ethanol production. C molasses is not valuable for sugar production because sugar extraction has reached a point of diminishing returns. Such a strategy would be chosen when the market value of sugar was generally higher than that of ethanol in production-equivalent terms, and was expected to remain higher for the foreseeable future.

In the optimization problem, decisions were also made to enable sugar production with flexible quantities. Namely, sugar extraction can be halted after the first or second stages, resulting in "A" or "B" molasses, respectively. These molasses streams have fermentable sugars that can still be economically extracted. However, the presence of additional fermentable sugar increases the efficiency of ethanol conversion. Consequently, if ethanol is expected to have a market value close to or greater than that of sugar, then it makes economic sense to prioritize ethanol production over some sugar production, by using A or B molasses as the ethanol feedstock.

The study of a combined sugar–ethanol production showed that opportunities still exist for increased profitability in the sugar industry, while decreasing environmental impacts through a holistic approach. The optimization model used in our study is very valuable for the producers who are using (or will be using) combined sugar–ethanol production, since they have the flexibility to switch among different alternatives of molasses use when the market prices are fluctuating over time. Consequently the decision whether to emphasize sugar or ethanol production can be easily made.

Towards Synthesis of an Optimal Thermal Cracking Reactor

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1. Summary

A fundamental approach to reactor synthesis for thermal cracking is presented, by firstly targeting an optimal reaction path and then deriving reactor geometry. As part of the targeting a new reaction-mixing model, called mixing kernel, is introduced. It is shown to be related to the attainable region theory. Preliminary results of the targeting approach to the thermal cracking process are discussed.

Keywords: reactor synthesis, targeting, attainable region, thermal cracking.

2. Extended Abstract

This paper outlines an approach to the synthesis of an optimal reactor for thermal cracking. The synthesis objective is, given the process reaction network and the feed sources, to maximise the amount of product per unit mass of feed.
We apply a fundamental approach which can be divided into two phases. The first targeting phase is the determination of the optimal reaction path along a reaction coordinate in composition space, using reaction and mixing operations. The results are the degree of mixing, the feed distribution function, the temperature profile, pressure profile and the residence time. In the second phase we translate this optimal path in geometry for equipment. In this paper we will concentrate on the first phase.

In our synthesis approach the determination of the optimal reaction path is decomposed in three stages:
a. Identification of the feasible window of physico-chemical conditions.
b. Find optimal distributive feed injection, product removal and internal mixing with reaction along a coordinate in the composition space and the residence time.
c. Determine the optimal temperature, pressure profiles and re-optimise the second stage till consistency is obtained.
This decomposition suffices for a single phase system. It is compatible with the more extensive design approach of Krishna and Sie (1994) for multi-phase systems.

Our motivation for the first stage (*a*) is to identify the feasible range of operating conditions, like: what type of heating is allowed, can we allow discontinuities in temperature & pressure profiles, what is the limiting temperatures for the materials available, catalyst used, number of phases, etc.. Physical considerations imply that the stages *b,c* should be computed all at once. Since we are researching a complex system, thermal cracking described by an extensive radical mechanism, we propose to separate stages *b* and *c* in order to obtain partial optimisation problems that can be solved more easily. The optimisation of the *T* and *P* profiles is difficult for large reaction systems. This decomposition in two stages requires verification and re-iteration if the outcome of stage *c* influence the results obtained at stage *b*.

The optimal degree of mixing for a given reaction system in the attainable region synthesis is determined by optimisation of discrete reactor superstructures, with geometric techniques, more recently with IDEAS and the method of bounding hyperplanes (Kauchali (2002), Zhou and Manousiouthakis (2006)). We prefer to use a continuous variant of the superstructure in the (isothermal, isobaric) composition space by introducing a so called mixing kernel (*M*) which defines the degree of internal mixing between locations along the system coordinate. Together with a distributive feed injection (*L*) and effluent removal (*K*) this yields the following reaction-mixing equations:

$$\frac{\partial C_{k,V}}{\partial t} = -\frac{\partial F_{net,k,V}}{\partial V} + L(V)F0_k + R_{k,V} - K(V)F_{k,V} + \int_0^{V_t} \left(F_{k,v} M(v,V) - F_{k,V} M(V,v) \right) dv$$

where t (s) time, V (m^3) is location in volume, V_t (m^3) is the total volume, C (mol·m^{-3}) is concentration, F_{net} (mol·s^{-1}) the net molar flow rate, F (mol·s^{-1}) the total molar flow rate, R (mol·m^{-3}·s^{-1}) the production rate, L (m^{-3}) the feed distribution kernel, $F0$ (mol·s^{-1}) the molar flow rate of the feed, $M(v,V)$ (m^{-6}) the mixing kernel (amount mixed from location v to V) and k is the identifier for k^{th} component. The mixing kernel M is independent of the species and subject to physical feasibility constraints, like conservation of mass and non-negative flows in the system. This equation embodies the CSTR, PFR and DSR models as special cases. We show that the attainable region for the Van Vusse reaction scheme can be reproduced with this equation.

Having introduced the mixing kernel we will discuss its application to thermal cracking of ethane. Preliminary results will be given and the impact on the design of this reactor will be shown. Further research directions are outlined for the geometric aspects of new reaction equipment.

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Optimisation-Based Design of Reactive Distillation Columns

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Summary

The conceptual design of reactive distillation columns is addressed by mathematical optimisation techniques. Difficulties in the optimisation are caused by the presence of discrete decision variables and by the nonlinearity and the complexity of rigorous column models. In this contribution, we discuss the influence of the modelling of the discrete decisions on the solution effort and the quality of the solution. The problem of local solutions is tackled by using a multi-start solver to initialise the optimisation.
Keywords: conceptual design, reactive distillation column, mathematical optimisation

Abstract

In a reactive distillation column, a chemical reaction is coupled with the distillation of the reaction mixture. This offers the opportunity to overcome chemical and thermodynamic limitations, such as a chemical equilibrium or distillation boundaries. On the other hand, the design of such an integrated process is challenging because the feasibility of the separation depends critically on the design parameters. In the conceptual design of reactive distillation columns, the operating parameters, the dimensions and the structure of the column are determined. Structural variables correspond to the number of column trays, the location of the reaction zone and the existence of feed streams on the trays. The design is evaluated by its total annualised profit that is composed of product revenues reduced by raw material costs, operating costs and investment costs that depend nonlinearly on the design parameters. The conceptual design constitutes an optimisation problem with complex constraints, implicitly given by chemical and thermodynamic equilibria and reaction kinetics. It can be tackled by mixed-integer nonlinear programming techniques. In the literature, different approaches to the modelling of the existence or non-existence of structural elements in the optimal solution have been proposed, e.g. the multiplication of constraints or variables by binary variables [1, 2] or disjunctive programming [3]. Besides the presence of strong nonlinearities in the model, the existence of binary or integer variables causes significant difficulties in the computation of feasible and optimal solutions. Different initialisation strategies can be used to speed up the optimisation which are usually based on insights into the process at hand.

Here we discuss different approaches to the modelling of the aforementioned structural decisions. Besides a conventional approach in which binary decision variables are assigned to the column trays in a superstructure that describes their existence [4], an approach with a minimal number of binary variables was studied. Although the number of binary variables is reduced considerably, the solution effort increases. Similarly, the existence of a feed stream or the presence of catalyst (i.e. chemical reaction) on a tray can be modelled via binary variables. Modelling the presence of feed streams via continuous variables that become zero if there is no feed considerably reduces the computing time but leads to a large number of nonzero feed streams, which is not realistic (cf. Fig. 1b). An efficient alternative is to optimise the number of column trays and the location of the feed trays successively, i.e., first the number of column trays is optimised for an unrestricted number of feed streams and then the locations and the values of a restricted number of feed streams are optimised for a fixed number of trays. A typical result is shown in Fig. 1c. In contrast, the distribution of the reaction zone can be efficiently described by continuous variables. The optimisation problem was implemented in GAMS and solved by the branch-and-bound solver SBB, the reduced gradient solver CONOPT, and OQNLP [5]. OQNLP implements a scatter search algorithm that generates a series of promising initial values with which the optimiser is started, thus increasing the probability of a good solution at the price of a largely increased solution time. The different approaches were applied to the production of methyl tertiary butyl ether and of methyl acetate.
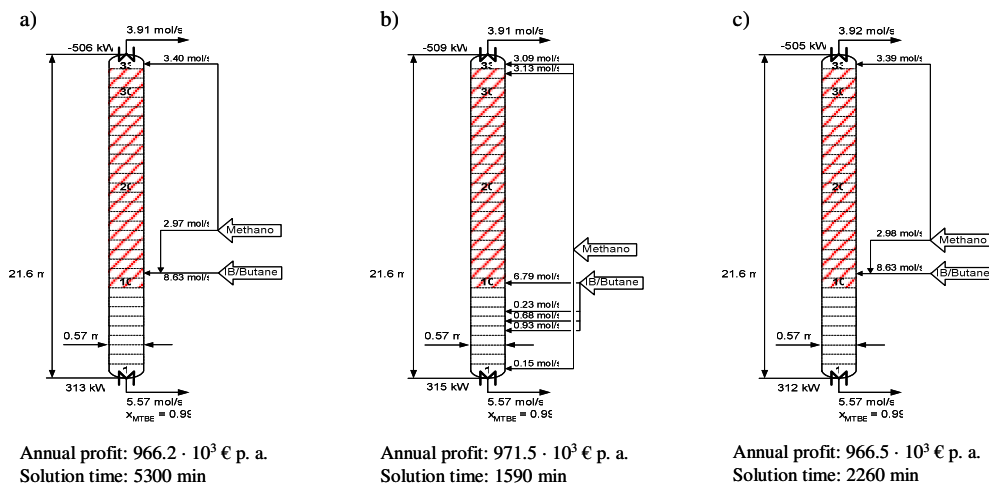
Figure 1: Comparison of different formulations of the optimization problem: a) binary variables for the presence of column trays (max. 40) and feed trays, b) column trays (max. 40): binary, feed trays: continuous, c) number of column trays: fixed from b), binary variable for the existence of feed trays.

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Multicriteria optimization under uncertainty – considering insufficient process data at the operation stage

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1. Summary

Inherent in chemical process models are parameters that have uncertainty associated with them. In an earlier paper the authors addressed multicriteria optimization (MCO) in the presence of model and process uncertainty at the design stage. Specifically the authors discussed extensions of the average criterion method, the worst-case strategy and the ε-constraint method under the following conditions: (a) at the design stage the only information available about the uncertain parameters is that they are enclosed in a known uncertainty region T, and (b) at the operation stage, process data is rich enough to allow the determination of exact values of all the uncertain parameters. The suggested formulation assumed that at the operation stage, certain process variables (called control variables) could be tuned or manipulated in order to offset the effects of uncertainty. This formulation made the conventional assumption that there was only one type of uncertain parameters. In this follow up paper, the authors consider the more realistic case where the uncertain parameters fall under at least two classes at the operation stage, namely (a) those that can be determined with enough accuracy and (b) those that cannot be determined with such accuracy given the available process data. In the full paper three illustrative examples (two benchmarks and one direct methanol fuel cell) will be presented.

Keywords: flexibility analysis, uncertain parameter, two-stage optimization, multi-criteria optimization, direct methanol fuel cell.

2. Extended Abstract

We distinguish between two types of variables, namely the design and control variables. The design variables correspond to design stage and can vary only at this stage. While the control variables can be tuned during both stages of the chemical process (CP). This work is focused on the case when at the operation stage we have incomplete information about uncertain parameters. This means that at the operation stage we do not have enough process data for determination of accurate values for all uncertain parameters. In this case we define two groups of uncertain parameters. The first group represents parameters which can be determined exactly at any time instant at the operation stage; at the design stage the only available information about this

group is given by the associated domain T^1. The second group represents uncertain parameters which cannot be determined accurately enough at any time instant at the operation stage. Thus the only information at both stages is given by the associated domain T^2. The presence of the second group of uncertain parameters complicates derivations of MCO under uncertainty. To solve the resulting MCO problem under uncertainty, we employ extensions of the average criterion (AC, Sophos et al., 1980) method, the worst-case strategy (WCS, Clark and Westerberg, 1983) and the ε-constraint method (Haimes, 1975).

We will use the following general approach for the extension of the AC and the WCS methods. First, we will transform each criterion $f_i(d, z, \theta^1, \theta^2)$ to a new criterion $\bar{f}_i(d)$, which depends only on the design variables. With $\bar{f}_i(d)$ $(i = 1, ..., p)$ we will be able to use either the AC method or the WCS method for solving the MCO problem under uncertainty. From now on we will use the phrase "convolution method" to denote the phrase "AC or WCS method".

Consider the following optimization problem

$$\min_z \int_{T^2} F(f_1, ..., f_p, \alpha)\mu(\theta^2)d\theta^2$$

$$\max_{\theta^2 \in T^2} g_j(d, z, \theta^1, \theta^2) \leq 0 \quad j = 1, ..., m$$

(1)

Here $F(f_1, ..., f_p, \alpha)$ is a convolution of p criteria $f_1, ..., f_p$, which is constructed using the convolution method and a is a vector of parameters. We will suppose that at the operation stage, Eqn. (1) is solved for each θ^1. In the full paper these ideas will be fully fleshed out.

Notation

a_i	Scalar constant
a	Vector constant
d	Vector of design variables (with dimension n_d)
f_i	Performance criterion
g_j	Scalar constraint
z	Vector of control variables (with dimension n_z)
θ	Vector of uncertain parameters over the domain T
θ^1	A subset of θ

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Decision suport system for unsteady-state reactors design using case-based reasoning approach

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1. Summary

The design and simulation of forced unsteady-state chemical reactors involves the mathematical modelling of transport phenomena and reactions in processes that take place in multi-phase systems. The detailed mathematical models of these systems that account for inter and intra-phase gradients as well as exchange or interaction between the phases are often complex and may be expressed in the form of several partial differential equations in two or three spatial coordinates and in time.

Despite a large body of literature in this field, there is no standard procedure developed for the design of reverse flow reactors. The design is often carried out by trial and error, coupled with extensive and tedious detailed numerical simulations.

This work attempts to provide a method for new problems solving by adapting solutions that were used to solve past similar problems. To illustrate this a case based reasoning (CBR) approach have been used in order to provide the insight into reverse flow reactor behavior needed for design decisions; taking into account the experience and solutions provided by the most similar past cases in order to solve new ones.

This approach generates automatically the alternative representations, provides computational information for modeling using previous design experiences, generates new ideas, frames the problem, and evaluates and adapts design alternatives. An example of methodology of design characteristics retrieval related with forced unsteady-state reactors was given to illustrate the proposed design method.

Keywords: case-based reasoning, unsteady-state reactors, decision suport system

2. Extended Abstract

The chemical engineering problems especially the design and modeling tasks are often quite difficult to be represented as a structured list of features of one or two data types. The forced unsteady state reactor and processes are highly complex. In order to

obtain relevant information a CBR system was implemented and in its library have been stored significant literature cases dealing with processes involving forced unsteady state operation.

The input information consists of numerical value representation of the technical characteristics and implicit information, and some textual aspects related to the description of the problem.

The problem is defined by a list of features with their values and weights of importance. Expert opinion was used in order to set up the most important feature for the correct identification of the forced unsteady state systems statement. The design experience of existing forced unsteady state process was stored as cases. The data of each case representation are schematized depending on specific information, i.e. substance class and name, process type, reactor characteristics, process and operating parameters, catalyst characteristics, solution description, comments or suplimentary information, etc.

The unsteady state reactor operation problem was submitted to the engineering analysis by structuring it on stages. This has been implemented in a CBR tool with interactive querying and abstractness procedure.

The following algorithms have been used in the framework of the CBR mechanism implementation: the *CBR-query support algorithm, the case retrieval algorithm, the similarity computation algorithm and the case adaptation algorithm* which uses rules and similarity paths.

The CBR-query support algorithm allowed to reduce the amount of the routine work needed to input information and to enforce domain model integrity. It supports inheritance of the components, properties and relations from classes, creation of virtual components corresponding to complex structural relations, etc.

The case retrieval algorithm, which is the key part of the CBR system, was based on the similarity measure [1].

The similarity computation algorith features the selection of the most appropriate mapping between the relation sets of the compared individuals by testing all possible paths against the maximal similarity criterion. Also, the use of weighting coefficients for relations allowed flexible tuning of the algorithm and similarity functions.

The CBR tool processes the problem description of a new forced unsteady state process matching it in comparison with all the cases in the CBR system library. The most similar cases are retrieved and the best one is selected in two steps, the first one - *tool based* corresponding to the usual CBR retrieval and the second one - *expert based* taking into consideration the specific supplementary information or comments related to specific features in order to improve the reliability of a possible new solution.

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Uncertainty Analysis during the Multi-criteria Evaluation of Wastewater Treatment Plant Design Alternatives

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1. Summary

The objective of this paper is to present the application of a systematic procedure to evaluate wastewater treatment plant (WWTP) design alternatives under uncertainty by multiple objectives. The motivation of this approach is to provide the designer with a tool to handle the deviation that prevails around the possible values that technical, economical, legal and environmental parameters can assume in the early stages of design. Decision making in these early stages is especially difficult when several design objectives must be taken into account simultaneously i.e. the evaluation of the alternatives is a multi-criteria problem. The usefulness of this approach is demonstrated with a case study where the type of biological nitrogen removal process in an existing activated sludge plant is evaluated

Keywords: Process Design, Wastewater, Uncertainty, Multi-criteria Decision Analysis, Monte Carlo Simulation

2. Extended Abstract

As in many other engineering applications, the evaluation of design alternatives in wastewater treatment plant (WWTP) design must take into account several objectives i.e. it is a multi-criteria problem (see for example Belton and Stewart, 2002). Moreover, in WWTP design there is generally a high uncertainty associated to the values that can be assumed for economical, environmental, technical and legal parameters

Nowadays, the analysis of activated sludge WWTP design alternatives is supported by the use of numerical simulators (Salem *et al.*, 2002; Beck *et al.*, 2005). However,

commercial process simulators assume deterministic rather than stochastic parameters and thus do not consider the influence of parameter variance on simulation results. Uncertainty is a central concept when dealing with biological systems such as a WWTP, a plant that is typically subjected to large natural load variations. Thus, both identification and understanding of the influence of parameters presenting uncertainty is essential for the correct assessment of a WWTP design and for the analysis of existing designs.

The objective of this paper is to present a systematic procedure to evaluate WWTP design alternatives under uncertainty.

The set of new results are illustrated with a case study, where the bioreactor of a WWTP is retrofitted to achieve simultaneous carbon and nitrogen removal. This plant is comprised of five aerobic continuously stirred tank reactors (CSTRs), a settling tank, a recycle and a purge. A number of simulations are carried out coupling a deterministic model with a Monte Carlo engine to explore the WWTP response with respect to the evaluation criteria. The knowledge generated during this process is extracted automatically and is quantified in terms of risk. This estimated risk provides a wider picture of the design space and the resulting decisions based on such information are more solid, since more information has been taken into account.

The significance of the proposed procedure resides in the advantages of integrating deterministic and probabilistic methods for multi-criteria decision making. Detailed numerical models (Henze *et al.*, 2000) are used to investigate the effect of parameter uncertainty on the overall process performance. As a result, it is possible (a) to provide the designer with a tool to handle the uncertainty inherent in the early stages of WWTP design, b) to demonstrate how the different uncertainties are propagated through the model and how they affect the effluent streams, and (c) to make more informed and rational decisions on whether or not to implement a specific wastewater treatment technology by quantifying its influence on the design under uncertainty.

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Session T4-1P: Process Synthesis & Design - Poster

Abstract Number	Paper Title & Authors	Included
149	The system analysis of multiassortmental manufacturings of phosphorus – containing products based on CALS – technologies A Bessarabov, L Puigjaner, E Koltsova, T Ogorodnikova	Yes
256	About new type of multiplicity of steady states in the recycle system: Reactor - Separating unit S Duev	No
686	Practical application of the methodology of integrated design for the synthesis of continuous flexible automated turbulent reactor units in the production of azo dyes and pigments G Ostrovsky, D Dvoretsky, S Dvoretsky	Yes
1460	Use of glycerol from biodiesel production: Conversion to added value products C Cardona, J. Posada, M Montoya	Yes
1651	Mineral process design under uncertainly: A case study approach L Cisternas, N Jamett, E Gálvez	Yes
2186	Norm norm-based approaches for Integrated Design of WWTP M Francisco, P Vega	Yes

The system analysis of multiassortmental manufacturings of phosphorus – containing products based on CALS – technologies

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1. Summary

An information system has been designed for monitoring the quality of multiassortmental manufacturings of phosphorus – containing products substances. The information system is based on the international CALS standard (ISO-10303 STEP). It contains the following information for the main elements of analytical monitoring: a list of elements to be monitored (substance classifier), details of the analytical procedure (including the sampling and sample preparation steps), performance parameters of the instruments, metrological support, and normative documentation (GOST standards, technical specifications, and others).

Keywords: phosphorus-containing products, multi-assortimental manufacturings, CALS, ISO 10303, system analysis

2. Extended Abstract

Multi-assortimental manufacturings phosphorus-containing products were examined. The first manufacturing consists of four products production by phosphoric slag processing. Four target products are examined during the investigation: sodium hipophosphite, sodium phosphite and lead hydrophosphite and phosphorous acid received at further processing. Second manufacturing is a multiassortmental six-products manufacturing of phosphoric acid of various qualifications.

For these schemes the system analysis at four levels of hierarchy is made: nomenclature level, productional-technological level, organizational-technological level and organizational-productional level. Three kinds of flexibility correspond to hierarchical structure: technological, structural and organizational.

The organizational-technological level's attribute is a united compartment. Tasks: apparature optimization and production cycle minimization.

The organizational-productional level's attribute is a separate workshop as a complex cybernetical system. Tasks: stabilization of material and informational flows

between the united compartments; distribution of raw materials, energetical and human resources.

The productional-technological level's attribute is a multiassortmental production. Tasks: optimal application of semiproducts and of common source materials; application of flexibility elements with the purpose of productional groups' extension; the power varying of the technological process in common.

The greatest interest for us represents a nomenclature level. Its characteristic attributes: a product of one aspect or one technological stage. Primal problems: expansion of a set of qualifications on parallax purity of one product; a variation of power of a technological stage. The operation of the given level is ensured with technological flexibility, which is determined by ability on the available equipment to execute some technological problems at the expense of flexible technological methods of deriving of preset substances (under the nomenclature) or at insignificant expenditures on returning of the equipment (stopping on washing, recommunication of pipelines and other operations).

For system analysis and control information of phosphorus-containing products, there carried out the development of a software package, including standard output documents (GOST (State Standards of Russian Federation), TU (technical standards), protocols, certificates etc.). Development was carried out within frameworks of the most modern and perspective computer aided system - CALS-technologies (Continuous Acquisition and Life cycle Support). In the basis of the CALS concept there is a complex of uniform informational models, standardization of methods to access information and its correct interpretation according to international standards (ISO-10303 STEP). In our work, the CALS concept usage allows to accomplish effective analytical monitoring of a wide class of phosphorus-containing products, essentially reduce time of analytical research and to increase quality of performed scientific operations.

Grouping of input information in CALS-system is performed by following categories: analyzable substance;documentation; used method of the analysis. In each category there is a little subcategory for data systematization by criteria, by respective category. Thus, in a category "substance" the following groupings were included: liquid-phase - solid phase; organic - inorganic; acids - salt - oxides etc.

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Practical application of the methodology of integrated design for the synthesis of continuous flexible automated turbulent reactor units in the production of azo dyes and pigments

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1. Summary

Statement of the problems and example of integrated synthesis of optimal turbulent reactor installation of continuous azo-dyes and pigments synthesis under uncertainty are presented. The analysis of insights into practical application of the methods of one- and two stage stochastic optimization problems solving with "hard" and "soft"(probability) constraints is given.

Keywords: integrated design, turbulent reactor unit, azopigment synthesis

2. Extended Abstract

During the integrated design of installation's units and control system of azo-dyes synthesis [*Ostrovsky G.M. et al.*] it is necessary to define design and process variables as well as the vector of tuning parameters of the control system to fulfill the efficient work of the installation and process constraints under uncertainty of process variables and model coefficients (kinetic parameters, heat and mass transfer coefficients etc.).

The process mechanism includes dissolution of the solid phase and aggregate of the chemical reactions. The goal product is diazocompaund, a secondary – nitrous gases, diazo-rosins etc. Aromatic amine in the form of hydrochloric suspension flows continuously into reactor, together with aqueous dissolution of sodium nitrite distributed along the reactor unit.

A number of tube modules and their sizes represent **design** variables of the installation, temperature and distribution of diazotization agent are **regime** (control) variables, and concentration of amine solid phase $[C_a^{(0)}]_s$ =370,0(±4%) mole/m^3,

kinetic coefficient of amine solid phase dissolution A=5,4·10^5(±5%), and kinetic coefficients of diazocompound decomposition (activation energy E_{04} = 87150(±0,2%) J/mole, E_{05}=63690(±0,2%) J/mole) are **uncertain** parameters. Influence of uncertain parameters has been considered according to the normal law of distribution. A class of *b automatic control systems* (ACS) with closed structure *h* is a possible control system. Mathematical model of a continuous synthesis process in a turbulent reactor unit has a form of non-linear differential equations system.

The choice of ACS structure was carried out with the use of the region of controllable (observable) variables and actions obtained from the analyses of structural matrix of chemical process dynamic equations. Also observability of the output variables, evaluation of the expenses for the development of the control devices, possibility and accuracy of the output variables forecast were considered. Alternative classes and structures of the ACS were explored using imitation modeling method in the order of their costs ranging.

Investigation of dynamic indicators of chemical process (controllability, inertance, etc.) in terms of control was carried out for admissible ACS structures. In the case when controllable in static chemical processes have poor dynamic characteristics, design and regime parameters (determined at the first stage) are corrected or new types of process units are chosen.

The analysis of the results of integrated synthesis for different problem statements proves that for reactor unit design of azo-dyes and pigments synthesis under uncertainty extra reserve of technical resource (comparing with the design without taking into account uncertain factors) is required. It is necessary to increase the design volumes of the reactor units: for the one stage optimization problem with "hard" and "soft" constraints overdesign is 50 % and 38 % respectively; for two stage problem with "hard" and "soft" constraints it is 45 % and 34 % respectively.

The final stage of integrated design consists of solving optimization problem for alternative variants of CP-ACS complexes. Attainability of the set goals for process running and feasibility of design specifications are proved by imitational research.

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Use of Glycerol from biodiesel production: Conversion to added value products

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1. Summary

A detailed study of main stages of a novel non-conventional process to obtain 1,3-Propanediol (*PD*) from Glycerol (*Gly*) has been made. Initially the volumetric productivity of *Gly* fermentation with *Klebsiella pneumoniae* bacterium was optimized for two continuous stages of fermentation, where was necessary to study the multiplicity of stable steady states for fermentation system. For PD recovery from fermentation broth it has been proposed a reactive-extraction with iso-butyraldehyde (iBAld) for produce 2-iso-propyl-1,3-dioxane (iPDOx) and water. iPDOx is removed in organic phase with aldehyde that acts simultaneously as reagent and solvent. Finally Static analysis for iPDOx hydrolysis system shows that is possible to obtain PD of high purity in a reactive-distillation tower, where also aldehyde is recovered.

Keywords: Glycerol fermentation; 1,3-Propanediol production; Reactive–extraction; Static analysis; Reactive–distillation.

2. Extended Abstract

Glycerol (Gly) is side product in biodiesel production, which is obtained in a ratio 1/10 (Gly/biodiesel) in weight. The growing biodiesel demand makes unavoidable an increase of Gly in the market and consequently a fall of its price, for this reason is necessary to transform it into a product of more added values and of high demand. An analysis about the different possibilities of Gly transformation available in the bibliography was carried out previously (*Posada et-al, 2006*), where both aspects were considered, operational and economics. This analysis showed that the most suitable option is the anaerobic fermentation with *Klebsiella pneumoniae* bacteria. Cellular growth model (*eq. 1, Zhi-Long Xiu et-al, 2004*), is based in a variation of *Monod* equation which consider the critical concentrations of all compounds (C_i^*) in which cellular activity ceases.

$$\mu = \mu_{max} \frac{C_{Gli}}{C_{GLI} + K_S} \left(1 - \frac{C_{HAC}}{C_{HAC}^*}\right)\left(1 - \frac{C_{EtOH}}{C_{EtOH}^*}\right)\left(1 - \frac{C_{PD}}{C_{PD}^*}\right)\left(1 - \frac{C_{Gli}}{C_{Gli}^*}\right) \qquad eq\ (1)$$

An analysis of multiplicity of stable steady states was carried out to optimize the volumetric productivity for one and two stages, selecting the conditions where higher concentrations of PD are found. In this case were analyzed three variables, feed *Gly* concentration, dilution rate in first and in second fermentation stage. PD outlet concentration and global yield in optimal operation are 0.4833 mol/l and 0.5481 molPD/molGly. For PD purification from fermentation broth a new no-conventional separation scheme was proposed that consists first in changing the hydrophilic character of PD with a reversible reaction of an aldehyde producing *2-alkyl-1,3-dioxanes* easily extractable by an organic phase. This was initially proposed by Malinowski (2000) and extended by Liu et-al (2005) where aldehyde acts simultaneously as reagent and solvent. In this work was found that iso-butyraldehyde (iBAld) is the most appropriate due to the low solubility in water (7g/100gH2O) and its mild boiling temperature (64.3 ℃), where the 2-iso-propyl-1,3-dioxane (iPDOx) produced is less soluble in water between the evaluated dioxanes. The yield of reactive-extraction is 85%. For iPDOx hydrolysis reaction the static analysis proposed by Pisarenko et-al (2001) is carried out. This is a short method that allows to study reactive distillation operations where a qualitative synthesis of technological scheme is obtained. The analysis showed that the adequate feeding ratio is 0.378/0.622 (iPDOx/Agua), with total iPDOx conversion for a reactive-distillation tower, packed in a great proportion on the inferior section due to self-extractive phenomenon, then pure PD is obtained as bottom and iBAld-water heterogeneous azeotrope is obtained as distillate; where can be recovered iBAld to 88%. This was confirmed with simulations to ∞/∞ conditions (100 stages and reflux 35) in ASPEN PLUS. For finite conditions the simulations showed that for a tower of 45 stages, packed between stages 8 and 44, with reflux of 5.73, a conversion of 69% is reached. When the water feeding is distributed and a reflux of 9.5 is used, a conversion of 97.5% is reached.

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Mineral Process Design Under Uncertainly: A Case Study Approach

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1. Summary

One of the presently existing difficulties in designing a process through optimization techniques is the estimation of the parameters needed for composing a selected model. In general, these parameters are not constants over time, and may be subject to degrees of uncertainty when they are estimated, either because they are represented by a known distribution of values or because the model is not a representation of the entire phenomenon. The objective of the present study is to analyze if this uncertainty influences the design of mineral processing systems. Following this theme we applied stochastic programming to the designs of copper mineral flotation circuits and compared them with results obtained by using deterministic programming. Three case studies were examined, two of which contained uncertainty in one parameter each, and a third study which had uncertainty in both of these parameters simultaneously. With all the cases, we first obtained an optimal deterministic solution using a mean value for the uncertain parameter. Then an optimal stochastic solution was obtained using the distribution of the parameter, examining various scenarios and their probabilities of occurrence. The results showed that when comparing the profits from circuits obtained by the deterministic versus the stochastic method, the results favored the use of the latter method. It is thus concluded that the stochastic programming method is able to provide better results than the deterministic method in designing certain mineral treatment processes.

Keywords: mining technology, flotation circuits, systems optimization, uncertainty evaluation, deterministic models, stochastic models

2. Extended Abstract

Flotation is a physico-chemical process which allows the separation of minerals from the remaining minerals which form most of the parent rock substrate. The separation is carried out using flotation circuits between flotation cells, flotation columns and auxiliary steps (milling and classification). The behavior of the entire process depends

on the configuration of the circuit and the chemical and physical nature of the pulp treated. None of the methods for designing flotation circuits, available in the literature (Cisternas et al, 2004, 2006), has considered that the design may contain parameters which cannot be completely defined, or values which may be subject to degrees of uncertainty. These usually involve external factors such as product demand, economic factors, environmental factors, or internal plant conditions including kinetic and diffusion constants (among others) which may lead to an inefficient process design (Kraslawski, 1989). In the specific case of the design of flotation circuits, large numbers of variables are handled, of which some may involve uncertainty, such as the grade of the feed stream carried into the circuit, the metal or product price, distribution of mineral particle size, and others.

Using two-stage stochastic programming with recourses (Sahinidis, 2004) three cases studies are analyzed. One of these includes uncertainty in the determination of the feed stream grade, the second uncertainty in the metal price (copper), and the third uncertainty in both parameters. The objective in all the cases was to determine the optimal configuration of the operation of the superstructure proposed by determining the correct distribution of streams (input and output from the equipment, recirculation, and mixing), and the operational condition in the Cleaner flotation stage. The mathematical problem is a mixed integer stochastic linear programming.

The examination of case studies has now shown that in all cases the application of only deterministic programming using mean parameter values results in losses of profits in the process, in comparison with methods employing stochastic programming. For this reason it is concluded that the use of stochastic programming is probably a necessary tool for process design, and in the present study, that of mineral processing since it creates flexible circuits with regard to operational and economic variations which are better suited to the variability of uncertain parameters.

Acknowledgements

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Norm Norm-based approaches for Integrated Design of WWTP

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1. Summary

In this work the Integrated Design (ID) of the activated sludge process of a wastewater treatment plant has been performed, including a linear multivariable predictive controller with constraints. In the ID procedure, the process parameters are obtained simultaneously with the parameters of the control system by solving a multi objective constrained non-linear optimization problem, taking into account investment, operating costs and a set of performance indexes based on the weighted sum of the H∞, l1 and H2 norms of different closed loop transfer matrices of the system, subject to a set of constraints (process, controllability, physical constraints).

Key words:
Integrated design, dynamic optimisation, activated sludge process, H8, l-1, H2 norms, Sensitivity transfer function, Control Sensitivity Function

2. Extended Abstract

2.1 Motivation and Objectives

Traditionally, process design and control system design have been performed sequentially. It is only recently displayed, that a simultaneous approach to the design and control leads to significant economic benefits and improved dynamic performance during plant operation. The Integrated Design methodology allows for the evaluation of the plant parameters and control system at the same time, making the designed system more controllable. Some good examples of Integrated Design applied to the activated sludge process are given in [1,2,3,4,5] where the plant dimensions, an optimal working point and the parameters of the controllers were obtained simultaneously. Despite of the complicated dynamics of the process under design, works adding advanced controllers to the Integrated Design procedure have not been reported in the literature even though it could be a good way to improve control performance. The reason for that it could be related to the complexity of the resulting optimization problem.

Within this context, the aim of this work was to tackle problems directly related to the Integrated Design of Activated Sludge Processes and Advance Control Systems to support engineers during the complex task of designing and control Wastewater Treatment Plants. The integration of Numerical Optimization, Dynamical Model Simulation and Model Based Predictive Control, is the most relevant feature of the work and, in our opinion, the key point to success in the design of flexible processes reducing the operation costs while legal specifications on the quality of the treated water are fulfilled.

2.2 Integrated design methodology

In this work, the Integrated Design problem is stated mathematically as a constrained non-linear multi-objective optimization problem, in which economic and control objectives and are considered together with some constraints. The solution of the ID problem is obtained following a constrained numerical cost optimization procedure that uses dynamic models and real data records of disturbances together with a set of predefined constraints to evaluate the plant dimensions, the optimal operation points and the control system parameters.

The cost functions include the investment, operation costs, and dynamical indexes based on the weighted sum of the H∞, l1, H2 norms of different closed loop transfer functions matrices of the system subject to a set of constraints. The constraints are selected to ensure that the process variables and some closed loop controllability measures and several closed loop performance criteria lay within specified bounds.

The methodology for the integrated design is subdivided in several steps:
1. Initial plant information: where all the information necessary is defined to carry out the WWTP design. It includes wastewater and control system characterisation (plant and control type, models, plant load,…)
2. Definition of design objectives, performance and controllability criteria and constraints: where the preliminary goals and the corresponding measurement criteria are proposed and classified according to different categories (environmental, economic, operational, control..).
3. Optimization procedure:
4. Validation of results: where the optimal plant can be simulated, several criteria evaluated, and comparison with other plants can be carried out.

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Session T4-2: Process Operation, Monitoring & Analysis

Abstract Number	Paper Title & Authors	Included
66	On the control problem in fluid energy milling and air classification processes: approaches for experimenting and modeling particulate systems in an industrial scale plant. L L Coutinho, M Embiruçu	Yes
630	Modeling and simulation for correlation between operational conditions and end-use properties of high density polyethylene resins M C B Costa, A L Jardini, M Embiruçu, R M Filho	Yes
821	Start-up of Empty Cold Reactive Distillation Columns by means of Feedback Control Strategies: the Discontinuous Stage S Sommer, J Raisch, K Sundmacher	Yes
939	Dynamic Evidence of Multiplicity in a Reactive Distillation Column for Ultra-Low Sulfur Diesel Production J C Cárdenas, T López-Arenas, R Lobo-Oehmichen, E S Pérez-Cisneros	Yes
1891	Diagnosis-based Sensor Network, Design and Retrofitting R Angelini, I Yelamos, L Puigjaner	Yes
2007	Evaluation of the potential of Periodic Reactor Operations Based on the Second Order Frequency Response Function A Markovica , A-S Morgenstern, M Petkovskac	Yes

On the control problem in fluid energy milling and air classification processes: approaches for experimenting and modeling particulate systems in an industrial scale plant.

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1. Summary

The objective of this paper is to study the control problem in particulates process, specifically opposed air jet milling followed by particle size classification using a forced vortex classifier. An overview of both processes is given and the control problem is defined based on the input variables, output variables and disturbances and from a perspective of experimenting and modeling those processes in an industrial scale plant. The multivariable control problem and causality diagrams are presented for each operation and the proposed experiments to model both plants are described. The interactions existing between both operations are considered in order to identify a control strategy that enables increase energy efficiency and maintain or improve product quality. Difficulties in performing model identification of dynamic processes without considering the availability of a laboratory scale pilot plant and without using an on- line particle size measurement device are discussed and results from preliminary experiment are presented.

Keywords: Fluid energy milling, fluid classification, modeling, particulate systems.

2. Extended Abstract

Particulate processes and powder materials are used in many different industries such as pharmaceutical products, food processing, powder metallurgy, painting, mineral processing and chemicals in general. Size reduction or comminution is the operation to reduce the particle size of solids. In the most of the cases, size reduction is based on applying mechanical energy to reduce the particles throughout producing compression, collisions or friction to promote particle breakage. As an intrinsic result of the breakage phenomena, different sizes of particles are generated. It means that it is not possible to define a unique particle size for the outcome material, but a particle size distribution. In the majority of the cases of comminution, it is not quite simple, or even possible, to control the shape of the size distribution by manipulating process

variables. Thus, when size distribution is a requirement for the particulate, subsequent particle size classification is necessary to separate the coarser particles from the fine fraction and adjust the shape of the size distribution. For the material in study, the excess of fine particles has bad influence in the product quality and the classification process objective is to reduce the fine fraction in the final product.

Particle size distribution and energy efficiency are important performance outputs for size reduction and classification operations. Many authors have reported that less than one percent of the total energy input is used in the breakage process. A considerable effort has been put in by many scientists and powder processing researchers in order to obtain suitable models for this branch of industrial systems. Most of the works describing those systems are based on population balance models, process rate models, and more recently approaches using Markov chains theory. It is not very common to find works in open-literature dealing with multiple inputs and output variables models and only very little research has been conducted based on black-boxes and nonlinear identification methods. Difficulties in performing model identification of dynamic processes without considering the availability of a laboratory scale pilot plant and without using an on-line particle size measurement device are discussed and results from preliminary experiment are presented.

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Modeling and simulation for correlation between operational conditions and end-use properties of high density polyethylene resins

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1. Summary

The development of mathematical relationships to allow the prediction of end-use properties of polymer resins as functions of the polymerizations conditions may be very useful for the production of resins with consumer specified properties. In this work is to build-up empiric models relating intrinsic and end-use properties of high density polyethylene (HDPE). Statistical correlation analysis was performed for all variables and used as the basis for proper choice of inputs to each outputs model. Subsequently, a process composed of two tubular reactors and a non-ideal stirred tank reactor, representative of many industrial plants, where different operational modes may be used as case study. Polyethylene resins produced in a second generation petrochemical industry and applied in the injection plastic molding were evaluated experimentally, since it is an important commodity nowadays. The developed models were compared to experimental data and good predictions were obtained.

Keywords: modeling, empirical models, polymerizations conditions, end-use properties, polyethylene

2. Extended Abstract

Resins produced in a polymerization process are approved by industrial quality control routines only if they meet a package of specifications needed for certain applications. Specifications are usually defined in terms of end-use properties, such us tensile strength and stiffness. If resin properties do not meet the defined specifications, resin lots are discarded, reprocessed or used for other applications, bringing some disadvantage to the company. Therefore, the development of mathematical relationships to allow the prediction of end-use properties of polymer

resins as functions of the polymerizations conditions may be very useful for the production of resins with assured specified properties. The problem, however, is that there is a lack of theoretical knowledge regarding how process operation conditions and end-use properties are related. The approach used here to bridge this gap is to identify the relationship between the some molecular and morphological properties (FI and density) of polyethylene resins and then to accommodate the desired end-use properties with those properties to develop suitable correlations. Continually, it is necessary to correlate operation conditions with FI and density of resins. According to this strategy, the first step may be regarded to be the most important one, as the second step may be performed with the help of process simulators.

The predictions from the empirical models were compared to the experimental values. Figure 1 illustrates the performance of the empirical models, which in fact is quite satisfactory, the models with representative parameters obtained for resins applied in the injection plastic molding and the multiple correlation coefficients for each model. It is possible to conclude that the empirical models developed may be useful to be used in either product development or for the definition of operation strategy to obtain the products with the desired property. With the empiric models, an analysis of the final properties behavior related to the intrinsic properties was carried out.
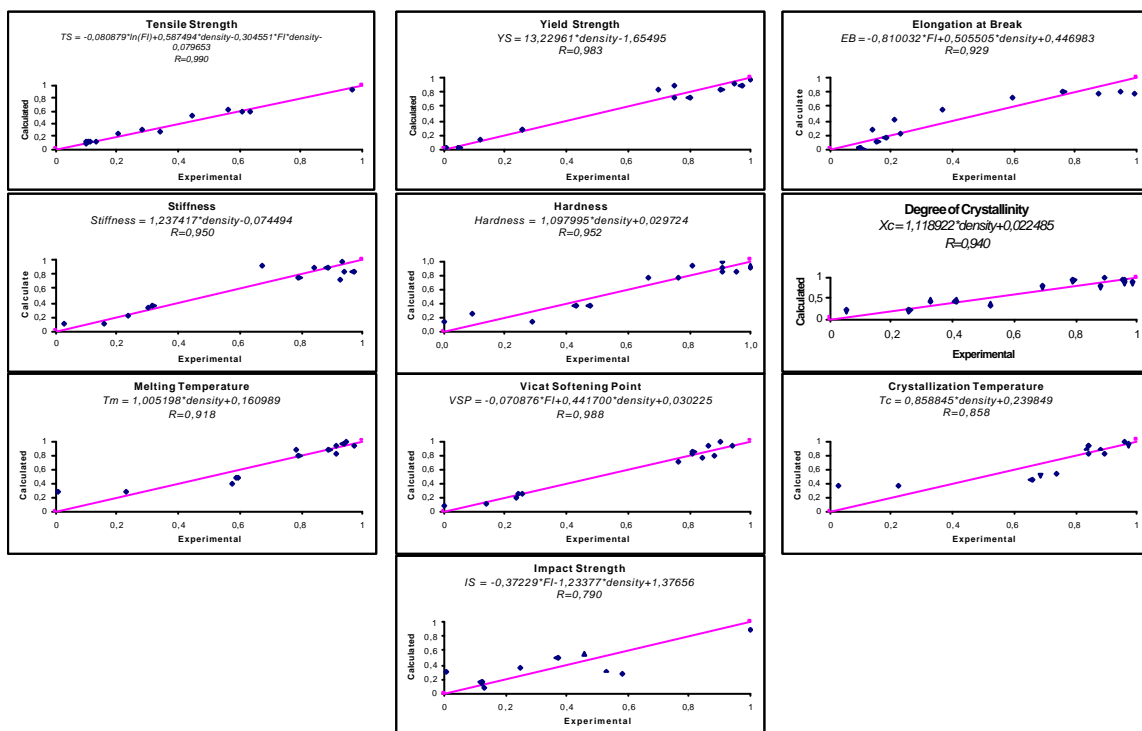
Figure 1 - Comparison between experimental values and calculated values for end-use properties.

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Start-up of Empty Cold Reactive Distillation Columns by means of Feedback Control Strategies: the Discontinuous Stage

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1. Summary

A new approach for start-up of empty cold reactive distillation columns by means of feedback control strategies is presented. In this paper, the discontinuous stage of start-up is taken into account. This stage begins with the fill-up and heating process of the empty cold column and ends if vapour reaches the condenser. A corresponding model for the start-up process is developed. The control strategy is based on servo-control of the process variables temperature and liquid level of the reboiler with PI controllers and is combined with bottom product recycling. The proposed strategy is demonstrated and tested with the reactive distillation process of esterification of ethanol with acetic acid.

Keywords: reactive distillation, start-up, discontinuous stage, feedback control

2. Extended Abstract

Reactive distillation (RD) processes integrate chemical reactions and distillation in the same process unit. This has several positive implications. However, the dynamic behaviour of reactive distillation columns (RDC) is quite complex, especially during the start-up stage. The start-up process of RDC is of environmental and commercial importance, and represents an active field of research. For RD operation, start-up should be finished as fast as possible since all process variables are changing during this stage, and the product has to be disposed. So far, there are only few publications addressing start-up of empty cold RDC, for instance Reepmeyer et al., 2003.

The motivation of this contribution is to solve the problem of the start-up process of the cold empty column by means of feedback control strategies. Thus, an automatic start-up strategy is obtained, which implies several potential advantages when compared to the existing open loop strategies: for example the start-up process can be

made insensitive against disturbances, operating safety can be improved, and a desired steady state can be reached exactly. It is convenient to model different stages of the start-up procedure separately and to apply a different control strategy for each stage. The outcome is a switching scheme consisting of several control policies based on different models.

In this contribution, we investigate the first part of start-up. It is called the discontinuous stage and consists of two single stages. Stage I is the fill-up and heating process. After achieving boiling conditions, stage II starts and ends if vapour reaches the condenser. The discontinuous stage is relevant, because in most works on start-up of RDC the trays are filled and warm.

The control strategy is based on servo-control of the process variables (controlled variables) liquid level $h_R(t)$ and temperature $T_R(t)$ of the reboiler with switching PI controllers including anti-reset-windup, and can be summarized as follows (see figure). The manipulated variables are the feed flow rate $F(t)$ and the reboiler heat duty $Q_R(t)$. Two switching procedures are necessary during the automatic start-up of the discontinuous stage. Before the feed tray and the trays below, except the reboiler have been filled completely, $F(t)$ is set to its maximum value F_{max} and $Q_R(t)$ is set to zero. When the liquid arrives at the reboiler, the liquid level control and the temperature control are switched on. The second switching procedure occurs at the beginning of stage II, because the dynamic behaviour of the column is changing when vapour is rising. In the strict sense, the controller parameters are changing when boiling conditions have been achieved in the reboiler: $p_{bub,R}(t) > p_0$.
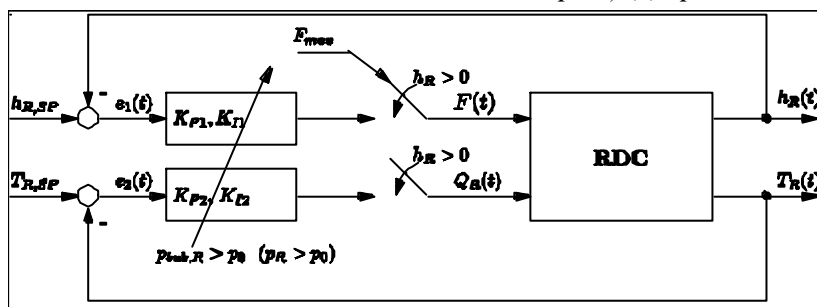
The control scheme is combined with recycling partial bottom product back to the feed (bottom product recycling). The recycle can reduce the amount of waste during start-up.

A corresponding model is developed to describe the discontinuous stage of start-up. For each tray, one total mass balance, one energy balance, and nc-1 component mass balances are formulated (nc = number of components). The generated equations are a rather complex, nonlinear, and implicit differential algebraic equation (DAE) system.

Our start-up strategy has been tested for an example where ethyl acetate and water is produced from ethanol and acetic acid. Promising simulation results have been obtained. The approach with bottom product recycling is recommended for the presented discontinuous stage.

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Dynamic Evidence of Multiplicity in a Reactive Distillation Column for Ultra-Low Sulfur Diesel Production

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1. Summary

The objective of the present work is to analyze and predict the multiple steady states through dynamic analysis when the reactive distillation column is subject to different input disturbances. The dynamic simulations are carried out to analyze the open loop dynamic responses of the system using step changes in the manipulated variable (reflux ratio, holdup, hydrocarbon mixture feed stage, hydrocarbon mixture feed flowrate, reboiler duty) and recording the dynamic behaviour of the product conversions (DBT and 4,6-DMDBT, called controlled variables). The magnitude of the change in the manipulated variables should be reduced to around 0.5% or less than its nominal value.

Keywords: reactive distillation, multiple steady states, HDS, dynamic simulation

2. Extended Abstract

A preliminary bifurcation analysis (López-Arenas et al., 2006) reveals the existence of multiple steady states in a reactive distillation process for ultra-low sulfur diesel production. It was found that, the main variables that affect the steady state behavior are the feed stage and flowrate of the fed hydrocarbon mixture (HC), reflux ratio and holdup. Furthermore, the holdup, sulfur composition in the HC feed stream and the H_2/HC feed ratio determines the final steady state achieved. The steady state design of the reactive distillation column (RDC) described here is based on the work by Viveros-García et al. (2005), in which the optimal design was achieved through a rigorous optimizing procedure using Aspen Plus 11.1^{TM}. This configuration (Figure 1) consists of 14 stages with two reactive zones and three non-reactive zones. It was fixed an operation pressure of 30 atm in the reactive column and a H_2/HC feed relation of 3 was used. The non-ideality of the system is accounted through the use of Peng-Robinson equation of state. Target conversion of 99% for the DBT and 4,6-

DMDBT were assumed. We used the Aspen Dynamics 11.1 ^{TM} to study the dynamics and control of the process. The equilibrium stage model is used in the simulation with bubble cap stages in the non-reactive zones and catalytic Rasching Rings in the reactive zones. The residence time of each device internal is about 5 min. This design is intended to have a high holdup and liquid phase residence time so that the regime of operation at each device internal is in the bubbly flow regime.
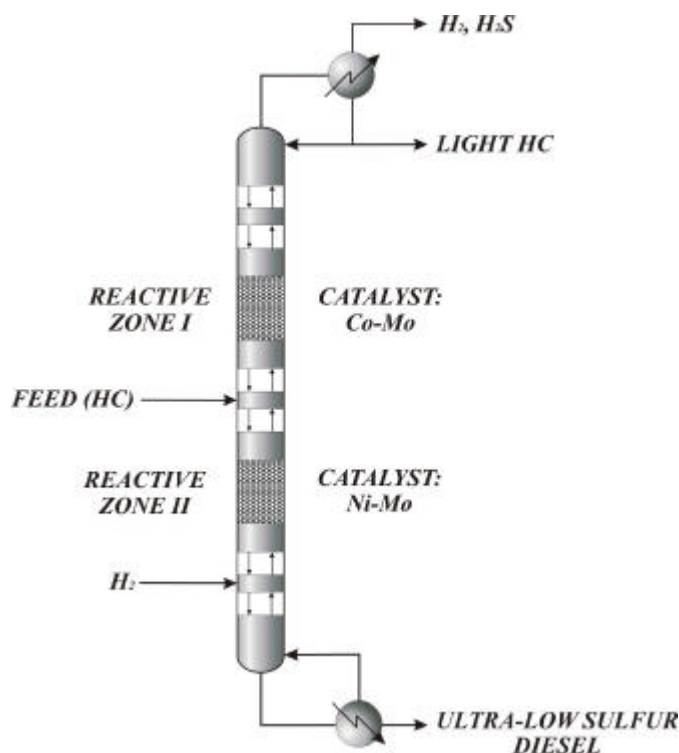
Figure 1 Design of a RDC for ultra-low sulfur diesel production.

As part of results obtained by the dynamic analysis we can conclude that one way to overcome the hardware and controllability design conflicts in the RDC, while maintaining the benefits of *in-situ* separation with reaction, is to employ the *Distillation-Side Reactor Concept* (DSRC).

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Diagnosis-based Sensor Network, Design and Retrofitting

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1. Summary

In this work the design and retrofitting of a sensor network (SN) is arranged by minimizing the sum of investment costs while keeping the performance of the plant Fault Diagnosis System (FDS). It is achieved by reducing the number of measured process variables according to some FDS constraints. The benefits of the methodology presented are demonstrated in an industrial case study, the Tennessee Eastman process (TEP).

2. Extended Abstract

The optimal design of sensor networks (SN) has received an increasing attention during last years. A wide variety of approaches relying on exhaustive enumeration, rigorous mathematical models, etc., were developed to address the complexity of SN placement problem. Within this context, the sensor placement can be regarded as a high combinatorial optimization problem where the main goal is to find the optimal balance between the indicators cost and performance. On the other hand, in most of the papers dealing with fault diagnosis it is assumed that the SN is in place and the relationship between sensor location and the FDS performance is rarely discussed. Here, both issues are considered and a method to optimally design a SN which on-line supplies reliable data to a FDS is presented. Sensors are placed to minimize the sum of investment costs while keeping the FDS performance when all original measured variables are considered.

The proposed method just measures some process key variables while maintaining the FDS performance. These variables must gather the essential process information from the diagnosis viewpoint. Then, an optimization method that assures the process observability and the minimum reliability of process key variables estimation is applied to allocate the required instrumentation. The methodology has been checked in a challenging diagnosis problem (TEP, Downs and Vogel, 1993) by using a data based FDS. The FDS is based on a Principal Component Analysis (PCA) detection module integrated with a rules based fuzzy logic system that on-line interprets the statistics calculated from PCA (Musulin et al., 2006). In order to estimate its performance, the accuracy, defined as the rate of right diagnosis and the total diagnosis responses, was evaluated. The formulated sensor placement optimization problem is solved using an MINLP-based approach (Angelini et al., 2006). Three cases were taken into account: design with and without knowledge of the FDS key variables and retrofit using the key variables knowledge, from the SN solution obtained without any knowledge. The results show how the knowledge of the key variables in the design phase, make it

possible accomplishing with the reliability requirements for them with less investment than that needed during the retrofitting phase. Results obtained by applying the MINLP (Angelini et al., 2006) take into account the sensor catalogue depicted in Table 1 (LM and FM stand for level and flow meters). Within the process variables involved in the flow balances, only F2, F9, F10, F14, and F15 (variables in TEP) were evaluated as key variables by the FDS.

Table 2 shows the costs of the optimal SNs in the three mentioned cases. The optimal solution 1 (Sol. 1 on Table 2) accomplishes with the reliability constraints depicted in first row of Table 3. The total cost (TDk) is 5400 monetary units, where 3900 correspond to the sensor acquisition cost (ACk) and 1500 are the installation costs (ICk). The solution was achieved by using 12 sensors of s1 type and 3 sensors of s6 type. Sol. 2 shows the retrofitting cost obtained from the previous design solution whereas the new reliability constraints are shown in Table 3 second row. Here, the minimum reliability requirements for the FDS key variables are higher than before. In order to accomplish with the new reliability constraints an additional cost of 2200 monetary units is required. The extra cost is due to the ACk (1550), ICk (600) and DCk (50) (de-installation cost). To enhance the functional reliability of the key variables to 0.98, one needs of 5 more sensors (3 S1, 1 S2 and 1 S6) than in the design solution. Sol. 3 shows the optimal design SN solution under constraints of Table 3 second row. It counts on 16 S1, 1 S2 and 3 S6, summing a total cost of 7400: 200 less than the previous solution evaluated in a retrofitting phase. Thanks to the advance key variables knowledge, it is possible to accomplish the reliability requirements investing less.

Table 1. Tennessee Eastman Process: Sensor catalogue

Sensor FM	Ack (€)	ICk (€)	DCk (€)	Reliability	Sensor LM	ACk (€)	ICk (€)	DCk (€)	Reliability
S1	250	100	50	0.7	S6	300	100	50	0.75
S2	500	100	50	0.75	S7	500	100	50	0.8
S3	800	100	50	0.8	S8	800	100	50	0.85
S4	1700	200	100	0.85	S9	1000	100	50	0.9
S5	200	200	100	0.9					

Table 2. SN solution Cost

	ACk	ICk	DCk	TCk
Sol. 1	3900	1500	0	5400
Sol. 2	1550	600	50	2200
Sol. 3	5400	2000	0	7400

Table 3. Tennessee Eastman Process Reliability Constraints

	F1	F2	F3	F4	F5	F6	F7	F8	F9	F10	F11	F14	F15	L1	L2	L3
r	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
r	0.8	0.98	0.8	0.8	0.8	0.8	0.8	0.8	0.98	0.98	0.8	0.98	0.98	0.8	0.8	0.8

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Evaluation of the potential of Periodic Reactor Operations Based on the Second Order Frequency Response Function

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1. Summary

The concept of higher-order frequency response functions (FRFs), which is based on Volterra series expansion of nonlinear functions is used to analyse the outlet concentration properties of perfectly mixed (CSTR) and plug-flow reactors (PFTR) after introducing periodic input concentration for several simple homogeneous and heterogeneous reaction mechanisms. The second order frequency response function which corresponds to the dominant term of the non-periodic (DC) component, $G_2((\omega_1,\omega_2))$, is mainly responsible for the average performance of the periodic process. Based on that, in order to evaluate the potential of such operation it is enough to derive and analyse $G_2((\omega_1,\omega_2))$. The sign of the function $G_2((\omega_1,\omega_2))$ defines the sign of the DC component and reveals whether the periodic operation is favourable compared to conventional steady state operation.

Keywords: Frequency response functions, Non-periodic component (DC), Mixed and plug flow reactors, n-th order reaction

2. Extended Abstract

Testing whether a periodic process is favourable or unfavourable, generally demands long and tedious experimental and/or numerical work. This paper presents a new, fast and easy method to receive this information based on the Volterra series approach, nonlinear frequency response analysis and the concept of higher order frequency response functions (Weiner and Spina, 1980).

Without going into details, just remind that the frequency response (quasi-steady state response to a co-sinusoidal input change) of a nonlinear system, in addition to the basic harmonic, contains a nonperiodic (DC) term, and an indefinite number of higher harmonics (Weiner and Spina, 1980):

$$x = x_s + A\cos(\omega t) \xrightarrow{t \to \infty} y = y_s + y_{DC} + B_I \cos(\omega t + \varphi_I) + B_{II} \cos(2\omega t + \varphi_{II}) + \cdots \qquad (1)$$

On the other hand, any nonlinear model with polynomial nonlinearity (**G**), can, in the frequency

domain, be replaced by an indefinite sequence of frequency response functions (FRFs)of different orders ($G_1(\omega)$, $G_2(\omega_1,\omega_2)$, $G_3(\omega_1,\omega_2,\omega_3)$,…). These functions are directly related to the DC component and different harmonics of the response. The DC component, which is responsible for the average performance of the periodic process, has a dominant term which is proportional to the asymmetrical second order function $G_2(\omega,-\omega)$:

$$y_{DC} = 2(A/2)^2 G_2(\omega,-\omega) + 6(A/2)^4 G_4(\omega,\omega,-\omega,-\omega) + \cdots \tag{2}$$

In this work the functions $G_2(\omega,-\omega)$ have been derived and analysed for several simple homogenous and heterogeneous reaction mechanisms, with introducing periodic input concentration variations to perfect mixed and plug-flow reactors. The following functions are obtained for the two simplest cases: n-th order reaction of the type A→B performed in a CSTR and PFTR, respectively:

$$\text{CSTR:} \quad G_2(\omega,-\omega) = -\frac{1}{2}n(n-1)\frac{k\tau C_{A,s}^{n-1}(1+k\tau C_{A,s}^{n-1})^2}{(1+k\tau C_{A,s}^{n-1}n)((1+k\tau C_{A,s}^{n-1}n)^2+\omega^2)} \tag{3}$$

$$\text{PFTR:} \quad G_2(\omega,-\omega) = \frac{n}{2}(e^{-\tau k C_{A,s}^{n-1}(n-1)}-1)e^{-\tau k C_{A,s}^{n-1}(n-1)} \tag{4}$$

(k is the rate constant, τ is the residence time, $C_{A,s}$ is the corresponding steady-state concentration of the reactant A and ω is the frequency).

By analysis of eqs (3) and (4), the following can be concluded:

- For $n<0$ or $n>1$: $G_2(\omega,-\omega)<0$, which corresponds to improvement of the reactor performance due to periodic modulation of the input concentration compared to steady state operation (i.e. the periodic operation is favourable).

- For $0<n<1$: $G_2(\omega,-\omega)>0$, which corresponds to reduced averaged performance due to periodic modulation of the input concentration compared to steady state operation (i.e. the periodic operation is unfavourable).

For illustration, some simulation results, based on eqs. (3) and (4) are shown in Fig. 1 for three values of the reaction order n. They confirm the previous conclusions, which are valid for both reactor types. Consequently, an analysis of the perfectly mixed reactor, which is generally simpler than an anlysis of a tubular reactor, can be used in order to investigate the usefulness of a periodic operation, no matter which type of reactor would be used in practice.
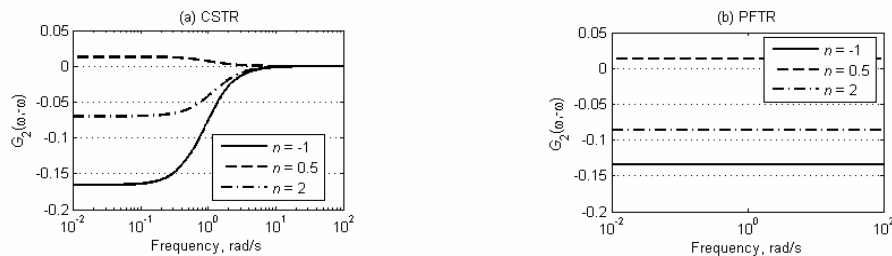
Figure 1. The second order functions $G_2(\omega,-\omega)$ for: (a) CSTR and (b) PFTR for 3 different reaction orders (τ=100 s, $C_{A,s}$=1 mol m^{-3} and k=0.001 s^{-1}mol^{1-n})

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Session T4-2P: Process Operation, Monitoring & Analysis - Poster

Abstract Number	Paper Title & Authors	Included
691	Control and track of melting process by QVI S Martinovic, P Jovanic, M Vlahovic, T Boljanac, V Vidojkovic	Yes
1674	Strategies To Compare Stationary Bonded Phases Of Hplc For The Preparative Or Semi-preparative Separation Of Unsaturated Polycyclic Hydrocarbons By Groups In Products Derived From Petroleum J M Segura	No
1764	Optimal off-line measurement schedule to support process and quality management J Gren, K Konkarikoski, R Ritala	Yes
3379	Scheduling of flexible multipurpose back-up chemical/assembly process systems E Capón, A Bonfill, A Espuña, L Puigjaner	Yes
4029	Dynamic Simulation of Plate and Frame Heat Exchanger Undergoing Rapid Fouling P Triratana, P Narataruksa, K Pana-Suppamassadu	Yes

Control and track of melting process by QVI

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1. Summary

This paper is occupied by track and control of single component melting process. Experiments were performed in an electric-resistance furnace with a horizontally placed movable graphite electrode (heater). Used raw material was floated quartz sand, and obtained material was electrofused SiO_2, also called quartz glass. Height of the electrode elevation and total melting time were varied. The process is considered as non-stationary process due to existence of captured gas bubbles in the viscous melt and many accompanying effects, as well. Tracking of processing parameters was enabled by thermovision as the source of information. In that regard, infrared camera was used. On the basis of these measurements, temperature profiles in the system during the melting process were obtained. Working models of the process were defined by correlation of the temperature changes with time at distances of 1, 3 and 5 cm from the heater. The "black box" method that correlates temperature and time in a model was applied. Powered functions are obtained as models of proposed system. These models were the base for processing control. Namely, based on virtual process defined by different models, sets of parameters for the process control are determined.

Keywords: non-stationary process, ThV camera, working models, process control

2. Extended Abstract

Melting of single-component raw material with clearly defined composition is examined in means of process parameters analysis, while the properties of raw materials can be considered as a constant of process. Since the melting and cooling are considered as non-stationary processes, the temperature distribution in the rector space was the main parameter that needed to be observed. Use of thermocouples would not provide reliable results because of non-stationary character of the process, so that preference was given to the application of a method that enabled visual tracking of the process i.e., quantification of visual information (QVI). Thermovisual (ThV) method was selected to record temperature fields and dissipations. Based on recorded visual and thermal images, temperature distributions vs. time were obtained.

In order to control the process, working model of time-temperature profile was made at the distances of 1, 3, 5 cm from the heater. Since the process was completely non-stationary and dynamical, definition of mathematical model regarding the processing parameters was almost impossible. It was the main reason for applying "black box" method. There are numerous mathematical equations and the most appropriate one should be defined. The term "degree of correlation" used in mathematical analyses shows the level of confirming how well the model describes experimental data. However, since the measured values present physical dimensions, the analyses should include simple models (equations). Linear models were applied in this analysis. Changes at the distance of 1, 3, 5 cm from the heater were presented in Figure 1.

$$Y=a+bx^{c} \quad Y=a+b\,exp(-x/c) \quad \text{Polynomial}$$

$$Y=a+bx^{c} \quad Y=a+b\,exp(-x/c) \quad \text{Polynomial}$$
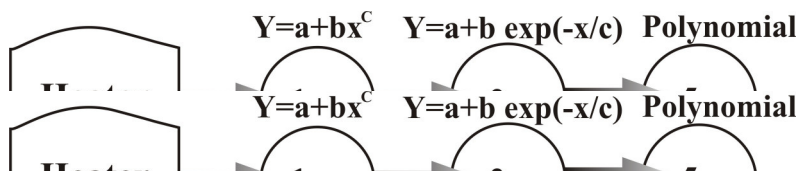
Figure 1: Changes of models at the distances of 1, 3, 5 cm from the heater

At the distance of 1 cm from the heater, three-parameter powered function was obtained. Similarly, at the distance of 3 cm, model has the form of three-parameter exponential function. However, at the distance of 5 cm, the first obtained model with the greatest correlation coefficient was polynomial expression of 5-th degree and six parameters. Obtained profiles showed minor differences in heating/cooling mechanisms at distances of 1 and 3 cm from the heater axes, while significant differences were observed at distances of 3 and 5 cm. It can be explained by faster cooling at larger distances due to heat loss through the walls of reactor and reduced "influence" of heater on process tendency. It indicates that it is not important to track temperature changes at the distance more than 5 cm according to the process control. Processing control implies series of experiments on virtual model to get various sets of processing parameters. It means that model or set of models should be defined as more accurately as possible. Real parts of the system are furnace and measuring and regulating devices, also called executive parts of measuring and regulating system. On the basis of various information obtained from the virtual part of measuring and regulating system, real parts of the system do control of the process. The essence of control system is based on feedback principle with very high level of data processing. In this case, two aspects of process control are proposed. The first one is static model with control elements placed in fixed spots in material. Process control is performed by comparing of response on the control element and values obtained with modeling. Another model, dynamic model, implies moving of measurement system together with heater. This is technically easier and more efficient way for processing control.

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Optimal off-line measurement schedule to support process and quality management

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1. Summary

Laboratory measurements are an integral part of process and quality management. Quite commonly, variables measured are statistically dependent and thus measurement of one variable is an indirect measurement of the others. In this presentation we formulate the cost-optimal measurement scheduling problem of laboratory measurements under the constraint that variable uncertainties at all times are less than specified. We solve this problem in the case when the joint probability density of variables is Gaussian, and when uncertainty evolves according to Ornstein-Uhlenbeck process. The optimum is independent on the measurement values obtained and thus the optimal schedule is a policy.

Keywords: quality management, scheduling, stochastic differential equations

2. Extended Abstract

In industrial processes, such as in papermaking, the product quality is measured from end product samples in laboratory. This information is typically used for three purposes: firstly to validate on-line sensors, secondly to manage quality parameters not measurable on line – e.g. strength of paper – and thirdly to decide whether to accept or reject the product batch. Each of the purposes set requirements on how much uncertainty may be tolerated in the quality estimate. It is a common practice to measure all quality parameters at regular time intervals. However, this is costly and may limit possibilities to measure those quality parameters that would be most important for overall uncertainty management and thus for decision support. Earlier work has considered minimizing a weighted covariance matrix (Mehra 1976; Bicchi, Canepa, 1993; see also Gupta et al, 2006).

Quality parameters are typically statistically dependent and thus measuring a subset of them provides information about the others. A measurement schedule describes which of the quality parameters are measured at which time instants, and will be

denoted as binary valued vector *k(t)*. We seek for optimal measurement schedule over a time horizon such that it minimizes the costs of measurement while maintaining the uncertainty within the constraints set by the application. Our quality information dynamics consists of continuous degradation towards the joint *a priori* probability density of quality, and occasional updates when new measurements are made. We describe the degradation with probability density function dynamics, Fokker-Planck equation, and the updating with probabilistic description of measurement and by applying Bayesian combination of earlier degraded information and of fresh measurement information. With this information dynamics we are able to assess the quality uncertainty at any time with any measurement schedule.

We show that if a priori information is multivariate Gaussian, the natural degradation between the measurements is according to Ornstein-Uhlenbeck (OU) process. Assuming that measurement uncertainties are normally distributed and that a subset $X^{(2)}$ is measured while $X^{(1)}$ is estimated, we derive the recursion for covariance matrix of measurement information about $X=[X^{(1)}\ X^{(2)}]$ at $t+\boldsymbol{D}t$ and t to be

$$[\Sigma(t+\Delta t)] = \left[\left[\Sigma(t) + (\Sigma^{(ap)} - \Sigma(t))\left(1 - \exp\left[-\Sigma^{(ap)^{-1}}D\Delta t\right]\right)\right]^{-1} + \begin{bmatrix} 0 & 0 \\ 0 & C_{22}^{-1} \end{bmatrix} \right]^{-1} \tag{1}$$

where Σ (and $\Sigma^{(ap)}$) are covariance matrices for the quality information (resp. a priori information) about X, whereas C_{22} is the covariance matrix of measurement uncertainties in $X^{(2)}$. D is the symmetric diffusion matrix for the OU process. The optimization problem now reads as

$$\min_{\{k(t_0+i\Delta t)\}_{i=0}^{H-1}} \sum_{i=0}^{H-1} c(k(t_0+i\Delta t)) \tag{2,}$$

$$\Sigma_{ii}(t) < \boldsymbol{s}_i^2 \quad \forall i, \forall t \in [t_0, t_0 + H\Delta t]$$

where c(k(t)) is the cost of measurement set k(t), H is the optimization horizon (maximal length of policy), and Δt is time discretization interval. The optimization problem is an integer programming task that we have solved with simulated annealing (SA). For example, if we consider five variables and there are 40 time steps in the optimization horizon, the search space has 2^{200} alternatives. The solution first checks if measuring all variables at all time instants is a feasible solutions: if it is not feasible solution, then no feasible solution exists; if it is feasible it will be chosen as the staring point of SA. SA converges to a near-optimal schedule with a Matlab implementation in a few minutes. The full paper provides examples of optimal policies with synthetic and real data from papermaking process.

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Scheduling of flexible multipurpose back-up chemical/assembly process systems

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1. Summary

This paper focuses on the scheduling of flexible multipurpose back-up chemical/assembly process systems in a fully robotized environment. The problem is modeled using both mathematical programming and heuristic rules, which are compared in terms of optimality and computation time. Stochastic data is also considered to take into account production environmental dynamics and identify robust schedules. The results obtained suggest that the two strategies should be combined to achieve well balanced results in terms of optimality and time.

Keywords: flexible systems, multipurpose scheduling

2. Extended Abstract

The effective configuration and coordination of operations is crucial in process and manufacturing industries in order to increase their quality and productivity. This paper deals with the scheduling of flexible multipurpose back-up chemical/assembly processes in a robotized environment with the aim to allocate resources (robotized units, intermediate storages and other resources) to assembly activities and determine the sequencing and timing of operations to optimize makespan and resource use. Flexible assembly systems and multipurpose plants scheduling have been extensively studied[2,3]. However, most of contributions do not consider the interaction of constraints from both industries, such as temporal and capacity restrictions and robotized tools. In this approach, alternative production sequences are considered along with constraints on resources availability and simultaneity requirements.

2.1. Modelling and solution approach

The problem has been modelled defining a set of process and storage stages for each process sequence. Each process stage consists of a set of operations to be performed sequentially and must be performed by one of the available robotized units. Resource consumption and simultaneity restrictions between operations of different stages are contemplated. A rigorous MILP mathematical model has been developed based on a continuous time representation. The schedule has also been obtained using heuristic

rules such as the less used unit for the assignment decisions, and the shortest processing time for sequencing. Dynamic variables such as variable processing and transportation times can be considered as a two stage approach, with the simulation of different scenarios to eventually identify a robust schedule.

For illustration purposes consider the case study based on an assembly process with 5 raw materials (*M*), 5 intermediate products (*i*), 17 stages (*e*) with three operations, and a single sequence as represented in Figure 1. Three robots are available for all the stages, and a limited resource is associated with the first operation of each stage. Simultaneity links exist for the operations of the stages previous to an intermediate.
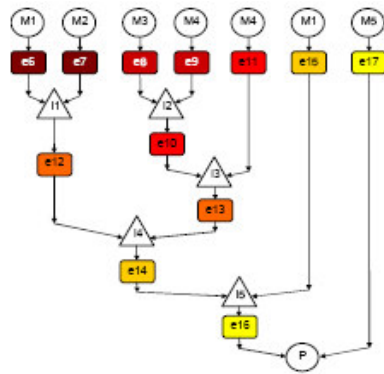
Figure 1-. Tree-representation of the sequence of the case study
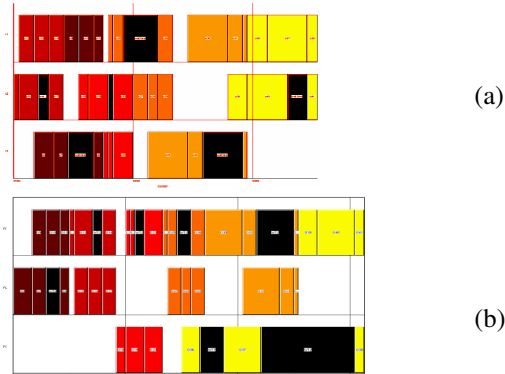
Figure 2-. Gantt chart representation for case study: (a) Mathematical approach (b) Heuristic approach

The mathematical model has been implemented in GAMS and solved using the MILP solver of CPLEX (9.0) on AMD Athlon 3000 computer. A schedule is obtained with an optimum makespan of 61 TU in 22.4 s CPU time (Figure 2a). On the other hand, the heuristic rules have been implemented in C++ as an integrated module of the scheduling system developed by Cantón (2003)[1]. A schedule with a difference about 23% in makespan is obtained in 0.2 s CPU time (Figure 2b). Despite the resources usage is not optimum, the computational requirements are significantly lower. Combining both approaches offers the best solution compromise.

2.2. Conclusions

Flexible multipurpose back-up chemical/assembly process systems are very attractive for the efficient management of resources and to replace labour in short series production and production peaks. However, their optimum production scheduling implies large computational effort due to the combinatorial nature of the problem. The use of a hybrid approach that exploits the capabilities of rigorous and heuristic methods offers the optimum strategy.

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Dynamic Simulation of Plate and Frame Heat Exchanger Undergoing Rapid Fouling

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1. Summary

General thermal model and dynamic simulation of plate heat exchangers (PHEs) with rapid fouling effects were presented. Cranck Nicolson's method and the ghost node technique were used to solve the thermal model. Effects of fouling were added to model through the overall heat transfer coefficient correlation. Rung Kutta 4th was used to receive the integral value of the fouling model. An experimental study of coconut milk pasteurization section by Pichitwitayakarn (2006) was used as a case study. Evolution of the coconut milk outlet temperature with time from the simulation agreed well with those obtained from the experiments. The algorithm presented in this research work can be used to provide a result of step change of selected input variable(s), i.e. fluid flow rate and temperature. The feature allows control strategy to be specified when the process is undergoing fouling. The algorithm was used to simulate the case of a commercial plate pack for coconut milk pasteurization. The results of this case study indicated that adjustment of hot water inlet temperature was appropriate in term of energy consumption.

Keywords: dynamic simulation, plate heat exchanger, rapid fouling

2. Extended Abstract

The plate heat exchangers (PHEs) have been widely utilized in diary and food processing plants, chemical industries, power plant, and cooling system due to the ease of maintenance and cleaning, their compact designs and their excellent heat transfer coefficient characteristic. However, the PHEs used in food processes always have a problem due to a disturbance called food fouling. Fouling from food fluids has shown it significant effects on PHE performance resulting in significant increase in capital and operating costs of plants. A number of authors have tried to simulate the effects of fouling by generating fouling models for various food fluids (Fryer (1985), Deplace (1995,1997) and Grispeerdt (2002), and Pichitwitayakarn et. al.(2006)). A number of authors also presented algorithms for dynamic simulation of PHEs (Laksaman (1990), Shrafi (1997), Das (2000,2002), and Georgiadis (2000)). However, the proposed algorithms were prepared to support a specific purpose of study such as an algorithm for using with kinetic models of protein denaturation. In general cases, fouling models can be simply obtained from the experimental works which have shown the rate of decrease of thermal performance as function of operating parameters such as processing time, fluid temperature, and fluid flowrate. This work then presents a fundamental dynamic model which can be used in conjunction with simplified fouling models. A simulation program was constructed in order

to predict temperature profiles when a plate pack was suspected for fouling effects. The methods of calculations were Cranck Nicolson, Centre Finite Differences and the ghost node technique. The program was tested for a case of pasteurization section of coconut milk by hot water which was the experimental work done by Pichitwitayakarn (2006). The plate pack had 1 pass 2 channels of hot water counter current with 1 pass 1 channel of coconut milk. The experimental data was compared with the simulation data with 100 grids and 1 second time interval as shown in Fig.1. Another case study was a commercial plate pack (50 thermal plates) used for coconut milk pasteurization section. The program was used to predict the outlet temperature of coconut milk that varied with time. After that it was used to identify an optimum control strategy from a set of step changes which were hot water temperature and hot water flowrate. The change of these parameters was preferred when the outlet coconut milk temperature was less than an acceptable temperature. The results have shown that, changing of hot water temperature (see Fig. 2) was a good option with respect to the energy consumption of this specific case.
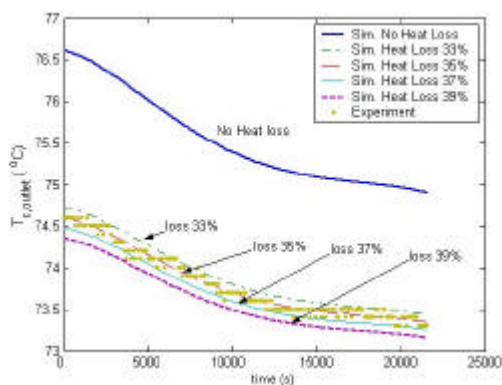
Fig. 1 Comparison of coconut milk outlet temperature obtained from simulation and experiments
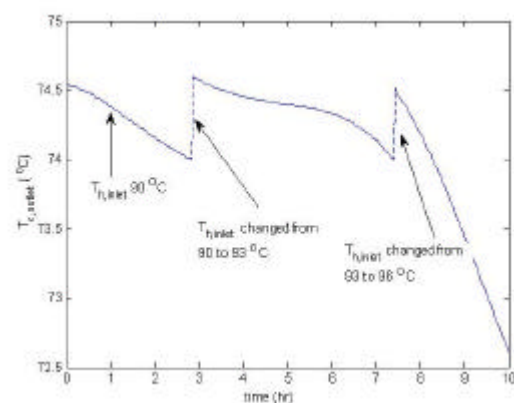
Fig. 2 Evolution of coconut milk outlet temperature when changing hot water inlet temperature

Acknowledgement

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Session T4-3: Supply Chain Management & Business Decision Support

Abstract Number	Paper Title & Authors	Included
25	Matching gasoline supply with distribution requirements optimizes depot storage capacity E O Okeke	No
536	Real world pipeline scheduling with inventory management: a combined MILP and sequencing heuristic approach S Relvas, H A Matos, A P Barbosa-Póvoa,b J. Fialhoc	Yes
2956	2956 - Operations and logistic planning considering vendor uncertainties to enhance the flexibility and reduce the risk of chemical supply chain networks G Kopanos, J M Lainez, M Badell, A Espuña, L Puigjaner	Yes
3730	A Milp Decomposition Approach For The Risk Management Within A Flexible Recipe Framework S Ferrer-Nadal, G Guillén-Gosálbez, M Graells, L Puigjaner	Yes

Real world pipeline scheduling with inventory management: a combined MILP and sequencing heuristic approach

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1. Summary

This work focuses on the medium-term scheduling of a system comprising a pipeline that connects a refinery to a tank farm. The pipeline transports six different oil products and the tank farm manages their inventories in order to accomplish lot approval, settling periods and clients' satisfaction. Relvas *et al.* (2006) developed a MILP model that describes this system using continuous time and volume representations. These authors applied this model to a real world scenario of a Portuguese oil derivatives' distribution company – Companhia Logística de Combustíveis (CLC). The sequential approach that is used to build the continuous time scale has a large impact in model performance, mainly for a medium-term horizon of one month. The pipeline pumping sequence of products was identified as one of the main sources of this problem. One of the possible solutions is the establishment of an initialization heuristic that focuses on the derivation of feasible starting points for products' sequence, which is the aim of this work.

Keywords: multiproduct pipeline, tank farm, MILP, heuristic, continuous formulation

2. Extended Abstract

This work explores the transportation and distribution of refined products, which is a challenging problem. However, studies in this field are scarce. Examples are the works by Rejowski and Pinto (2004) and Magatão, Arruda and Neves (2004) as discrete approaches, and Cafaro and Cerdá (2004) as a continuous approach. The focus of these authors is mainly the pipeline schedule, in contrast with the work by Relvas *et al.* (2006) where the pipeline schedule is combined with inventory management at the destination tank farm. The current work presents an initialization heuristic (Figure 1), which uses system general features and specific scenario data on the following purposes i) obtain a sequence of products' beginning and bounds on number of lots or ii) obtain complete and feasible products' sequences.
Given the initial inventory and daily clients' demands on each product, it is possible to determine priorities on products' reposition, being the first result of the heuristic.
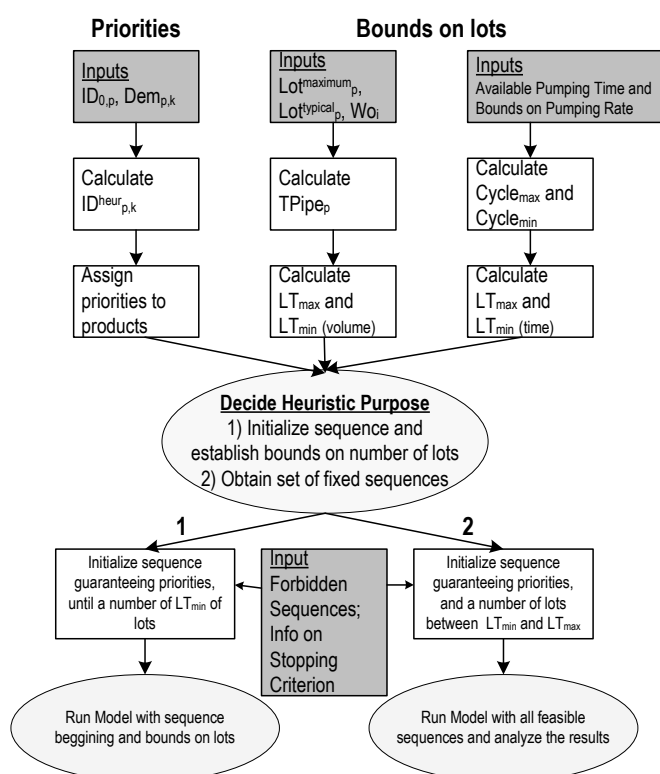
Figure 1 – Initialization heuristic procedure

The remaining results establish bounds on lots, either using information on typical and maximum lots' volumes or considering available pumping time and bounds on pumping rate. One important system condition is the forbidden products' pairs due to product contamination. The stopping criterion can be important if there is a specific ending condition to verify, inside of the pipeline, at the end of the time horizon.

This heuristic is validated considering a period of 6 months from June to November 2006. The data used for each month corresponds to the final client's demands and real pipeline stoppages. It was considered the initial inventories for June 2006 and the heuristic combined with the MILP model supplies the transition between consecutive months. At the end, the obtained results are compared with the real situation. The heuristic will provide 4 different products' sequences for each month, the best candidate will be chosen based on model performance (using GAMS/CPLEX relative gap and CPU time) and operational indicators (final and minimum inventory levels, medium flowrate, pipeline usage and interfaces during pipeline stoppage).

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Operations and logistic planning considering vendor uncertainties to enhance flexibility and reduce risk in chemical supply chain networks

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1. Summary

The coordination between manufacturers and suppliers in a supply chain (SC) network is an important link in the distribution channel. In fact, suppliers are manufacturer's external organizations, and indeed their performance will strongly determine the future performance of the whole SC. Otherwise, any deficiency in the process will lead to excessive delays and poor customer service[1]. Thus, an effective methodology for assessing the impact of suppliers' operations uncertainties is a request from the current business and a pending issue for the academics. The impact of demand uncertainty[2] has been studied by a large number of authors. Instead, in this study the incorporation of uncertain parameters introduced by vendors operations, such as lead times and delivered quantities, are examined in order to shed light on how they could influence the SC optimization and management. In this work a multi-stage stochastic MILP approach[3] is applied to deal with planning of SC systems capable to support the decision making process under uncertainty in chemical process industries and where supplier uncertainties are specifically incorporated.

Keywords: supply chain planning, stochastic programming, uncertainty, vendors operations, financial risk.

2. Extended Abstract

A scheduling and planning model for multiproduct chemical batch plants was adopted from the literature[4] and it was appropriately modified in order to incorporate supplier's operations impact on the whole entity of the SC network. Suppliers operations lead times or delivered quantities are considered uncertain, and in order to model the effects of these uncertainties in the SC decision making system, a two stage stochastic approach is used. The first stage decision variables are the ones concerning scheduling and ordered raw material quantities meanwhile the variables concerning production planning, inventories, transportation and vendors operations are considered second stage.

An academic case study was developed in order to compare the deterministic and the stochastic approaches. This comparison is based on the financial risk (Ω) associated with a specific planning under uncertainty, which is defined as the probability of not meeting a certain target profit level[5]. A supplier, a chemical batch plant, 2 warehouses and 3 markets are the echelons of the studied SC network. Three different realizations of vendors lead times and 5 planning periods are considered. This results into a scenario tree with 243 leaf nodes (scenarios).
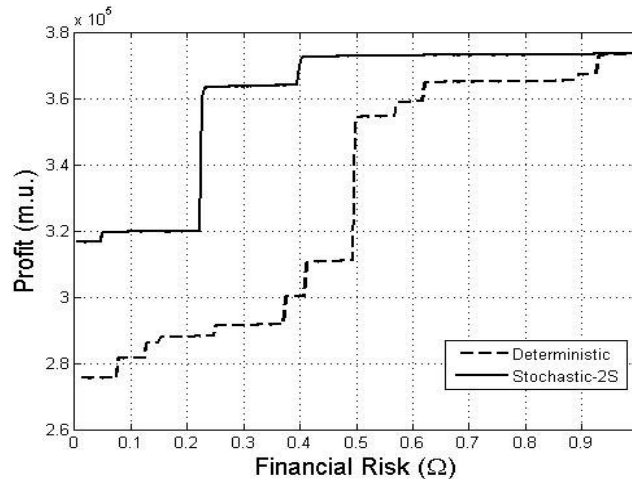
Figure 1: Comparison of Financial Risk curve for the deterministic and the 2-stage stochastic approach.

Fig.1 explicitly illustrates the superiority of the stochastic approach, since the financial risk is reduced when compared with the deterministic approach. Moreover, the expected profit (Table 1) is 9.5% higher in case of the stochastic approach, while the value of the stochastic solution (VSS) is equal to 31216.6 m.u. and the expected value of perfect information (EVPI) is 536.25 m.u..

Strategy	Equations	Variables	Discrete	CPU time (s)	E[Profit] (m.u)
Deterministic	663[*]	575[*]	288[*]	17.5	328200.26
Stochastic - 2S	91897	106087	43122	677.28	359416.85

†Solved in GAMS 22.3/CPLEX in a 1.24 GHz AMD , 1 GB of RAM.   [*] for each scenario

Table 1: Computational results of deterministic and 2-stage stochastic approach.

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A MILP Decomposition Approach for the Risk Management within A Flexible Recipe Framework

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1. Summary

The aim of the present work is to provide a tool to support the scheduling under uncertainty of batch chemical processes taking full advantage of a flexible recipe framework. To address this problem, a large scale multi-objective stochastic Mixed-Integer-Linear-Programming (MILP) model is presented. This model is based on the general precedence model and explicitly includes the trade-off between risk and profit. The outcome of such formulation consists of a set of Pareto-optimal solutions from which the decision-maker should choose the best one according to his/her preferences. A decomposition strategy based on the sampling average approximation (SAA) has been studied as a way of overcoming the numerical difficulties associated with the application of the proposed strategy to large scale industrial scenarios.

Keywords: demand uncertainty, risk management, flexible recipe, sample average algorithm

2. Extended Abstract

Batch processes have received great attention over the last years because of their higher flexibility compared to continuous processes and the increasing demand for specialty, high added-value chemical and pharmaceutical products. Within this context, the short-term scheduling deals with the optimal allocation of a set of scarce plant resources over time to manufacture one or more products following a batch recipe. Most of the scheduling approaches assume that batch processes are operated at nominal conditions following predefined fixed production recipes. However, in many cases a flexible recipe operation may be a suitable way of incorporating systematic recipe adaptations depending on the actual process conditions (Romero et al., 2003). Furthermore, the complexity of the scheduling problem is increased by the high degree of uncertainty brought about by external factors, such as continuously changing market conditions and customer expectations, and internal parameters, such as product yields, qualities and processing times. Although it has been widely

recognized the importance of incorporating uncertainties in the scheduling formulations, most of these models are deterministic, i.e. they assume that all the problem data is known in advance. Thus, the accuracy of the solutions generated using deterministic models may depend on the degree of uncertainty. Moreover, most of the stochastic models devised to date to address scheduling under uncertainty optimize the total expected performance measure, and do not provide any control on its variability over the different scenarios. That is to say, they assume that the decision-maker is risk neutral. However, different attitudes towards risk may be encountered (Bavaro and Bagajewicz, 2004).

The aim of the present work is to provide a tool to support decision making during the development of a scheduling policy in an uncertain market environment while incorporating the trade-off between risk and profit at the decision level. To achieve our goal, this work propose an efficient MILP-based framework that manages the risk in the decision-making strategies by incorporating as an additional feature the flexibility of the batch processes recipes is presented. The problem is mathematically posed as a multi-scenario multi-objective two-stage stochastic model, which accounts for the maximization of the expected profit and minimization of a risk measure. The former metric is indeed appended to the objective function to allow controlling its variability over the entire range of scenarios. In our stochastic formulation, the decisions associated with the scheduling tasks are represented by first-stage variables whose value must be determined before the uncertainty is unveiled. On the other hand, the sales are computed once the uncertain events take place at the end of the time horizon. The resulting model suffers from the "curse of dimensionality" since it is indeed very sensitive to the number of scenarios considered. To overcome the numerical difficulties associated with such mathematical formulation, a decomposition strategy based on the Sample Average Approximation (SAA) is introduced. This decomposition technique provides near optimal solutions and incurs in much less CPU time than the monolithic formulation. The main advantages of our approach are highlighted through a case study, in which a set of solutions appealing to decision makers with different attitudes toward risk are obtained. Moreover, the convenience of exploiting the capabilities of the flexible recipe framework as a way of hedging the financial risk associated with the batch process operation is also discussed through comparison with the traditional approach which operates at nominal conditions.

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Session T4-4: Advances in Computational & Numerical Methods

Abstract Number	Paper Title & Authors	Included
1853	A computational approach to solvent selection M Peters, A C Spiess, W Leitner, L Greinera	Yes
1930	Constrained Gibbs energy methods in process modeling P Koukkari, R Pajarre, K Penttilä	Yes
2053	Solution of nonlinear reaction-diffusion systems based on Green's functions F J Valdes-Parada, M Sales-Cruz, J Alvarez-Ramirez, J A Ochoa-Tapia	Yes
3375	The function of functional modelling in (bio-)chemical engineering S B Jørgensen, N Jensen, M Lind	No
3537	Dynamic optimization based on adjoint sensitivity analysis J B Jørgensen, M R Kristensen, P G Thomsen, K Johansen	Yes
4142	DEM – Discrete Element Method, modelling active pharmaceutical ingredient powder behaviour J Fiedler, D J Taylor, F X Ricard	Yes

A computational approach to solvent selection

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1. Summary

The combination of a thermodynamic model for conversion and yield in biphasic systems in combination with the *ab initio* prediction of thermodynamic properties is a straightforward and cost-effective way of solvent screening.

Keywords: multiphase reactions, phase equilibria, optimization, solvent selection

2. Extended Abstract

Multiphase reaction media are a promising strategy to push the approach of homogenous catalysts to an industrial scale. Important examples for industrial processes on ton-scale using the advantages of liquid/liquid biphasic metal-catalysis are the oligomerisation in the Shell Higher Olefin Process (SHOP)[1] and the Ruhrchemie / Rhône-Poulenc process[2,3]. Biphasic systems also play an important role in separation processes in the chemical industry such as in the butadiene extraction[4].

To use biphasic reaction conditions effectively, a distinct knowledge of the equilibrium thermodynamic boundaries is of great value. In order to obtain reliable data, a large number of time-consuming and expensive experiments are necessary. To minimize the amount of experimental work but also to reduce the environmental impact, a modern approach to solvent selection is sketched below:
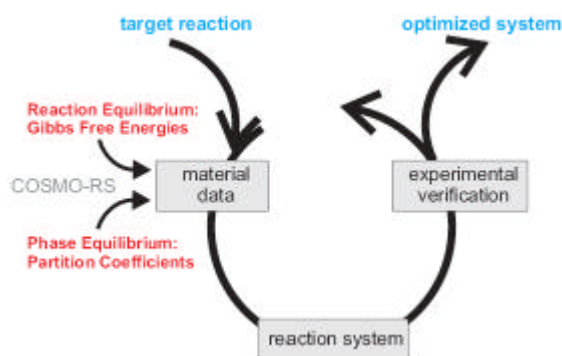
The approach starts with the selection of a target reaction that can be described with adequate material data. Having those data available, the reaction system can be modelled to compute the behaviour of the reaction system in various solvents. Finally, after choosing the best systems, an experimental verification for the optimal system choice, or alternatively, a further optimisation round will take place.

A good starting point for such an optimization is the mathematical modelling of an ideal system. For an ideal reaction system, an analytical solution was derived to calculate and predict equilibrium conversion and product yield in biphasic reaction mixtures with only one reactive phase[5,6]. This mathematical expression was validated using a numerical model for the ideal case. In order to move on to non-ideal systems, a numerical model for the non-ideal case will be set up.

For the collection of material data, partition coefficients were calculated using COSMO-RS[7]. Furthermore, a method for the *ab initio* prediction of standard reaction Gibbs energies in solution was set up using a combination of quantum mechanics and statistical thermodynamics. From the standard reaction Gibbs energies, the calculation of equilibrium constants is possible and thus the calculation of conversion using the above model for the reaction system.

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Constrained Gibbs energy methods in process modeling

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1. Summary

Computation of chemical equilibria and phase diagrams for multi-phase and non-ideal systems by the material-balance constrained Gibbs free energy minimization is a modern application of the thermodynamic theory, which has an increasing number of practical uses. Yet, in many prospective applications, the behaviour of matter is influenced by additional constraining factors, such as kinetic inhibitions, or electrochemical, charge transport as well as surface phenomena. For these situations, an extended Gibbs energy method can be applied. In this technique, the supplementary work-coefficient or affinity related condition is introduced to the Gibbs energy calculation as an additional undetermined Lagrange multiplier, which represents the constraint potential. The potential energy is introduced to the Gibbs energy calculation as a Legendre transformed work term divided into substance specific contributions. A number of new phenomena can then be included in multi-component Gibbs'ian calculations.

Keywords: Multi-phase Gibbs energy minimisation, constraint potentials, reaction kinetics, surface energy, ion exchange

2. Extended Abstract

The Gibbs energy minimisation requires the use of the chemical potentials (partial molar Gibbs energies) of the constituents of the system. Usually, these appear at their equilibrium values as a result of the minimisation calculation, the mass balance constraints being the necessary subsidiary conditions. Yet, there are several such physical circumstances, where chemical potentials appear constrained also by other factors. Then, immaterial constraints for chemical potentials can be applied together with multi-phase Gibbs energy minimisation software. The constrained potentials arise typically due to an additional work or energy effect or they are due to a pre-defined affinity. In the Gibbs energy minimisation performed by the Lagrange method the new constraints are set with additional Lagrangian multipliers. They assume the same mathematical form as the mass balance conditions, yet they must not be affixed

to a given molecular mass. The equations governing the chemical potentials and their respective constraints in the multi-phase system become as follows:

$$\boldsymbol{m}_k = \sum_{j=1}^{l} a_{kj} \boldsymbol{p}_j \quad (k = 1,2,...N) \tag{1}$$

$$\sum_{\boldsymbol{a}=1}^{\Omega} \sum_{k=1}^{N_a} a_{kj} n_k^{\boldsymbol{a}} - \boldsymbol{b}_j = 0 \quad (j=1,2, l) \tag{2}$$

where Ω is number of possible phases, N_α is number of different chemical constituents in a given phase ($\boldsymbol{a}$) as formed from l system components by means of the conservation matrix $\{a_{kj}\}$. Equation (2) includes in addition to the mass balance constraints the necessary immaterial conditions, such as electroneutrality, conservation of surface area, metastability of a given constituent etc., as denoted here with the symbol $\boldsymbol{b}_j$ /1/. Equations (1) and (2) can then be used to solve for the unknowns $(n_k^{\boldsymbol{a}}, \boldsymbol{p}_j)$. Generally the $n_k^{\boldsymbol{a}}$ represent molar amounts of constituents in different phases, while the Lagrange multipliers $\boldsymbol{p}_j$ are potentials of the system components, including those due to immaterial effects. For equilibrium problems, the Gibbs energy minimisation with given input amounts and the system temperature and pressure is sufficient to solve for the constraint potential and system composition. In non-equilibrium systems, an external algorithm of e.g. reaction kinetics is necessary to set the extent of change /2/.

The constrained Gibbs energy applies to modeling of such systems as the electrochemical Donnan equilibria in aqueous systems containing semi-permeable interfaces, phase composition in surface-energy controlled systems and in systems with affinities controlled by chemical reaction kinetics. The new method has been successfully applied in calculating distribution coefficients for metal cations together with pH-values in pulp suspensions, in calculation of surface tension of various mixtures and in thermochemical process modelling involving chemical reaction rates (Figure 1). It can be used in assessment of thermodynamic properties, service and design applications, process scale-up, study of new chemical concepts and search for new, more economic process alternatives.
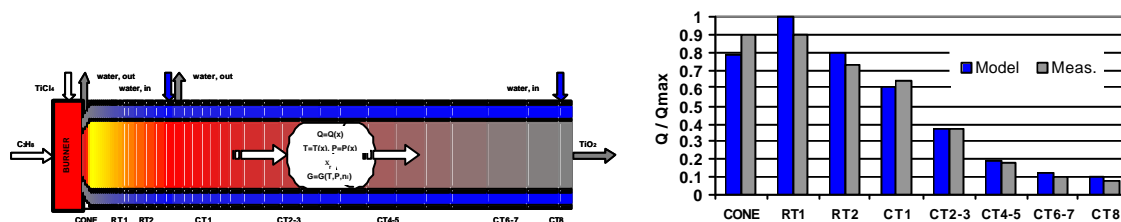
Figure 1. The combination of an immaterial reaction rate constraint and Gibbs energy minimisation was used for the scale-up model of a TiCl$_4$ burner. The model couples endo- and exothermic reactions with the thermodynamic conditions of the industrial reactor and can be validated with both measured heat transfer and temperature data.

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Solution of nonlinear reaction-diffusion systems based on Green's functions

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1. Summary

In this work an integral formulation based on Green's functions is used, which leads to numerical schemes that converge using less number of nodes and therefore less computational time than other traditional methods, specially when the diffusive effects are dominant. Among the advantages that this formulation offers, in comparison to the classical one, are: i) avoiding the spatial numerical differentiation, the error propagation due to the rounding off is reduced significantly; ii) the boundary layer conditions are incorporated exactly, this is, low-order approximations are not used like in finite differences discretization.

Keywords: Green's functions, integral method, reaction-diffusion models, numerical solutions.

2. Extended Abstract

Modern computer-based process design, optimization and control methodologies require massive on-line solution of detailed, commonly distributed-parameter, models. For instance, optimization of chemical reactors with selectivity criteria involves the solution of reaction-transport models for catalytic pellet and/or reactor scales. At each step of the optimization cycle, the underlying reaction-transport models must be solved numerically by means of stable and robust schemes. Finite-differences and finite-elements schemes are widely used given the existence of both theoretical results of stability and computational techniques for implementation. However, recent studies have shown that the use of classical discretization techniques (e.g., orthogonal collocation, finite-differences, etc.) for reaction-diffusion models cannot be stable in a wide range of parameter values as required, for instance, in model parameter estimation (Asteasuain et al., 2001, Agrawal et al., 2006). The main

source of instability is the lower order approximation used in the domain of the differential equations compared to the one for boundary conditions. Hence, the development of stable and robust numerical procedures for distributed parameter processes is still of most importance within advanced process design and optimization methodologies.

It is well known that differentiation-based techniques tend to magnify the propagation of approximation errors, while integral-based techniques tend to smooth round-off errors. In this paper, a further exploration of integral equation formulation for nonlinear and non-isothermal reaction-diffusion transport is carried out. This kind of analysis has been previously reported in the Chemical Engineering literature (Amundson and Schilson, 1961, Kesten, 1969, Mukkavilli et al., 1987a,b). To this end, the Green's function problem is posed and solved for three geometries (i.e., rectangular, cylindrical and spherical), and two representative examples are worked out to illustrate the ability of the method to describe accurately the phenomena with respect to analytical and numerical solutions via finite-differences. In Figure 1, we show the dependence of the predictions of the effectiveness factor of the number of mesh nodes using finite differences and Green's functions. The results clearly show that for a diffusive dominant process $(\Phi \leq 1)$, the results from the differentiation-based technique converge more rapidly to the exact solution, while for a reaction rate-dominated process, the results from both approximation methods are merely the same.
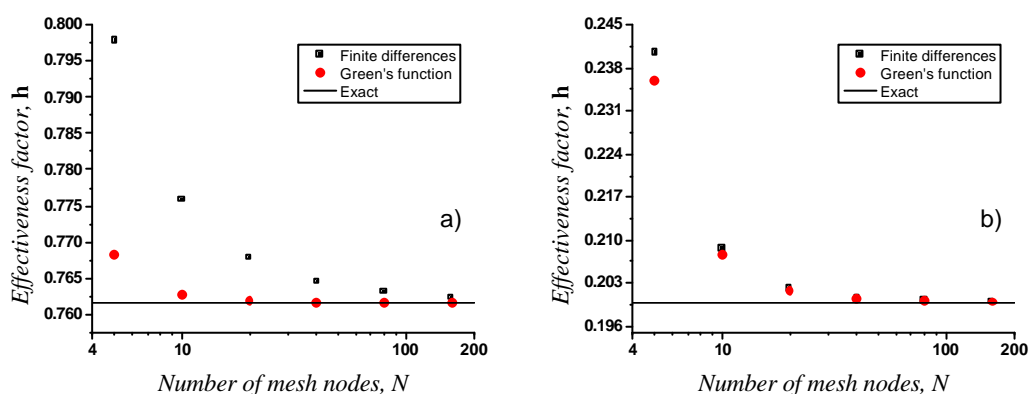
Figure 1: Effectiveness factor for a slab (considering first-order reaction rate) vs. number of mesh nodes for a) $\Phi = 1.0$, b) $\Phi = 5.0$.

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Dynamic Optimization based on Adjoint Sensitivity Analysis

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1. Summary

We present a numerical robust and efficient method for optimization of dynamic systems. The method is based on the ESDIRK integration method and the sensitivities are computed using the adjoint method. The method is demonstrated for nonlinear moving horizon estimation and nonlinear model predictive control on a continuous stirred tank reactor system.

Keywords: Dynamic optimization, ordinary differential equations, sensitivity computation, numerical methods

2. Extended Abstract

The applications of sensitivity analysis in systems of ordinary differential equations are ubiquitous in science and engineering. The applications include model development, optimization, parameter estimation, model simplification, data assimilation, optimal control, uncertainty analysis and experimental design. Consequently, there is an interest in algorithms which compute sensitivities for systems of ordinary differential equations in a robust and efficient manner.

In dynamic optimization, a considerable amount of CPU-time is spent in integrating the system of differential equations as well as computing the sensitivities (gradients). In this paper, we describe sensitivity computations for systems of ordinary differential equations using the adjoint approach and an ESDIRK integration algorithm. Furthermore, we apply the developed algorithm to dynamic optimization of chemical process systems and demonstrate its computational efficiency compared to other methods for sensitivity computation.

Using a CSTR case study, the developed adjoint approach for sensitivity computation is applied to the continuous-discrete nonlinear smoothing problem as well as the nonlinear optimal control problem. These problems constitute the mathematical kernel of moving horizon estimation and control. We demonstrate the remarkable computational efficiency and simplicity obtained when the gradients are computed using our adjoint ESDIRK integration algorithm. Compared to forward methods for sensitivity analysis such as staggered direct, staggered corrector and simultaneous corrector methods, the adjoint approach is most efficient when the number of parameters (decision variables) is large. This is exactly the case in applications of nonlinear model predictive control of chemical processes. We benchmark several sensitivity computation algorithms applied to dynamic optimization problems and conclude that the adjoint sensitivity approach is most efficient for certain large-scale problems in nonlinear model predictive control applications.

The adjoint sensitivity algorithm using ESDIRK integration method is implemented in the ESDIRK software package for dynamic simulation and optimization.
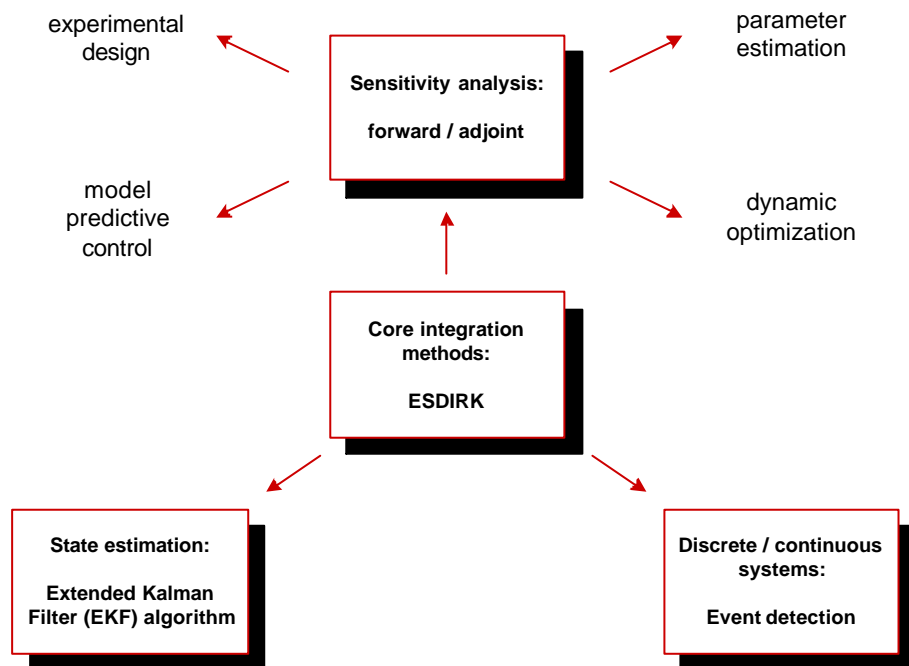
Figure 1: The ESDIRK software package for dynamic simulation and optimization.

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DEM – Discrete Element Method, modelling Active Pharmaceutical Ingredient powder behaviour

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1. Summary

Process unit operations such as filtration, drying and sieving are critical powder handling operations in primary pharmaceutical processes development. Due to the differences in physical properties (size, shape, density etc.) of Active Pharmaceutical Ingredients significant variations in terms of mixing, segregation, packing or flow can be observed in these granular systems. The Discrete Element Method (DEM) offers the opportunity to model the kinetic of granular systems and it has been used to characterise bulk properties and the flow inside a hopper and a conical dryer.

Keywords: DEM, Discrete element method, powder behaviour, API - Active Pharmaceutical Ingredient

2. Extended Abstract

In recent years, granular flow modelling has become possible using DEM. DEM uses Newton's laws to calculate the position, velocity and acceleration of each discrete particle. Individual particles can be tracked as they interact with other particles and/or the geometry. The DEM technique offers the opportunity of gaining data from optical dense systems for better understanding of the particle kinetics. Is also allows to visualise the impact of intrinsic particle properties such as particle shape, PSD - Particle Size Distribution to bulk properties (density, angle of repose). This is beneficial in equipment design optimisation. Within this work, a commercial Software package (DEM-Solutions) has been used. The following paragraphs will give a quick introduction to DEM modelling and to the first initial results achieved.

- Model setup:

Each model requires setting up the mechanical/physical properties of the particles/geometry in use, as well as the definition of the particle shape. Figure 1 illustrates the method of particle shape

Figure 1: particle generation

definition by means of a particle template (outer ellipsoidal mesh). The particle template has been used as a guide tool to meet the particle shape by fitting in the spherical base particles. Any shape can be defined by a set of spherical base particles. The free surface of the spheres is used to calculate the single particle volume and mass. After setting the particle generation parameters (location, generation rate, number, orientation, PSD, initial velocities etc.) the input to the model is complete. The performance of a simulation/post-processing strongly
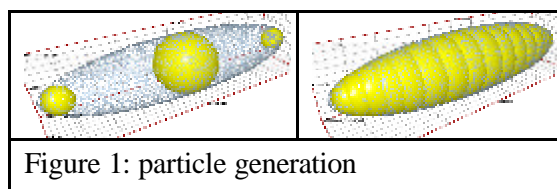
depends on the number of CPU's in use. Therefore a memory-rich multiprocessor system is required.

- Bulk properties (bulk density):

DEM has been used to simulate the packing of 2 different particle types in order to evaluate the capability to predict bulk densities. Prolate and spherical particles have been chosen as an initial particle system to be studied, since both could be found as normal distributed and easy to validate. In order to generate the particle population to be modelled, the spherical particles has been assumed as ideal spheres (parent particle shape) and the prolate particles has been assumed as an ellipsoid (Figure 1). The PSD has been obtained and applied to both types of particles. Figure 2 shows the DEM
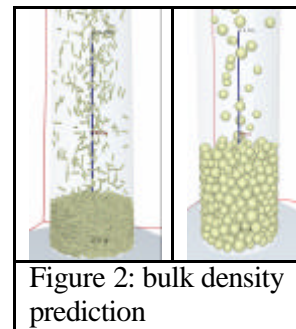
Figure 2: bulk density prediction

results. A 500mL measuring cylinder has been filled (random orientation) with the specified particles. From the fill height and the total particle mass the bulk density has been calculated. The experimental validations of the modelled bulk density have shown a good agreement for the spherical particles (7% error) and a prediction error of 20% for the prolate particles. The error observed was due to the derivation of the real particle shape to the modelled particle shape. Hence, only for real crystalline powder with an almost ideal geometric shape (pipes, spheres etc.) an acceptable prediction error seems achievable.

- Hopper discharge process:

Figure 3 shows a powder discharge process out of a silo down to an inclined chute. The 3D kinetic energy plot visualizes the impact of the particle against the second chute. The line plot shows the averaged kinetic energies of 10 tracer particle over the time. The negative gradient of the kinetic Energy at t=2sec (located in the middle of the line plot) identifies the energy lost (impact energy) due the impact against the second chute. This data could form the base to predict breakage probabilities.
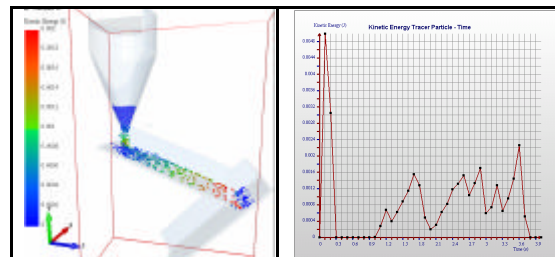
Figure 3: hopper discharge process (kinetic energy 3D/line plot)

- Conical dryer:

Figure 4 shows the particle trajectories from a set of tracer particles defined during post-processing at the bottom of a conical dryer. Since the orbital kinetic of the screw has not been modelled, only the turnover time could be obtained from the trace plot. From the tracer trajectories it could be found, that particle within the screw show the highest lift velocity. The right picture of Figure 4 illustrates the mixing performance of the

Figure 4: conical dryer (particle flow traces/ mixing evaluation)

conical dryer at t=0sec and t=30sec. The slowest mixing could be found within the centre of the conical dryer.

It can be summarised, that DEM shows a large potential with the remaining challenges of considering particle breakage, true PSD and heat and mass transfer. The CPU and memory intensive character of a DEM simulation should also be noted as possible limitation.

Session T4-4P: Advances in Computational & Numerical Methods – Poster

Abstract Number	Paper Title & Authors	Included
145	Modeling and Optimization of Crude Oil Fouling Based on Artificial Neural Networks and Genetic Algorithms J Aminian, S Shahhosseini, M Azarmi, M Molaei, A Ghaemi	Yes
305	Infotherm: A Thermophysical XML-Database of Mixtures and Pure Compounds J Homann	Yes
350	Numerical simulation for the heat transfer of a helical double-pipe vertical evaporator D Colorado-Garrido, J A Hernadez, D Juárez-Romero, O García-Valladares, J Siqueiros	Yes
3035	Dynamic Optimization of a Batch Reactor using the capabilities of an MINLP process synthesizer MIPSYN M Ropotar, Z Kravanja	Yes
3528	A Family of ESDIRK Solvers for DAE Systems J B Jørgensen, M R Kristensen, P G Thomsen	Yes
3532	Enhanced performance of ant colony algorithm compared with other metaheuristics in batch scheduling E Capón, A Espuña, L Puigjaner	Yes
3691	Application of Genetic Algorithm in Kinetic Modeling of Fischer-Tropsch Synthesis M Masoori, R B Boozarjomehry, M J Sarnavi	No

Modeling and Optimization of Crude Oil Fouling Based on Artificial Neural Networks and Genetic Algorithms

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1. Summary

For industrial preheat train, the feedstock variability and presence of different species and operating conditions increase the fouling influence on heat exchanger performance. Prediction of crude oil fouling behavior in industrial preheat exchangers have been extensively studied by various researchers. However, a general, effective and robust method has yet been demanded. This paper illustrates a method based on combination of artificial neural networks (ANN) and genetic algorithms (GA). In this approach, the optimal structure of ANN is constructed using a GA code. The ANN model was then applied to a set of experimental data for predicting crude oil fouling behaviour in an industrial shell and tube heat exchanger. The overall mean relative error of ANN was 94.1% lower than the model presented by Panchal (1997). Another GA optimization algorithm was developed, to minimize fouling formation. The results indicate significant improvement in reduction of fouling formation at 5 constant tube diameters.

Keywords: Fouling, Modeling, Optimization, Neural networks, Genetic algorithms

2. Extended Abstract

Fouling of crude oil in preheat train of crude distillation unit (CDU) is a serious problem for oil refineries, which leads to increased energy consumption, increased pressure drop, reduction or complete loss of throughput and increased maintenance cost. The conventional regression models are generally unable to analyze extremely complicated processes, such as crude oil fouling which is involves a considerable number of independent variables with poorly understood interactions. This study aims to implement the powerful artificial neural network method for an industrial crude oil fouling data bank.

Due to strongly complicated relationship between fouling formation and governing process parameters, training of the ANN takes a long time. To overcome this problem, a GA optimization called GA-1 was performed. The target of GA-1 is to select the best structure of ANN for minimizing overall mean relative error (OMRE) between predicted and experimental data. After optimizing ANN structure, employing GA-1, the GA code was implemented again to optimize operating conditions of heat exchanger aiming to minimize fouling formation. Hereafter, this code is referred to as GA-2. Summery of GA-1 and GA-2 are shown in Table 1.

Table 1. Genetic Algorithms parameters

	GA-1	GA-2
Objective function	Minimize $\dfrac{1}{N}\left(\sum_{i=1}^{N}\left(\dfrac{y_i - t_i}{t_i}\right)\right)\times 100$ N= 1,2,3,…,50	Minimize R_f
Decision variables	1) No. of hidden layers 2) No. of neurons in each hidden layer 3) Type of transfer function in each hidden layer	At 5 constant diameters: 1) Bulk temperature 2) Fluid velocity

In this study 50 experimental data of fouling resistance proposed by Panchal are used to develop ANN architecture. They were obtained for crude oil with 5 tube diameters and different velocities and bulk temperatures ranging from 0.91 to 3.17 m/s and 232 to 467 °C correspondingly. Three parameters including tube diameter, velocity and bulk temperature of the crude are defined as inputs to the network and one output which is the fouling resistance. Figure 1 shows result of the well established GA-1-ANN.
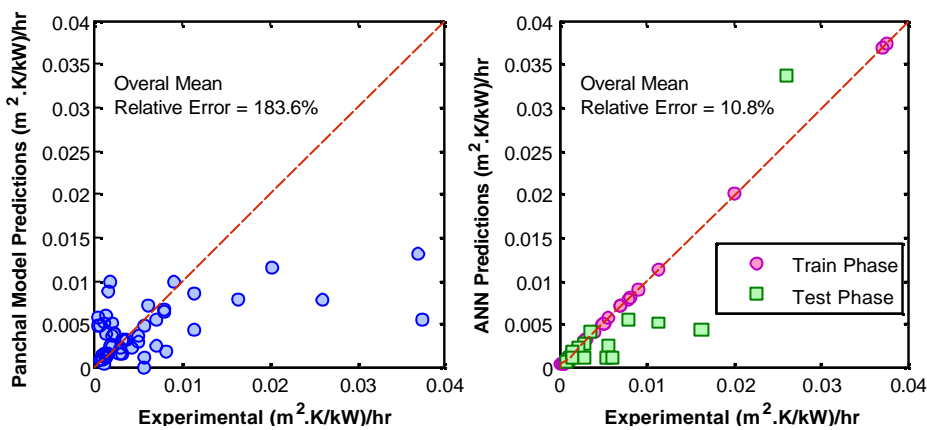
Figure 1. Comparison between ANN and Panchal model predictions

Table 2. Optimal operating conditions applying GA-2

Tube diameter (mm)	Crude Velocity (m/s)	Bulk Temperature (^{o}C)	Minimum Reported R_f	Optimum R_f (m^2.K/kW)/hr
21.1	2.98 (1.16)	354.5 (260)	5.00e-04	1.65e-07
15.2	1.24 (2.53)	251.4 (376)	1.20e-03	7.09e-07
9.5	2.49 (1.68)	410.9 (288)	1.00e-03	4.73e-07
9.4	1.28 (1.01)	436.6 (376)	3.00e-04	2.09e-06
5.5	1.83 (1.37)	441.3 (358)	2.00e-04	2.04e-08

Bracketed values in table 2 are operating conditions of actual experiment before GA optimization. Optimized values applying GA-2-ANN are presented in 5th column in which, the maximum percentage reduction of R_f (relative error) is 99.99% at diameter 5.5 mm.

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Infotherm: A Thermophysical XML-Database of Mixtures and Pure Compounds

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1. Summary

The database Infotherm comprises more than 180,000 tables of PVT-properties, phase equilibria, transport and surface properties, caloric properties, acoustic and optical properties of 26,000 mixtures and 7,000 pure compounds taken from journals, data collections, manuals and measurement reports some of which exclusive to Infotherm.

This database contains search functions in order to combine about 150 properties, conditions and types of equilibria with definable value ranges, substance names, formulas and CAS registry numbers by boolean operators.

Infotherm has a download possibility in ThermoML-Format, an XML-based IUPAC standard for experimental thermodynamic property data storage and exchange.

Keywords: database, thermophysical data, mixtures

2. Extended Abstract

There are numerous sources for thermophysical data currently available on the market in printed and electronic form summarizing results from scientific articles in tables and diagrams in order to support the chemical engineer by easing the data inquiry and data processing. Apart from some few exceptions in "Beilstein", the "CAS-Registry-File", some handbooks or the Inhouse-Versions of the TRC-Group from NIST there are just two* comprehensive sources for mixture data aside from the original articles and simulation software.

Reliable experimental data on mixtures are essential for nearly every chemical process in order to check the results of the widely used simulation models and to fit the parameters of their mathematical approaches.

Reliable parameters are available for less than 10 % of all relevant compounds.

Additional simulation models often neglect the weightage of crucial data, excess charges for the process robustness and the analysis of stability limits while exactly calculating with partly unknown correctness.

Infotherm® offers more than 120,000 tables with experimental numerical data on mixtures with special consideration of phase equilibria and more than 70,000 tables referring to pure compounds.

For approx. 10,000 substances there are 22 types of equilibria and states of aggregation (such as VLE, LLE, SLE, solid state, glass state etc.), 26 conditions of measurement and states (e.g. critical state, isobaric, binodal, excess state, azeotropic state etc.) and 97 properties (e.g. Gibbs energy, enthalpy of vaporization, Antoine constants, viscosity, boiling points etc.) which are freely combinable with bibliographic data and the type of system (pure compounds and mixtures up to denary systems) by Boolean operators in order to narrow down the search exactly to the desired system.

The dataset consists currently of 75% organic, 20 % inorganic and 5 % organometallic compounds with the focus on solvents. There are also approx. 2000 tables with properties of ionic liquids which become increasingly important as solvents and absorbents.

To estimate properties of a system which are not exactly covered by the dataset all available derivatives of a searched compound are displayed. The range of the searched numeric data can be varied until the closest corresponding experimental value (e.g. for the temperature of measurement) is found. An interactive graphical display of the tabular values enables the user to interpolate between the measured values.

The currently monitored sources are the most important European and American journals of chemistry and chemical engineering as well as leading Russian, Korean, Indian and Chinese journals in original language. International university journals, conference minutes, white papers, e-journals and other so called "grey literature" via the Internet are also analyzed. The present dataset bases on approx. 14,000 articles selected from about half a million papers from all available qualified sources.

With a growth rate of approx. 1000 tables per month every relevant detail of an article is quantitatively registered, evaluated and qualitatively weighted. This ensures the availability of every information via the retrieval system and a quality oriented listing of the reported tables.

A short abstract describes the method of measurement as well as the type of used instruments and the pureness of the substances if these parameters are given in the original article. Values derived from experimental values (e.g. the entropy or Antoine constants) and calculated values are specially indexed . In addition, the correctness of basic constants, the numeric trend and the range of the values is checked. Further criteria are the topicality of the paper and the number of measuring points. Thus a table published 50 years ago giving a vapour-liquid-equilibria based on 10 measuring points gets a lower ranking than one (dealing with the same substances) with 50 measuring points and given pureness from today. The monitored period of publishing starts in 1919.

In order to pace the input of data from e-journals published via the internet, which is expected to become a standard in the near future, and to ease the data exchange with customized databases the so called ThermoML-format was implemented in 2005 [4].

ThermoML is aimed at standardizing and structuring thermophysical data for electronic communication with maximum detail of information.

This format, developed by the TRC-Group from NIST, was declared as a standard format by the IUPAC in 2005 and refined by FIZ CHEMIE in co-operation with TRC and the IUPAC regarding detailed bibliographic data, data on the compound system and the graphical display.

Numerical simulation for the heat transfer of a helical double-pipe vertical evaporator

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1. Summary

A dynamic model is developed to describe the thermal and fluid dynamic behavior of a helical double-pipe vertical evaporator used in a waste energy recovery heat transformer by water purification process. The evaporator uses water as working fluid connected in countercurrent. The heat transfer by conduction in the internal tube wall is considered; in addition the change of phase is carried out in the internal tube. The dynamic model considers equations of continuity, momentum and energy in each flow. A model by Artificial Neural Network is proposed for the thermodynamics properties required in each point of the grid in which the domain is discretized. The results of this model are compared with the experimental data of the evaporator in the process.

Keywords: evaporator, heat transfer, helical tube, numerical simulation.

2. Extended Abstract

A heat transformer is a thermal device that increments the thermal level of a heat flow of low quality stream to a higher level, with the purpose of recover this heat to another application. A water purification process by simple distillation is used in the absorber heat transformer while the heat obtained by the auxiliary condenser is recycled [1]. This heat transformer has four components one of them is an evaporator. In the experimental process the evaporator is a compact helical double pipe. To improve overall model of heat transformer, the dynamic model of helical evaporator was developed.

The scope of this model does not consider different flow regimen of evaporations phenomenon, for example sub-cooled boiling and post-dryout. The heat transfer with the surrounding ambient is neglected.

Mathematical formulation in two-phase inside the control volume, fig. 1**,** was used. Where de "i" and "i+1" represent the inlet and outlet sections of control volume and

"m" is the mass flux through the pipe in the direction of flow. The governing equations with two-phase flow fluid have been integrated considering the following assumption: One-dimensional flow, pure fluid, separated flow model and axial heat conduction inside the fluid is neglected [2].
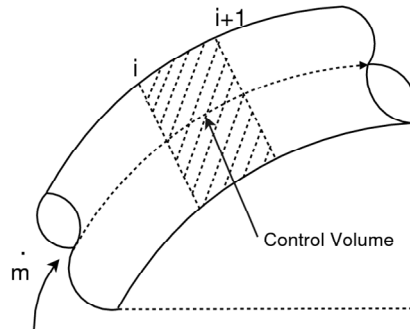
Figure 1: Control volume in helical pipe

The void fraction (ε_g), shear stress (τ) and convective heat transfer (α) are obtained by empirical correlations for helical systems as reported in the literature. The domain of flow fluid is discretized spatially based on a strict couple fully implicit step by step method over a control volume. A first order approximation of the dynamic equations was used to solve the mathematical formulation.

The differentiation between the liquid, two-phase and vapor flow inside the internal pipe is given by the enthalpy, pressure and vapor quality. The change from to one to two phases is assigned at boundary section (i+1) of the control volume.

The calculation of thermodynamic properties is on the basis of neuronal models (ANN) where the input layer is pressure and enthalpy. One, two or three neurons in hidden layer are used depending on the property calculated. The formulation and discretized equations over control volume for solid elements was used over the internal wall and solver with tri-diagonal matrix algorithm. Simulated data of the model in steady-state are compared with experimental data of the evaporator.

The results obtained by the model in steady-state, compared with experimental data produce an error calculated for Q (power = kJ/s) is lower than 0.8%. For the output heat (kJ/s) of the working fluid (steam) is lower than 0.6%. Nevertheless, to deviation in the temperature of single-vapor flow is easy with a small amount of sensible heat. Therefore, these results together with others obtained by the authors allow using this model as an important tool to design and optimize this kind of evaporators.

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Dynamic Optimization of a Batch Reactor using the capabilities of an MINLP process synthesizer MIPSYN

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1. Summary

This contribution describes the development of various strategies for the dynamic optimization of a batch reactor in order to obtain a robust model, suitable for nonlinear (NLP) or mixed-integer nonlinear programming (MINLP) problems. Different schemes for Orthogonal Collocation on Finite Element (OCFE) and various model formulations have been studied to increase the robustness of the model. Various strategies have been applied to NLP and MINLP models, and in addition, their efficiencies and robustness have been compared.

Keywords: Batch reactor, orthogonal collocation, NLP, MINLP, process synthesis

2. Extended Abstract

In recent research (Ropotar and Kravanja, 2006) NLP and MINLP models were developed for the dynamic optimization of batch reactors. Differential-algebraic equations were converted into an algebraic system of equations by the use of Orthogonal Collocation on Finite Element (OCFE).

Different OCFE schemes with a fixed (NLP) or changing number of finite elements (MINLP), with moving or fixed finite elements, and with an end and/or inner optimal point in the Legendre polynomial representation are investigated in order to further increase the efficiency of the NLP and MINLP models. In the case of NLP formulation with moving finite elements, additional nonlinearities of algebraic constraints are introduced in the model due to the presence of the variables, which represent finite element's lengths. Therefore, inequality constraints for approximation error were included in the model. In the case of NLP optimization, the number of finite elements has to be set in advance and is, thus, usually oversized in order to satisfy a given error tolerance, whereas, in the MINLP cases it is explicitly modeled in order to adjust it simultaneously during the optimization process to the minimal number of elements. Finally, in the case of the MINLP model, the robustness of the

model is studied with respect to the use of different model formulations. Different model formulations are then compared, in order to find out which of them are more efficient and robust. The results are gathered in Table 1.

Table 1: Comparison among different schemes and strategies.

schemes/ strategies	NLP (fixed FE)	NLP ($\varepsilon = 1$) (flexible FE)	NLP ($\varepsilon = 10^{-3}$) (flexible FE)	MINLP ($\varepsilon = 1$)	MINLP ($\varepsilon = 10^{-3}$)
c_A^{opt} (mol/l)	0.101	0.101	0.101	0.101	0.097
c_B^{opt} (mol/l)	0.605	0.605	0.605	0.605	0.610
c_C^{opt} (mol/l)	0.094	0.094	0.094	0.094	0.093
T^{opt} (K)	369.1	369.3	369.6	369.3	361.9
t^{max}	200	200	200	200	200
t^{opt} (s)	142.55	139.95	152.56	140.00	192.00
Z (k\$)	36.996	36.998	36.714	36.999	36.617
CPU time (s)	11.461	7.072	33.957	7.422	22.146

It can be seen that the results are very similar. Small differences occur in temperatures, total optimal time, profit and, as expected, in CPU time. When 50 finite elements were used, the NLP and MINLP models were able to tolerate an approximation error tolerance up to 10^{-3}. It can be seen that CPU time for solving MINLP model is smaller than NLP when tolerance 10^{-3} was used.

2.1. Conclusions

The results represent optimal time-operation (concentration, temperature) profiles, optimal raw material consumption, and optimal number of batches. The NLP model with a fixed number of moving finite elements is most suitable for the optimization of stand-alone reactors when the approximation error is large. Since, the disjunctive MINLP model can adjust automatically an appropriate number of finite elements in order to tolerate given approximation error, it can be more efficient than the NLP model when the approximation error is small. This could be especially significant when MINLP synthesis of reactors is performed within the overall process schemes where it is important not to burden the NLP computation by carrying unnecessary final elements through MINLP iterations.

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Ropotar, M., Kravanja, Z., *Optimization of a Batch Reactor using NLP and MINLP*, Proceedings of ICCMSE 2006, Chania, Crete, Greece, 27 October - 1 November 2006.

A Family of ESDIRK Solvers for DAE Systems

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1. Summary

We present a new software package called ESDIRK for simulation and optimization of dynamic systems described by index-1 differential algebraic equations.

Keywords: Dynamic optimization, ordinary differential equations, sensitivity computation, numerical methods

2. Extended Abstract

Efficient and reliable software for solving differential equations is important for a wide range of process engineering disciplines including model development and process and product design. Increasingly large models are being solved on powerful computers, and the solvers are often nested in sophisticated optimization loops requiring many repeated solutions of the underlying equations. In addition, these optimization loops require derivative information of the solution to the equations. Thus, the differential equation solver must be capable of computing not only the solution to the equations, but also the sensitivities with respect to problem parameters, initial conditions or control inputs. Efficient computation of sensitivities is essential to applications such as parameter estimation, dynamic optimization, nonlinear model predictive control and experimental design. Apart from applications requiring sensitivity information, the differential equation solvers are often required to integrate hybrid dynamic systems in which discrete events occur causing discontinuities in the solution. In this talk we will present a software package for dynamic simulation and sensitivity analysis of differential-algebraic equation (DAE) systems. The package is based on the family of ESDIRK (Explicit Singly Diagonally Implicit Runge-Kutta) methods [1]. The one-step nature of these methods makes them particularly well suited for problems with frequent discontinuities, as in discrete event systems and optimal control applications using zero-order parameterization of inputs. Moreover, the strong stability properties (A- and L-stable) of ESDIRK methods make them suitable for index-1 DAEs. The ESDIRK solver package includes a range of methods

of varying order, all equipped with continuous extensions for generation of dense output and location of discrete events. Discrete event problems are handled by detecting and locating zero-crossings of event functions defining switches to other system states. Finally, the methods are equipped with sensitivity analysis algorithms for both forward [2,3] and adjoint sensitivity analysis. The sensitivity analysis algorithms have been applied to nonlinear model predictive control applications [4] as well as in the construction of a very efficient extended Kalman filter algorithm for state estimation in continuous-discrete stochastic systems [5,6].
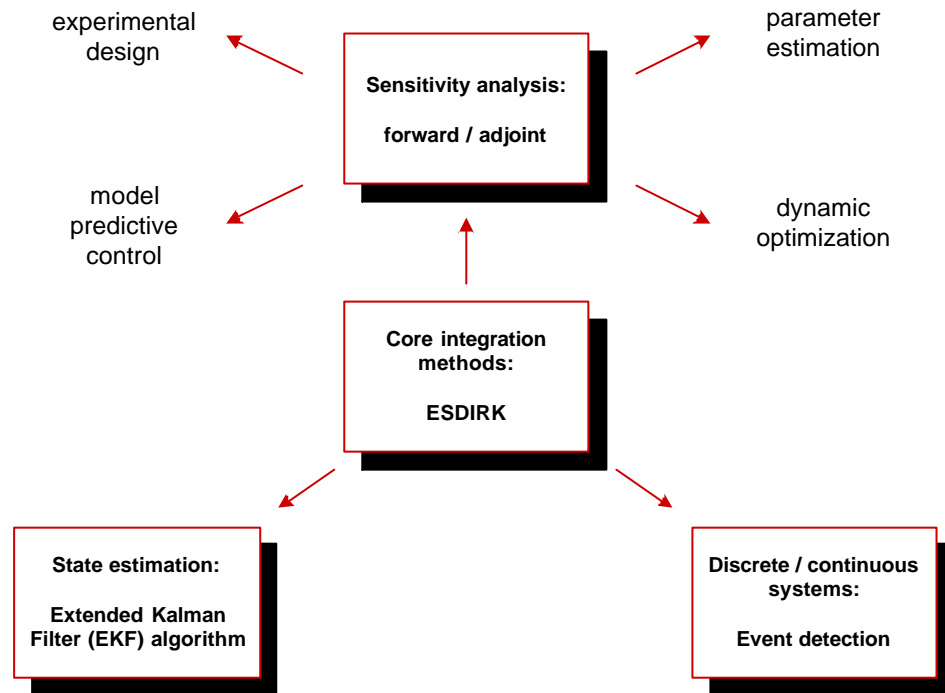
Figure 1: The ESDIRK software package for dynamic simulation and optimization.

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Enhanced performance of ant colony algorithm compared with other metaheuristics in batch scheduling

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1. Summary

This paper deals with the application of heuristic and exact approaches to the scheduling of batch plants. Different case studies are modeled using both mathematical programming and heuristic rules combined with local search in order to compare both approaches in terms of efficiency. Moreover, a substantial improvement of the ant colony algorithm proposed by Jayamaran[4] is also introduced.

Keywords: scheduling, metaheuristics, ant colony optimization

2. Extended Abstract

Scheduling plays a central role in short and medium-term activities of manufacturing and process industries. Regarding the combinatorial nature of the problem, obtaining the optimal solution for large problems consumes considerable computational effort. Therefore, finding fast and effective solution strategies to solve scheduling problems has been recently deeply studied[2]. Available algorithms are classified into either exact or approximate. Approximate algorithms, such as heuristic rules and metaheuristics, sacrifice optimal solutions for the sake of lower computation times.

A metaheuristic means a general algorithmic framework which can be applied to different optimization problems with relatively few modifications in order to be adapted to a specific problem[3]. Jayaraman et al. (2000)[4] describe an ant colony algorithm for flow shop problems and continuous functions optimization of batch plants. This paper proposes a modification of this previous algorithm in order to achieve higher performance. An additional objective is the comparison, in terms of efficiency of two metaheuristic methods, ant colony optimization (AC) and genetic algorithm (GA) in solving scheduling problems. Moreover, the proposed examples are modelled using MILP in order to calculate the optimum solution. Thus, a comparison of the optimum results is made with those obtained with metaheuristics.

2.1. Modelling and solution approach

A rigorous MILP mathematical model has been developed based on a general precedence continuous time representation[2]. Heuristic rules have also been used,

namely the less used unit for the assignment decisions, and the shortest processing time for sequencing. The initial heuristic schedule has been iteratively solved by local search, applying the genetic algorithm and ant colony algorithm. Both Jayamaran and a proposed modified ant colony algorithm are considered. The proposed modification consists of setting the initial value of pheromone proportional to the fitness value of each region instead of a fixed value for all individuals of the population.

Hereafter, two case studies are considered. On the one hand, a batch plant that produces three products (A-C) in 5 units. On the other hand, a batch plant[5] with 4 stages, 10 units and 20 orders to process, without any other constraint, is also presented. The objective function in both cases is makespan minimization.
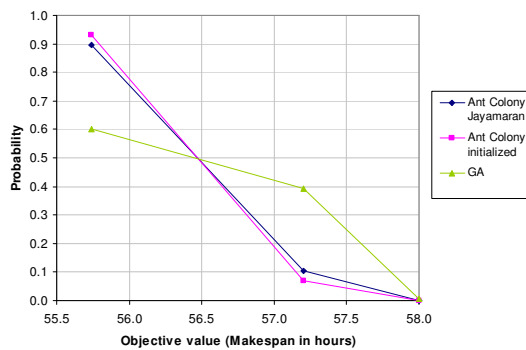
Figure 1-. Comparison in effectiveness of the three metaheuristics for case study 1

The mathematical models have been implemented in GAMS and solved using the MILP solver of CPLEX (9.0) on AMD Athlon 3000 computer. The heuristic rules and metaheuristic procedures have been implemented in C++ as an integrated module of the scheduling system developed by Cantón (2003)[1]. In the current proofs, AC obtains better results, for the same computational time (4s CPU time each iteration) than those of GA (Figure 1). In addition, the improved AC algorithm entails better results in the objective function value. Namely for case study 2, the modified algorithm has over 3% more solutions which are lower than 5% from the best value obtained, and in general, solutions are closer to better values. However, with ant colony algorithm, it was not possible to reach better values as good a value as the obtained with the mathematical model at the expense of high computation time (over 3600s CPU time).

2.2. Conclusions

Although exact approaches can achieve optimal results, their computation times can be so large, that metaheuristics become advantageous for obtaining good solutions in less computation time. The enhanced ant colony algorithm proposed, provides the worst initial individuals are not given from the beginning the same importance as the better, thus search is focused on better results.

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Session T4-5: Safety & Risk Management Systems

Abstract Number	Paper Title & Authors	Included
492	Dangerous industrial installation and critical managerial elements: the inspections on safety management systems B Vincenzo, B Sergio, M Loredana, V Fabrizio, M Sergioa	Yes
1074	Enhancing abnormal events management by the use of quantitative process hazards analysis results I Yélamos, A Bojarski, G Joglekar, V Venkatasubramanian, L Puigjaner	Yes
1079	The relation between size of plant and risk: traditional processing versus intensive continuous processing P Khoshabi, P N Sharratt	No
3658	An easy evaluation method for reaction hazard Y Fujimoto	No

Dangerous industrial installation and critical managerial elements: the inspections on safety management systems

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1. Summary

The work is based on theme of relevant industrial risk management, regarding the development of an integrated inspections systems for industrial installation. The work affords also a critical analysis about the politic of prevention of relevant accidents and the safety management system.

In the paper the techniques utilized to identify potential hazards caused from human faults and estimate their possible consequence have been reported. Some indications useful to select safety measure and also to predispose a risk management planning have been compared.

The starting point of the work is the application of general system of inspections provided by the Italian Ministry of the Environmental Protection (MATTM) to perform a detailed and systematic examination of technical, organizational and management systems applied in the industrial installation sited in Sicily.

The safety management system data has been extracted from official safety reports.

Keywords: industrial installation inspection, safety management systems, safety analysis

2. Extended Abstract

Many hazard events derived from critical managerial elements represent main sources of uncertainty in risk analysis of industrial installation.

The identification of the critical managerial elements could be the evaluation of criticality of the single managerial elements in the specific reality considered, by:
- analysis of operational experience
- outcomes of safety analysis

- outcomes of inspections.

The ART. 18 of European Directive 96/82/CE (Seveso II) requires to members States, the application of a system of inspections (or similar control measures) so to perform a detailed and systematic examination of technical systems, and also of organizational and management systems applied in the industrial installation.
The control systems should to guarantee:
- adequate safeguards, adopted by industrial installation manager, in order to prevent relevant incidents;
- adequate safeguards to control the possible consequences of important incidents inside and outside;
- data and the information contained in the safety reports describe the situation of the plant;
- information to the population.

The inspection system, besides, must answer to the following dispositions:
- all the industrial plants should be subordinates to a program of inspections. The program of inspections should consider at least one annual inspection visit for all industrial installation plants subject to the presentation of the safety reports;
- after every inspection the inspectors write up formal relation;
- the results of inspection should be estimated in cooperation with the manager of the industrial installation.

The inspecting visit on the SGS system, started in Italy from 2000, are ordered by Italian Ministry of the Environmental Protection with bimonthly mandate.
These visits are carried out by several commission formed by National and Regional Agency for environmental protection, National Corps of Fire Brigades, National Institutes for Safety ISPESL. In order to carry out the inspection Some Guidelines produced from APAT and MATTM are systematically used to perform the check of system SGS.
Campeti G. et al., have been presented a paper reported the results of some inspections applied in Italy starting from 2000.
General critical aspects emerged during the inspection activity, regarding the organizational and managerial factors, are referred to: the operative experience in comparison with similar industrial installations, the specific activity of information, formation and training, useful to prevent important incidents, last the operational control.

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Enhancing abnormal events management by the use of quantitative process hazards analysis results

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1. Summary

This work, presents a framework for integration of Abnormal Events Management (AEM) and Process Hazard Analysis (PHA) to enhance on-line plant safety. The framework consists of a decision making module which uses an off-line extended HAZOP analysis, a fault diagnosis system (FDS) and a plant dynamic model, to generate a corrective actions (CA) protocol. The protocol is influenced by the fault(s) diagnosed and the plant status.

Keywords: Abnormal events management, process hazard analysis.

2. Extended Abstract

Significant progress has been made in the identification of the causes of abnormal plant conditions during past 15 years. However, AEM continues to be dominated by experiential techniques, which are not necessarily based on the understanding of the underlying process. Automation of AEM not only requires accurate fault diagnosis but also a complete response with CA that may be derived from the knowledge of the causes and consequences of the diagnosed faults. PHA provides qualitative answers about causes (fault sources) and consequences (variables crossing their allowable bounds). However, it does not provide the time at which specific variables will cross the bounds after an abnormal event.

In this work, a technique for AEM is demonstrated which combines dynamic simulation with PHA to take advantage of the HAZOP analysis. The HAZOP analysis is extended to generate quantitative information in form of thresholds for key variables. The crossing of a threshold by the associated variable constitutes an event. Also, a set of CA is associated with each event to correct its consequences. Such information from PHA is used to set up an original CA protocol. In addition, this technique uses a plant dynamic model to simulate the effect of the diagnosed fault under the current plant conditions. The dynamic simulation is crucial in predicting the time at which the variable(s) will reach the specified safety threshold(s), thereby helping the system to decide which corrective actions to implement first. Therefore, a new protocol may potentially emerge for each abnormal event since the fault severity and current plant status may be different every time. The information flow scheme and the system architecture are summarized in Figure 1.

An industrial sour water stripper plant is used as case study. It is simulated in ASPEN dynamics® and a simplified simulated scheme is used as the plant dynamic model. The HAZOP analysis of this

plant (Vaidhyanathan, 1995), was extended for use in this case study. The rest of tools (FDS, Extended HAZOP and Decission Support System (DSS)) in the framework were implemented in Matlab®. The fault tested in this study consisted of an upstream flow increase labelled as 'Deviation 1.1' on the original HAZOP analysis (from Table 5.2 on Vaidhyanathan, 1995). The fault strength was evaluated on-line by the DSS and was simulated using the dynamic model. The results of the dynamic model were analyzed by the DSS. Thus, the original CAs are ranked and presented to the process operator along with additional information (time to thresholds, variable deviations, causes-consequences, etc.) so that the operator can take the most suitable counter-measure(s). The fault was introduced at the second operating hour and its cause was quickly identified by the FDS. A summary of the report generated by the system is given in Table 1. CAs on that protocol are ordered by urgency time and should be applied if the problem remains on the specified times. Different protocols were attained with the same fault but under different intensities and/or plant conditions.
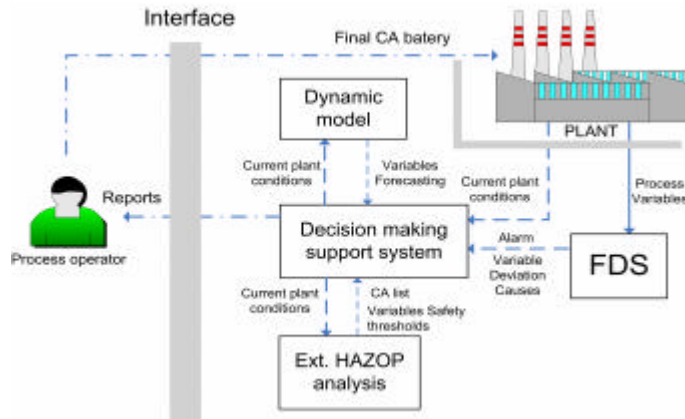
Figure 1. System architecture and information path.

Table 1. Report information summary facing a Sour Water plant inlet flow increase.

Consequences	Time to Thresh.	CA protocol
Inlet Pipe rupture	> 50 h	1. Solve upstream problems (Now).
Inlet Pipe leakage	23.5 h	2. Alarm to slop oil plant (On 9 h ahead)
High decanter level (HDL): high impurities flow	9 h	3. By-pass inlet flow and shut down process (On 18 h ahead).
HDL: decanter overflow	18 h	4. Turn on safety ventilation (On 23 h ahead).
Decanter leakage	34.5 h	5. Shut down inlet to plant. Re-drive flow (On 34 h ahead)

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Session T4-6: Process Analytical Technology

Abstract Number	Paper Title & Authors	Included
197	Process Analytical Technology, quality by design and scientific-risk based approaches - fundamental change in the pharmaceutical industry A Brindle, L Linderg-Nielsen	Yes
878	Simultaneous monitoring of crystal and mother liquor phase properties during batch crystallization using in-line Raman spectroscopy H Qu, M Louhi-Kultanen, J Kallas	Yes
2613	Acoustic chemometrics monitoring of chemical production processes – Systematic methods and tools for managing the complexity M Halstensen, K Esbensen	Yes
2692	Application of tBTEM and other multivariate techniques to quantitative in-situ UV-Vis measurements F Gao, H Zhang, L Guo, M Garland	Yes
2870	Design of process monitoring and analysis systems, using a model-based computer aided framework R Singh, K V Gernaey, R Gani	Yes

Process Analytical Technology, Quality by Design and Scientific-Risk Based Approaches - Fundamental Change in the Pharmaceutical Industry

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1. Summary

The pharmaceutical industry is undergoing a fundamental change in the way it develops, manufactures and how it is regulated by the authorities. These changes are being driven by the regulators and the industry itself as they strive to understand more about products and processes to improve quality and reduce overall costs. Process Analytical Technology (PAT), Quality by Design (QbD) and scientific-risk based approaches are representative of the new way of thinking and in dealing with regulatory authorities.

Keywords: pharmaceutical, Process Analytical Technology (PAT), Quality by Design (QbD), risk

2. Extended Abstract

The pharmaceutical industry has some of the poorest OEE (overall equipment effectiveness) figures in the manufacturing sector. Add to this the steadily declining amounts of drugs being successfully submitted (despite increased spending) and an increase in the amount of recalls of unsafe product from the marketplace and all seems less than ideal for the pharmaceutical sector.

However, the pharmaceutical industry, backed by the regulators, is driving towards a fundamental shift in attitude to the way it thinks about processing.

The key force driving this change is the desire to understand more about current processes and those still under development. Increased process understanding will help optimise current processes and improve the design of new processes with the result of reduced variability, improved quality and reduced cost.

Processes in development will target the scientific-risk based understanding of their fundamentals - leading to scientific rich, documentation light submissions to the authorities. The regulatory authorities (such as FDA) offer significant incentives in

doing this; that of regulatory relief. The FDA has already stated that increased scientific understanding in a submission documented with tools from QbD and PAT will give flexibility to manufacturers to change and improve processes without the need for the typically complex and costly updates to the regulatory authorities.

This presentation will seek to highlight some of these fundamental changes (being driven by the PAT, 21st century GMP and QbD initiatives) and detail what this means for the billions of dollars that is spent on pharmaceutical processes and their development each year.

Simultaneous monitoring of crystal and mother liquor phase properties during batch crystallization using in-line Raman spectroscopy

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1. Summary

The *in-line* probe of a Raman spectrometer was applied to the monitoring of batch cooling crystallization of carbamazepine (CBZ) from ethanol-water solution. The simultaneous monitoring of both the anhydrate/hydrate phase of the crystals and the concentration of the mother liquor was implemented. Two different cooling strategies and the effect of one surfactant were studied. The onset of the primary nucleation of CBZA or CBZH from solution can be clearly identified from the *in-line* measured Raman spectra data. The initiating of the phase transformation can be easily observed from the solid phase monitoring. The kinetics of the crystallization of CBZA and CBZH, and the phase transformation can be followed. The Raman spectroscopy was proved to be a powerful tool for the *in-line* monitoring of anhydrate/hydrate crystallization process. The information obtained from the Raman spectroscopy leads to improved understanding of the process and the effects of thermodynamic and kinetic factors on the hydration phase of the crystals. The *in-line* monitoring of the process also offers great potential for the optimization of the process and the control of the crystalline quality.

Keywords: Crystallization, Raman spectroscopy, Pseudopolymorphism, *in-line* Monitoring

2. Extended Abstract

Two different cooling strategies and the effect of one surfactant were studied. The information about the solution phase and the crystallized solid was interpreted from the collected *in-line* spectra. The calibration of Raman spectra for the quantification of the crystal phase has been introduced in previous work (Qu et al. 2006a, 2006b and 2007). With the stepwise cooling mode, the solution saturated at 48.6°C was cooled down from 55°C and the anhydrate carbamazepine (CBZA) was crystallized out at 37°C. The CBZA was subsequently transformed into dihydrate form (CBZH) when the solution was further cooled to 17°C. A cooling-heating mode was utilized to

investigate the dehydration of CBZH. The solution saturated at 35°C was first cooled from 40°C to 15°C and then it was heated to 35°C. The crystallization of CBZH was encountered at 20.5°C and then the CBZH transformed to CBZA at 34°C. The effect of the surfactant on the crystallization of both CBZA and CBZH was not significant in the present study. The *in-line* measured evolution trend of the supersaturation level was in good agreement with the off-line measurement.
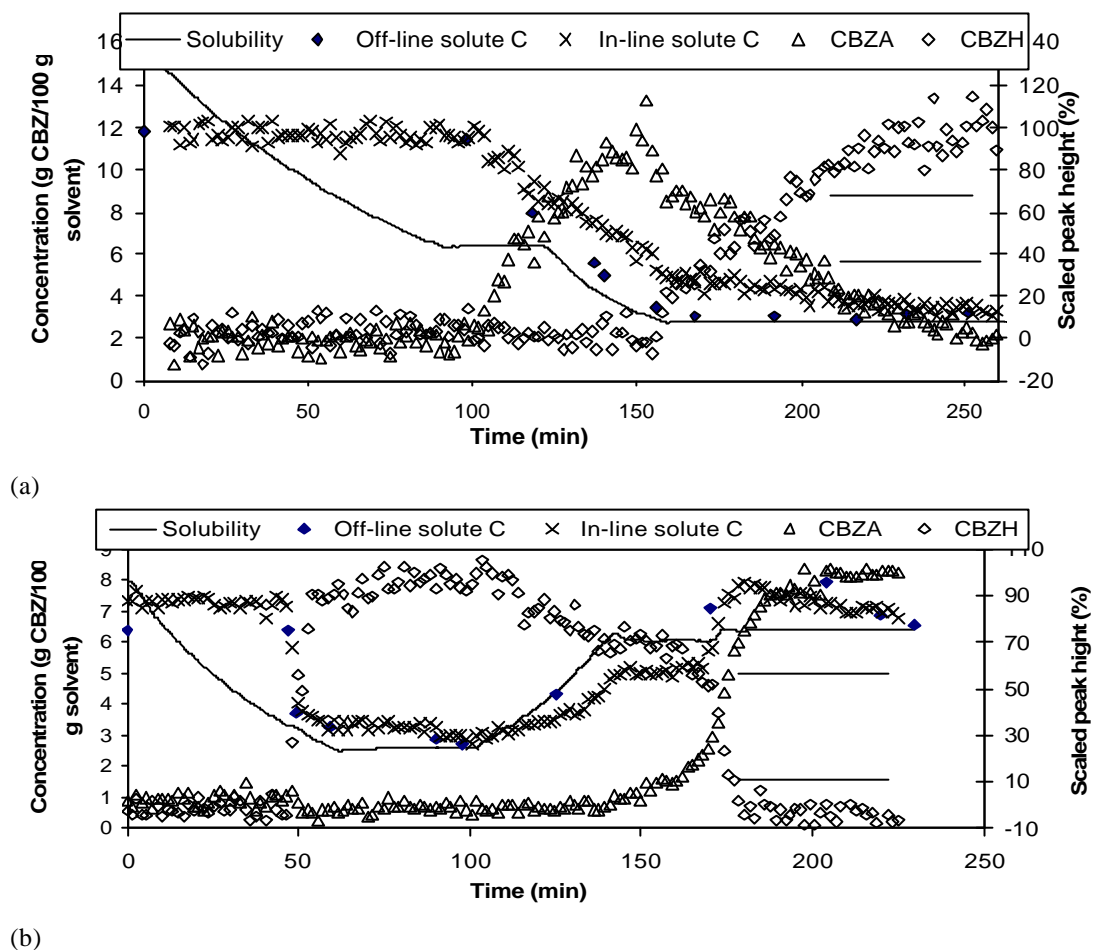
(a)

(b)

Fig. 1 Solubility, off-line measured solute concentration, and scaled peak height with respect to solute CBZ, CBZA and CBZH crystal phase during the batch crystallization with (a) step cooling and (b) cooling-heating mode.

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Acoustic chemometrics monitoring of chemical production processes – Systematic methods and tools for managing the complexity

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1. Summary

Acoustic chemometrics (a.c.) is a new general Process Analytical Technologies (PAT) approach for on-line monitoring of industrial processes. Acoustic chemometrics concerns capturing system vibration characteristics, e.g. from two-phase systems (gas-solids/liquid-solids) generated by the manufacturing process or by transportation. The resulting vibrations can easily be measured by non-intrusive, "clamp-on" sensors (e.g. accelerometers). Acoustic signatures carry embedded information about physical and chemical parameters, such as composition (oil, fat, ammonia, buttermilk, glycol, ethanol), mixing progress, fiber length, flow, density, temperature - as well as system state. For extraction and quantification of these types of specific analytes and parameters of interest, domain transforms (FFT, WT) and PLS-regression is essential for multivariate calibration (process chemometrics).

Keywords: Acoustic chemometrics, process monitoring, ammonia, urea, PAT, multiphase flow

2. Extended Abstract

Acoustic chemometrics is here applied for monitoring of industrial production processes, wiz. a feasibility study of fluidized bed granulation of a fertilizer product (urea) (in a Semi-Industrial Pilot Plant: SIPP), illustrating the main acoustic chemometrics features and benefits. We have also included industrial examples of monitoring of ammonia flow in pipelines and how it is possible to predict fat content in milk directly from acoustic vibration signatures caused by turbulent flow in pipelines. Conventional process monitoring and control is sub-optimized by slow and labour-intensive laboratory analysis: particle size distribution, liquid urea-concentration (correlated with water content), which are typically delayed by up to some 2+ hours of analysis time. It is also critical to be able to detect process transients and upsets. The new acoustic chemometrics approach goes directly into the real-time,

on-line domain. In this exemplar study we focus on:

1. Optimal sensor localization in the semi-industrial granulator plant
2. Assessment of the feasibility to predict:
        Fluidized bed movement
        Crystallisation point of liquid feed to the granulator
        Moisture content in the granules
        Fat content
3. Monitoring for visualization of critical situations - early operator warnings

With acoustic chemometrics it is possible to monitor both process state and product quality for industrial process control. Relevant early warnings trigger the process operator to change relevant process parameters to control product quality or to prevent critical shut-down situations. Successful validation of this type of PLS-prediction models signify that acoustic chemometrics has matured into a proven on-line technology in the Process Analytical Technologies (PAT) domains. Figure 1 shows predicted vs. reference values for particle moisture content inside an industrial scale granulator.
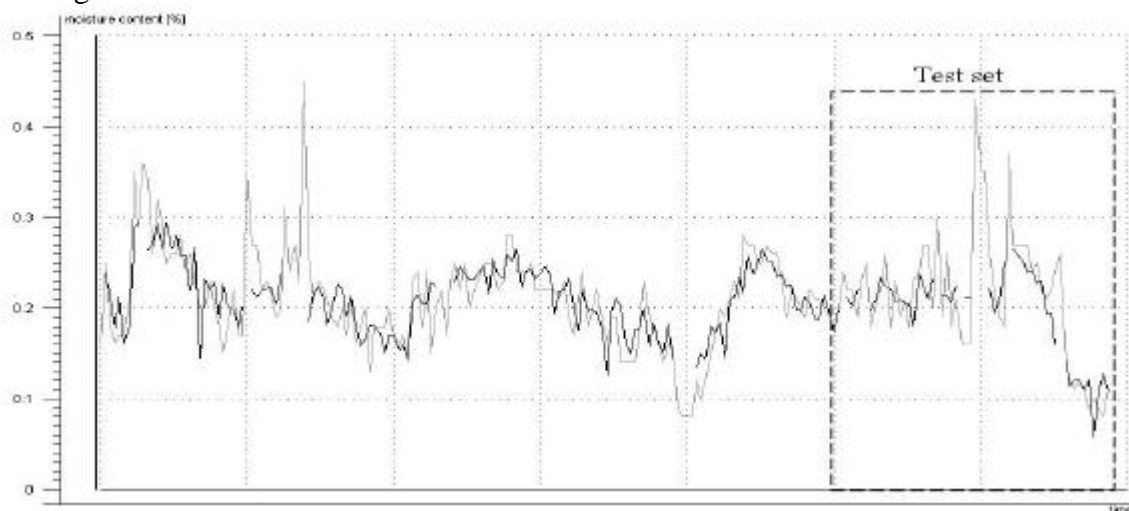
Figure 1: Predicted vs. measured plot for granule moisture content [% water], calibrated on data from five months of production.

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Application of tBTEM and other multivariate techniques to quantitative in-situ UV-Vis measurements

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1. Summary

One recently proposed self-modeling curve resolution algorithm, two-band targeting entropy minimization (tBTEM), was applied to UV-Vis spectral analysis, for blind source separation of the pure spectra and to calculate the corresponding concentrations from the mixtures. Nine spectra were collected in one semi-batch experiment with multiple perturbations of three highly-overlapping dyes, namely, bromophenol blue (Bblue) sodium salt, bromocresol green (Bgreen) sodium salt and methyl orange. Good estimated pure spectra, compared to experimental references, were recovered without any *a priori* information. This result demonstrated that tBTEM can be successfully used to reconstruct the pure component spectra from broad and highly overlapping spectral data.

Keywords: In-situ UV-Vis spectroscopy; Multiple perturbations, tBTEM

2. Extended Abstract

Many interesting chemical processes involving tautomeric equilibria, short-lived intermediates, and kinetically labile complexes can not be analyzed by classical spectrophotometry since the species in the solution can not be separated experimentally. In such cases, a combination of appropriate spectroscopic method and chemometrics can be useful. When the concentrations of solutes are very low, and when these solutes have chromophores, UV-Vis provides some distinct advantages. Due to the broad spectra of many electronic transitions, multi-component UV-Vis spectra are usually highly overlapping. Consequently, resolution of the overlapping bands can provide valuable qualitative as well as quantitative information.

BTEM is a self-modelling curve resolution (SMCR) programme. It has been successfully applied to deconvolute various spectroscopic data, such as FTIR [1], Raman [2] and MS [3] data, based on an information entropy minimization concept. The main advantage of this algorithm is that the deconvolution can be achieved without any *a priori* information.

Experimental Apparatus and Experimental Design The general experimental system consisted of a Schlenk tube (100 ml) equipped with a magnetic stirrer, a pump and UV-Vis spectrometer, all in a closed recycle configuration. One set of well defined experiments with perturbations of three dyes were conducted in deionized water. Stock solutions for these three dyes were used in the perturbations.

Pure Component Spectral Reconstruction and Concentration Calculation The total 9 UV-Vis spectra in the interval 265-800 nm were assembled into one matrix of size $A_{9 \times 1071}$. A spline was first applied to get rid of some noise in the raw data matrix. Singular value decomposition (SVD) was then used to decompose the processed data matrix. After decomposition, the right singular vectors V^T were inspected and 5 extrema were chosen as targets in the tBTEM algorithm. For most of the spectral reconstructions performed (vida infra), only 4 right singular vectors of information were needed. The experimental pure component reference spectra and the tBTEM estimates for Bblue (Fig. 1a, targeting both ca. 590 and 310 nm), Bgreen (Fig. 1b, targeting both ca. 618 and 402 nm) and methyl orange (Fig. 1c, targeting only ca. 460 nm) are plotted in Figs. 1a-1c.

A combination of tBTEM spectral estimates (Bblue, Bgreen and methyl orange) and experimental reference spectra (water plus quartz cell and background) were used in the multivariate quantitative analysis. The corresponding calculated concentration profiles of three different dyes are plotted in Figs. 1d-1f. As a comparison, the corresponding real concentrations are also plotted.

From Fig. 1, it can be seen that good tBTEM estimates were obtained compared to their corresponding experimental references. Almost 100% signal recovery was also obtained in the least squares fitting. In conclusion, the present contribution shows that a combination of tBTEM and other multivariate tools can be successfully applied to deconvolute the UV-Vis spectral data matrix.
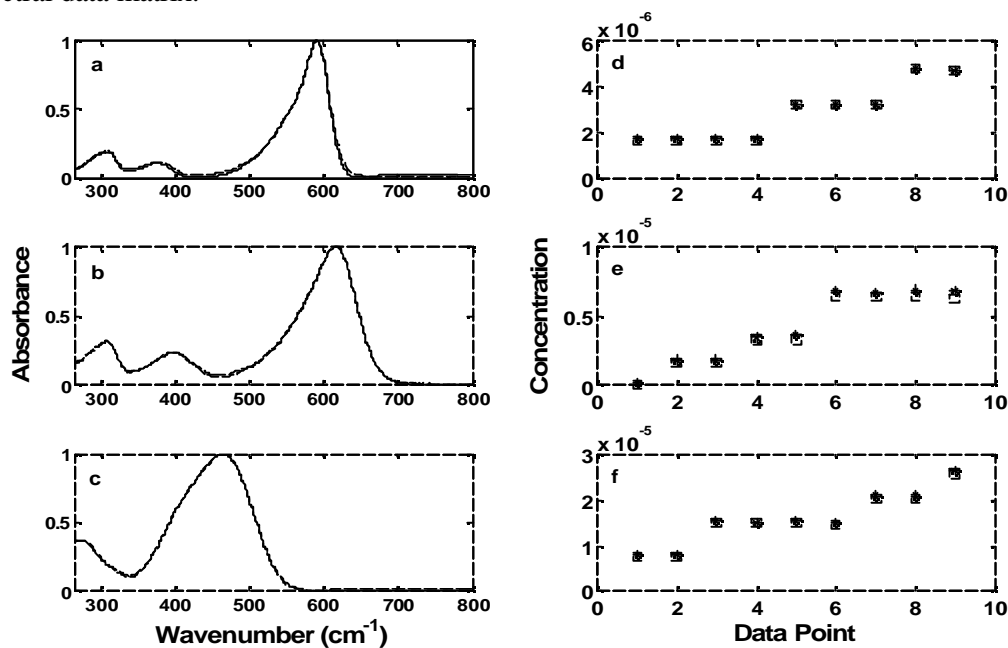
Fig. 1. tBTEM spectral estimates and estimated concentrations (see text for details)

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Design of Process Monitoring and Analysis Systems, using a Model-based Computer Aided Framework

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1. Summary

In the manufacturing industry, for example, the pharmaceutical industry, obtaining a consistent end-product quality is mandatory. A thorough understanding of the process as well as a properly designed monitoring and analysis system are required to obtain the desired end-product properties. This work focuses on developing a *model-based computer-aided framework* that will provide the methods and tools through which methodology for the design of the monitoring and analysis systems related to product quality control as an add-on to traditional chemical process design methods, can be developed. The *design of a process monitoring and analysis system* is a step-wise procedure consisting of the selection of critical process variables, followed by the proper selection and placement of suitable monitoring and analysis equipments to keep track on the behavior of these critical process variables, and finally, also including the coupling of the monitoring and analysis system to a control system to ensure that critical process variables can be controlled.

Keywords: PAT, process analytical technology, process monitoring, process analysis, design, framework, fermentation, tablet manufacturing

2. Extended Abstract

The starting point for the *design methodology* is the problem definition in terms of data related to the process specifications and the desired product quality, which are provided by the product manufacturer (or PAT system designer). A knowledge base and a model library are two important supporting tools within the framework. The knowledge base provides the necessary data during the design. It contains information related to process monitoring and analysis systems and includes for each unit process, a list of critical process variables that should be monitored, a list of the corresponding manipulating variables (actuators), and the corresponding equipments typically used for their measurement (including data related to accuracy, robustness, time, etc.). The model library contains the models which relate the process variables. These models

will support the analysis, for example by predicting process variables which are not measurable, thus generating the additional or missing data needed to obtain the final design. The framework guides the user through a systematic analysis (design methodology) related to the process-product and the important process-product variables to obtain the desired design for the product monitoring and analysis system. Optimization of the design can be achieved in terms of product data analysis time, cost of monitoring equipment subject to the maintenance of the desired product quality. The design methodology together with the model-based computer-aided framework has a potentially wide industrial application range, has the ability to assist in faster product-process development, and to allow identification of potential problems in the early stages of process-product development.

The objective of this paper is to highlight the design methodology together with the model-based computer-aided framework. First, the structure of the knowledge base has been developed. Later on, information was introduced in this knowledge base on the basis of an extensive literature search combined with an industrial survey and data collection. A collection of the necessary process operational models have been created through a computer-aided modeling tool (ICAS-MOT, developed at CAPEC). Process analysis, identification of critical points and process variables and selection of the appropriate monitoring and analysis system for the product-process will be illustrated through two case studies: a first case study, a tablet manufacturing process, is mainly focused on the pharmaceutical industry; a second case study, a fermentation process demonstrates the applicability of the framework for the bio-based process industries.

Session T4-7: Software Architecture, Standards & Interfaces

Abstract Number	Paper Title & Authors	Included
2970	Update on CAPE-OPEN standards and CO-LaN activities (Keynote) M Pons	Yes
595	Designing with CAPE-Open M P Breil, J Gabrielsen, N von Solms, G M Kontogeorgis, E H Stenby	Yes
1313	ProSimPlus: New CAPE-OPEN capabilities in process simulation S Déchelotte, A Vacher, O Baudouin, G Hameury	Yes
1617	Use of CAPE-OPEN standards in the interoperability between modelling tools (MoT) and process simulators (ProSim) R Morales-Rodríguez, R Gani, S Dérchelotte, A Vacher, O Baudouinb	Yes
3177	Use of CAPE-OPEN standards in the coordinated optimization of plant production scheduling and supply-chain planning J M Laínez, C Benqlilou, A Espuña, B. Ivanov, N. Vaklieva, L. Puigjaner	Yes

Update on CAPE-OPEN standards and CO-LaN activities

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1. Summary

The CAPE-OPEN Laboratories Network (CO-LaN) organizes worldwide activities related to the CAPE-OPEN standards. Recognition of the CAPE-OPEN standards is measured through its continuous adoption by the market. CO-LaN maintains actively the CAPE-OPEN standards, expanding its range of applicability. In order to ease up the adoption process, CO-LaN is actively developing a suite of software tools helping developers to progress on CAPE-OPEN implementation. CO-LaN brings together regularly CAPE-OPEN experts and beginners either in dedicated conferences or training courses.

Keywords: CAPE-OPEN, CAPE, interoperability, standards

2. Extended Abstract

CAPE-OPEN standards are the widely recognized industry standards through which interoperability is achieved between pieces of software used in process systems engineering. The CAPE-OPEN standards have been first beta-released in mid-1999, then officially released (version 1.0) in March 2002. The CAPE-OPEN standards are increasingly implemented in process modelling environments and process modeling components. The market penetration of the CAPE-OPEN standards is increasing year after year: the most prominent software vendors in the process simulation domain, as well as many niche vendors or academic suppliers of process simulation code, have adopted CAPE-OPEN as their preferred means of interoperating.

The CAPE-OPEN standards are maintained and supported by the CAPE-OPEN Laboratories Network (CO-LaN), a not-for-profit organization strong of 60+ members where half of them are software vendors. The continuous growth of this organization reflects the progress made in the adoption of the CAPE-OPEN standards for enabling interoperability between process modelling environments and process modelling components. CO-LaN is seeking actively new members.

While the initial CAPE-OPEN standards, as released in 2002, were meant already to cover most of the process simulation domain, CO-LaN has taken recently a number of steps to extend the existing standards and to facilitate their implementation and use.

Advances have been made in the thermodynamic domain with the release of version 1.1 of the Thermodynamic and Physical Properties interface specification (October 2006). A Special Interest Group on Refining Reactors has been created mid-2006 and its first significant results have been presented in March 2007. Further implementations have occurred on the extension to dynamic unit operations of interfaces developed at first only for steady-state unit operations. Guidelines on interoperability between .NET and COM middleware have been issued.

Software tools supporting the implementation of CAPE-OPEN interfaces have been developed by CO-LaN and distributed to the CO-LaN membership: first a new version of the Wizard for Unit Operations in Visual Basic has been released. The Wizard is now fully compliant with version 1.0 of the CAPE-OPEN standards. The Wizard simplifies the process of developing a CAPE-OPEN compliant Unit Operation by writing automatically most of the source code necessary. Secondly the production version of the CAPE-OPEN Logging and Testing Tool (COLTT) has been released in March 2007 and maintained since then. COLTT helps making diagnostics on the communication taking place through CAPE-OPEN interfaces between a process modelling component and a process modelling environment.

Training in CAPE-OPEN concepts and implementation has developed through the sponsorship of CO-LaN while specifically targeted dissemination events have been organized in Europe and in the U.S. Two one-day training courses have taken place during the last year, one in the US and the other one in Europe, gathering altogether 30 participants. CAPE-OPEN conferences have been organized on an annual basis both in the US and Europe for the past four years with increasing participation.

For the future, additional areas have been defined where the CAPE-OPEN standards will be extended to serve the end-user community and the software vendor community: hydrodynamic modelling, solid thermodynamic physical properties for instance.

Visit www.colan.org for updated information on activities of the CAPE-OPEN Laboratories Network.

ProSimPlus: new CAPE-OPEN capabilities in process simulation

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1. Summary

Interoperability, integration and re-use are the most often met demands from engineering calculation software users. ProSimPlus, the general steady state process simulator developed by French software house ProSim and used by many industrial companies around the world, now provides new CAPE-OPEN capabilities. These capabilities will be demonstrated in the presentation.

Keywords: CAPE-OPEN, interoperability, ProSimPlus, process simulation, Simulis

2. Extended Abstract

The advantages of the component based software development and its implication on software interoperability will be first presented and illustrated with Simulis Thermodynamics, ProSim's thermodynamic properties server.

Then it will be shown how ProSimPlus inherits from the CAPE OPEN compatibility of Simulis Thermodynamics at the thermodynamic level. In effect, ProSimPlus is able to perform steady-state process simulation using external thermodynamic models as represented on Figure 1.

An example of use of a third-party CAPE-OPEN property package within ProSimPlus will be demonstrated.

Figure 1: CAPE-OPEN thermodynamic socket

Conversely ProSimPlus has the capability to create CAPE-OPEN property packages that can be used within other CAPE-OPEN compliant software as shown on Figure 2.

An example of use of a third-party CAPE-OPEN property package within ProSimPlus will be demonstrated.
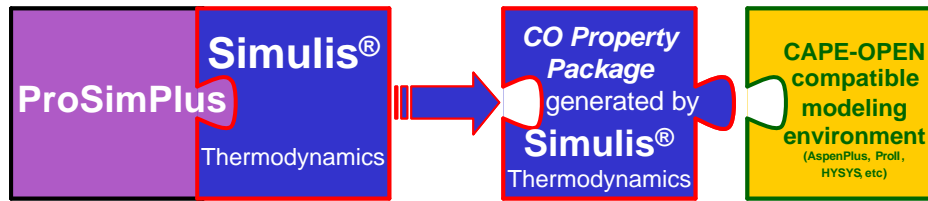
Figure 2: CAPE-OPEN thermodynamic plug

Furthermore, ProSimPlus also offers a CAPE-OPEN unit socket to call external unit operation models. These plugged external unit operations are then managed as "native" unit operation in the process simulation. An illustration of this capability will be presented with the use of CAPE-OPEN compatible unit operations.

Thanks to the CAPE-OPEN Laboratories Network (CO-LaN), successful tests have been performed with third parties CAPE-OPEN compliant components. Depending on the quality of the software component, the cost of the CAPE-OPEN compliance, in terms of calculation time, was demonstrated to be generally, very low.

ProSimPlus was already an open simulator in which the user could add its know-how, either with classical user modules (for instance Fortran DLL), or using the VB Script facility to add some functionalities. New CAPE-OPEN capabilities developed within ProSimPlus increase this openness and allows the use of external thermodynamic packages and/or unit operations. With this support of the CAPE-OPEN standard, ProSimPlus proposes a new way to integrate customers' know-how and to manage it in the long run.

References

www.colan.org   official web site of the CO-LaN

www.prosim.net ProSim web site

Use of CAPE-OPEN standards in the interoperability between modelling tools (MoT) and process simulators (ProSim)

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1. Summary

CAPE-OPEN organization is an association promoting open interface standards in process simulation software. In this work is shown the advantages of the use of CAPE-OPEN for the interoperability between MoT-Simulis Thermodynamics and MoT-ProSimPlus for thermodynamic calculations and unit operation calculation, respectively.

Keywords: CAPE-OPEN, interface, ICAS-MoT, Simulis, ProSimPlus

2. Extended Abstract

Up to now, it is well known that computer-aided tools play a vital role in the modelling/design/analysis/control of chemical processes and products thus manufacture. As these tools may come from different sources and disciplines, *how can they be used efficiently for the design/analysis of specific process-product?* The CAPE-OPEN interfaces, in this case, make the possible integration of the needed computational tools.

The objective of this presentation is to highlight the application of computer-aided modelling tools for generation and use of modelling objects in CAPE-OPEN compliant process simulators. This presentation will highlight the use of external modelling objects for unit operation models as well as thermodynamic property models. What we need are the following:

- A process simulator with a CAPE-OPEN socket (e.g. ProSimPlus).
- A CAPE-OPEN unit/property methods wrapper (link) that is able to receive an external model object from an external source.

- The model object representing any model (unit operation or thermo) generated for a computer-aided modelling tool for model translation, analysis and solution (ICAS-MoT).

The advantage of using ICAS-MoT (Sales-Cruz, M. and Gani, R., 2003) is that it is possible to transfer the model equations representing any new unit operation/thermo into a COM-object that can be used in some simulation engines (Icassim and Dynsim available within ICAS software), external software (i.e. EXCEL) or external simulators (ProSimPlus, etc) with a well defined interface without the user having to write any programming code. ICAS-MoT also carries out the analysis of degrees of freedom, determination of the structure of the equation system, index analysis, partitioning and ordering of the model equations and numerical analysis; and the solution of the model analyzed in the previous step, and thereby, producing customized simulators for a particular process.

The presentation will highlight the application of CAPE-OPEN interfaces for a model generated and tested in ICAS-MoT and then its equivalent COM-object is created. This COM-object is then wrapped by a generic unit-wrapper and plugged into the CAPE-OPEN socket of ProSimPlus (CAPE-OPEN compliant process simulator). It will also highlight the synergy between ICAS-MoT and Simulis Thermodynamics (from ProSim) through established generic CAPE-OPEN link.
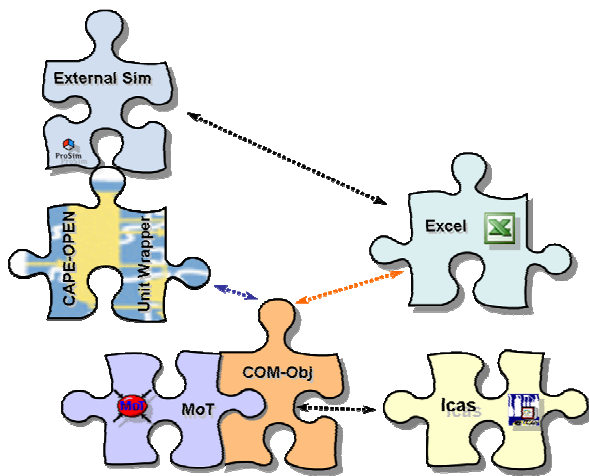

Figure 1. Software integration among MoT, external simulators, external software and modelling engines.

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Use of CAPE-OPEN standards in the coordinated optimization of plant production scheduling and supply chain planning

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1. Summary

Following different specific needs and research programs during last years, a considerable number of simulating packages and components for chemical engineering have been created. However, it has been accounted that these pieces of software are not straightforwardly suitable for integration with other complementary applications, which constitutes a basic need from the perspective of industrial use. Aiming to respond to this need, the CO-LaN (http://www.colan.org) laboratory was created in order to develop common standards (CAPE OPEN standards) which should allow transparent communication between different applications. On the other hand, although the historical trend in the management of single manufacturing sites has been driven by the integration of aggregate planning and detailed scheduling[1], current Advanced Planning and Scheduling (APS) systems support the decision making process at specific levels and functions, so that the consideration of their co-operative supply chain network (SC) requires a revised perspective and complementary decision making structures. Furthermore, additional SC key considerations (e.g. environment, finances, marketing), are not adequately covered or even disregarded by current approaches. Under such circumstances, CO standards for interfacing software components seem an adequate answer and proper strategy to propose a framework made up of a flexibly envelope of diverse applications to assess SC decisions at different hierarchical levels and functions. The structure proposed in this work is thus in consonance with the trend towards enterprise wide modeling (EWO) which aims to integrate all the functional decisions into a global model driven by an overall key performance measure.

Keywords: CAPE-OPEN; supply chain management; decision support systems

2. Extended Abstract

The nature of SC planning problem is quite similar to the plant production scheduling problem, this similarity enabling the extension of CO APS standard to the SC planning level. The dissimilarity arises when tactical and strategic decisions are considered. The latter broughts into play a broader aggregated view of the problem.

The considered network does not only contemplate equipments, but the whole echelons of a SC (i.e. processing plants, warehouses, suppliers). Also, the time scale in this type of problems is usually larger than the time required to process a product, transforming this way the sequencing-timing problem into a rough capacity problem. Capacity is one of the key sensitive information flows to take into account when communicating two applications which are solving SC planning problems at two different hierarchical levels.

The SC problems that this work undertakes are related to SC design, planning and scheduling. Due to the extension and complexity of present SC models considered in EWO systems, here is proposed the architecture depicted in figure 1. As shown, it is proposed an interface integrating the strategic and tactical SC decision making levels. The interfaces related to non-operational issues are defined separately, as it is usually done in practice. These non-operational modules can be utilized by any other class of problems where the metrics they comprise may be relevant; being this other reason to be treated in an isolated manner.
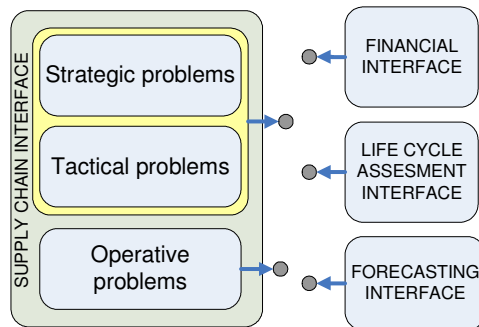
Figure 1: Architecture proposed

When considering that distinct software can solve SC problems at different decision levels and that a flow of information can be shared by them, the SC problem becomes solved in a sequential manner. A metaheuristic based methodology is proposed to drive local optima (solutions resulting from the previous elementary problems) towards a global result that, although it cannot guarantee global optimality, is offering not a merely feasible but "well balanced" compromise.

The information flow analysis between the modules has been carried out by examining the information exchange between a SC Planner developed by the BAS and a scheduler (MOPP) developed by UPC required to solve a diary SC case study[3].

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Acknowledgments

Designing with CAPE-OPEN

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1. Summary

The presentation will be a talk on the benefits of the CAPE-OPEN standard – illustrated by some examples of our developments on a thermo system (advanced thermodynamic models) and unit operations (PT-flash and CO_2 absorber).

Keywords: Thermodynamics, unit operation, CO_2 absorption

2. Extended Abstract

The CAPE-OPEN standard offers the developers of new thermodynamic models and new unit operations the possibility of providing these products as plug-ins to process simulators. The advantage is the elimination of the complex and lengthy step of computational implementation.

The steady increase in the number of CAPE-OPEN compliant thermodynamic modules tells us that the problem of making codes CAPE-OPEN compliant (while difficult) has been solved. Therefore the focus for thermodynamicists must be on good thermodynamic models. Ten years of experience of using the Cubic-Plus-Association (CPA) equation of state (Kontogeorgis *et al.,* 2006a and 2006b) have demonstrated that it is a very successful model for handling multi-component, multiphase equilibrium in systems containing hydrogen-bonding substances.

Besides the need for good thermodynamic models, there is also a need for the ability of making tailor-made unit operations. Towards this objective, the CAPE-OPEN standard is an obvious choice and a good example is the CO_2 capture using an alkanolamine solution (Gabrielsen *et al.*, 2006). This unit operation encapsulates the essential properties of most unit operations: thermodynamics, chemical reactions and mass transfer. The fundamentals of the unit operation have been validated using data obtained from a fully computerized pilot plant.

Normally, the performance of a unit operation will depend on the choice of the thermodynamic model. Unit operations based on the CAPE-OPEN technology can be developed so that user has the privilege of choosing among the thermodynamic models available in the process simulator.

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Session T4-8: Process Control

Abstract Number	Paper Title & Authors	Included
1052	Control structure selection of a deethanizer column with partial condenser E S Hori, S Skogestad	Yes
1679	A multi-parametric programming approach for dynamic programming and robust control N Faísca, O Exler, J Banga, E N Pistikopoulos	Yes
2174	Norm based approaches for Automatic tuning of Model based Predictive Control P Vega, M Francisco, E Sanz	Yes
2349	Inferential control of a chaotic autocatalytic reaction in a continuous stirred tank reactor A Mukherjee, D P Searson, M J Willis, A R Wright	Yes
3061	Design and Performance Evaluation of an Explicit Parametric Controller for a Solid Oxide Fuel Cell (SOFC) System: A Comparative Study D I Gerogiorgis, K I Kouramas, N Bozinis, E N Pistikopoulos	No
3281	Estimation of noise covariances and identification of disturbance structure using the autocovariance least-squares method B M Åkesson, J B Jørgensen, N K Poulsen, S B Jørgensen	Yes

Control structure selection of a deethanizer column with partial condenser

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1. Summary

The selection of a good control structure for a distillation column is important for the plant operation. In this work, it is studied the control structure selection of a deethanizer column with partial condenser from Statoil/Norway. The objective is to separate ethane (C_2) from propane (C_3). This is a multicomponent column with a partial condenser and vapor distillate flow. The column has 36 trays and is fed in tray 26. As the feed is already very low concentrated in ethane (2.1%), the distillate flowrate is very small (around 1% of the feed). Although this could cause some difficulties for pressure control, the results show that this is not a big problem if we also close a temperature loop. The simulations are done in ASPEN Plus and ASPEN Dynamics. The main objective is to find a structure that minimizes the effect of disturbances and implementation error (noise and bias) in both top and bottom compositions (indirect control). The results show that it is better to control temperatures in the top section where the gains are higher and, as this is a multicomponent column, the two-point temperature control does not improve the control system performance (Hori and Skogestad, 2007).

Keywords: deethanizer, partial condenser, control structure selection, indirect control

2. Extended Abstract

2.1. Steady-state simulation

The steady-state simulation was done in ASPEN Plus. The simulation shows that the temperature profile is very flat in the bottom section. It implies that the temperature slope (temperature difference between neighbouring stages) is very small, so we shouldn't control a temperature in this region (Luyben, 2005).

2.2. Dynamic simulations

The stabilizing control structure used (pressure and level controllers) is:
- control bottom level by bottom flowrate B
- control pressure by distillate flowrate D
- control reflux drum level by reflux flowrate L

The two degrees of freedom available (condenser Q_c and reboiler Q_b duties) are used for temperature control (the stages are counted from bottom to top):
- Q_c /T37: use Q_c to control the temperature after the condenser (T37)
- Q_b /T4: manipulate Q_b to control temperature in tray 4
- Q_b /T36: manipulate Q_b to control temperature in the most sensitive tray (T36)

The control structures are compared in Figure 1 for a disturbance in feed flowrate. In this plot, we compare the indirect control of the top and bottom compositions. The objective is to choose the control structure that gives the smallest composition deviation. It is possible to see that the best structure is Q_c/T36, which gives almost zero deviation for top composition and the smallest for bottom composition. This result confirms that it is better to control a temperature in the top section (highest gain and large temperature slope). Although it can seem a bit strange to control a temperature in the top section manipulating the reboiler duty, Hori and Skogestad (2007) present some examples of columns that have this same characteristic.
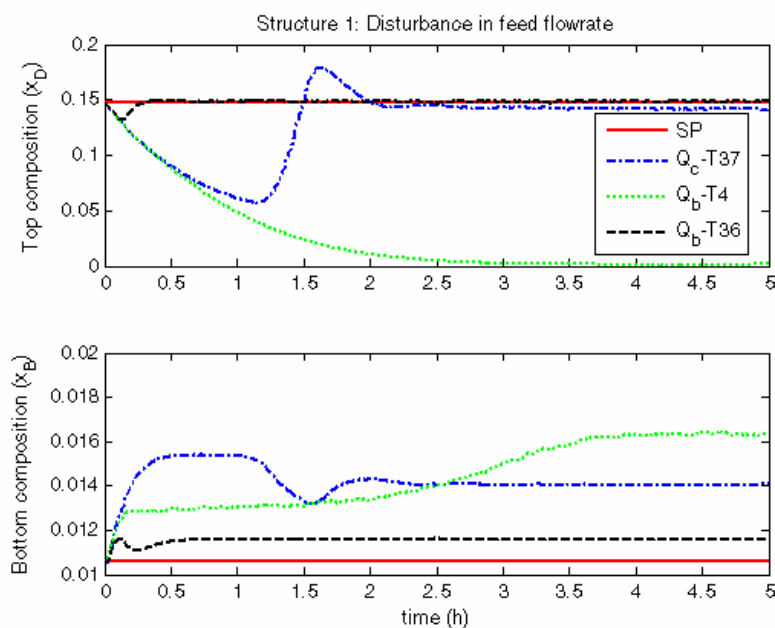

Figure 1: Composition response to disturbance in feed flowrate.

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A multi-parametric programming approach for dynamic programming and robust control

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1. Summary

In this work, we present a new algorithm for solving complex multi-stage optimization problems involving hard constraints and uncertainties, based on dynamic and multi-parametric programming techniques. Each echelon of the dynamic programming procedure, typically employed in the context of multi-stage optimization models, is interpreted as a multi-parametric optimization problem, with the present states and future decision variables being the parameters, while the present decisions the corresponding optimization variables. This reformulation significantly reduces the dimension of the original problem, essentially to a set of lower dimensional multi-parametric programs, which are sequentially solved. Furthermore, the use of sensitivity analysis circumvents non-convexities that naturally arise in constrained dynamic programming problems. The potential application of the proposed novel framework to robust constrained optimal control is highlighted.

Keywords: pharmaceutical synthesis, green chemistry, green engineering, solvent selection

2. Extended Abstract

P Dynamic Programming is well-documented (Bellman, 2003; Bertsekas, 2005) as being a powerful tool to solve multi-stage decision problems. Based on the optimality principle, the original problem disassembles into a set of small dimension problems. This strategy has been successfully applied to numerous problems, however, the presence of hard constraints is an obstacle. Presence of hard constraints implies non-linear decisions with respect to the present state, which is why the conventional implementation of the dynamic programming procedure would require the solution of global optimisation algorithms. Furthermore, the presence of uncertainty in the dynamic model of the problem, imposes further challenges for the solution of the

dynamic programming problem. Although some researchers have dealt with this problem (see Borrelli et al, 2005), it is an open research topic.

In the present work, a new algorithm is proposed to solve the convex multi-stage problem with hard constraints based on dynamic programming and parametric programming procedures. Each echelon of the dynamic programming procedure is interpreted as a multi-parametric optimisation problem (Pistikopoulos *et al.*, 2007*a,b*), with the parameters being the states at the current stage and future optimisation (control) variables. Preserving the dynamic recursive procedure, the dimension of the optimisation problem is reduced to a set of sequential lower dimensional multiparametric programming problems, constrained by fewer inequalities; whereas the use of sensitivity analysis circumvents possible non-convexities. Therefore, the robust solution for convex multi-stage decision problems in the presence of uncertainties is easily computed with this new algorithm. The underlying mathematical theory is described and numerical examples are presented to illustrate the potential of the new approach.

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Norm based approaches for Automatic tuning of Model based Predictive Control

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1. Summary

In this work an automatic procedure to obtain the parameters of a Model Based Predictive (MPC) control system sheme is presented. The tuning procedure has been developed within a multi objective constrained non-linear optimization framework taking into account several performance indexes for the optimal tuning of MPC. Among them, the weighted H∞ norm of several closed loop disturbances transfer function and the ∞ norm of different signals are considered. The mathematical optimization to obtain the control system parameters is tackled in two iterative steps using the clasical Sequential Quadratic Programming (SQP) method and, also, a special type of random search method (MOAM).

Keywords
Model predictive control, Robust Control Theory, l1 norm, H∞ norm, Mixed Sensitivity Problem, Sensitivity Matrix, Control Sensitivity Matrix, constraints Multiobjective Optimization

2. Extended Abstract

2.1 Motivation and Objectives

Model predictive control schemes (MPC) are the most widely used advanced control techniques in industry because of its easiness to deal with multivariable systems and constraints together with difficult dynamics and delays. Several successful applications in activated sludge control have been reported in ([4]). Usually, the tuning of the parameters in linear Model Based Predictive Control schemes has been performed using expert knowledge and a trial and error procedure.
Recently, some works dealing with automatic tuning of MPC.have been published some of them using the Optimization Theory but without considering output and inputs constraints on the on-line optimization step. ([1], [2]). In [3] we have already proposed a methodology for the on-line automatic tuning of the whole set of parameters of linear Model Based Predictive Control Systems was carried out but by minimizing the Integral Square Error (ISE) norm as performance index. The main

tuning parameters are those affecting the behaviour of the closed loop combination of plant and MPC. (control efforts weights, prediction and control horizons, time constant for the reference trajectories,..). An important drawback of this work was that within the optimization procedure a dynamical simulation has to be carried out as a means of computing the objective function or any other dynamical performance indexes including real data records as disturbances. The control strategy is applied during the simulation. This makes the procedure extremely slow.

The objective of this work was to develop more efficient procedure to tune MPC algorithms. The approach presented here uses linear models and norms to avoid the resolution of a dynamic optimization problem

2.2 Main Contributions.

At the view of previous works, we propose a new approach for the optimal automatic tuning of MPC. The more relevant aspects of the actual proposal are:

1) The proposed methodology is based on the minimization of a set of indexes based on the weighted sum of the H_1, H_2 and H_∞ norms of several closed loop transfer functions matrices of the system subject to a set of constraints. In this sense no dynamical simulation is needed and therefore the algorithm is very fast The methodology proposed here is a general one and the formulation is a multivariable one. The use of linear models for the control also allows for the specification of any other convex performance criteria within an LMI framework to state stability conditions and some desired closed-loop behaviour.

2) The optimal evaluation of the whole set of real (Weighting factors) and integer parameters (horizons) of the linear MPC control scheme is carried out by solving a MINLP/DAE optimization problem by using a random search based method (MOAM).

3) The use of the proposed automatic tuning approach within an Integrated Design framework can be easily stated.

The approach has been validated on a simulated example based on a real wastewater treatment plant. Real scenarios for the main disturbances have been considered in the simulated model to make a more realistic analysis of the results.

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Inferential control of a chaotic autocatalytic reaction in a continuous stirred tank reactor

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1. Summary

Control of chaos in chemical reaction systems is crucial to mitigate long term unpredictability and non-uniform system performance, e.g. irregular product concentration/selectivity at any given time. Chaos in chemical systems may be controlled by stabilising unstable periodic orbits (UPOs) in the reaction state space. This paper investigates whether product concentrations of an autocatalytic reaction, simulated in a continuous stirred tank reactor, may be stabilised by feedback control of a single state variable. An inferential control algorithm based on a secondary state variable is proposed. This state variable, derived from rate of heat evolution time series data, is used in the simple proportional feedback (SPF) algorithm (Davies and Scott, 2001). The performance of the algorithm is evaluated when noisy heat evolution data are sampled for the feedback law.

Keywords: control of chaos, simple proportional feedback, reaction calorimetry

2. Extended Abstract

Control of chaos in reacting systems is critical to mitigate long term unpredictability and inconsistent system performance (Boccaletti et al., 2000). Chaos may be controlled by stabilising unstable periodic orbits by temporal perturbations to an accessible process parameter. A common characteristic of most control of chaos studies involving reactions is the assumption that concentrations of the reactants and products can be measured on-line without any significant time delay. However, this is often infeasible due to extensive use of analysers with long cycle times or off-line laboratory assays. An alternative strategy, comprising an inferential control algorithm based on measurements of a secondary state variable, is proposed in this paper. The secondary state variable derived from the time series of rate of heat evolution data from the reactor is used in the feedback control law.

2.1. Algorithms to control chaotic oscillations

The SPF control algorithm, first proposed by (Peng et al., 1991), is a geometrically inspired variant of the Ott, Grebogi and Yorke (OGY) chaos control technique (Ott et al., 1990). The SPF algorithm directly targets the fixed point of the Poincaré map by applying appropriate manipulated variable perturbations. The magnitude of the control action is directly proportional to the deviation of the current measurement on the Poincaré map from the desired fixed point. It has been shown by Davies and Scott, (2001) and Mukherjee et al.

(2007) that a perturbation of the manipulated variable may be designed such that it will direct the system to the fixed point on its next return to the Poincaré section.

2.2. Autocatalytic reaction model

The model consists of five reaction steps and the overall reaction converts reactant A (autocatalysed by B and C) to products P_1 and P_2 in a CSTR. The presence of nonlinear feedback in the reaction kinetics results in chaotic oscillations for certain reaction conditions. Assuming that isothermal conditions are maintained (e.g. by power compensation reaction calorimetry) and that the inlet feed temperature is equal to the reactor temperature, then the total heat generated by the reactions $(Q_r)_t$ is equal to negative of the heat supplied $(Q_c)_t$, i.e. $(Q_r)_t = - (Q_c)_t$. Hence, $(Q_c)_t$ may be used to calculate the total heat liberated by the reactions.

2.3. Inferential control of product concentration by rate of heat evolution

In the inferential control algorithm, the inferred rate of heat evolution $(Q_r)_t$ is used for the chaos control technique. When $(Q_r)_t$ reaches its nth local peak Q_n, (i.e. the maximum of an oscillation cycle), the SPF control algorithm perturbs the manipulated variable by $\boldsymbol{dq}_n$ according to:

$$\boldsymbol{q}_n = \overline{\boldsymbol{q}} + \boldsymbol{dq}_n \quad \text{and} \quad \boldsymbol{dq}_n = \frac{Q_n - Q_F}{g} \tag{1}$$

Where $\overline{\boldsymbol{q}}$ is the nominal value of the manipulated variable (i.e. the residence time of the reactor, which may be adjusted using the feed flow rate), $?_n$ is the value of the manipulated variable at the nth maximum of $(Q_r)_t$ and Q_F is the fixed point of the Poincaré map. The constant of proportionality term in the control law is denoted by g.

2.4. Conclusions

Product concentrations in a chaotic mutating autocatalytic reaction have been successfully regulated by controlling the rate of heat evolution from the reactor. It has been shown that the proposed algorithm performs satisfactorily, even in the presence of noise in the measurement data.

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Estimation of noise covariances and identification of disturbance structure using the autocovariance least-squares method

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1. Summary

The Kalman filter requires knowledge about the noise statistics. In practical applications, however, the noise covariances are generally not known. The purpose of this paper is to present a method for Kalman filter tuning and disturbance structure identification for use with model-based control. The method yields least-squares estimates of the noise covariances, which can be used to compute the Kalman filter gain. Furthermore, the method can be used for identification of the disturbance structure.

Keywords: Kalman filter, covariance estimation, state estimation

2. Extended Abstract

In state estimation the state of a system is reconstructed from process measurements. State estimation has important applications in control, monitoring and fault detection of chemical processes. The Kalman filter and its counterpart for nonlinear systems, the extended Kalman filter, are well-established techniques for state estimation. However, a well-known drawback of Kalman filters is that knowledge about process and measurement noise statistics is required from the user. In practical applications the noise covariances are generally not known. Tuning the filter, i.e. choosing the values of the process and measurement noise covariances such that the estimation error is minimized, is a challenging task. If performed manually in an ad hoc fashion it represents a considerable burden for the user. Since better estimates result in better control there is a motivation for developing methods for Kalman filter tuning.

The filter tuning problem is essentially a covariance estimation problem where the Kalman filter gain is computed based on the estimated covariances. A promising technique for covariance estimation is the autocovariance least-squares method proposed recently by Odelson and co-workers for linear time-invariant systems (Odelson et al. 2006). This method is based on the estimated autocovariance of the output innovations, which is used to compute a least-squares estimate of the noise covariance matrices. The approach has the advantage that routine operating data from the process can be used. The estimation problem can be stated in the form of a convex semidefinite program, which can be solved by interior-point methods which guarantee positive semidefiniteness of the covariance matrices. The estimation method has been generalized to systems where the process noise and the measurement noise are mutually correlated.

The structure of the noise that enters the system is likely to be unknown as well. Generally there are only a few independent disturbances affecting the states and by minimizing the rank of the process noise covariance matrix the noise structure can be identified. The trace is used as an approximation of the rank and is added as an objective to the least-squares problem. The minimum rank can be determined by plotting the trace versus the fit to data for different values of a weight parameter (Rajamani and Rawlings 2006). To extract information about the number of disturbances and the structure of the disturbances, singular value decomposition can be applied to the combined covariance matrix for both process and measurement noise. The number of disturbances is the number of nonzero singular values and the noise shaping matrices for process and measurement noise are obtained from the orthogonal matrices containing the singular vectors.

The performance of the noise covariance estimation method and the disturbance identification technique is demonstrated on numerical examples from the chemical process industry.

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Session T4-8P: Process Control - Poster

Abstract Number	Paper Title & Authors	Included
363	Design of PID Controller Cascaded with Filter for First Order Time Delay Process M Shamsuzzoha, M Lee	Yes
990	Robust stabilization of an exothermic CSTR M Bakosova, D Puna, J Zavacka	Yes
1044	A Novel Mixed Product Run-to-run Control Algorithm – Dynamic Ancova Approach M-D Ma, C-C Chang, D S-H Wong, S-S Jang	Yes
1407	Fuzzy Model-based Predictive Control of a Chemical Reactor A Vasickaninová, M Bakošová	No
1715	PD and PID Fuzzy Logic Controllers. Application to Neutralization Processes M C Palancar, L Martín, J M Aragón, J Villa	Yes
2201	Nonlinear model predictive control strategies applied to a fed-batch sugar crystallizer L S Dediós, P Georgieva, S Feyo de Azevedo	Yes
2234	Development of Soft Sensors for Debutanizer Product Quality Estimation and Control I Jerbic, N Bolf, H Pavelic	Yes
2524	Neural Network Modeling and Control of an Etherification Hybrid Reactor P Kittisupakorn, P Thitiyasook, K Konakom	Yes
2838	Control and Optimization of a Fluid Catalytic Cracking Process: An Industrial Case J L Fernandes, C I C Pinheiro, N Oliveira, J Inverno, F Ramôa Ribeiro	Yes
2877	Data Driven Tuning of Lower Level Controllers for Disturbance Rejections J K Huusom, N K Poulsen, S B Jørgensen	Yes
3520	A Critical Discussion of the Continuous-Discrete Extended Kalman Filter J B Jørgensen	Yes
3560	Modeling and Control Solutions for Riser Slugging in Offshore Oil Fields O Q F Araújo, J Luiz de Medeiros, G C Nunes	Yes

Design of PID Controller Cascaded with Filter for First Order Time Delay Process

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Abstract

The majority of controllers used in the process industries are still proportional, integral, and derivative (PID). There are many reasons for this, including the fact that they are well understood by many industrial operational, technical, and maintenance individuals, and, in many applications, the fact that a properly designed and well-tuned PID controller meets or exceeds the control objectives. Although advance control techniques such as model predictive control can provide significant improvements, a PID controller that is properly designed and tuned has proved to be satisfactory for the vast majority of industrial control loop.

The well-known internal model control (IMC) PID rules have the advantage that a clear tradeoff between closed-loop performance and robustness to model inaccuracies is achieved with a single tuning parameter. The reported literatures show that IMC-PID provides good setpoint tracking but very sluggish disturbance response for tuning the process with a small time-delay/time-constant ratio. However, for many process control applications, disturbance rejection is much more important than setpoint tracking. Therefore, controller design that emphasizes disturbance rejection rather than setpoint tracking, is an important design problem that has received renewed interest recently.

Recently Skogestad, (2003) proposed a rule for modification of the integral terms to improve disturbance rejection for integrating processes and also proposed the simple analytical rules for the model reduction to obtain a model in this form. Chen and

Seborg, (2002) proposed a design method for PID controllers based on the direct synthesis approach. Some of the workers (Lee et al. 1998; and Horn et al. 1996) proposed the same kind of lead lag filter to resolve this problem, but still it has lack of consistency in result.

Therefore, in this article, we have proposed an analytical tuning method for the PID controller cascaded with a lead/lag filter for the FOPDT process based on the IMC design principle. The controller is designed for the disturbance rejection and two-degree-of-freedom control structure is used to slacken the overshoot in the set-point response. The simulation study shows that the proposed design method provides better disturbance rejection than the conventional PID design methods when the controllers are tuned to have the same degree of robustness by the measure of maximum sensitivity (Ms). A single tuning parameter closed-loop time constant (λ) guideline is provided for several different robustness levels.

Robust stabilization of an exothermic CSTR

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1. Summary

The paper deals with an application of robust static output feedback control to an exothermic continuous-time stirred tank reactor with parametric uncertainties and multiple steady states. The problem of robust controller design is converted to solution of linear matrix inequalities and a computationally simple non-iterative algorithm is presented. The possibility to use robust static output feedback for control of reactors with uncertainties and comparison of a robust controller with an optimal controller is demonstrated by simulation results.

Keywords: chemical reactor, multiple steady states, uncertainty, robust control, static output feedback

2. Extended Abstract

Exothermic reactors are very interesting systems because of their potential safety problems and the possibility of exotic behavior such as multiple steady states. Furthermore, operation of chemical reactors is corrupted by many different uncertainties. The goal of this paper is to present the possibility to stabilize a continuous-time stirred tank reactor (CSTR) with an exothermic reaction (hydrolysis of propylene oxide to tri-propylene glycol) in its unstable steady state using robust static output feedback control (RSOFC). The CSTR is an uncertain system because of two inexactly known parameters, reaction rate constant and reaction enthalpy.

Robust controller design is based on a linear state-space representation of the CSTR in the form of a linear time-invariant polytopic system with system matrices situated into a convex envelope of 2^n vertices, where n is the number of uncertain parameters. Necessary and sufficient conditions for stabilization of an uncertain polytopic system via static output feedback are presented at first (Vesely, 2004). The problem of RSOFC design is reduced to solution of two matrix inequalities, which are further

transformed in two linear matrix inequalities (LMIs). These LMIs must be solved for everyone of four vertex systems obtained for two uncertain parameters of the CSTR. The stabilizing robust controller is obtained via solutions of two sets of LMIs. A computationally simple non-iterative algorithm for obtaining a robust controller is also presented. If the solution of the first set of LMIs is feasible, the polytopic system is simultaneously stabilizable via a static output feedback. If the solution of the second set of LMIs is feasible, then the uncertain closed-loop system is quadratic stable with a guaranteed cost. The design procedure guarantees with sufficient conditions the robust quadratic stability and guaranteed cost.

The possibility to use robust static output feedback for control of the CSTR with uncertainties and comparison of a designed robust controller with an optimal LQR controller is demonstrated by simulations. The controlled variable is the temperature in reactor T_r, control inputs are volume flow rates of reaction mixture and coolant. The main aim is to stabilize the reactor in its unstable steady state represented by the $T_r = 343,1K$. Fig.1 shows the open-loop response of the CSTR, the closed-loop response of the CSTR obtained with one of the designed robust static feedback P controllers and the closed-loop response of the CSTR with an optimal LQR controller. Simulation results are presented for a nominal model of the CSTR obtained for mean values of reaction rate constant and reaction enthalpy and for four vertex models obtained for all combinations of minimal and maximal values of reaction rate constant and reaction enthalpy. Simulation results confirm that the described design procedure gives robust controllers, which are able to stabilize chemical reactors with uncertainties.
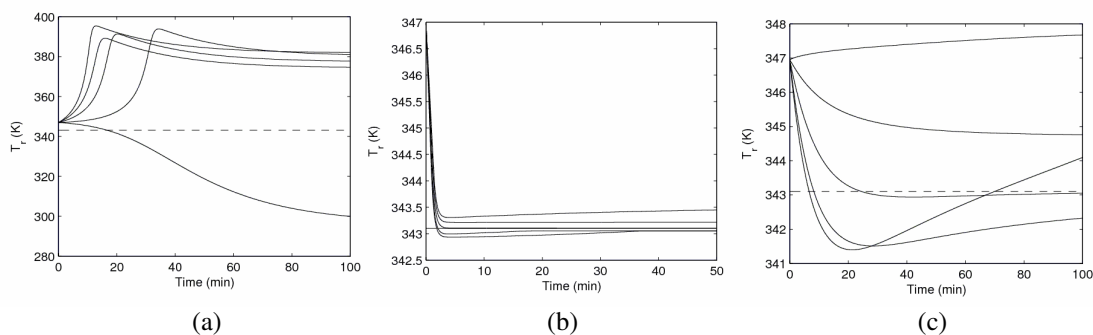

| (a) | (b) | (c) |

Figure 2: Open-loop response (a), closed-loop response with a robust controller (b) and closed-loop response of the CSTR with a LQR controller (c)

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A NOVEL MIXED PRODUCT RUN-TO-RUN CONTROL ALGORITHM – DYNAMIC ANCOVA APPROACH

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1. Summary

In semi-conductor manufacturing industry, production resembles an automated assembly line in which many similar products with slightly different specifications are manufactured step-by-step, with each step being a complicated physiochemical batch process performed by a number of tools. This constitutes a high-mix production system for which effective run-to-run control (RtR) and fault detection control (FDC) can be carried out only if the states of different tool and different products can be estimated. However, since in each production run, a specific product is performed on a specific tool, absolute individual states of products and tools are not observable. In this work, a novel state estimation method based on analysis of variance (ANOVA) is developed to estimate the relative states of each product and tool to the grand average performance of this station in the fab. The method is formulated in a form of recursive state estimation using Kalman filter. The advantages of this method are demonstrated using simulations to show that the correct relative states can be estimated in production scenarios such as tool-shift, tool-drift, product ramp-up, tool-offline and preventive maintenance. Furthermore, application of this state estimation method in a minimum variance based RtR control scheme shows that substantial improvements in process capabilities can be gained, especially for products with small lot counts.

Keywords: state estimation, ANOVA, Kalman filter, run-to-run control

2. Extended Abstract

The run-to-run (RtR) controller is a model-based process control system that integrates concepts in statistical quality control (SPC) and engineering process control (EPC). It is achieved by adjusting process inputs (recipes) at the beginning of each run based on information obtained from previous runs. In the last decade, RtR control has been extensively deployed in the semi-conductor industry. Research and development in this area have been summarized by many authors in books and review

articles (Castillo and Hurwitz, 1997; Moyne, et al., 2001; Edgar, et al., 2000; Castillo, 2002, Qin, et al. 2006).

For a multi-tool (*n=1,…,N*) multi-product (*m=1,...,M*) operation, according to ANOVA, the process model may be described as

$$y_k = bu_k + \mu + \tau_{n_k} + p_{m_k} + \varepsilon_k$$

where *b* is the process gain which relate the change in manipulating variable u_k to the change in output quality variable y_k; μ is the overall mean of all observed tool and product combinations, τ_n (*n=1,…,N*) represent the difference between the average results of all possible products on n^{th} tool and the overall mean, and p_m (*m=1,…,M*) represent the difference between the average results on all possible tools of the mth product and the overall mean. Unlike absolute states of the particular tool and product, τ_m and p_m are relative contributions subject to the constraints

$$\sum_{n=1}^{N} \tau_n = 0 \qquad \sum_{m=1}^{M} p_m = 0$$

The above model plant can be expressed in a state space form. The ANOVA states can be estimated in a recursive way using Kalman filter which leads to the unbiased minimum mean-square estimator if the observability matrix is full rank.

Conclusion

In this paper a novel state estimation method based on statistics method ANOVA is developed to estimate the relative states of each product and the relative states of each tool to the grand average of this station in the fab. The method is formulated in a form of recursive state estimation using Kalman filter. Simulation results show that the correct ANOVA states can be estimated in production scenarios such as tool-shift, tool-drift, product ramp-up and offline. Furthermore, application of this state estimation method in a minimum variance based RtR control scheme shows that substantial improvement of quality of products with small run counts. This makes the proposed method highly suitable for mixed product control system.

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PD and PID Fuzzy Logic Controllers. Application to Neutralization Processes

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1. Summary

The performance of a Fuzzy Logic Controller (FLC) for the pH control is studied. The process used to test the controller performance is the continuous neutralization of aqueous solutions of acetic and propionic acids with an aqueous solution of sodium hydroxide. The best results are obtained when the FLC uses the pH error, pH error derivative and pH cumulative error as input variables. For perturbations up to 50% on the acidic stream flow rate and concentration, the controlled pH of the outlet stream shows overshot lower than 1 pH unit.
Keywords: Process control, neutralization, fuzzy logic, pH-control

2. Extended Abstract

Introduction

pH control plays an important role in several industrial processes. Neutralization is subjected to many difficulties (non linearity, high sensitivity to small perturbations, etc). These special characteristics lead to a great number of strategies about pH control that have been reported in the literature. So, several alternatives to classical PID controllers for pH control have been considered, including different types of linear and nonlinear models (Palancar *et al.* 1996) and artificial neural networks (ANN) (Palancar *et al.* 1998). The FLC has been applied to control diverse processes during the last years, Chen et al. (1993), Edgar and Poslethwaite (2000) and Regunath and Kadirkamanathan (2001). The aim of this work is to compare the performance of two FLCs, PD-FLC and PID-FLC for the pH control in a neutralization process.

Neutralization Process and Controller Model

The process used to test the controller performance is the continuous neutralization of an aqueous stream of a mixture of acetic and propionic acids with an aqueous solution of sodium hydroxide. The neutralization vessel is a Continuous Stirred Tank Reactor (CSTR) of 1750 cm^3 and the mean residence time of the liquid was between 300 and 1800 s. The whole process was simulated by a numerical model already described in a previous paper (Palancar *et al.* 1996).

The control system is a feedback loop in which the measured variable is the pH inside the neutralization vessel, the manipulated variable is the flow rate of the alkaline stream and the control action is based on PD or PID FLCs. The PD-FLC considers the error (set point minus actual pH) and the error derivative as the two input variables of the controller. The PID-FLC considers the pH error, pH error derivative and pH cumulative

error as the three input variables of the controller. For both controllers, the output variable is the valve stem position, which regulates the flow rate of the neutralizing agent stream. The PD-FLC has 5, 3 and 7 membership functions for the error, error derivative and valve stem, respectively. The PID-FLC has 7, 3, 3 and 7 membership functions for the error, error derivative, error integral and valve stem, respectively. The valve stem position after each sampling is calculated by defuzzification, using the "centroid" method.

Results

The study has been made currently by the numerical simulation of the controlled neutralization process. The simulation has been made by using LabView$^{©}$. The robustness and adaptability of the controller were studied under three different circumstances: 1) start up; 2) acid flow rate perturbations and 3) acid concentration perturbations.

When the PD-FLC is used, the response settling time ranges between 0.28 and 0.9 min; these values are lower than the ones obtained with ANN based controllers (Palancar et al. 1998). The overshot of the pH response to perturbations that drives to a pH decreasing is lower than 0.5 pH units. When the perturbations drive to a pH increasing, the overshoots are greater than 3 pH units. The overshot is lower with the PID-FLC and the settling time is similar with both controllers. An example of the results obtained for the system start up and after perturbations is shown in figure 1.
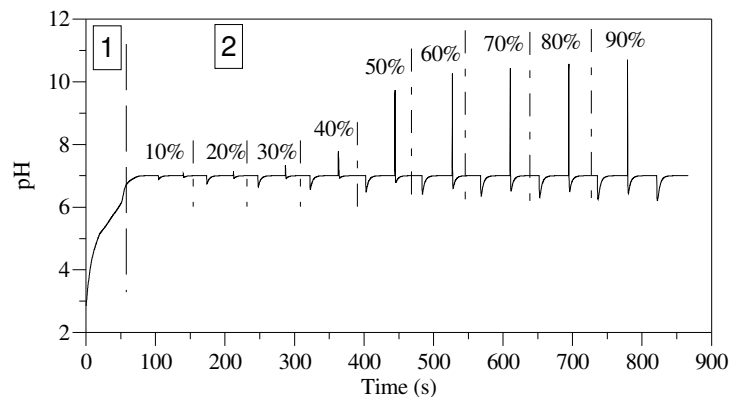
Figure 1. - Variation of pH *vs* time during the systems start up and after acidic concentration perturbations. Zone 1: Start up. Zone 2: acidic concentration perturbations. The % are referred to the steady state value before perturbation.

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Nonlinear model predictive control strategies applied to a fed-batch sugar crystallizer

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1. Summary

Two nonlinear model predictive control (NMPC) strategies are applied to an industrial sugar production process: i) NMPC that does not exploit the batch nature of the process (termed as classical NMPC) and ii) the Batch NMPC (BNMPC) that takes into account the end-point control objectives. They are also compared with the classical PI controller and one linear MPC (LMPC) scheme. A number of tests are performed covering most relevant practical issues as the choice of control and prediction horizons, operation without and with disturbances (in the vacuum pressure) and variations in the initial conditions (purity of syrup of the feeding). The main conclusions are that while the process runs under nominal conditions, NMPC, PI, LMPC and DNMPC demonstrate practically insignificant differences and any of these controllers can be tuned to respond satisfactorily. However, in the presence of disturbances or changes in the initial conditions the DNMPC demonstrate better performance with respect to the final product quality. This is due to the explicit consideration of the end point objectives in the performance function. However, the price to be paid is a high CPU . Work, which is now going on, is to reduce the computational time and to consider not only final time specifications but also tracking objectives over the batch duration in the framework of a more complex cost function.

Keywords: nonlinear model predictive control, fed-batch sugar crystallization, shrinking nonlinear discrete time optimization

2. Extended Abstract

During the last decade the model based predictive control (MPC) became an attractive control strategy implemented in a variety of process industries. However, it can be considered as industrial alternative only for continuous and predominantly linear processes (Qin and Badgewell, 2003). The application of MPC for batch nonlinear cases is still far from being an industrial reality and represents an interesting theoretical and practical control challenge (Balasubramhanya and Doyle, 2000). The batch or fed-batch mode is a typical production scheme for a large group of pharmaceutical, biotechnological, food and chemical processes. It is related with the

formulation of a control problem in terms of economic or performance objective at the end of the process (Nagy and Braatz, 2003). For example, the crystallisation quality is evaluated by the particle size distribution (PSD) at the end of the process which is quantified by two parameters - the final average (in mass) particle size (MA) and the final coefficient of particle variation (CV). The main challenge of the batch production is the large batch to batch variation of the final PSD. This lack of process repeatability is caused mainly by improper control policy and results in product recycling and loss increase. MPC, being one of the approaches that inherently can cope with process constraints, nonlinearities, and different objectives derived from economical or environmental considerations, has the potential to overcome the problem of the lack of repeatability and drive the process to its optimal state of profit maximization and cost minimization. These problems are the main motivation for the present work, which is focused on a comparative analysis between two Nonlinear MPC (NMPC) schemes implemented to a batch white sugar crystallizer – i) NMPC that does not exploit the batch nature of the process (termed as classical NMPC) and ii) the batch NMPC that takes into account the end-point control objectives, i.e. the prediction horizon is equal to the batch final time. Three control scenarios were studied. In the first scenario the nominal case without disturbance and noise is considered. In the second and the third scenarios the effect of disturbance in the vacuum pressure and the noise in the vacuum pressure were studied.

The results demonstrated that in general the batch NMPC outperforms the classical NMPC but to the expense of heavy computational burden due to the high prediction horizon (Fig. 1).
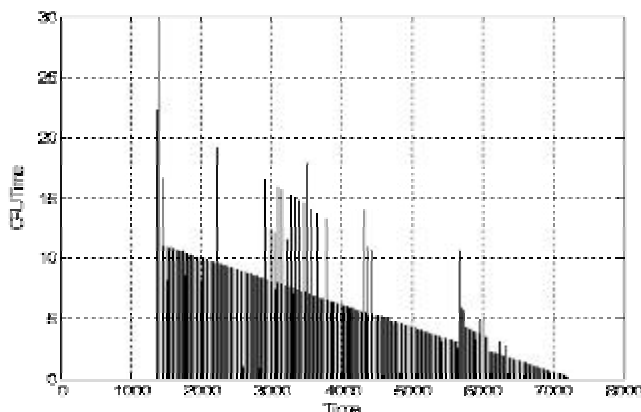
Fig. 1 CPU time per iteration [s] along the process duration

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Development of Soft Sensors for Debutanizer Product Quality Estimation and Control

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1. Summary

This paper demonstrates soft-sensor design for product quality monitoring and process control of debutanizer column of INA Refinery Sisak, Croatia. The column is fed by unstabilized FCC gasoline, and products are Liquefied Petrol Gas (LPG) and stabilized FCC gasoline. Method of estimation of pentane fraction in liquefied petrol gas (LPG) and Reid vapor pressure of stabilized FCC gasoline using inferential model is elaborated. The aim is to control debutanizer thus pentane fraction in LPG is kept under 2 mass percent and RVP of FCC gasoline on desired value (50 kPa). Two neural soft sensor models are developed based on available process measurements and laboratory analysis – first for estimation of pentane fraction in LPG and second for estimation of RVP of stabilized FCC gasoline. For the building of the neural networks the cascade learning based on the cascade-correlation learning paradigm is developed. Developed soft sensors have been additionally validated by additional experimental data and achieved results have been analyzed and compared with laboratory analysis results.

Keywords: identification, process modelling, soft sensor, neural network, debutanizer column

2. Extended Abstract

Debutanizer column is located at Gas Concentration Unit of FCC plant in INA Sisak Oil Refinery. It is used for FCC gasoline stabilization, precisely for separation of LPG from FCC gasoline.

The column is fed by unstabilized FCC gasoline, and products are Liquefied Petrol Gas (LPG) and stabilized FCC gasoline. After treatment on DEA and MEROX plant LPG becomes commercial. Stabilized FCC gasoline is used as a component for gasoline blending.

The aim is to control debutanizer thus pentane fraction in LPG is kept under 2 mass percent (LPG quality specification) and RVP of FCC gasoline on desired value (50

kPa). Variables that affect debutanizer's product quality are temperatures on top and at bottom, temperatures on specific trays and reflux flow. Temperature of fifth tray is controlled by temperature control loop TRC-93 in cascade with reflux flow control loop FRC-101. Temperature at bottom and on 35th tray is controlled by hot flow through column reboiler. Disturbances are flow, temperature and composition variations of column feed.

Neural soft sensor models are developed based on available process measurements and laboratory analysis and using software simulation model. Process variables are measured continuously and saved in DCS memory so there is available temperature and flow database. Pentane fraction in LPG and RVP value of FCC gasoline database is limited by dynamics of laboratory analysis (once per day). Two neural soft sensor models are developed for continuous product quality monitoring. First one for estimation of pentane fraction in LPG and second for estimation of RVP of stabilized FCC gasoline. It is constructed by input and output layer and hidden layer with five neurons. Network input vector consist of the temperatures on the column's top, T_t, on the 5th tray, T_5, on the 35th tray, T_{35}, and reflux flow rate. Output is the RVP value of stabilized FCC gasoline. Similarly, neural network for estimation of pentane fraction in LPG is constructed.

Developed soft sensor neural models have been additionally validated by experimental data saved in DCS memory and achieved results have been compared with laboratory analysis results. Comparison of laboratory analysis and results achieved by soft sensor for predicting RVP value of stabilized FCC gasoline is shown. Soft sensor follows satisfactory the trend of changing RVP values, but certain deviations still persist. These deviations can be explained with the model non-perfection and also with the fact that the values of majority experimental data are situated around 50 kPa. Therefore, the neural network has better approximation characteristics within these values.

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Neural Network Modeling and Control of an Etherification Hybrid Reactor

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1. Summary

The etherification processes are improved by a hybrid reactor which combine separation with chemical reaction. As a result, the process yields are higher while their process dynamic behaviors are more complex. A conventional Proportional Integral Derivative (PID) controller is able to control the non-linear and complex processes but with slow responses and low performances. In addition, its performance is not guaranteed in the cases of disturbance changes and plant-model mismatches as well. In recent years, the neural network (NN) control techniques have been successfully applied to those highly non-linear and complex systems due to the present availability of advanced computer technology. However, those investigations did not apply to any hybrid reactors. In this paper, neural networks are used to not only develop a black box model but also formulate neural network internal model controller in a Proportional Integral-Nonlinear Internal Model Control (PI-NIMC) cascade strategy. The objective of this study is aimed at controlling the reactant concentration in the reactor during the etherification to obtain a high yield of the desired product. Simulation results indicate that PI-NIMC provide better control performance than the conventional PID in set point tracking and disturbances rejection in both nominal and plant-model mismatches cases. Besides, the results justify the use of NN control technique in a highly non-linear and complex process.

Keywords: neural network modeling, neural network control, internal model control, hybrid reactor

2. Extended Abstract

Etherification hybrid process

An etherification hybrid process (Fig.1) integrates a pervaporative membrane into a conventional Continuous Stirred Tank Reactor (CSTR). Every component excepts for the desired product is separated while the reaction takes place, therefore, the product shifts to higher levels of quantity and quality. The reactions taken place in the reactor consist of reaction 1, which is a reversible reaction, and reaction 2, which is an irreversible side reaction as follows:
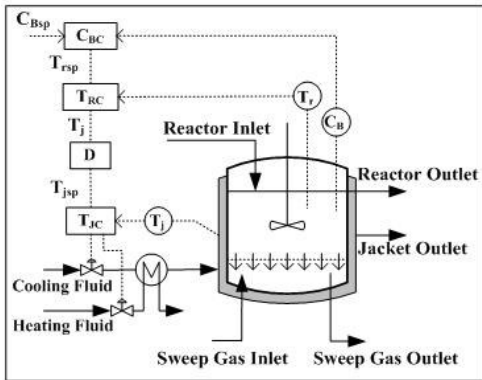
Fig. 1. Process Schematic Diagram   **Fig.2.** Cascade PI-NIMC Topology
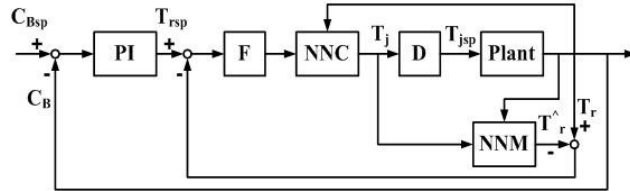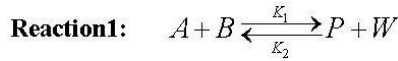
In this work, the neural networks are used as an internal model and a controller in the Nonlinear Internal Model Control (NIMC) strategy (Fig.2).
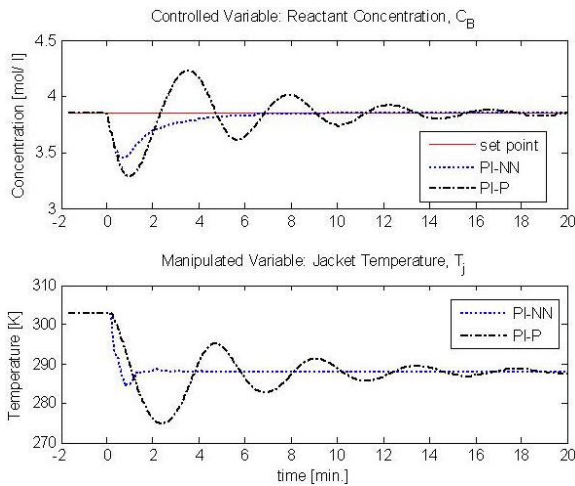
Fig. 3. Disturbance Change, -20% C_{Bin} **Fig. 4.** Plant-Model Mismatch,-30% k_1
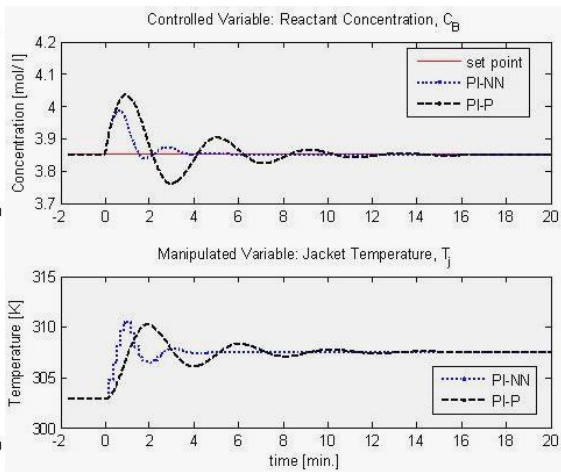
Simulation Results

Fig. 4 and 5 show the simulation results of PI-NN and Pi-P Controllers in the change of – 20% C_{Bi} and plant-model mismatch of -30 % k1. It can be seen that the PI-NN provides better control response than the PI-P controller does.

Conclusion

This work presents the use of neural network approach as a model and a controller for the control of a continuous etherification process. Simulation results show that the PI-Neural Network controller gives better control performance and much more robust than the PI-P controller.

Control and Optimization of a Fluid Catalytic Cracking Process: An Industrial Case

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1. Summary

Fluid Catalytic Cracking (FCC) is an important refinery process. Therefore the economical incentives to operate near optimal conditions are high; however FCC units' optimal performance is usually achieved near physical and operating constraints of this process, which makes the FCC a challenging task for control and optimization studies. A model that can predict both the steady and dynamic states of an UOP FCC unit with high efficiency regenerator was developed and validated with industrial data from an operating unit. The regulatory control was implemented in the dynamic process simulator, considering the same control loops as the ones in the operating unit. On-line optimization was then implemented to find the optimal steady-state operating point, and integrated to the regulatory control that brings the process to the new optimal steady-state.

Keywords: fluid catalytic cracking, industrial process, process control, process optimisation, nonlinear dynamics.

2. Extended Abstract

The increasing oil price and the stringent environmental regulations are forcing the refining industry to perform significant modifications in its operation, namely by the use of advanced process engineering tools, such as advanced process control and process optimization. However, the use of these tools requires the development of models that can realistically simulate the refinery processes (Moro, 2003).
A model that can predict both the steady and dynamic state of an UOP FCC with high efficiency regenerator was developed and presented in previous papers (Fernandes et al, 2006; Fernandes et al., 2007). This model was therefore validated with steady-state data of a real industrial unit operating in Galpenergia Sines Refinery, and compared to dynamic data after the implementation of the main regulatory control.

The regulatory control implemented consists of three main control loops, where the reactor temperature is controlled by manipulating the regenerated catalyst slide valve; the regenerator pressure is controlled directly by regulating the flue gas valve; and the reactor catalyst level is controlled by manipulating the spent catalyst slide valve.

Figure 1 shows the dynamic responses of the riser reactor temperature, pressure and regenerated catalyst slide valve opening to changes in the feed flowrate for a real period of 12000 seconds (3h20min).
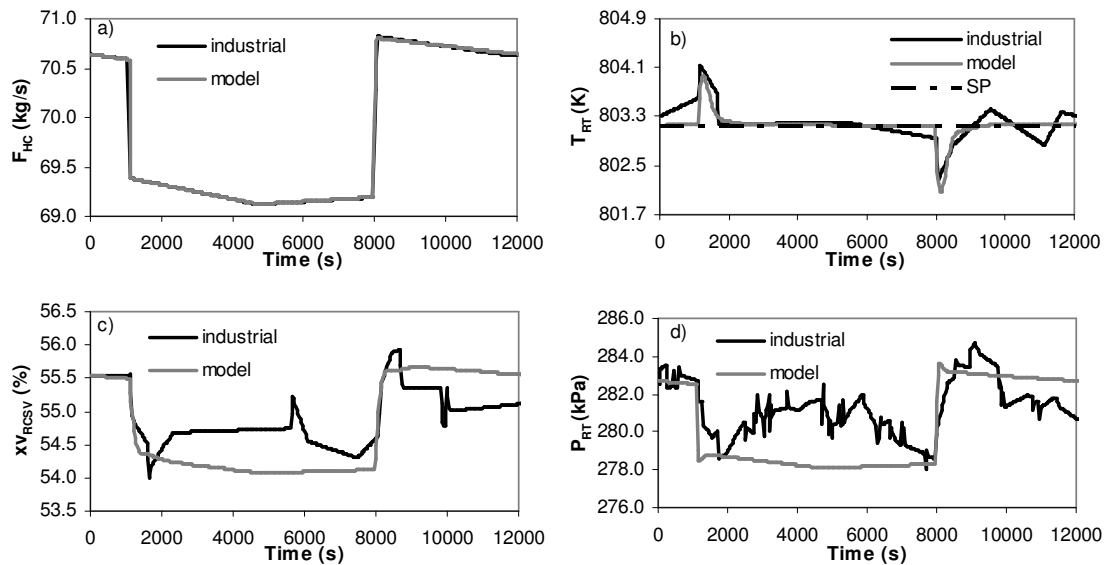
Figure 1: Plant and model responses to changes in the feed flowrate. a) Feed flowrate; b) Riser reactor temperature; c) Regenerated catalyst slide valve opening; d) Riser reactor pressure.

By comparing the simulated data to the industrial data it is possible to see that there is a very good agreement in the trends of the process variables presented and that the dynamic characteristics of the system, such as the time constants and gains are also in good agreement. As expected, there is some noise in the industrial data, and probably unmeasured disturbances that are not included in the model and that contribute to some of the differences found between the simulated and the real behaviour of the unit.

With the validated model, on-line optimization was then carried on and integrated with the regulatory control in order to maximize the unit profit margin by optimizing the operating conditions and other variables such as atmospheric residue incorporation in the fresh feed flowrate.

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Data Driven Tuning of Lower Level Controllers

for Disturbance Rejections.

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1. Extended Abstract

Optimal operation in chemical industry requires a (plant wide) model based, multivariable, control strategy such as Model Predictive Control (MPC). This optimal multivariable controller handles the interaction between the lower level loops. These loops are single input single output (SISO) control loops and their set points are set by the MPC according to the production objectives. For this multilevel control scheme to be effective, it is crucial that the lower level SISO controllers are working faster that the higher level MPC and that they are properly tuned for disturbance rejection.

Iterative Feedback Tuning (IFT) is a data driven method for optimization of the performance of simple controllers given a criterion expressed as a classic quadratic cost function. The method was first publish in [1] and have since been extended and tested for a number of applications [2]. IFT iteratively minimizes the cost function using a gradient based search method. The key feature of IFT is how to achieve the unbiased estimate of the gradient of the cost function with respect to the controller parameters. It an advantage that all data are collected from closed loop operation since it is the closed loop performance that is subject to optimization. The IFT method does not rely on external perturbation, due to a special design of the experiments which provide the gradient estimate. Unfortunately the IFT method only converges slowly when a controller is tuned for disturbance rejection problems. Therefore this contribution proposes to combine IFT with classic system identification and employ external perturbation in order to increase the information content in data. That leads to a faster convergence which renders the method amenable for a number of practical

problems where the convergence of the standard formulation is too slow, which results in a too many of plant experiments.

The probing signal generated to excite the process is evaluated as a constraint optimization problem. It is desired to achieve data with the highest possible information content of the process dynamics without bringing the process too fare from the operating region. This optimization problem is solved based on a model of the process or the loop itself in contrast to the tuning optimization problem which only relies on data. Having a model for the plant will allow check on nominal stability of a new controller before implementation, or could even be used in a line search algorithm to improve the update of the controller parameters in the tuning method.

The tuning of PID control loops of a four tank system [3] is considered as an example of an underlying control level. The liquid flow out of each tank has a nonlinear dependence on the level in tank, and tank system can be configured to exhibit different types of dynamics. The controllers are manipulating a pump in order to control the liquid level in the tanks. All variables are measured online, but the measurements are affected by noise. IFT tuning of the controllers for the four tank system with external perturbation are investigated and the disturbance rejection properties of the system are tested both in simulation and in practice on the pilot plant.

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A Critical Discussion of the Continuous-Discrete Extended Kalman Filter

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1. Summary

In this paper, we derive and apply a novel numerically robust and computationally efficient extended Kalman filter for state estimation in nonlinear continuous-discrete stochastic systems. The continuous-discrete extended Kalman filter is applied to the Van der Vusse reaction example. This example is a well-known benchmark for nonlinear predictive control. Using the Van der Vusse example, we demonstrate inherent limitations of the extended Kalman filter and sensor structure for unbiased state estimation. In particular, we demonstrate that the convergence rate of the concentration estimate in the Van der Vusse system is limited by the frequency of concentration measurements. These limitations limit the achievable performance of any closed-loop system including nonlinear model predictive control.

Keywords: State estimation, extended Kalman filter, stochastic differential equations

2. Extended Abstract

This paper presents the computational challenges of state estimation in nonlinear stochastic continuous-discrete time systems. The extended Kalman filter for continuous-discrete time systems is introduced by *ad hoc* extension of a probabilistic approach, based on Kolmogorov's forward equation, to filtering in linear stochastic continuous-discrete time systems. The resulting differential equations for the mean-covariance evolution of the nonlinear stochastic continuous-discrete time systems are solved efficiently using an ESDIRK integrator with sensitivity analysis capabilities. This ESDIRK integrator for the mean-covariance evolution is implemented as part of an extended Kalman filter and tested on several systems. For moderate to large sized systems, the ESDIRK based extended Kalman filter for nonlinear stochastic continuous-discrete time systems is more than two orders of magnitude faster than a conventional implementation. This is of significance in nonlinear model predictive control applications, statistical process monitoring as well as grey-box modelling of systems described by stochastic differential equations.

Stochastic differential equations are introduced for modeling of chemical systems. The proposed extended Kalman filter algorithm is a methodology to filter and predict such a system based on noise corrupted measurements at discrete times. This paradigm is ideally suited for state estimation in nonlinear model predictive control as it allows a systematic decomposition of the model into predictable and non-predictable dynamics. The application of the extended Kalman filter as the predictor in grey-box modeling of process systems using the prediction-error approach is emphasized in the presentation. We demonstrate the proposed algorithm and methodology in detail using the Van der Vusse reaction system as example.

The continuous-discrete extended Kalman filter is implemented in the ESDIRK software package in a numerically robust and efficient way.
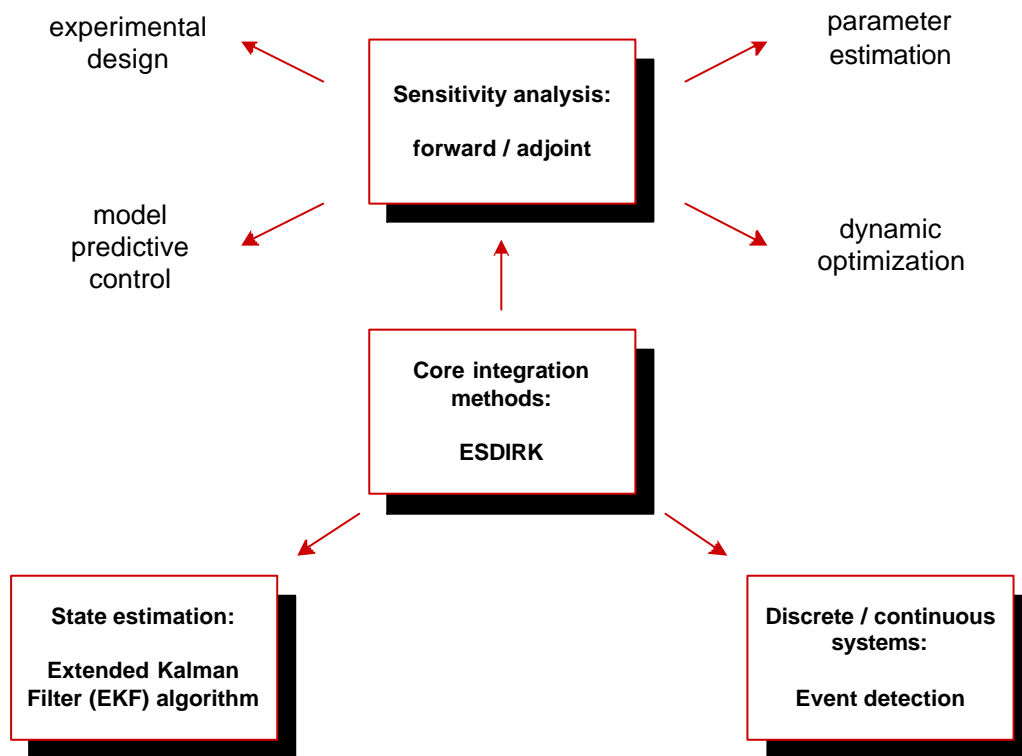
Figure 1: The ESDIRK software package for simulation, state- and parameter-estimation, and optimization in dynamic systems.

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Modeling and Control Solutions for Riser Slugging in Offshore Oil Fields

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1. Summary

A highly transient flow regime called *riser slugging* can develop in pipelines from wellheads to separation tanks which introduces severe oscillations of pressure and flow rates in off-shore processes. Mitigation of the intensity of *riser slugging* may be achieved via anticipative control actions on valves positioned at the entrance and at gas/oil exits of the separators. In *Phase 1*, this work is concerned with the development of a simplified phenomenological model for the producing system, including a set of wells performing gas-lift, their corresponding risers, entrance manifold and a gas-oil separator. The input variables to this integrated model are the percentage of opening of choke and exit valves on the separator. The corresponding output variables are its internal pressure and liquid level in the separator. The oscillating slugging in the pipelines arises naturally as a consequence of the values chosen for specific model parameters like down-hole pressures, gas injection flow rates, fluid properties and geometry of wells and lines. In *Phase 2*, this work is involved with the mitigation of slugging consequences via determination of optimum adaptive decentralized control strategies actuating on the choke and exit valves on the gas-liquid separator. Finally, in *Phase 3*, we approach the identification of a stochastic predictor for the entire system (risers + tanks) adopting an ARX MIMO structure, periodically tuned to the real process by using recorded time series of inputs and outputs. With a tuned ARX predictor, optimum anti-slugging control strategies can be periodically established for the real process.

Keywords: riser slugging, gas-lift, slugging control, ARX predictor

2. Extended Abstract

In offshore oil fields, risers are used to transport a multiphase mixture (composed by oil, gas, water and sand) from the wellheads to separation tanks on producing platforms. In case of inexistence of separation and pumping facilities near the wellheads, on the sea bottom, this multiphase mixture must be propelled to the sea surface at expenses of the reservoir pressure. For deep water, a common situation is that the reservoir is not sufficiently pressurized to promote the flow of oil at satisfactory rates, requiring artificial ascension of oil via gas-lift techniques, where injection of compressed natural gas is maintained at some points in the well column. In consequence, high flow rates of gas have to be accommodated in the system of

risers for further recovery by gas-liquid separators at the platform, before re-compression and re-injection. In this scenario, and depending on the flow conditions, a flow regime called riser slugging can develop in the pipelines. This regime, naturally highly transient, introduces severe oscillations of pressure and flow rates into the system. Mitigation of the intensity of riser slugging requires anticipative control actions on valves at the entrance and at gas/oil exits of the separators.

Simplified Modeling of Oscillating Producing Wells and Reception System

We firstly addressed the development of a simplified phenomenological model for the producing system, including a set of wells performing gas-lift, their corresponding risers, entrance manifold and a gas-oil separator. The input variables to this integrated model are the percentage of opening of choke and exit valves on the separators. The corresponding output variables are the pressure and liquid level in the separator. The oscillating slugging in the pipelines arises naturally as a consequence of the values chosen for specific model parameters like down-hole pressures, gas injection flow rates, fluid properties and geometry of wells and lines. The well model uses a non-distributed approach based on the division of the well into annular and tube compartments. The risers adopt a pseudo-stationary two-phase (slug) flow model. The separators are described via conservation equations for gas and liquid compartments coupled to valve flow rate models.

Control Structure for Reception of Slugging Feeds

We now consider the mitigation of slugging consequences in the separation system via optimum adaptive decentralized control strategies actuating on the choke and exit valves on the gas-liquid separators. In offshore production plants, gravity separators, compressors, hydrocyclones (de-oilers) and electrostatic treaters are used to specify oil, gas and water for exportation. A simple structure of vessels in series results, which indicates that substantial attenuation of feed disturbances can be obtained if proper control is done. Merely fast acting control loops, designed for disturbance rejection, facilitate propagation of downstream disturbances in the flow rates. In this work, an adaptive control law of a PI level controller was employed and tuned to optimize a control performance criterion subject to minimum and maximum limits on level, with penalty imposed on control movements. The level controller was tuned according to the following adaptation law:

$$K_C = f\, K_{C0}; \quad \tau_I = \frac{\tau_{I0}}{f}, \quad f = (1 + \frac{1}{1 + e^{(\lambda_1(E_1 - abs(e)))}} + \alpha(1 + \frac{1}{1 + e^{(\lambda_2(E_2 - abs(e)))}}) + \beta(1 + \frac{1}{1 + e^{(\lambda_3(E_3 - abs(e)))}}).$$

K_{CO} and τ_{CO} are the proportional gain and the reset time for zero error (e). The remaining parameters allow for smooth transition of controller behavior along three plateaus of intensity defined by values 1, α and β. Parameters λ_1, λ_2 and λ_3 regulate the sharpness of transition between neighboring plateaus, while E_1, E_2 and E_3 represent the respective error thresholds. Tuning of level controller parameters (K_{CO}, τ_{CO}, α and β) and conventional PI pressure controller (K_C and τ_C) parameters was posed as an optimization problem, with objective function defined as the weighted sum of level controller error, pressure controller level and control effort, subject to minimum and maximum limits on separator level. The resulting *averaging level control* stood both a quiescent feed condition and a slugging feed condition.

Stochastic Prediction of the Dynamic Behavior of the Producing System

Finally, the identification of a stochastic predictor, capable of representing the entire producing system, was accomplished via ARX MIMO structures. The ARX predictor was chosen because it is simple, accurate and can be periodically tuned to the real process through recorded time series of inputs and outputs. The utilization of the ARX predictor was demonstrated with simulated data generated with the simplified model above. In the real process, optimum anti-slugging control strategies can be periodically established by using permanently tuned ARX predictors.

Session T4-9a: Process Simulation & Optimization - I

Abstract Number	Paper Title & Authors	Included
585	Modeling of high and low-pressure separator units in high-pressure LDPE plants P Pladis, A Baltsas, C Kiparissides	Yes
1268	Automated inference of chemical reaction networks P J English, D P Searson, M J Willis, A R Wright	Yes
2215	Distributed moisture content in a continuous fluidized bed dryer C Kettner, M Peglow, T Metzger, E Tsotsas	Yes
2306	One dimensional modelling of conical spouted beds D Rivera, G Lopez, M J San José, S Alvarez, H Altzibar, M Olazar	Yes

Modeling of High and Low-Pressure Separator Units in High-Pressure LDPE Plants

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1. Summary

A comprehensive dynamic mathematical model is developed for the simulation of high and low-pressure separation units in LDPE plants. Various equation of state (e.g. Sako-Wu-Prausnitz, SAFT, PC-SAFT) are employed simulate the operation and phase equilibrium in flash separation units. The capability of the proposed model to describe the phase-equilibrium of ethylene-polyethylene mixture and the dynamic operation of flash separators is demonstrated by comparing model predictions with available experimental data.

Keywords: modeling, high-pressure, LDPE, separator

2. Extended Abstract

Low Density Polyethylene (LDPE) has been commercially produced in high-pressure reactors for more than five decades. Two reactor technologies (i.e., tubular and autoclaves) are employed in the high-pressure polymerization of ethylene. The polymerization of ethylene is typically carried out at very high temperatures (120-320ºC) and pressures (1500-3000 atm). Thus, in the presence of a mixture of initiators (e.g., peroxides, azo compounds), ethylene can be polymerized via a free-radical mechanism. A large variety of LDPE grades is usually produced from a single reactor line, with varying degree of polydispersity, branching and density (0.915-0.935 g/cm^3).

In a high-pressure LDPE process, fesh ethylene after its primary compression is commonly mixed with the recycled ethylene stream from the flash separators. This combined stream is pressurized to the desired pressure, in the second compression stage, and is then fed to the reactor. Polymerization of the monomer is initiated by adding free-radical initiators (usually organic peroxides). Due to the short reactor residence time (30-90 s), the monomer conversion is relatively low, between 15 and 35 %. The separation of unreacted ethylene from the LDPE is performed in two

successive separation stages. In the first stage, the reactor let down valve drops the pressure of the outlet stream to 150-300 atm which is then directed to the high-pressure separator. The ethylene-polyethylene mixture entering the high-pressure separator is split into a polymer rich liquid phase (containing 70-80% per weight polymer) and an ethylene rich gas phase (containing ethylene and amounts of wax). The polymer rich liquid phase from the bottom of the high-pressure separator is directed to the low-pressure separator. In the second flash separator, the pressure is further reduced to about 1.5 atm. The ethylene gas and waxes stream leaving the low-pressure separator is fed to the primary compressor, and the liquid bottom stream is sent to the extruder. The phase equilibrium of the ethylene-LDPE mixture is calculated using various equations of state models (e.g., Sako-Wu-Prausnitz, SAFT, PC-SAFT). The capability of the proposed model to describe the phase-equilibrium of ethylene-polyethylene mixture and the dynamic operation of the flash separator is demonstrated by comparing model predictions with available data. The dynamic model of the separator is able to predict deviations from the theoretical phase equilibrium state as it has been observed in real plant data.

In Figure 1 the equilibrium ethylene solubility in polyethylene is compared with the actual ethylene fraction inside the high-pressure separator. The plant measurements represent several LDPE grades, while the simulations represent the model output using different mass transfer constants. Figure 2 illustrates the dynamic behavior of ethylene and LDPE mass fractions in the high pressure separator. It is clear that an equilibrium model severely underpredicts the fraction of ethylene in the polymer stream, that leaves at the bottom of the high-pressure separator.
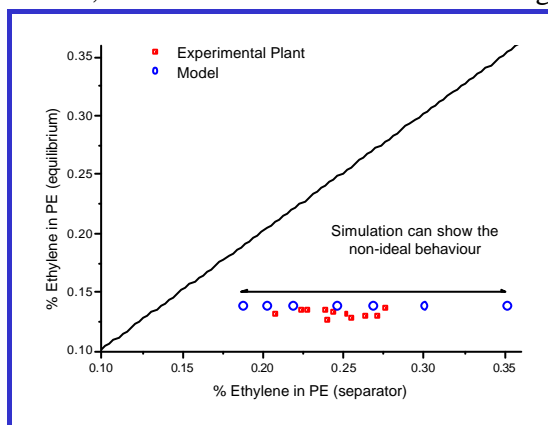
Figure 1. Comparison of predicted solubilities and actual measurements in high-pressure separators.
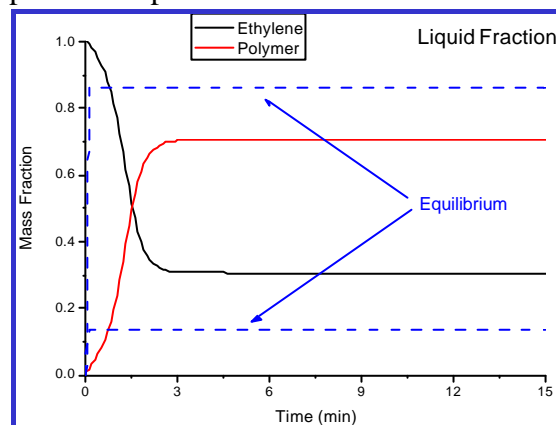
Figure 2. Comparison of model predictions with actual measurements in high-pressure separators.

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Automated Inference of Chemical Reaction Networks

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1. Summary

This paper demonstrates, using simulations, a novel procedure that searches for mass action kinetic models corresponding to plausible chemical reaction networks (CRNs). The procedure requires only time series concentration data sampled from batch reactors. Firstly, a branch and bound algorithm - guided by an information entropic objective function and kinetic heuristics - is used to create candidate sets of kinetic model topologies. Subsequent techniques use statistical indices and heuristics to reduce the candidate sets in order to form a coupled set of physically consistent kinetic models representing the identified CRN.

Keywords: chemical kinetics, network inference, chemical reaction network, kinetic model identication

2. Extended Abstract

Methods to automatically reverse engineer chemical or biochemical reaction networks from experimental data are the subject of considerable interest (Crampin et al., 2004). Research into these techniques has, to date, largely been confined to the biosciences, but such methods could have significant commercial implications for the chemical and process industries. Software for kinetic fitting - once the structure of the reaction network is known - is widely available, but the initial inference of this structure is a bottleneck within the development cycle that requires considerable expertise. Hence, methods that can accelerate the discovery of chemical reaction networks from data have substantial commercial and academic potential. In particular, the burgeoning use of high throughput technologies (HTT) in chemical process research and development (e.g. automated robotic workstations for performing many experiments in parallel) coupled with improved chemical sensor technology will provide an increase in the quantity and quality of experimental data available during the product development lifecycle. This trend suggests that effective methods for the reverse engineering of reaction networks from data will become of increasing importance in the future.

This paper describes one approach to the problem: a novel automated method for efficiently searching the space of a specific class of kinetic rate expression models. This class of models corresponds to unimolecular and bimolecular elementary reactions occurring in a well-mixed isothermal reactor (Burnham et al., 2006; Searson et al., 2006). The only experimental data required are time series concentration measurements, and virtually no prior knowledge of the reaction mechanism or chemical properties of the reactants and products is assumed. However, prior chemical knowledge can be incorporated into the procedure when available. The methodology can be applied in reactors operating in batch or semi-batch modes rendering it suitable for a variety of experimental configurations. The methodology comprises 3 stages: (1) A branch and bound algorithm – guided by information entropy and kinetic heuristics - is used to search the space of mass action kinetic rate models in order to construct a set of candidate models for each chemical species. (2) Standard and robust regression methods are used to detect model terms with a low statistical significance. These are removed to yield a refined set of candidate models. For each chemical species, the refined candidate model with the best information entropy measure is extracted and combined with the others to form a trial model of the kinetics of the chemical reaction network. (3) A final screening stage identifies any inconsistencies within the network kinetics and employs heuristics to resolve them. The elementary reaction steps comprising the reaction network are then inferred directly from the identified kinetic model.

The procedure is demonstrated, in simulation, with noisy data from a hypothetical reaction network comprising 5 chemical species involved in 4 simultaneous reactions within a batch reactor. It is shown that the automated procedure is able to correctly identify the structure of the reaction network and estimate the reaction rate constants. Some advantages of the method are, firstly, that it is guaranteed - in the worst case scenario - to be as least as efficient as an exhaustive search of the space of kinetic rate models. Usually, however, it is between 4-20 times more efficient. Secondly, it has the potential to scale well to larger and more complex systems (such as those involving higher order kinetic rate terms corresponding to multi-step reactions involving short-lived intermediates). Finally, the procedure is almost entirely automated; making it a suitable basis for a software tool to aid chemists and chemical engineers in the discovery of chemical reaction networks from laboratory scale data.

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Distributed moisture content in a continuous fluidized bed dryer

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1. Summary

In this study the influence of residence time distribution on the moisture content of disperse solids in continuous fluidized bed drying is investigated. To describe this process a population balance model has been applied. In this model particles with different residence times are allocated to different classes of the entire population. Furthermore, experimental methods to determine the moisture content of single particles are presented. Results of measured and simulated moisture distributions are compared.

Keywords: population balances, granular material, moisture measurement, fluidized bed

2. Extended Abstract

In chemical industry, fluidized bed drying of particulate solids is very common. A uniform moisture content of the dried product is highly desired. In continuous operation, the particles may have a non uniform moisture content distribution due to different residence times in the apparatus. On the one hand a short residence time might cause a very high moisture content, on the other hand too long exposition time might damage the product. Latter may degrade the quality of material, especially in such cases where the solids are thermo-sensitive.

To gain a better understanding of the interaction between process conditions, material properties and product quality the traditional drying models basing on averages need to be extended to describe the effect of distributed material properties. For this extension the concept of population balances provides the adequate framework. In a first step three internal coordinates of the population, namely the enthalpy h, the moisture l and the residence time t are considered. Thus, one can derive a three dimensional population balance (PBE) for a well mixed vessel

$$\frac{\partial f(t,\tau,h,l)}{\partial t} = -\frac{\partial G_\tau f(t,\tau,h,l)}{\partial \tau} - \frac{\partial G_l f(t,\tau,h,l)}{\partial l} - \frac{\partial G_h f(t,\tau,h,l)}{\partial h} + \dot{f}_{in} - \dot{f}_{out}.$$

The term on the left hand side denotes the temporal change of number density distribution f. The first three terms on the right hand side of the equation represent the aging, the drying and the heating of particles, respectively. The parameter G indicates the temporal change of the particle properties with respect to corresponding internal coordinate, e.g. $G_l = dl/dt$ or $G_\tau = d\tau/dt$. The two last expressions correspond to the conveyed and discharged particle flux at the inlet and outlet of the dryer. To reduce the numerical effort, the 3D PBE can be simplified using the marginal distribution approach. This simplification yields a set of three 1D PBE (number distribution, enthalpy distribution and moisture distribution) where only the residence time is kept as internal coordinate. To complete the model one needs to combine the PBE with an adequate model for the gas phase. Therefore, mass and enthalpy balances and appropriate kinetics of heat and mass transfer have to be defined. In our studies an heterogeneous fluidized bed model suggested by Burgschweiger and Tsotsas [1] was applied, which assumes that the gas passes the solid phase in plug flow while the solid phase is perfectly mixed. Axial dispersion in the gas is considered in the kinetic coefficient (Sherwood number).

The experiments were carried out in a continuous lab scale dryer (diameter 150 mm, batch size 3 liters). For different process conditions the moisture distributions in the product flow were determined by single particle measurements.

These measurements were conducted using the nuclear-magnetic-resonance (NMR) technique. The free induction decay (FID) after 34.5 µs was chosen to determine the total amount of water in the sample qualitatively. The NMR signal was converted into absolute amount of water by calibration of the FID with a coloumetric moisture measurement.

Figure 1: Influence of particle flow rate on moisture distribution. Test material: g-Al_2O_3 particles ($Æ$ 1.8 mm, initial moisture 2.2 mg).

In the framework of this study the influence of particle flow rate on moisture distribution has been investigated. Beside other effects an increased particle flow rate reduces the residence time of solids in the dryer. Consequently, the moisture distribution in the product will change significantly. This result is depicted in Figure 1. Furthermore the comparison between measured and simulated moisture distributions are presented. For all process conditions satisfactory results were obtained.
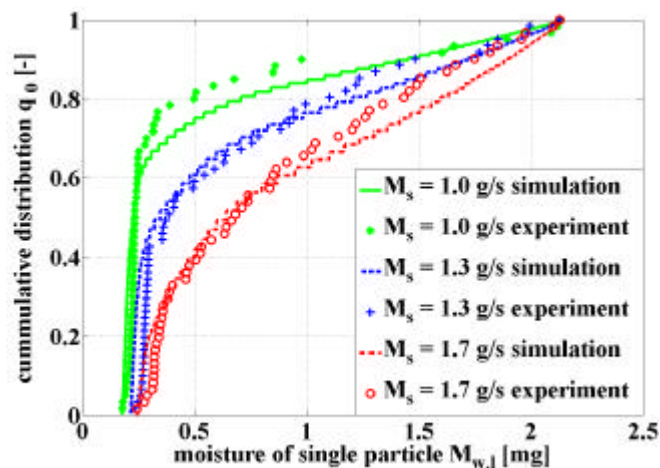
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One dimensional modelling of conical spouted beds

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1. Summary

A one-dimensional model that considers the solid cross-flow from the annulus into the spouted has been developed. The model is based on mass and momentum balance equations for the gas and solid in both the annulus and spout and empirical. The great advantage of the model is the requirement of only two empirical equations, one for obtaining the minimum spouting velocity and the other one for obtaining the pressure gradient through the bed. Based on the data obtained at the top of the spout, the model allows for calculating properties in the fountain, namely fountain height and the voidage at the axis of the fountain.

Keywords: spouted beds, conical spouted beds, modelling

2. Extended Abstract

Conical spouted beds have good perspectives for operations and processes where gas-solid contact is required, as in addition to the characteristics of the conventional spouted beds (cylindrical with conical bottom) they may operate in a wider range of gas velocities, which allows for attaining a vigorous gas-solid contact (Olazar et al., 1992). This versatility makes conical spouted beds especially useful for treatment of solids that are difficult to handle due to their irregular texture or because they are sticky. Likewise, conical spouted beds allow for attaining low gas residence times. A good behaviour of conical spouted beds has been proven in combustion of bituminuous coals (Tsuji et al., 1989), treatment of sawdust and agroforest residues (Olazar et al., 1994a) and pyrolysis of waste plastics and tyres (Aguado et al. 2005)

To improve the knowledge about the gas-solid contact in conical spouted beds a mathematical model has been developed. The aim of the model is to obtain velocity distributions of gas an particles in the different regions of conical spouted beds. Furthermore, design of conical spouted bed reactors for pyrolysis of biomass, plastics and tyres requires to couple the kinetic model with the hydrodynamic one. For this purpose, a simple but reliable hydrodynamic model should be used.

The model incorporates two levels of complexity: The simpler version considers constant bed voidage along the spout, given that this is a dilute region. For this

purpose, mass balances have been applied in the spout and annulus for gas and particles but momentum balances have only been applied in the spout region both for gas and particles. In the second version, bed voidage along the spout has been considered to increase with bed level. To obtain the evolution of bed voidage along the spout, the momentum balance for the gas in the annulus has been used.

The great advantage of the model is the requirement of only two empirical equations, one for obtaining the minimum spouting velocity and the other one for obtaining the pressure gradient through the bed. Apart from that, only the geometrical factors of the conical spouted bed and the physical properties of gas and particles are required.

A comparison of the results predicted by the model with the experimental ones shows the version with constant voidage gives poorer predictions except for the solid cross-flow from the annulus into the spout with bed level. The predictions of the second version are quantitatively much better. Figure 1 shows the values predicted by the model and the experimental ones for gas velocity and bed voidage along the spout (San José et al., 1998).
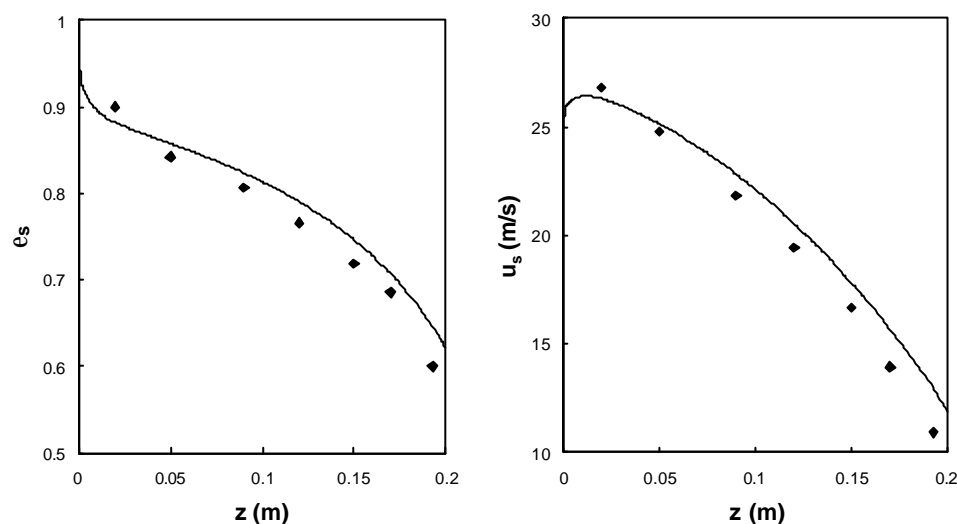
Figure 1. Experimental values (points) and those calculated with the model (solid lines) for bed voidage (left graph) and gas velocity (right graph) along the spout.

Based on the data obtained at the top of the spout, properties in the fountain have also been calculated, namely fountain height and the voidage at the axis of the fountain.

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Session T4-9b: Process Simulation & Optimization – II

Abstract Number	Paper Title & Authors	Included
560	Dynamic Monte Carlo simulation of batch free-radical linear and non-linear copolymerization systems. D Meimaroglou, A Krallis, C Kiparissides	Yes
2255	Application of integrated process and control system model for simulation and improvement of an operating technology B Balaskoa, S Nemetha, G Nagyb, J Abonyia	Yes
3257	Periodic optimization of continuous microbial growth processes: Higher-order corrections to the Pi criterion I Dermitzakis, C Kravarisa	Yes
3302	Performance of reduced distillation models in dynamic real-time optimization L Würth, A Linhart, H Preisig, W Marquardt	Yes
3524	Dynamic optimization of modelica models J Åkesson, Karl-Erik Årzén	Yes

Dynamic Monte Carlo simulation of batch free-radical linear and non-linear copolymerization systems.

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1. Summary

A Monte Carlo (MC) algorithm is developed to calculate the distributed molecular properties in batch free-radical polymerization reactors, in terms of a comprehensive kinetic mechanism. The various diffusional effects, appearing during polymerization (i.e., gel effect, glass effect), are also included in the kinetic model. The method is first applied to linear (polymethyl methacrylate, PMMA) and branched (polyvinyl acetate, PVAc) polymerization systems. Subsequently, the method is extended to free-radical batch co-polymerizations (e.g., styrene-methyl methacrylate (Sty-MMA)). Simulations are carried out, under different reactor conditions, to calculate the monomer conversion, the leading moments of the "live" and "dead" polymer chain distributions as well as the distributed molecular polymer properties (i.e., molecular weight distribution, MWD, long chain branching distribution, LCBD, copolymer composition distribution, CCD, etc.). The accuracy of the proposed method is tested via a direct comparison of theoretical predictions with available experimental data. Furthermore, a number of comparisons are made with simulation results obtained from the solution of the governing population balance model, using the fixed pivot technique, (FPT). It is clearly shown that the proposed dynamic MC algorithm is very efficient in simulating batch free-radical homo-polymerization and co-polymerization processes up to very high conversions.

Keywords: polymerization, Monte Carlo, sectional grid methods, copolymerization.

2. Extended Abstract

A well-known approach for the calculation of the distributed molecular properties of polymers (e.g., MWD, LCBD, CCD etc.), is the use of bivariate population balance equations (PBEs), (Kiparissides, 2006). In principle, based on the polymerization kinetic mechanism, one can derive dynamic PBEs to describe the time evolution of the "live" and "dead" polymer chains in a polymerization reactor. However, the total number of the resulting dynamic molar species balances is commonly of the order of thousands equations, thus making the analytical solution of the complete set of nonlinear differential equations extremely difficult, if not impossible, for most cases of interest.

To deal with the above high dimensionality problem, in the present work, two novel numerical methods are employed for the numerical solution of the bivariate PBEs. Specifically, a Monte Carlo algorithm is developed to calculate the dynamic evolution of the univariate MWD of linear polymers as well as the dynamic evolution of the bivariate MW-LCBD and MW-CCD of branched polymers and copolymers, respectively. The algorithm is based on the original developments of Gillespie (1977) and provides complete dynamic simulation of the "live" and "dead" polymer chain populations, in terms of a comprehensive kinetic mechanism (Meimaroglou et. al., 2007). Furthermore, the fixed pivot technique (FPT) of Kumar and Ramkrishna (1996) is specially adapted to calculate the dynamic evolution of the "live" and "dead" polymer chain populations in free-radical batch polymerization reactors.

A direct comparison of simulation results with experimental measurements as well as some representative simulation results are shown in Figs. 1-4. From the comparisons it is clearly shown that the proposed dynamic MC and FP algorithms are capable of simulating with accuracy batch free-radical homo-polymerization and co-polymerization processes up to very high monomer conversions.
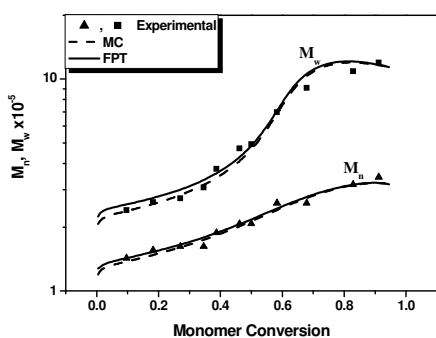
Figure 1. Average molecular weights of pSty-MMA.
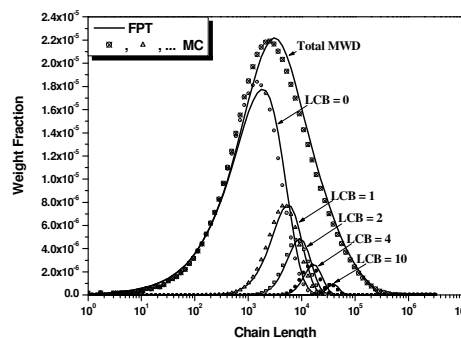
Figure 2. MWD of pVAc for different LCB values.
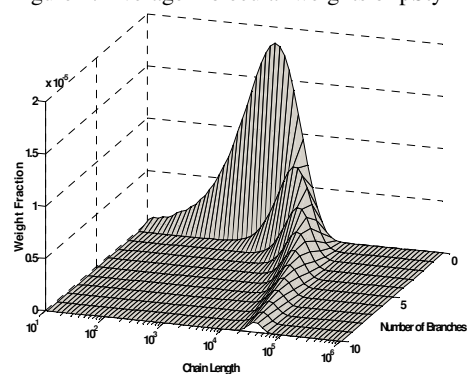
Figure 3. MW-LCBD of pVAc.
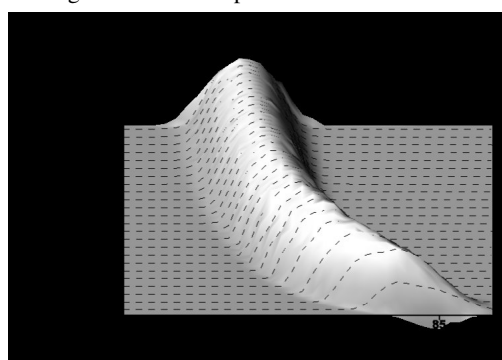
Figure 4. MW-CCD of pSty-MMA.

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Application of integrated process and control system model for simulation and improvement of an operating technology

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1. Summary

Leading chemical product companies stand for life-cycle modeling, where an overall model is applied at every level of the production system, i.e. "the model integrates the whole organization". Contrary to the fact that this approach is fulfilled during design phase of a technology, integrated application for model-based simulation is unnoticed during continuous process analysis and improvement.

The methodology proposed in this paper integrates production systems, where integration means information, location, application and time integrity. Models of process and control systems are integrated to a process Data Warehouse. This structure support engineering tasks related to analysis of system performance, process optimization, operator training (OTS), reverse engineering, and form decision support (DSS) systems.

The aim of this work is to present the effective usability of such framework in an operating polymerization process to emphasize how integrated modeling and simulation of process and control systems and information flow among the production units can improve the overall performance of complex process systems. The case study used for this purpose deals with the development of a new soft-sensor used for the estimation of the product quality.

Keywords: model-based optimization, offline simulator, process analysis

2. Extended Abstract

The application of process models is typical in planning areas of chemical engineering, where steady-state process design and dynamic control strategy development are the main tasks [1], but at the operational level the recycled usage of models in automation and control is not widely realized, thus it might be concluded that the profitability of life-cycle-modeling and model re-usage is not widely recognized. [2].

For all these purposes, an integrated process methodology was developed. This methodology integrates the system, where integration means information, location, application and time integrity. Obviously, the solutions are rather system-specific but the systematic methodology can be generally applied to handle the complexity and get relevant knowledge.
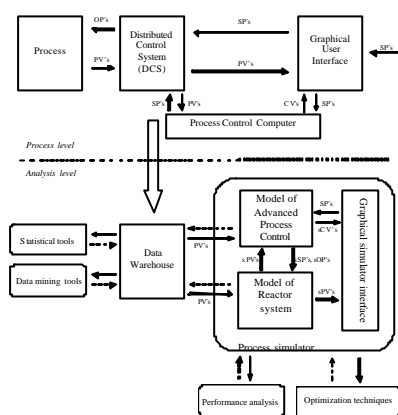
Figure 1: the integrated methodology of process analysis

Figure 1 shows our methodology scheme for process analysis. Process Data Warehouse (DW) is a data analysis-decision support and information process unit, which operates separately from the databases of the Distributed Control System (DCS), which contains trusted, processed and collected data. The data collected into DW indirectly creates a basis for optimization and system performance analysis techniques through a process simulator. In order to achieve such an offline process simulator, one needs to integrate models and information of the system or re-create them if they do not exist anymore.

For particular analysis, the applied components decide whether the result is a soft sensor, process monitoring, reasoning or reverse engineering tool, operator training/qualification or decision support system application.

The proposed methodology was applied as a theoretical basis for a research project in a polymerization plant of Tisza Chemical Group Plc., Hungary. The dynamic process simulator was realized in MATLAB$^{®}$ Simulink$^{®}$ environment to get it flexible, expandable and easily restructurable. The model of the advanced control system has been also implemented in Simulink. These simulators communicates through a Graphical User Interface (GUI) with the user and ODBC connection with the process data warehouse that stores almost two years of data historical collected from the DCS. The components of the models were validated on this real industrial data. Considering several validating simulations, it can be stated that the productions of the same products mostly differ from each other, so to get useful information about the optimal operating regimes of these diverse products sensitivity analysis techniques need to be done either in steady or dynamic manner. Based on steady state values of state variables and the corresponding product quality (melt flow index - MFI) measures, a sensitivity function of quality with respect to state variables was identified which can be easily visualized by e.g. Self-Organizing Map (SOM).

Since the advanced process control system does not have originally implemented transition strategy, transitions are managed by plant operators. To handle this problem, our process simulator has besides the re-simulation with real valued data input downloaded from DW the dynamic simulation capabilities as well to freely choose transition trajectories as set points between steady state values of process variables, thus it is an adequate basis for multi-objective optimization.

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Periodic Optimization of Continuous Microbial Growth Processes: Higher-order corrections to the Pi criterion

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1. Summary

The method presented in this work aims at determining higher-order corrections to the Pi-criterion, thus allowing for greater accuracy under a wider range of forcing amplitudes. This extension also provides a natural framework to analyze the effect of various complex periodic inputs on the long-term response of the dynamic system. The theory is applied to a model of a biochemical reactor under periodic forcing.

Keywords: optimization, periodic operation, Pi criterion, continuous operation, bioreactors

2. Extended Abstract

We utilize basic results of centre manifold theory [Carr, 1981] in order to predict the optimal forcing frequency of a system of differential equations of the form $\dot{x} = f(x,u)$. Important assumptions for the method employed are the existence of a stable steady state and the analyticity of f. u is a periodic function of time with a cyclic frequency of ω and an amplitude of M. Performance is measured in terms of an objective function of the form $J = \dfrac{\omega}{2\pi} \displaystyle\int_{0}^{2\pi/\omega} g(x(t),u(t))\,dt$.

The solution method, originally suggested by Kravaris et al (2002), is as follows: The centre manifold differential equation is formed and then solved via recursive Taylor series. The solution describes the long term response of the system to the periodic forcing. The solution is then substituted in the expression for *J*. The result is a power series in *M* with coefficients being functions of ω.

In the present work we briefly examine two different types of inputs: (a) sinusoidal wave, (b) square wave approximated by a truncated fourier series. The model used is a third order system for biomass production proposed by Abulesz & Lyberatos (1987). It can be seen from figures 1 and 2 that higher order approximations of J provide a different optimal frequency than the one suggested by the 2nd order approximation (which is equivalent to the Pi-criterion in the sinusoidal input case).

The performance improvements relative to the optimal steady state provided by our method for M=0.075 are of the order of 50% in the sinusoidal input case and 100% in the square wave input case.
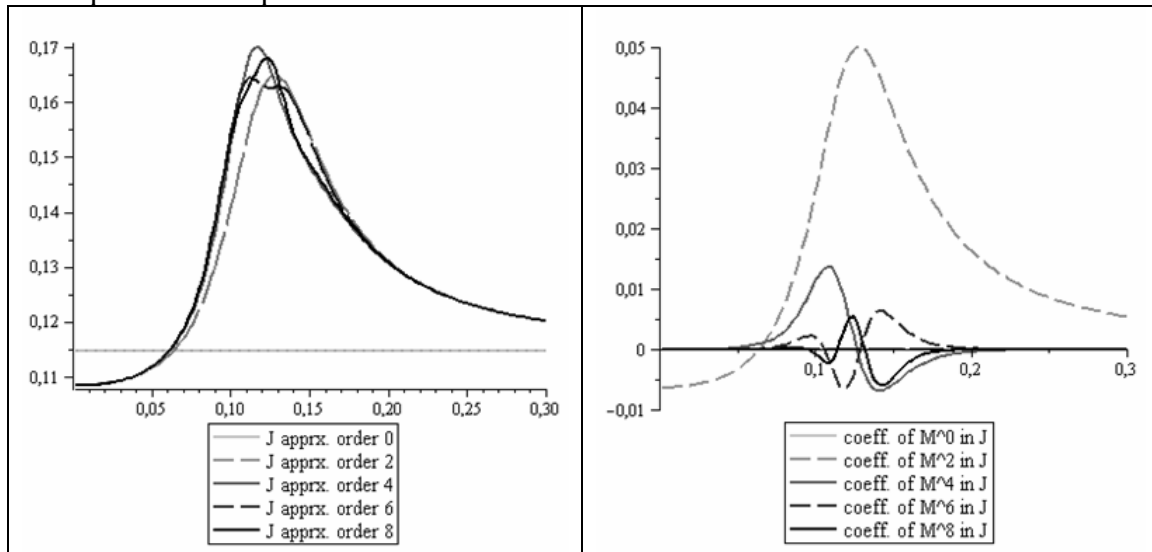
Figure 1: (a) Objective function for different approximation orders as a function of ω and (b) coefficients of the power expansion in M as a function of ω for sinusoidal input
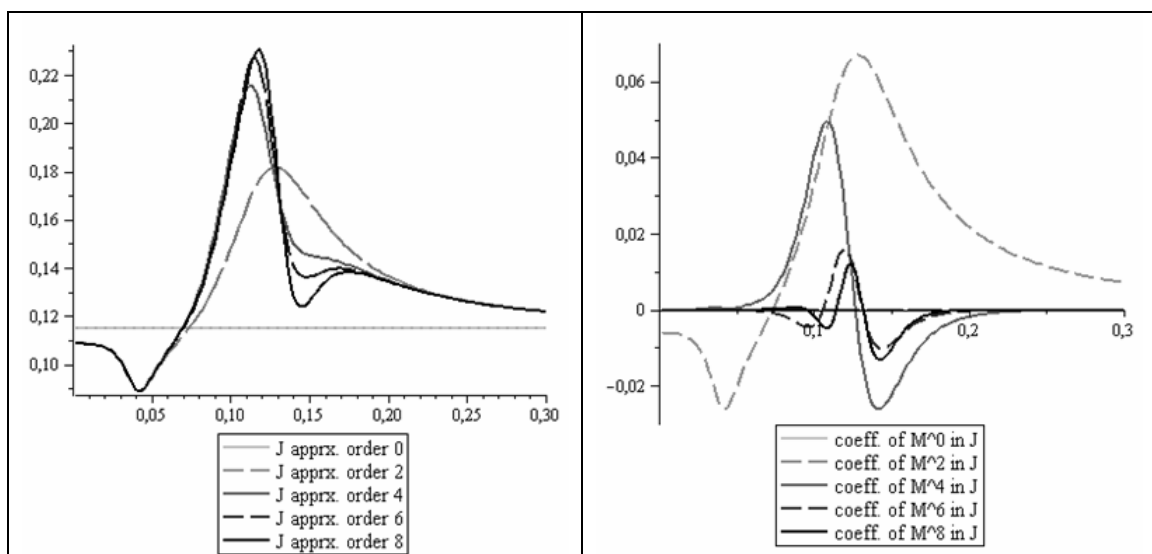
Figure 2: (a) Objective function for different approximation orders as a function of ω and (b) coefficients of the power expansion in M as a function of ω for square wave input

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Performance of Reduced Distillation Models in Dynamic Real-Time Optimization

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1. Summary

Real-time optimization (RTO) and model predictive control are state-of-the-art technologies for efficient and economically optimal operation of process plants. In order to make this computationally demanding technology applicable to large-scale chemical plants, models of significantly reduced computational complexity compared to the complexity of the original problem have to be employed. However, because of their reduced accuracy, the benefits of using reduced models in real-time optimization and control have to be investigated carefully. In this study, a tray aggregation method is used to derive reduced models of order 3, 5 and 7 of a 74-dimensional binary distillation column model. These models are used in a receding-horizon controller for economically optimal disturbance rejection, and their respective closed-loop performance is compared to that of the full model. It is found that with a careful implementation of the reduced models, a gain of roughly one order of magnitude in computational speed can be obtained, to the cost of slight constraint violations.

Keywords: real-time dynamic optimization, model reduction, aggregated models, distillation

2. Extended Abstract

2.1. Aggregated Tray Distillation Model

The full model used in this study models a binary distillation column with 72 trays with refluxdrum and reboiler using one material balance per tray and assuming constant molar holdups and overflows. The assumed vapour-liquid equilibrium on each stage is described by constant relative volatilities. From a model of this type, reduced models can be derived by tray aggregation (1). The resulting models are differential algebraic equation models where the number of dynamic variables equals the number of compartments in the column. Recently this method has been successfully extended to more complex distillation models (2).

With this method, three models of order three, five and seven were derived. The dynamic response of the models of order 5 and 7 is influenced by the compartment sizes and the position of the aggregation centres. Several possible configurations and a procedure to find an optimal selection of these parameters have been investigated in this study. As a crucial step to

increase the simulation speed, the algebraic equations were substituted into the differential equations, storing the off-line calculated solutions in a look-up table with cubic interpolation.

2.2. Real-Time Dynamic Optimization

The optimization problem is solved online at each sampling time t_j on a receding horizon after a set of measurements of the currents states and uncertainties has become available. All states are assumed to be measurable, as state estimation is not considered in this work. An economic objective function minimizes the energy supplied to the reboiler over time, whereas the product quality is controlled by path constraints on the reboiler and refluxdrum concentrations. The degrees of freedom for the optimization are the reflux rate and the vapour flow from the reboiler.

The dynamic optimization problem is solved numerically by the dynamic optimizer DyOS (3) using a control vector parameterization approach. The dynamic optimization problem is converted into a nonlinear programming problem by discretizing the controls on the time horizon $[t_j, t_f]$ using piecewise polynomial approximations, which is solved by an sequential quadratic programming (SQP) algorithm. The objective function, the constraints and their gradients are evaluated by a simultaneous integration of the DAE model combined with the sensitivity equation system. After starting with a coarse discretization, the parameterization is adapted online at each sampling interval by adaptively refining the grid (3) to reject disturbances rapidly.

2.3. Results

The process operation is simulated using the full distillation model, whereas the optimizations are carried out at a sampling rate of 120 seconds using the reduced order model. The process starts from the nominal, optimal steady-state and a disturbance (20% step change) is introduced in the feed concentration at time zero.

An important reduction in computational time of roughly one order of magnitude was obtained using the reduced models, which is mainly due to the fact that the sensitivity integration of the reduced model is significantly faster. Nevertheless, the mismatch between the reduced and the full model leads to slight constraint violations and a small offset from the optimal steady-state values. This error is to some extent affected by the choice of the compartment sizes and positions, and leads in some cases to oscillations around the operating point. Although the reduced model's performance seems promising for RTO regarding its solution times, further research has to be done to match the properties of the reduced models during transient operation with the requirements of RTO.

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Dynamic Optimization of Modelica Models

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1. Summary

This contribution gives an overview of the JModelica project. One of the primary objectives is to extend the modeling language Modelica, to also support formulation of complex dynamic optimization problem. While Modelica offers convenient abstractions for modeling of physical systems, it contains no language support for optimization. Since a major effort in the formulation of a dynamic optimization problem is often devoted to encoding the dynamical model, a modular extension which enables formulation of optimization problems, based on Modelica models, is attractive. A language based approach enables optimization problems to be specified formally, and in addition, efficient transformation techniques from the area of compiler construction can be applied. The project deals with three different aspects of the problem; *i)* a language extension of Modelica for dynamic optimization, entitled Optimica, *ii)* prototype software for translating a Modelica model and a complementing Optimica description into a canonical mathematical representation and *iii)* code generation for efficient numerical algorithms. In addition, case studies are performed to demonstrate the effectiveness of the concept.

Keywords: Modeling, Dynamic optimization, Modelica, JModelica

2. Extended Abstract

High-level modeling languages are receiving increased industrial and academic interest within several domains, such as chemical engineering, thermo-fluid systems, power systems, and automotive systems. One such language is Modelica [1]. Modelica is an open language, specifically targeted at multi-domain modeling and model re-use. Key features of Modelica are object-oriented modeling, declarative equation-based modeling, a component model enabling a-causal connections of sub-models, as well as support for hybrid/discrete behavior.

While there are very efficient software tools for simulation of Modelica models, tool support for static and dynamic optimization is often less developed. Furthermore, specification of optimization problems is not supported by Modelica. Since Modelica

models represent an increasingly important asset for many companies, it is of interest to investigate how Modelica models can be used also for optimization, by utilizing cutting-edge numerical algorithms, in order to increase return of investment.

This paper contributes an overview of a project targeted at defining an extension of Modelica, Optimica, which enables high-level formulation of optimization problems. In addition, the project is concerned with development of prototype tools for translating a Modelica model and a complimentary Optimica description into a representation suited for numerical algorithms, as well as performing case studies demonstrating the potential of the concept. One of the main benefits of the suggested approach is that the high level descriptions are automatically translated into an intermediate representation by the compiler front-end. This intermediate representation can then be further translated to interface with different numerical algorithms. The user is therefore relieved of the burden of managing the often cumbersome API:s of numerical algorithms. The flexibility of the architecture also enables the user to select the algorithm most suitable for the problem at hand.

The prototype software which is developed in the JModelica project is based on the JastAdd framework for extensible compiler construction, see [2] for an overview. A first version of the Optimica extension has recently been defined. In addition, a prototype compiler supporting a subset of Modelica has been developed. The compiler enables translation of the high level Modelica and Optimica descriptions into the language AMPL [3], where the continuous dynamical states have been transcribed by means of a simultaneous optimization approach based on collocation over finite elements, [4]. The resulting algebraic optimization problem is then solved by the numerical algorithm IPOPT [5]. The tools have been successfully used e.g. to find optimal start-up trajectories for a plate reactor [6].

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Session T4-9c: Process Simulation & Optimization - III

Abstract Number	Paper Title & Authors	Included
1316	Local approximation to complex models for efficient optimisation: application to crystallisation processes A Yang, X Ou, G Montague, E B Martin	Yes
1914	Robust MINLP optimization model for petrochemical network design under uncertainty K Al-Qahtani, A Elkamel, K Ponnambalam	Yes
2634	Performance of esterification system in reaction-distillation column E A Edreder, I M Mujtaba, M.M. Emtir b	Yes
2853	Optimisation parameters of the reactive separations with very fast chemical reaction J Slava, Marcel Kotora, J Markos	No
3131	A hybrid modelling approach in the simulation of integrated urban wastewater systems B Ráduly, E Lindblom, K V Gernaey	Yes

Local approximation to complex models for efficient optimisation: application to crystallisation processes

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1. Summary

Recent advances in mathematical modelling have enabled the development of detailed mechanistic models to support the design and analysis of chemical processes or products. However in those cases where the resulting model is highly complex, it can be very time consuming to solve the model numerically, thereby limiting its practical applicability. This is especially the case where a complex model is used for the numerical optimisation of a process thereby necessitating the execution of a large number of evaluations of the model. To make such an optimisation task computationally tractable, the idea of approximating complex mechanistic models with statistical models is investigated. In particular, an iterative optimisation procedure is implemented which makes use of a Gaussian process model (GPM) to locally approximate the complex mechanistic model. The GPM is successively updated according to the results obtained from evaluating the original model at locations in different sub-regions searched by the optimisation algorithm. The potential of this method in reducing the number of evaluations of the original model, and hence lowering the computational cost, is confirmed by its application to the optimisation of a batch cooling crystallisation process.

Keywords: mathematical modelling, local approximation, statistical modelling, Gaussian process model, simulation-based optimisation

2. Extended Abstract

Model reduction and simplification treatments are important for realising the practical application of complex mathematical models in optimisation-based process engineering tasks (Marquardt, 2002). Where an optimisation task utilises a complex model, but with no structural or derivatives information available, this problem is generally referred to as the optimisation of expensive black-box objective functions and have been handled by a number of simulation-based optimisation methods (Jones et al., 1998).

In this work, an iterative optimisation procedure based on a method developed by Bueche et al. (2005) is implemented and its applicability for the optimisation of chemical processes is evaluated. The approach makes use of a Gaussian process model (GPM) to locally approximate a complex mechanistic model (CMM). Within each iteration of the optimisation procedure, the GPM is trained using data generated from a number of executions of the CMM, where the inputs to the CMM are selected from a sub-region of the entire optimisation domain. It is thus assumed that the GPM is valid within this sub-region, where the optimisation is subsequently to be performed using the GPM instead of the CMM. The GPM computes both the mean and the standard deviation of its prediction, with the latter metric providing an indication as to the accuracy of the GPM. This information is utilised to determine the next sub-region for approximate modelling and optimisation such that the improvement in the objective function and the GPM's accuracy are well balanced. This process continues until a particular stopping criterion is satisfied.

A consequence of using the local approximation model is that the optimisation procedure requires fewer evaluations of the original CMM, compared with the number required when the optimisation is based solely on the CMM, hence the optimisation is computationally more efficient. This method treats the CMM as a black box when the CMM is being approximated. Therefore, unlike the model reduction–based methods, it virtually requires no knowledge as to the structure of the CMM. This method also differs from those based on the global approximation of the CMM: it successively constructs local approximation models that are easier to build than a global model, especially when the dimensionality of the input space is high.

This procedure is successfully applied to the optimisation of the temperature profile of a batch crystallization process. The process was modelled through a set of two-dimensional partial differential-algebraic equations using the modelling tool gPROMS. The optimisation was first carried out on the CMM model using a Genetic Algorithm (GA). A GA was selected in order to avoid being trapped by a local optimum too quickly. The same problem was then solved by applying the local approximation based procedure, where both the maximum likelihood based training of the GPM and the optimisation using the GPM, at each iteration in the procedure, were carried out using the same GA. A number of comparative studies were performed with different initialisations. The results showed that, to achieve the same optimum, the number of evaluations of the CMM required by the local approximation based method is around 1/3 of that required using the CMM model directly.

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Robust MINLP Optimization Model for Petrochemical Network Design under Uncertainty

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1. Summary

This paper addresses the strategic planning, design and optimization of a network of petrochemical processes under uncertainty and risk consideration. The problem was formulated as a two-stage mixed-integer nonlinear model (MINLP) with parameter uncertainty considered in the process yield, raw material and product prices, and upper and lower product market demand. Operational risk was accounted for in terms of variance in both projected benefits in the first stage variables and deviation from forecasted demand in terms of the recourse variables. For each term, a different scaling factor was used to analyze the sensitivity due to variations in each component on the petrochemical network. The study showed that the final petrochemical network bears more sensitivity to variation in product demand. However modeling the uncertainty in process yields and prices provided a more robust and practical perspective of the problem.

Keywords: Petrochemical planning, planning under uncertainty, robust optimization

2. Extended Abstract

The Petrochemical industry is a network of highly integrated production processes. The products of one plant may have an end use but may also represent raw materials for another process as well. This multiplicity of production schemes offers the sense of switching between production methods and raw materials utilization. This flexibility in petrochemical products production and the availability of many process technologies require adequate strategic planning and a comprehensive analysis of all possible production alternatives.

In this paper we study and compare the strategic planning, design and optimization of a network of petrochemical processes under deterministic conditions, uncertainty and uncertainty with risk consideration. The problem was formulated as a two-stage mixed-integer nonlinear model (MINLP) with nonlinearity arising from modelling the risk components. Both endogenous uncertainty, represented by uncertainty in the process yield and exogenous uncertainty, represented by uncertainty in raw material

and product prices, and upper and lower product market demand were considered. The considerations of uncertainty in these parameters provided a more robust and practical analysis of the problem especially at a time where fluctuations in petroleum and petrochemical products prices and demands are souring.

The case study presented in this paper is based on Al-Sharrah et al. (2006). The petrochemical network included 81 processes connecting the production and consumption of 65 chemicals. The uncertainty is considered through discrete distribution with a total number of 200 scenarios for each random parameter. The modeling system GAMS (Brooke et al., 1996) was used for setting up the optimization models. The model was solved with DICOPT (Viswanathan & Grossmann, 1990). In this study, operational risk was accounted for in terms of variance in both projected benefits, represented by first stage variables, and forecasted demand, represented by the recourse variables. Different scaling factors were used to analyze the sensitivity due to variations in each term. Projected benefits variation was scaled by θ_1 and deviation from forecasted demand was scaled by θ_2 where different values of θ_1 and θ_2 were used to observe the sensitivity of each term on the final petrochemical complex.

The study showed that the problem bears more sensitivity to variations in product demand for values of θ_1 and θ_2 that maintain the final petrochemical structure. However, as the values of θ_1 and θ_2 increase, some processes became too risky to be included in the petrochemical network and instead importing some final chemicals became a more attractive alternative. Figure 1 and 2 illustrate the variations in expected profit with risk in terms of standard deviation at different θ_1 and θ_2 values, respectively.
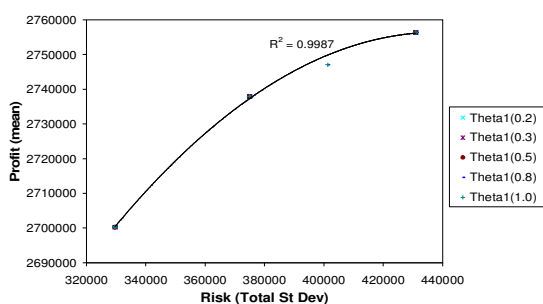
Figure 1: Risk vs. projected benefits at different θ_1 Figure 2: Risk vs. projected benefits at different θ_2

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Performance of esterification system in reaction-distillation column

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1. Summary

In this work a comparative study of the performance of conventional and unconventional (semi-batch configuration) batch reactive distillation column 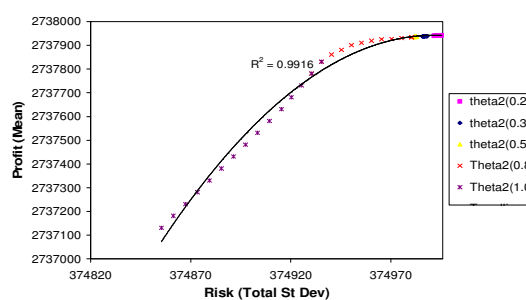is presented for esterification reaction of ethanol and acetic acid to produce ethyl acetate (main product) and water. Dynamic optimisation problem is formulated to maximise the conversion of ethanol to ethyl acetate subject to product purity constraints for different amount of feed reactants while optimising reflux ratio of operation for conventional operation and both reflux ratio and the amount of acetic acid feed rate for semi-batch operation. Flooding condition has been added as a constraint to the system for the semi-batch operation. It is found that there are cases when semi-batch operation can be more effective in maximising the conversion.

Keywords: Batch reactive distillation, Conventional column, Semi-batch column, Modelling, Dynamic optimisation

2. Extended Abstract

The esterification process is modelled using detailed mass and energy balances and thermodynamic properties within gPROMS modelling software. The basic model was taken from Mujtaba (2004) which is linked with Physical Properties package (IPPFO) of gPROMS and kinetic and vapour-liquid equilibrium models from Bogacki et al. (1989) and Suzuki et al. (1970). For conventional column, five cases with varying amount of reactants are utilised to study the effect of feed change on the maximum conversion of ethanol to ethyl acetate. The feeds <Acetic Acid, Ethanol, Ethyl Acetate, Water> are: Base Case - <2.25, 2.25, 0.0, 0.50>, Case 1 - <2.375, 2.125, 0.0, 0.5>, Case 2 -<2.5, 2.0, 0.0, 0.5>, Case3-<2.625, 1.875, 0.0, 0.5> and Case4 - <2.5, 2.25, 0.0, 0.025>. The other input data are shown in Table 1. For a given batch time (between 15 to 25 hrs) with given product purities (0.7 molefraction of ethyl acetate) the results are summarised in Tables 2 and 3. The results show that the conversion has

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been improved with changing feed amount (including the case with the reduced amount of water in the feed).

Table 1. Column Specifications for Ethanol Esterification Process

No of ideal stages		Internal plate hold up (kmol)	= 0.0125
(including reboiler and condenser)	= 10	Condenser hold up (kmol)	= 0.10
Feed Location (Semi-batch)	= 8	Vapour boil up rate (kmol/hr)	= 2.50
Total fresh feed (kmol)	= 5	Column pressure (bar)	= 1.013

Table 2. Maximum Conversion and Optimal Reflux Ratio at Different Batch Time

t_f, hr	Base Case	Case 1	Case 2	Case 3	Case 4	Semi-batch
15	69.9 (0.943)	72.8 (0.943)	75.2 (0.944)	77.2 (0.946)	73.7 (0.938)	76.7 (0.936)
20	74.2 (0.953)	77.0 (0.953)	79.3 (0.954)	81.2 (0.956)	77.8 (0.949)	81.6 (0.947)
25	76.9 (0.960)	79.7 (0.960)	81.9 (0.962)	83.7 (0.963)	80.5 (0.958)	-

Note: Conversion is in % and Optimal Reflux Ratio is shown in brackets.

Table 3. Amount of Distillate Product at Purity of 0.7

t_f, hr	Base case	Case 1	Case 2	Case 3	Case 4	Semi-batch
15	2.14	2.14	2.10	2.04	2.32	2.40
20	2.37	2.36	2.30	2.21	2.53	2.65

For semi-batch column, the amount of initial charge to the reboiler is same as the base case. Pure acetic acid is charged at the rate of F = 0.12 kmol/hr to the column. The following constraint must be satisfied to avoid column flooding (Mujtaba, 1999).

$L_D \geq F$, where $L_D = Vc(1-R)$ leading to $R \leq 1-(F/Vc)$ and. $R_{max} = 1-(F/Vc)$ (1)

Where, V_c is the condenser vapour load, L_D is the distillate rate, R is the reflux ratio. The results show that about 10 % more conversion (compared to conventional) is achieved for semi-batch scheme up to batch time of 20 hrs. No solution was found for other batch times (Table 2) as higher than the maximum allowable reflux ratio (R_{max}) was needed to avoid column flooding. The optimal reflux ratio increases with increasing batch time and reducing initial amount of ethanol in the feed. The column can operate at lower reflux ratio (compared to the base case) with reducing amount of water (case 4) and with semi-batch case. Table 3 shows that the amount of distillate product increases with increasing batch time for all cases. Also for a given batch time, semi-batch operation produces more distillate product.

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A hybrid modelling approach in the simulation of integrated urban wastewater systems

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1. Summary

This work combines Artificial Neural Network (ANN) modelling and traditional (mechanistic) modelling of the urban wastewater system, in order to obtain a tool that allows for fast evaluations of the performance of such systems. It is shown that using this combined modeling approach no significant loss in the simulation accuracy can be detected (when compared to the pure mechanistic modeling approach), while the simulation speed increases by one order of magnitude.

Keywords: artificial neural networks, simulation speed, integrated urban wastewater system modelling, wastewater treatment plant modelling, hybrid modelling

2. Extended Abstract

Simulation of the integrated urban wastewater system is typically a computationally-demanding, and consequently a time-consuming task. Thus model-based evaluation of integrated urban water systems consists more of waiting for the simulation than actually processing and evaluating simulation data. In case of long-term simulations (= several years of data) and time-series analysis, this problem becomes even more accentuated.

The high computational demand of the traditional integrated urban wastewater models is a consequence of the high overall complexity of these models, and thus of the individual complexity of the sub-models making up the integrated model. Indeed, a mechanistic model of the integrated urban wastewater system typically consists of sub-models for the sewer system, the wastewater treatment plant (WWTP) and the receiving waters. Reduction of simulation times can be achieved by speeding up one or more of the sub-models of the integrated system. In this paper the use of a fast

neural network model instead of the mechanistic model of the WWTP is proposed for this purpose. The neural network is trained on a sequence of treatment plant input/output data generated by the mechanistic model of the WWTP. In other words, the trained ANN becomes a "fast copy", a reduced model of the original WWTP model. This ANN is then coupled to a mechanistic river model – representing the receiving waters – and to an influent model (Fig. 1). The influent model generates time series of typical WWTP influent flow rate and pollutant concentration disturbances. As a result of substituting the mechanistic WWTP model by the ANN, a reduction of the simulation time by a factor of 23 was achieved (0.9 minutes vs. 21 minutes for a simulation over one year). The results presented in this paper show that the errors of the hybrid model (in terms of predicted pollutant levels in the river) are of an acceptable level when compared to the results of the purely mechanistic model, confirming the practical usefulness of the proposed method.
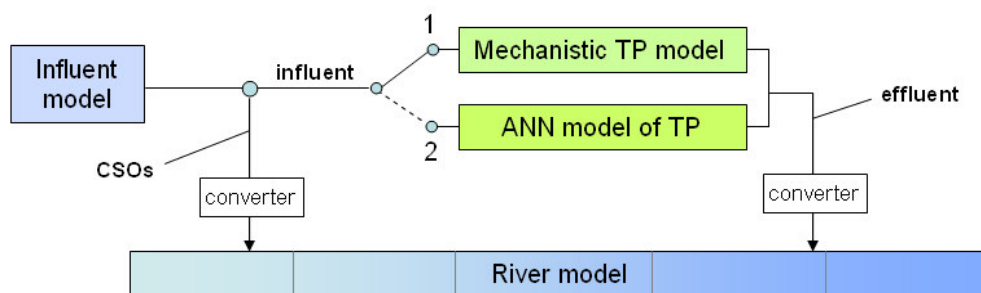

Figure 1: The integrated model configuration. When the switch is in position 1 the mechanistic Treatment Plant model is used, while in position 2 the ANN model is used. The converters "translate" the state variables of sub-models from one model to the other.

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Session T4-9P: Process Simulation and Optimization - Poster

Abstract Number	Paper Title & Authors	Included
781	Mathematical modeling of caustic treatment processes of zeolite's sorbents A Ermakov, D Dvoretsky, S Dvoretsky	Yes
1972	Compact Flat-Box Adsorbers for Air Separation by PSA Processes C-t Chou, W-T Chen, C-F Cheng	No
2237	Thermodynamic analysis of coupled methanol hydrocarbon cracking reaction D Mier, A T Aguayo, J Ereña, B Valle, J Bilbao	Yes
2506	Simulation of the Tetrahydrofuran Dehydration Process by Extractive Distillation in Aspen Plus P Gómez, I Gil	Yes
2592	Modelling and Simulation of an Industrial Continuous Naphtha Catalytic Reformer (CCR) M Mahdavian, S Fatemi	Yes
2638	Effect of Operating Decisions on the Design and Energy Consumption of Inverted Batch Distillation Column I Mujtaba, A Masoud	No
2852	Estimation of preliminary process parameters of reactive distillation device M Kotora, J Sláva, J Markoš	Yes
3090	Scheduling for maximum profits in the Icelandic cod industry A G H Guðmundsdóttir, B S Margeirsson, C P Jensson	No
3073	Evaluation of hydrogen production from metallurgical industry's flue gases using AspenPlus™ simulation software E Turpeinen, R L Keiski	Yes
3191	Optimization of Ammonia Synthesis Reactor using Genetic Algorithm B Hosseinzadeh, M T Sadeghi	Yes
3373	The Effect of Off-cut Recycle on the Multivessel Batch Distillation Column using Rigorous Dynamic Model I Mujtaba, M Mahmud, M Emtir	Yes
3438	A comparison of binary coding and real-coded genetic algorithms applied to a three-phase catalytic reactor M Rezende, A Costa, R Maciel Filho	Yes
3697	Optimization of the Culture Medium for the Bioethanol Production Using Genetic Algorithm B Zelic, A Vrsalovic Presecki, Z Findrik, Đ Vasic-Racki	Yes

Mathematical modeling of caustic treatment processes of zeolite's sorbents

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1. Summary

Adding caustic treatment stage to the traditional technologies of granulated zeolite sorbents (GZS) production allows to receive sorbents with improved properties: higher mechanical strength, static and dynamic capacity. To describe the process of caustic treatment a mathematical model has been developed. Using the developed model the problem of obtaining industrial prototype of zeolite sorbent 4A with improved properties has been stated and solved.

Keywords: granulated zeolite sorbents (GZS), caustic treatment

2. Extended Abstract

Changes in physical and chemical properties of granulated zeolite sorbents in the process of caustic treatment can be explained by the behavior of the following processes: source components of GZS, coupling agents (claying mineral) and adsorbent (synthetic zeolite) in the interaction with caustic solution are partially dissolved with the emergence of the simplest silicate and aluminate ions; as a result of the polycondensation reaction between ions, alumosilicate ions are formed and colloid alumosilicate structures appear; due to the continuous dissolution of the alumosilicate structures the crystallization centers are formed and the zeolite crystals grow in situ.

Aggregate of the described physical and chemical processes causes change of adsorptive and mechanical properties of sorbents. Partial recrystallization of the claying mineral into zeolite's phase allows increasing static adsorption capacity up to 25%. Along with the described phenomena, the process of caustic treatment of GZS is accompanied by increase of the effective adsorbate diffusion coefficient up to 70% and dynamic adsorbtion capacity due to the modification of the secondary porous structure with the appearance of the new porous (with the size variation from micro to macro values). Thus during the caustic treatment of GZS polymodal secondary structure is formed, which, in general, does not differ in type and character of porous effective radius distribution from the structure type of secondary porosity of initial

samples. At the same time increase of the volume of secondary porous is changing in the wide range (3-150%) and strongly depends on the concentration of caustic agent and duration of treatment. Increase of the mechanical crush strength up to 200% can be explained by the formation of amorphous alumosilicate and increased strength of claying particles of the formed gel structure.

Mathematical description of GZS caustic treatment process has been formulated taking into account of the following assumptions [*Ermakov A., 2003*]: 1) the process of single particle caustic treatment of GZS and process in the unit reactor behave the same; 2) the process runs in isothermal conditions; 3) the particle has a canonic shape (cylinder, sphere); 4) there is no gradient of concentrations in the fluid phase; 5) the particle is isotropic from the diffusion standpoint.

In compliance with the taken assumptions, taking into account physical and chemical processes, mathematical description of GZS caustic treatment includes the system of partial differential equations of controlled diffusion reactions and balance equations of liquid and solid phases.

Boundary problem of controlled diffusion reactions of GZS caustic treatment process has been solved by the finite-difference method of implicit type with four points model.

Using the developed model we have solved the problem of caustic treatment of GZS: for the initial type of GZS (percent content and type of claying coupling agent, shape and size of granules) it is required to define such conditions of caustic treatment process realization (concentration and temperature of caustic dissolute, frequency of mixer rotation, mass composition of liquid and solid phases in the unit), when the optimum of aggregate of adsorption and mechanical properties of GZS could be achieved.

Optimization problem has been solved for the industrial prototype of zeolite sorbent 4A, which is broadly used for refinement and drying of cooling agents. Comparison of adsorption and mechanical properties of the prototype zeolite sorbent produced with the traditional technology and zeolite example produced with the suggested optimal conditions of the caustic treatment showed the increase in the following properties: mechanical strength by 36,8 %, adsorption capacity by 14%, and effective diffusion coefficient by 4,3%.

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Thermodynamic analysis of coupled methanol hydrocarbon cracking reaction

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1. Summary

A thermodynamic analysis of the reactions that are involved in the simultaneous cracking of n-butane and methanol process, CMHC, [1] has been performed, with the aim of selectively obtaining C_2-C_4 olefins. The transformation of both raw materials in an integrated process has advantages such as energy compensation over industrial processes used for obtaining olefins from each raw material. This process combines the exothermic methanol conversion with the highly endothermic hydrocarbon cracking in a thermo-neutral reaction, which is important for the reactor design. A mathematical model [2] has been developed in MATLAB with the aim of obtaining the equilibrium constants of the main reactions, equilibrium olefin yield and the heat associated with the reaction system.

Keywords: methanol hydrocarbon cracking, equilibrium, thermodynamic

2. Extended Abstract

2.1 Thermodynamical model

The main reactions that take part in the coupled methanol hydrocarbon cracking have been considered to be: i) methanol dehydration reaction; ii) olefin formation from dimethyl ether; iii) olefin formation from n-butane cracking. The equilibrium composition of each compound is calculated by assuming the reaction rate to be zero at the equilibrium state:

$$\upsilon_i^j \frac{d\varepsilon_j}{d\tau} = k_j \left[\prod_{r=1}^{R} \left(f_r^{-\upsilon_r^j} \right) - \frac{1}{K_j} \prod_{p=1}^{P} \left(f_p^{\upsilon_p^j} \right) \right] \xrightarrow{eq} \upsilon_i^j \frac{d\varepsilon_j}{d\tau} = 0 \tag{1}$$

Where ε_j is the extent of each reaction (change in mol number of each, i, compound with the estequiometric coefficient υ_i^j). Fugacity f_i is determined by:

$$f_i = \Phi_i \cdot y_i \cdot P \tag{2}$$

where the fugacity coefficient, Φ, is calculated by Soave-Redlich-Kwong state equations. The mathematical model calculates the value of the composition, y_i, that makes the reaction rate zero under a certain operation pressure, P, by using a high kinetic constant, k_j in order to guarantee the equilibrium state. The equilibrium constant at any reaction temperature is calculated by using standard molar enthalpy ($\Delta H°$), free-energy ($\Delta G°$) and heat capacity of each compound (Cp_i).

2.2 Results

The combination of temperature and methanol/n-butane molar rate in the feed that makes zero the heat associated with the system has been calculated.
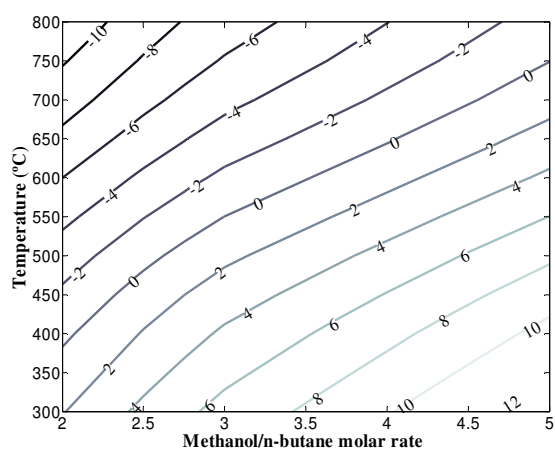

Figure 1 shows the heat generated in the CMHC process. The system is thermo-neutral at temperatures between 500-550 ºC and methanol/n-butane molar rate in the feed between 3-3.5, which is evidence of process synergy and viability.

The overall olefin yield is between 83-89% under these operation conditions.

Figure 1.- Heat realised $(kJ.mol^{-1}_{CH2})$ for different combinations of temperature and methanol/n-butane in the feed.

Finally, a comparison of the heat generated in the following processes has been made in order to determinate the energy compensation in the CMHC process: i) MTO process; ii) n-butane cracking; iii) CMHC process.

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Acknowledgements

Simulation of the Tetrahydrofuran Dehydration Process by Extractive Distillation in Aspen Plus

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1. Summary

The aim of this work is to simulate and analyze an extractive distillation process (extractive distillation and recovery columns) for separation of tetrahydrofuran(THF)-water azeotropic mixture using Aspen Plus® and Aspen Split simulators. Calculation of vapor liquid equilibrium of Tetrahydrofuran–Water–Entrainer system was done using the NRTL equation, which binary interaction parameters were regressed using experimental data. A methodology for the study and selection of different candidate entrainers was followed, determining that the most suitable is glycerol. The solvent to feed molar ratio, reflux molar ratio, feed stage, feed solvent stage, and feed solvent temperature, were determined and their effects on the separation and the energy consumption in the two columns was studied.

Keywords: extractive distillation, entrainer, tetrahydrofuran, simulation.

2. Extended Abstract

Tetrahydrofuran dehydration is a process of special economical concern, as anhydrous THF demand is increasing. There are a variety of suitable processes for the separation of azeotropic mixtures, being extractive distillation using 1,4-Butanediol the most commonly used method for THF dehydration (Xu et al, 2006). Extractive distillation uses a third substance (entrainer) that increases the relative volatility of the key components of the feed, breaking the azeotrope and producing high purity streams.

The solvent selection methodology was supported with Aspen Split entrainer selection tool. For this purpose NRTL model was chosen, following the appropriate criteria and regressing binary interaction parameters using experimental data. Pseudobinary diagrams and residue curve maps were drawn in Aspen Split, showing that the entrainers that most effect on the relative volatility cause are glycerol, ethylene glycol and propylene glycol. 1,4-butanediol, being suitable for the separation, does not increase the relative volatility enough to break the azeotrope at a

reasonable solvent/feed ratio. As glycerol is economically favourable, it is chosen as the entrainer for the extractive distillation process.

The operation conditions were settled, using the Sensitivity Analysis Tool in Aspen Plus. The process diagram of the simulation in Aspen Plus is shown in Figure 1. The input information of the simulation, as well as the results for the studied parameters are exposed in Table 1.
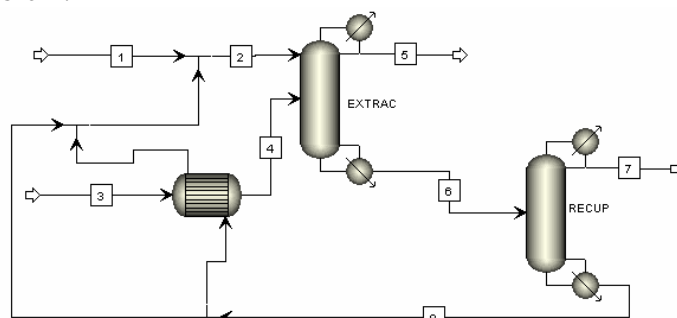

Figure 1. Process Flowsheet for the extractive distillation system used to dehydrate THF

	Extractive Column					Recovery Column		
Number of Stages	10					6		
Feed Stage	6					3		
Entrainer Feed Stage	2					-------		
Entrainer Feed Temperature °C	120,5					-------		
Reflux Ratio	0,5					0,1		
Entrainer/Azeotropic Feed Ratio	0,3					0		
Energy Consumption kJ/kgTHF in 5	0,34					0,11		
Streams	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Temperature C	20,00	120,48	20,00	63,43	65,95	120,73	11,27	208,00
Pressure bar	1,01	1,01	1,01	1,01	1,01	1,01	0,08	0,08
Mole Flow kmol/hr	0,18	30,00	100,00	100,00	81,90	48,10	18,28	29,82
THF	0,00	0,00	83,00	83,00	81,86	1,14	1,14	0,00
Water	0,00	0,00	17,00	17,00	0,03	16,97	16,97	0,00
Glycerol	0,18	30,00	0,00	0,00	0,00	30,00	0,18	29,82

Table 1. Simulation Results Summary

The composition of THF in the distillate is comparable with the one obtained in other studies with other entrainers (Xu et al, 2006), but using a more economical entrainer like glycerol and with a lower solvent to feed ratio.

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Modelling and Simulation of an Industrial Continuous Naphtha Catalytic Reformer (CCR)

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1. Summary

Nowadays, with worldwide increasing demands of the high qualitative gasoline, it is necessary to establish the new naphtha reforming units and develop the traditional units to the high efficiency processes. In this work, according to the recent progresses in naphtha reforming technology, a modelling and simulation of an industrial continuous catalytic reformer is performed. The applied kinetic model is based on Padmavathi model [1] with some modifications on kinetic constants as well as considering deactivation rate of the catalyst during the reaction. Current model is based on 25 lumped components (including C_6 to C_{10} hydrocarbons) in three categories of Paraffins, Naphthens and Aromatics, by using 60 reactions. The kinetic parameters of the reactions are tuned using data of the outlet temperatures and components flow rates in industrial operating conditions. Validation of derived model is carried out using a new feed with another composition in which the results show a good agreement with actual outlet data. This model can receive the feed property and determine the yield, composition and RON of the product (reformate). Hydrogen and LPG are the light fraction of the reforming process which is determined in this work. This reformer model could link to HYSYS software for further plant simulation and optimization.

Keywords: Naphtha reforming, gasoline, high RON, continuous catalytic reformer

2. Extended Abstract

Continuous catalytic reforming of naphtha is a new technology in recent years because of economic design, operability and product quality in comparison to the other types of catalytic reforming units. Today, all new units are designed based on this technology and old units are revamped to the continuous process or combination of both. The purpose of this work is to simulate properly these industrial units.
The kinetic model of this project utilizes lumped representation of the reactions that take place. These groups range from six to ten carbon atoms for normal and

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isoparaffins (P_6-P_{10}), from six to ten atoms of carbon for alkylcyclopentanes, alkylcyclohexans (N_6-N_{10}) and aromatics (A_6-A_{10}). The 12 sets of reactions are considered in different kinetic models such as dehydrogenation and dehydroisomerization of naphthenes to aromatics, dehydrogenation of paraffins, dehydrocyclization of paraffins to aromatics, isomerization or hydroisomerization to isoparaffins, isomerization of alkylcyclopentanes, and substituted aromatics and hydrocracking of paraffins and naphthenes to lower hydrocarbons. The rate equations of these reactions are considered as a simple equation in power law form [1].

The catalyst deactivation equation is also considered as model issued by Liu et al [2].

By the proposed reactor model 30 differential equations for material balances with one energy balance and a pressure drop equation (Ergun equation) were introduced for the plug model reactors. The model equations are used to predict temperature, hydrogen production, composition profiles and reformate yield, coke formation, pressure drop and velocity profile in a commercial continuous reforming unit consisting of a series of three radial catalytic reactors.

The reaction kinetic parameter values were estimated and tuned in order to fit to the outlet stream compositions and exit temperatures of each reactor to the experimental results of the industrial unit. After optimization of kinetic parameters to approach to the actual results, the extended model was validated by replacing the feed specification by a new naphtha feed stream (No.2) with different composition. The results showed a good agreement between predicted and commercially reported amounts with average deviation of 4%. A comparison between the model and actual results are presented by the average absolute relative deviation (%AARD) of the calculated values in Table1.

Table 1: % AARD for reformate, hydrogen and temperature in optimization of the kinetic parameters (No.1) and the new naphtha feed composition (No.2)

	Reformate				Hydrogen		Outlet Temperature of Reactors		
	RON	MON	Aromatic (Vol %)	Flow	H_2 (Mol%)	Flow	1st	2nd	3rd
Feed (No.1)	0.70	0.89	1.77	0.39	0.12	1.75	0.73	0.13	0.07
Feed (No.2)	1.00	1.68	3.56	0.23	0.20	4.88	0.99	0.56	0.30

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Estimation of preliminary process parameters of reactive distillation device

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1. Summary

Reactive distillation (RD) represents a complex process. The multicomponent nature of processed mixtures and also coexistence of reaction and separation at the same time, results in a complicated mathematical model. The major part of this equation system is composed of strongly non-linear equations, solving which an iterative technique has to be used. This is true for both of the different depth approaches, which are describing RD column. Namely, equilibrium (EQ) stage model and more complex non-equilibrium (nonEQ). To obtain solution of the most precise model (nonEQ) following strategy can be applied. The steady state solution from EQ model can be used as a first trial to initialize computation of nonEQ model. Nevertheless, the problem still remains in estimation of initial values for EQ model.

To fill this gap, in following work there will be introduced and explained algorithm, which will estimate preliminary parameters of reactive distillation device. The aim is that the results from this program could be used as first trial values for EQ model and consequently for more rigorous nonEQ model.

Keywords: reactive distillation, mathematical model, initialization parameters

Evaluation of hydrogen production from metallurgical industry's flue gases using AspenPlus™ simulation software

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1. Summary

With the aid of simulations using AspenPlus™, six different types of hydrogen production processes are investigated. Three of them are typical natural gas based processes and the rest use metallurgical industry's flue gases as a feedstock. Compared to the natural gas based processes, flue gas based processes are competitive in terms of the energy consumption. In addition, specific CO_2 emissions into the atmosphere in flue gas based processes are lower than in the reforming cases used as references.

2. Extended Abstract

Introduction

Hydrogen has a great potential as an environmentally clean energy fuel. Hydrogen can be produced from almost any carbon containing source ranging from natural gas to biomass [1]. Steam reforming of natural gas is the preferred process for hydrogen and synthesis gas production today [2]. In different industrial sectors, for example in metallurgical industry, many exploitable gas streams for hydrogen production exist. Coke oven gas, referred to as COG, is produced during the carbonization of coal in coke oven plants. It contains over 50% hydrogen and is a high potential source for pure hydrogen. The chemical conversion of coke oven gas into a hydrogen rich gas can be done by reforming of the crude gas. The objective of the present study is to evaluate, using Aspen Plus simulation software, different processes to produce hydrogen.

Simulations

Computer aided simulation is a useful and practical tool for designing new or alternative processes, particularly in evaluating required material and energy flows. In this study material and energy balances are calculated using AspenPlus™ simulation

software for different hydrogen production processes. Three of them, steam methane reforming (SMR), partial oxidation (POX) and dry reforming (DRY), use natural gas as a feedstock and the rest processes (COGCO$_2$, COGH$_2$O and COGO$_2$) use coke oven gas as a feedstock. The configuration of the reforming process in common form is described in Figure 1. The system comprises heater (1), reformer (2), heat exchanger (3), boiler (4), water gas shift reactor (5) and separator (6).
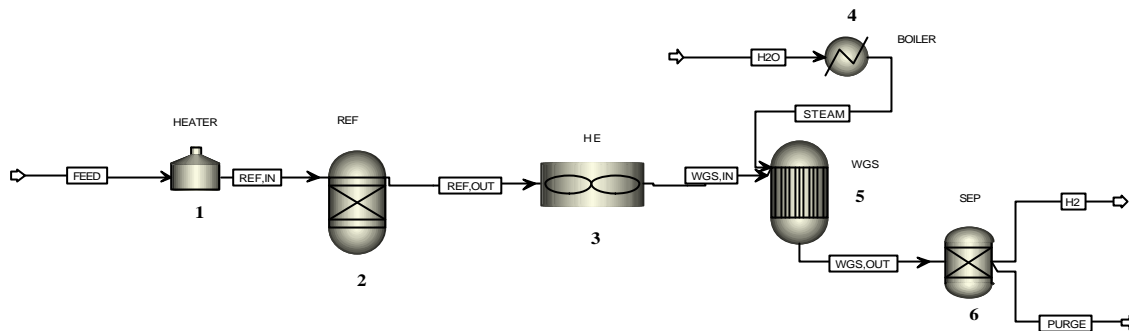

Figure 1: Schematic presentation of the reforming process

Simulation results

Material and energy balances and CO$_2$ emissions are summarized in Table 1

Process	H$_2$ yield [kmol]	Energy consumption [kW]	Specific energy consumption [kW/m^3 H$_2$]	CO$_2$ emissions [kmol]	Specific CO$_2$ emissions [kg/m^{3}H$_2$]
SMR	3.880	292.036	3.076	0.973	0.451
POX	2.777	209.018	3.076	0.988	0.640
DRY	3.780	293.269	3.172	0.979	0.466
COGCO$_2$	1.577	131.312	3.403	0.307	0.349
COGH$_2$O	1.582	131.268	3.391	0.310	0.352
COGO$_2$	1.345	112.473	3.418	0.306	0.409

Table 1: Calculated material and energy balances and CO$_2$ emissions in the reforming processes

Conclusion

The material and energy balances simulated by AspenPlus™ show that it is possible to produce hydrogen using metallurgical industry's flue gases as a feedstock. Compared to the mature natural gas based reforming processes, like e.g. steam reforming, flue gas based hydrogen manufacturing processes are competitive in terms of the energy consumption. In addition, specific CO$_2$ emissions into the atmosphere in flue gas based reforming processes are lower than in the reforming cases used as references.

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Optimization of Ammonia Synthesis Reactor using Genetic Algorithm

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1. Summary

In this work Genetic Algorithm was employed as a powerful method for optimization of an industrial ammonia synthesis reactor. The reactor consists of four adiabatic catalytic fixed equipped beds with three quench flows and an internal heat exchanger. Momentum and continuity equations as well as energy balance equations are solved by finite element discretization in order to obtain temperature and concentration profiles. The kinetics of reaction is assumed to have a Temkin-Pyzhev-type rate equation, whereas properties of the gaseous mixture are represented by the Redlich-Kwong equation of state. The optimization problem was defined based on plant data obtained from an operational ammonia reactor in Razi petrochemical complex at Bojnurd-Iran. An optimum ratio of H2/N2 was obtained from numerical solution of the problem in which Micro Genetic Algorithm was employed. However, for better performance, Simple Genetic Algorithm was used to find the quench flow rates configuration. The results show that the estimated optimum condition can improve the overall product yield by 4.5%.

2. Extended Abstract

2.1. Reactor

The studied Kellogg synthesis reactor is vertical type with four beds. Syngas with nitrogen, hydrogen, ammonia, methane and argon enters the bottom of the reactor. The input feed to the reactor, is first divided into two parts. One part is considered as feed and the other part as quench gas. Because of exothermic reaction in the reactor, quench gas is used to control the inlet temperature of the beds.

### 2.2. optimization of quench configuration with SGA

Simple genetic algorithm (SGA) is applied to reactor model with the following parameters:

Crossover probability=0.9 Mutation probability=0.05 Population size=125 Maximum generations=25.

Table1 shows the optimization results for the reactor and with this new quench configuration, overall product yield can improve 4.5%.

Table 1. Optimum condition of ammonia synthesis reactor

First quench(kg/s)	16.423
Second quench(kg/s)	17.516
Third quench(kg/s)	7.580
overall product(Ton/year)	229790
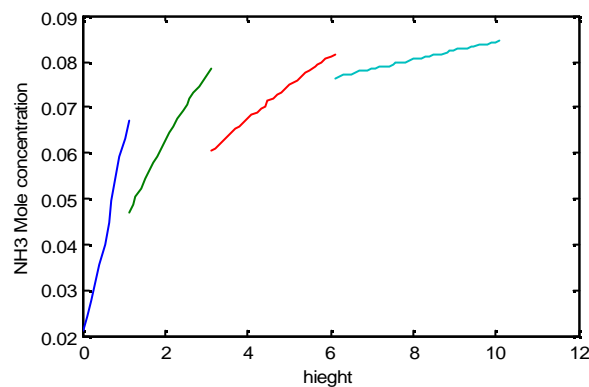
Figure 1. Ammonia concentration profile in four beds

Figure1 illustrates the prediction of concentration profiles for ammonia in four beds and ascention of the concentration profiles demonstrates that the optimum point is in good agreement.

2.3. Optimization of H2/N2 ratio in feed

Regarding to the complexity of the model, in order to find the optimum ratio of H2/N2 in feed, Micro Genetic algorithm with the following parameters is applied to the model, that reduces the number of function evaluations:

Crossover probability=0.9 Mutation probability=0.2 Population size=5 elite count=1.

The estimated *H2/N2* in this reactor is 2.778 and with this optimum ratio, overall product yield has been improved by 1.9%.

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A comparison of binary coding and real-coded genetic algorithms applied to a three-phase catalytic reactor

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1. Summary

Genetic Algorithms (GAs) have been often applied to solve many optimization problems. Such algorithms are based on Natural Genetic and Natural Selection mechanism and some fundamental ideas are borrowed from Genetic in order to artificially construct an optimization procedure. The classical form of Genetic Algorithm used to solve an optimization problem is a binary coding which works with binary strings. There is another form that uses the real values directly that is the real-coded Genetic Algorithm. This paper aims to compare the binary and real-coded Genetic Algorithm in respect to time consuming and the best value of the objective function, in order to point the suitable approach for a Real-Time optimization. That comparison is applied to a three-phase catalytic reactor that produces 2-methyl-cyclohexanol and the problem is postulated as a single objective and constrained optimization problem.

Keywords: binary code, real-coded genetic algorithms, three phase catalytic reactor, real-time optimization.

2. Extended Abstract

During the last decades, evolutionary methods have received a considerable attention and have experienced a rapid development. Genetic Algorithms have been the most popular form of evolutionary algorithms (Baskar *et al*., 2003). Genetic Algorithms work with a set of possible solutions, or chromosomes, called population. Weather the chromosomes are represented as binary strings or the real valued parameters are used. There are many papers that propose different forms to apply genetic operators in a genetic algorithm to both encodes, binary or real. The GA operators work closely with other factors such as population size and encoding in controlling the GA performance (Lowndes *et al*., 2005). Boozarjomehry and Masoori (2007) used both codification forms to a kinetic modeling of many reaction system and the results showed that real coded presented lower performance than binary coding GA.

The aim of this work is the evaluation of the binary coding and real-coded genetic algorithm optimization applied to a three-phase catalytic reactor, a single objective and constrained optimization problem.

In order to compare both codification forms, a Fortran code is used and the selected GA parameters are shown in Table 1.

Population size	50
Number of generation	50
Crossover rate	0.80
Mutation rate	0.05

Table 1 – Selected GA parameters.

Table 2 shows the comparison of the performance of the binary and real-coded GA.

	Binary	Real
Productivity (Kmol/m^{3}s)	$1{,}65 \times 10^4$	$1{,}22 \times 10^4$
Computational Time (min)	3	5
Implementation Difficulties	Codification in binary strings	Tuning of parameters

Table 2 – Comparison of the performance of the binary and real-coded GA.

In Table 1 is possible to see that binary coded GA is more efficient in the optimization of the reactor in terms of computational time and best value of the objective function and handling of the code. In this way, the real-time optimization of the three-phase catalytic reactor may be suitable when a binary coding Genetic Algorithm is applied.

Regards

FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo).

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Optimization of the Culture Medium for the Bioethanol Production Using Genetic Algorithm

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1. Summary

Fuel ethanol, which has a higher octane rating than gasoline, accounts for approximately two-thirds of the world's total annual ethanol production of more than 31 billion liter. The primary reasons for considering the expanded use of biofuel ethanol concern sustainable resource supply, enhanced security and the realization of macroeconomic benefits for rural communities and the economy at large. Bioethanol is generally produced from the fermentation of sugar or materials that can be converted into sugar such as starch or cellulose, with the ethanol extracted in its final form by distillation. One of the basic problems in the bioprocesses development is the optimization of initial experimental conditions. Considering that, there is a great deal of parameters that can influence the outcome of bioprocess, it is of general concern to find a good optimization method. Genetic algorithm (GA) is a stochastic optimization method based on the principals of evolution. Experimental optimization using GA was applied to investigate influence of the composition of synthetic culture medium on fermentation of sugars in the bioethanol production process.

Keywords: bioethanol, fermentation, *Saccharomyces cerevisiae*, optimization, genetic algorithm

2. Extended Abstract

Fermentation medium contained per liter: 20 g bakers' yeast, 50 g glucose, while $FeSO_4 \cdot 7H_2O$, $(NH_4)_2SO_4$, $CaCl_2$, KH_2PO_4, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, and $MgSO_4 \cdot 7H_2O$ were fed in according to the experimental plan. Anaerobic fermentation of glucose by *Saccharomyces cerevisiae* was carried out in shake flasks. 0.5-liter flasks containing 100 mL medium were incubated in the rotation shaker at 30 ºC and 160 rpm and samples were periodically withdrawn from the flasks. Each point of the experimental plan was performed in triplicate. Glucose concentration was analyzed using PAP method - an enzyme-based assay, while ethanol concentration was measured using GC. Effect of initial concentrations of medium composition on final ethanol concentration and ethanol productivity were analyzed using GA

(programme package GALOP). Investigated range of fermentation medium compounds and optimization steps are shown in Table 1. Weighting factor of target functions were set to 1 and written as linear combination of investigated parameters. Mutation occurrence in a program was set to 0.01, the crossover occurrence was set to 0.95 and the number of individuals in a generation was 10.

Table 1 Investigated range of medium compounds and optimization steps (concentrations in g L^{-1})

	$FeSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4$	$CaCl_2$	KH_2PO_4	$CuSO_4 \cdot 5H_2O$	$ZnSO_4 \cdot 7H_2O$	$MgSO_4 \cdot 7H_2O$
lower border	0.002	1	0.05	0.05	0.0005	0.002	0.2
upper border	0.05	20	0.1	5	0.005	0.012	2
optimization step	0.002	1	0.01	0.05	0.0005	0.002	0.02

The principle of experimental optimization was as follows: GA offers the first random population of 10 individuals with given characteristics. Experiments were performed under process conditions given by GA. Concentrations of glucose and ethanol were measured, and after glucose has been consumed experiment was stopped. Maximal ethanol concentration achieved and calculated ethanol volumetric productivity were written in GA as return information, which GA used for further adjustments of next generation. Experimental results obtained for the first (A) and second (B) generation are shown in the Figure 1. Procedure was repeated till process optimum was reached.
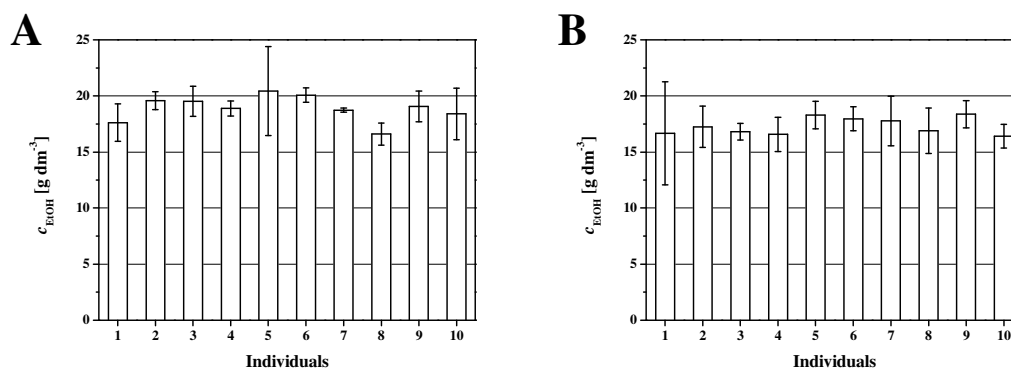

Figure 1. Final ethanol concentrations in first (A) and second (B) generations

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Session T4-10: Tools Integration - CAPE Methods & Tools

Abstract Number	Paper Title & Authors	Included
1603	Conceptual design and optimal tuning of decentralized control loops for chemical plants: Application to the Tennessee-Eastman Process L T Antelo, O Exler, J R Banga, A A Alonso	Yes
1698	A Tabu Search-based algorithm for the integrated process and control system design O Exler, N Faisca, L T Antelo, A A Alonso, J R Banga, E N Pistikopoulos	Yes
1948	A computer bsed tool for integrated design of wastewater treatment plants and advanced control systems P Vega, F Alawneh, L Gonzalez, M Francisco, B Perez b	Yes
2005	CFD-based analysis of the wall effect on the pressure drop in packed beds T Atmakidis, E Y Kenig, E S Kikkinides	No
2135	Systematic analysis and design of the hybrid processes P T Mitkowski, G Jonsson, R Gani	Yes
3218	Model-based optimal control of the production of polyvinyl acetate F Aller, G Kandare, L F Blázquez, D Kukanjac, V Jovana, M Georgiadis	Yes

Conceptual Design and Optimal Tuning of Decentralized Control Loops for Chemical Plants: Applications to the Tennessee Eastman Process

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1. Summary

In this work we describe a conceptual approach which has been recently developed to design efficient decentralized control structures for flexible chemical plant operation. The approach combines concepts from thermodynamics, inventory networks and process control to construct a set of stable and robust decentralized control candidate structures. Such candidates consist of inventory control loops designed so to ensure convergence of the mass and energy inventories to given references and thus guaranteeing stability of the extensive properties despite plant disturbances or even parameter uncertainty. Since the loops are defined over inventories, they contain almost every possible decentralized alternative. In this way, and by physically realizing the inventory control loops over the available degrees of freedom, the approach can be employed to construct a superstructure only containing stable (and robust) decentralized control candidates. It is on this set that NLP or MINLP problems can be defined to select the best operational alternative. The different aspects of the conceptual design approach will be illustrated on the well known Tennessee-Eastman Process.

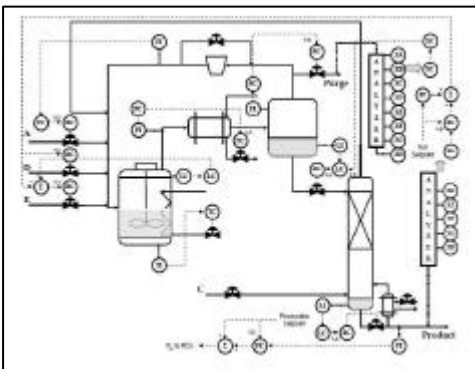*Keywords:* Plant-wide control, optimal tuning, plant stability.

2. Extended Abstract

The *thermodynamic-based control* (TBC) design procedure developed by Antelo *et al.* (2006, 2007) tried to provide a systematic to the framework of the plant-wide control. In this work, the *TBC* approach is applied to derive robust decentralized controllers for the Tennessee Eastman Process (Downs and Vogel, 1993), ensuring the global stability of the plant. As a first step in the design, the TEP is represented as a *process network* (PN) composed of coupled mass and energy inventory layers. After this formal representation of the process, *conceptual mass and energy inventory control loops* in every node (defined as a well-mixed homogeneous material region) of the network are designed to drive the system to a compact set ? defined by constant inventories, because it is over this set where we can ensure that the process system is passive and stability can be proved (Alonso and Ydstie, 2001). The next step in the TBC design is to *realize* the proposed conceptual inventory control loops using the physical inputs-outputs of the process since the total inventory fluxes can be the result of combining multiple convective outflow streams. This fact leads to a *superstructure* of control candidates for the TEP. It must be pointed out that all the TBC structures inside this superstructure satisfy that the inventories in the process will converge to a given convex set,

and therefore output stability is guarantee. We have considered a subset of the global set candidates, which are derived from the original TBC control proposal by Antelo *et al.* (2006) (Figure 1), and they are related to the reactor control loops. In the original control structure, the *E* Feed and the condenser coolant flow are used to close the reactor level and pressure control loops, respectively. As an alternative to establish these loops, we consider the *D* Feed and the purge flow, respectively. In order to determine the best control alternative among the proposed ones, a new binary vector *b* is added to our system dynamics. These 0-1 variables express which of the four control strategies is being used, and they are defined as: $b_1 \in \{0,1\}$ (*E* feed); $b_2 \in \{0,1\}$ (*D* feed); $b_3 \in \{0,1\}$ (Condenser coolant) and $b_4 \in \{0,1\}$ (Purge flow). Therefore, the TBC proposal by Antelo *et al.* (2006) will be characterized by the vector $b = (1,0,1,0)^T$. According to this discussion, the MINLP problem employed to set the best alternative can be stated as follows:

$$\min_{v,b} J(x,v,b) \quad s.t.\ f(\dot{x},x,p,v,b,t) = 0; \quad h(x,p,v,b) = 0; \quad g(x,p,v,b) \geq 0;$$
$$b_1 + b_2 = 1;\ b_3 + b_4 - 1 \geq 0;\ v_l \leq v \leq v_u;\ b_l \leq b \leq b_u \tag{1}$$

where *J* is the objective function (the operating costs of the TEP), *f* is the set of differential and algebraic equality constraints describing the system dynamics, and *h* and *g* are possible equality and inequality path and/or point constraints. Finally, $b \in \{0, 1\}^4$ is the vector of binary variables (0-1 variables) and $v \in \mathbb{R}^{36}$ are the continuous variables (the *PI controller parameters* to be optimal tuned). In order to solve this MINLP problem, and as the global component of the methodology, a procedure based on extensions of the Tabu Search (TS) algorithm is applied. Regarding the local solver, we have used an adaptation of TS to mixed-integer nonlinear optimization problems, called *Mixed-Integer Tabu Search* (MITS) (Exler *et al.*, 2007). The solution obtained by MITS for the binary vector is $b = (0,1,0,1)^T$. This vector defines the new realization of the control loops for the pressure and the level in the reactor by acting over the purge and the *D* Feed, respectively.

Figure 1. A TBC structure (Antelo et al.,2006)

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A Tabu Search-based algorithm for the integrated process and control system design

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1. Summary

In this contribution we focus on the area of integration of process and control system design. The interaction of process design and control is formulated as a mixed-integer dynamic optimization (MIDO) problem and by using the control parameterization approach we obtain as a result a finite dimensional mixed-integer non-linear programming (MINLP) problem. Because of the multimodal structure of these problems we use a global optimization strategy. The hybrid algorithm MITS is presented, which uses a combinatorial component, based on Tabu Search, to localize promising attraction basins, and a local solver, which is activated whenever such a promising area is located. Numerical results are presented for the optimization of the well-known Tennessee Eastman Process (TEP).

Keywords: Integrated Process and Control System Design, Mixed-Integer Nonlinear Programming, Metaheuristic, Tabu Search

2. Extended Abstract

During the last decade, the importance of a simultaneous (integrated) process design approach, considering operability together with the economic issues, has been widely recognized (e.g. Pistikopoulos and Ross, 1999). The aim is to obtain profitable and operable process and control structures in a systematic way. Both the process design characteristics, control strategies, control structure and controller's tuning parameters have to be selected optimally in order to minimize the total cost of the system while satisfying a large number of feasibility constraints in the presence of time-varying disturbances. The arising optimization problem is a challenging mixed-integer dynamic optimization (MIDO) problem. The multimodal (non-convex) nature of this problem has been highlighted in the open literature. As a result global optimization

(GO) techniques for nonlinear dynamic systems are used which have received increased attention from engineers, mathematicians and computer scientists.

There are different approaches to solve this MIDO problem, such as dynamic programming, control parameterization and complete discretization. This work focuses on the control parameterization approach, obtaining as a result a finite dimensional mixed-integer nonlinear programming (MINLP) problem. An adaptation of the metaheuristic Tabu Search (TS) which was originally developed by Glover (see Glover and Laguna, 1997) is used to solve the MINLP. The developed algorithm called Mixed-Integer Tabu Search (MITS) is an advancement of the approach proposed by Battiti and Tecchiolli (1996).

The basic idea of the algorithm MITS can be summarized as follows. MITS contains of a combinatorial component and a local solver. The aim of the combinatorial component is to locate areas in which good local minima are expected. To increase the quality of a local solution we use a Mixed-Integer Sequential Quadratic Programming algorithm called MISQP by Exler and Schittkowski (2006).

Numerical results are presented for the optimization of the well-known Tennessee Eastman Process (TEP) by Downs and Vogel (1993), which has been widely used in the literature as a case study due to its challenging properties from a control engineering point of view.

Acknowledgement

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Computer Based Tool for Integrated Design of Wastewater Treatment Plants and Advanced Control Systems

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1. Summary

The objective of this work is the development of a Computer Based Tool for the Simulation, and Integrated Design (ID) of Activated Sludge Processes and their Control Systems. Integrated Design methodology allows for the simultaneous design and evaluation of plants and control system parameters. In the paper, the ID problem is stated mathematically as a constrained non-linear multi-objective optimization problem, in which economic and control objectives are considered together with some constraints. The solution of the problem is obtained following a numerical cost optimization procedure that uses dynamic models together with a set of predefined constraints to evaluate plant dimensions, operation points and controller parameters. The constraints are selected to ensure that the process variables and some controllability measures lie within specified bounds. The integration of Numerical Optimization, Model Identification, Dynamical Model Simulation and Model Based Predictive Control, is the most relevant feature of the package and the key point to succeed in the design of flexible processes reducing the operation costs while legal specifications on the quality of the treated water are fulfilled. Some of the available models and data records, representing real Wastewater Treatment Plants, can be taken as starting point either for being redesigned or just as simulation models (to be compared with others, for its control system design, etc.).

Keywords: Process and Control Integrated Design, Advanced Control, Multi-Objective Optimisation, System Identification.

2. Extended Abstract

The public view concerning wastewater treatment these days is fairly positive. The EU Urban Water Directive (91/271/EC) adopted years ago, together with the recently adopted EU Water Framework Directive (2000/60/EC), define stringent requirements for urban wastewater treatment and a time frame for the step-wise implementation by the member countries. The application of the directive has lead to the construction of new plants and redesigning of existing ones with the aim of reducing the environmental impact as much as possible. The costs associated to these actions have been very important. In this sense, the norm imposes several objectives, to be achieved by engineers that should be pointed out. First, the design of more complex

but more flexible plants considering the new environmental restrictions facilitating their adaptation to future legislations, avoiding redesigns. Second, a stricter operation and control at must be guaranteed. To achieve the above mentioned aims, it is necessary the use of Integrated Design Techniques, combining Optimization and Advanced Control, together with Computer Aided Tools to allow for the simultaneous design of plants and control systems at lower costs.

Within this context, the objective of this work was the development of a Computer Based Tool for the Simulation and the Integrated Design of Activated Sludge Processes and their Control Systems to support engineers during the complex task of designing and controlling water Treatment Plants.

2.1 Integrated design methodology

Integrated Design problem is stated mathematically as a constrained non-linear multi-objective optimization problem, in which economic and control objectives are considered together with some constraints. The solution of the ID problem is obtained following a constrained numerical cost optimization procedure that uses dynamic models and real data records of disturbances together with a set of predefined constraints to evaluate the plant dimensions, the optimal operation points and the control system parameters.

2.2 The computer based tool

The objective of the application of an optimization procedure is to find values of the parameters describing the plant dimension, and to find values of the parameters describing the control strategy so that minimum possible adverse impacts of the strategy are applied to the environment. Solutions resulting not only in minimum impacts but also those leading to less detrimental impacts than the currently applied strategies minimizing a cost functions.

The tool contains considerable number of user options like Plant Design, Integrated Design (Plants + controller), various types of controllers (PID, MPC....etc), different optimization algorithms, several cost function formulae, simulation with/without faults, control system design (PID, MBPC, GMV…etc). The package is an integrated tool for system's optimization which integrates programs for the optimization and predictive control of WWTP (Activated Sludge Processes), simulators (SIMULINK), computer aided control system design (Matlab, toolboxes) and a very friendly user interface (GUIDE toolbox).

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Systematic analysis and design of the hybrid processes

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1. Summary

The hybrid processes involve integrated operations of at least two unit operations and offer opportunities for process improvements, which otherwise would probably make the original processing route infeasible. In general, two types of hybrid processes are distinguished: reaction-separation (R-S) and separation-separation (S-S). In the presentation the systematic model-based framework for design and analysis of hybrid processes is given along with the generic models developed for it and associated computer-aided methods and tools. The methodology is highlighted through application examples for R-S and S-S tasks.

Keywords: hybrid process design, process integration, conceptual design

2. Extended Abstract

The design of the R-S and S-S hybrid processes have to take into account the performance of each constituent element and the optimisation of the design must take into consideration their interdependency. The systematic model based framework for design of hybrid systems presented previously [1] has been extended and improved. The objective is to identify the best possible process set-ups for R-S and S-S systems with desired constraints of process parameters like yield, reaction time, selectivity, product purity, energy consumption, etc. The design algorithm consists of four main steps and it is presented on Figure 1 along with associated tools from ICAS family.

Depending on reaction requirements and/or selection of separation techniques, the methods for solvent and membrane selection are used. Steps 3 and 4 require appropriate models which would allow the simulation of various operational scenarios for different configuration of hybrid processes. Analysis of hybrid process operation requires analysis of different process models. These models could be sufficiently simplified by merging them, for example, embedding membrane sub-models into the reactor model and thereby leading to the easier hybrid process analysis. Note that the process models also consist of the property sub-models for both unit operations.

The proposed model-based framework is supported with two case studies. The enzymatic esterification of cetyl oleate is an example of R-S integration. In that case,

the possibility of integrating pervaporation with reactor is proposed because the product yield can be improved by the removal of water which is a by product. Impacts of several operational conditions at hybrid semi-batch configuration have been study. It is important to observe that the increase of membrane area from 0.0288 m^2 to 0.0576 m^2 does not give significant improvement of the process in terms of process yield. The feasible membrane which would meet that design is a commercially available polyvinyl alcohol membrane (PERVAP1005, GFT).
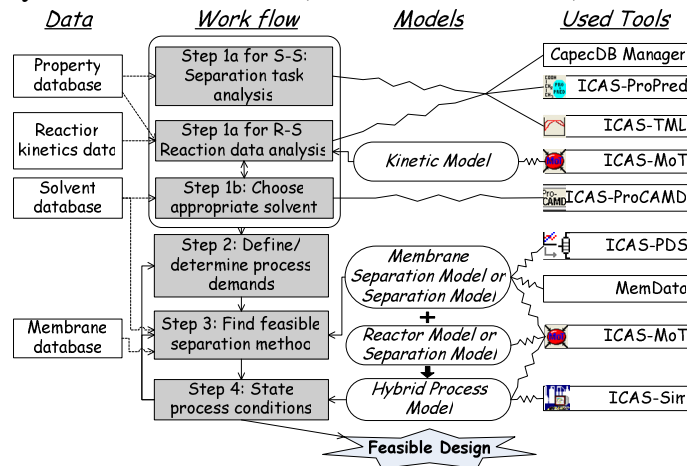

Figure 1 Methodology of design/analyze hybrid process system

The second case study is an example of S-S task. The dehydration of acetic acid is a difficult and high energy demanding part of solvent recovery in manufacturing of terephthalic acid. Based on the driving force approach [2] two process design alternatives have been identified. In the first design, DFM (distillation followed with membrane unit), the membrane-based separation (MBS) unit is use to enrich the top product of distillation column to the required purity. In the second design, DSM (distillation with side membrane unit), the MBS treats the draw stream from the distillation column in order to enhance the separation in the difficult region. The drawback of the first scheme is the necessity to use a highly selective MBS ($\alpha = 50$). However, for the low selective MBS modules ($\alpha = 2.25$) the second design will give improvement in terms of process heat duty in comparison to the base case design. The rather small influence of cut values (θ) on both designs is observed (Figure 2a and 2b)

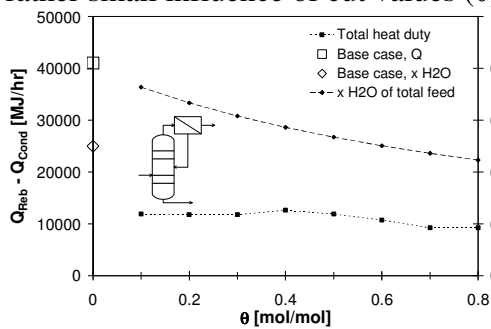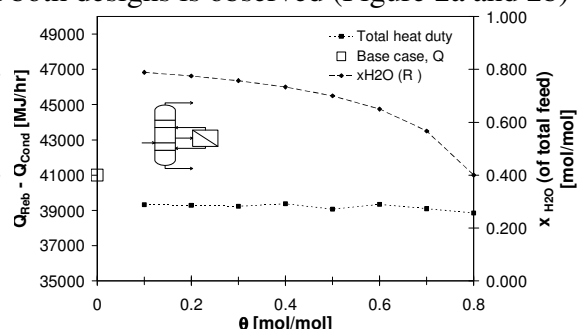

Figure 2a Heat duties for DFM configuration   Figure 2b Heat duties for the DSM configuration

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Model-based optimal control of the production of polyvinyl acetate

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1. Summary

The paper presents an optimal control strategy for the increase of polyvinyl acetate production in polymerization plant. The control strategy consists of two control loops: temperature control and control of monomer concentration in the aqueous phase. In the latter case the concentration is not measured, so it was estimated from the calorimetric data using a dynamic model. The control strategy has been evaluated by simulation using a complex model of polymerization process.

2. Extended Abstract

In the environment of increasing demand and competitiveness the polymer manufacturers need to augment the production at the lowest cost. This work considers the polymerization plant in Mitol factory in Sežana, Slovenia, which is nowadays working over ninety per cent of its capacity. The preliminary analysis of the production process of polyvinyl acetate in Mitol revealed that there are not bottlenecks in the process. To increase the production without further investments a reduction of the duration of the reaction should be achieved. The main variables affecting the duration of the reaction and thus the productivity are: the temperature in the reactor, the initial amount of monomer, the subsequent feed rate of monomer and the addition of initiator.

Currently the temperature is controlled by manually adding the initiator. This can lead to the offset and oscillations of the reactor temperature, affecting both the final quality and the duration of the reaction. The ratio between the amount of monomer charged in the beginning and the amount charged during the reaction is feasible, but it has never been optimised. The feed rate of the monomer is kept constant. The initiator is introduced manually at the operators' discretion. During the polymerization the operators have the responsibility to decide when to add more initiator, and when to start the addition of monomer. Therefore, the

possibilities to increase the production of polyvinyl acetate in Mitol are the enhancement of the temperature control through the optimal addition of initiator and the optimization of the monomer addition profile. The constraints imposed on the objective function consider the desired final conversion and particle size of the polymer product. Since the real plant cannot be used to perform experiments, a model has been developed on which the optimization algorithms can be applied. The details of this model can be found in a previous paper.

An optimal control strategy for the polymerization process has been designed. This strategy aims to reduce the time of the batch and so increase the productivity. The two variables controlled are the temperature (T) and the concentration of monomer (Maq) in the aqueous phase (Fig. 1). The temperature data are collected on-line by a sensor introduced in the reactor. The concentration of monomer is not directly measured; hence it has to be estimated. A dynamic model of the reactor estimates the rate of polymerization from the calorimetric data. The resulting control strategy has been validated off-line, based on the previously developed model, will be implemented in the factory. The four main variables identified by the Mitol Company as characteristic for the final product quality: the final conversion, particle size, solids content and viscosity, act as the end point constraints. The maximum temperature in the reactor constitutes the path constraint.

In this paper an optimal control strategy for the addition of the initiator and the monomer has been designed. The objective of the optimization is the reduction of the time of the reaction while keeping the quality variables within acceptable values.
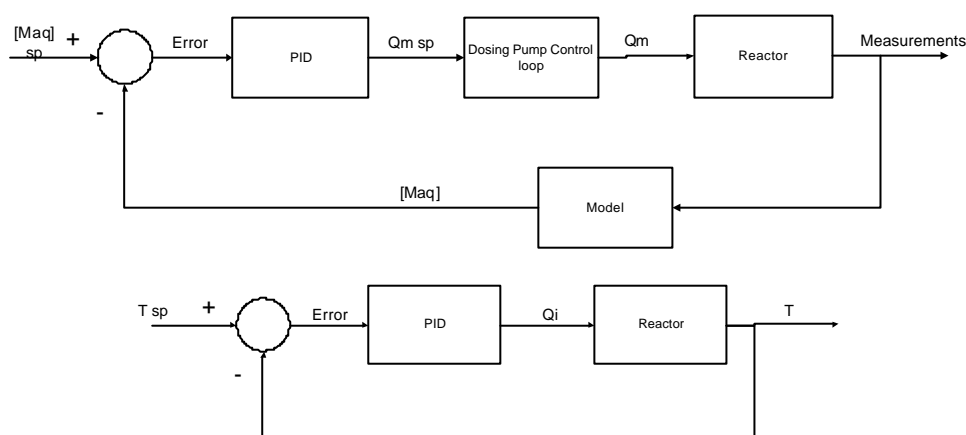

Figure 1: Control of monomer concentration in aqueous phase (Maq) and temperature (T) by adjusting the addition of initiator (Qi) and monomer (Qm).

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Session T4-10P: Tools Integration - CAPE Methods & Tools - Poster

Abstract Number	Paper Title & Authors	Included
215	Nonlinear Modeling Of A Reactor-exchanger By Using Narx Neural Networks Y Chetouani	Yes
1238	Design of Flexible Utility Systems D Zheng, J K Kim, W Kwapinski, S Perry, R Smith	Yes
2083	Design of experiments and empirical models for up to date burners design for process industries P Belohradsky, V Kermes, P Stehlik	Yes
2287	On the application of model reduction techniques for dynamic optimization of chemical plants operation B Dorneanu, C S Bildea, J Grievink, V Jovan	Yes
2829	Modelling and optimization of single and multi-layer pressure swing adsorption system D Nikolic, A Giovanoglou, M C Georgiadis, E S Kikkinides	Yes
3362	CAPE-OPEN – Aspen Plus based mathematical modeling for integrated simulation of an entrained bed gasifier M Pérez-Fortes, A Bojarski, G Kopanos, S Ferrer-Nadal, N Mitta, C A Pinilla, J M Nougués, E Velo, L Puigjaner	Yes
3437	Making value with order management for agent based systems M Badell, G Kopanos, J M Lainez, L Puigjaner	Yes
3752	Comparison of liquid discharge from a tank through circular and irregular shape orifices M Dziubinski, L Przelazly	Yes

Nonlinear modeling of a reactor-exchanger by using NARX neural networks

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1. Summary

The main aim of this paper is to establish a reliable model of a process behavior under its normal operating conditions. The use of this model should reflect the true behavior of the process and allow to distinguish a normal mode from an abnormal one. In order to obtain a reliable model for the process dynamics, the black-box identification by means of a NARX (Nonlinear Auto-Regressive with eXogenous input) model has been chosen in this study. It is based on the neural network approach. This paper shows the choice and the performance of the neural network in the training and test phases. An analysis of the inputs number, hidden neurons and their influence on the behavior of the neural predictor is carried out. Three statistical criteria; Aikeke's Information Criterion (AIC), Rissanen's Minimum Description Length (MDL) and Bayesian Information Criterion (BIC) are used for the validation of the experimental data. A reactor-exchanger is used to illustrate the proposed ideas concerning the dynamics modeling. The model is implemented by training a Multi-Layer Perceptron (MLP) Artificial neural network with input-output experimental data. Satisfactory agreement between identified and experimental data is found and results show that the model successfully predicts the evolution of the outlet temperature of the process.

Keywords: reliability, safety, modelling, neural network, ARX, nonlinear identification

2. Extended Abstract

Process development and continuous request for productivity led to an increasing complexity of industrial units. In chemical industries, it is absolutely necessary to control the process and any drift or anomaly must be detected as soon as possible in order to prevent risks and accidents. Moreover, detecting a fault appearance on-line is

justified by the need to solve effectively the problems within a short time (Chetouani, 2007a; Chetouani, 2007b). This research concerns the development of fault detection modules intended to supervise the functioning state of the system (Chetouani, 2006a). The former has to generate on-line information concerning the state of the automated system. This state is characterized not only by control and measurement variables (temperature, rate, etc.), but also by the general behavior of the process and its history, showing in time whether the behavior of the system is normal or presents drifts. In the context of numerical control, fault detection and isolation (FDI) proves a vital complement to the adaptive means of dealing with instationarities in nonlinear highly non-stationary systems. Under normal conditions, the fault detection module allows all information to be processed and managed in direct liaison with its general behavior. In other case, it detects any anomaly and alerts the operator by setting on the appropriate alarms. The intrinsic highly nonlinear behavior in the industrial process, especially when a chemical reaction is used, poses a major problem for the formulation of good predictions and the design of reliable control systems (Cammarata et al., 2002). Due to the relevant number of degree of freedom, to the nonlinear coupling of different phenomena and to the processes complexity, the mathematical modeling of the process is computationally heavy and may produce an unsatisfactory correspondence between experimental and simulated data. Similar problems arise also from the uncertainty for the parameters of the process, such as the reaction rate, activation energy, reaction enthalpy, heat transfer coefficient, and their unpredictable variations. In fact, note that most of the chemical and thermo-physical variables both strongly depend and influence instantaneously the temperature of the reaction mass (Chetouani, 2006b). One way of addressing this problem is the use of a reliable model for the on-line prediction of the system dynamic evolution. However, designing empirical models such as the black-box models is unavoidable (Leontaritis et al., 1985). The purpose of this identification is to establish a reliable model of the dynamic behavior of a process like a reactor-exchanger. This reliable model enables to reproduce the process dynamics under different operating conditions in a normal mode. The main aim of this paper is to establish a reliable model of a process behavior under its normal operating conditions. The use of this model should reflect the true behavior of the process and allow to distinguish a normal mode from an abnormal one

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2

Design of Flexible Utility Systems

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1. Summary

A novel methodology for the design and dynamic optimisation of site utility systems has been developed to improve operability and cost-effectiveness of utility systems. Site utility systems must satisfy steam and power demands that change significantly according to process users' demands. Decisions on operating scenarios should be made by considering variable conditions. There exist transient periods in which operating conditions of utility systems are changed from one scenario to another. In this study, such transient behaviour is systematically investigated by using dynamic modelling and simulation of site utility systems, which enables flexible utility systems to be designed. Operating policies at steady-state are optimised to maximise the system efficiency or minimise costs, while variation of steam conditions (flowrate, pressure) are kept within acceptable bounds. Transient analysis is performed to check the feasibility of utility system design, analyze the operability and reliability of utility systems, and provide operating strategies in both steady-state operations and transient periods. Better understanding of transient phenomena can lead to cost savings as better use of equipment and/or less using standby capacity. A case study is presented to illustrate significant benefits which can be gained from the modelling framework and transient analysis.

Keywords: flexible utility systems, transient analysis, dynamic models

2. Extended Abstract

The design and optimisation of site utility systems is one of the most challenging topics in process engineering, as the complexity of equipment networks and choice of operating conditions present significant challenges to optimise utility systems in practice.

Site utility systems are inevitably operated with different scenarios or operating conditions, due to variable conditions, such as different electric power tariffs, changing load in processes and variable ambient temperature. Therefore, utility systems should be flexible enough to change operating conditions (or scenarios) from one to another at minimum penalty and disturbance to the overall systems. Simplified dynamic models have been developed for transient analysis in the periods of such changes.
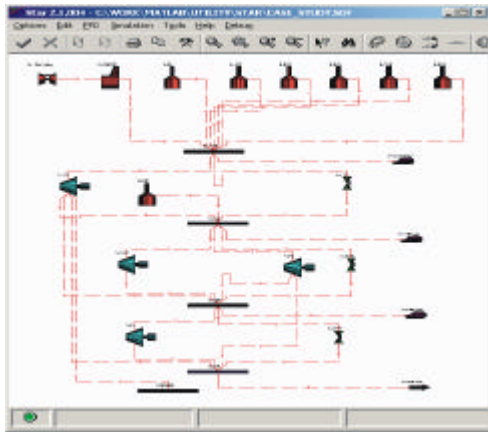
Figure 1: site utility system in case study

The proposed methodology aims to provide an optimised equipment network structure together with operating policies to minimise total operating cost, improving flexibility, operability and stability of the utility system. The design procedure is summarized as follows: (1) the site configuration is set up, including economic and physical conditions, equipment properties, site steam and power demands, and safety constraints, etc.; (2) equipment network structure design and operating scenarios identification are carried out based on steady state methodology; (3) operating policies, such as boiler working loads and steam distribution paths, are optimised to minimize operating cost, while variation of steam conditions in scenario-transition period, simulated based on dynamic models, is kept within acceptable bounds.

A case study (Fig. 1) presents the application of proposed methodology on a site utility system, which comprises of five working boilers, a gas turbine with heat

Figure 2: Power changes produced by turbine 4 for different scenarios

recovery steam generator and two spare boilers. A transient situation is considered by introducing an event of breakdown in Boiler 2 At time 100s, VHP steam generation decreases sharply and is later recovered by two spare boilers. In the transient period, the loss of site power or steam differs according to different operating policies, shown in Fig. 2. Finally, an optimised operating policy is achieved, which achieves minimum operating cost with acceptable power/steam loss.

Acknowledge

Design of experiments and empirical models for up to date burners design for process industries

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1. Summary

At present period the application of complex models based on computational fluid dynamics (CFD) increases. At the same time, the cost of full experiments with high number of factors grows rapidly. Due to high cost of experiments therefore grows the importance of properly designed experiments and statistical data analysis. Statistical experimental design and analysis is an indispensable tool for experimenters and one of the core topics in a statistics curriculum. The present work deals with the design of experiment with high number of factors for diffusion gas burners. In the experiment, purposeful changes are made to the individual design parameters of the system while observing the changes in the output response, especially concerning the formation of nitrogen oxides. Priority is however always given to the functionality of the burner (namely flame stability). This paper shows a convenient way how to set up the plan of expensive and time consuming experiments in testing industrial burners.

Keywords: design of experiments, statistical data analysis, empirical model

2. Extended Abstract

Experimental approach cannot be fully substituted by computational modelling, which applies also to tuning of design of new burners. Due to the high cost of experiments therefore grows the importance of careful experiment planning and statistical data analysis. But also the costs of carrying out computational parametric analysis are significant. Therefore, careful consideration must be given to planning of physical experiments as well as numerical parametric studies. For this purpose, advanced statistical tools should be used to minimise costs and maximise efficiency.

The present work deals with the design of experiment from its preparation, through experiment planning, that follows preliminary considerations about the model, implementation of the experiment and subsequent evaluation. Furthermore, we point

out the problems of the performing of full experiment with high number of factors and outline the possibilities of creating the basis for fractional experiment. The considerations are demonstrated on experiments with diffusion gas burners, where investigation focuses on the influence of individual design parameters on the formation of nitrogen oxides. Importance for industrial practice, equipment and consequently processes is demonstrated.

A common goal in many types of experiments is to characterize the relationship between a response and a set of quantitative factors of interest to the researcher. The experiment presented in this work is conducted at the most up to date experimental research facility for testing diffusion gas burners. The test facility and experimental burner enable to set up high number of design parameters, such as direction of secondary fuel jet, radial and axial shift of secondary fuel jet and others. The execution of full experiment is not reasonable due to high number of runs, high cost and time consuming character of the experiments.

Response surface methodology is an effective mathematical and statistic technique useful for the modelling and analysis of such problem. The objective of response surface methodology is to determine the optimum operating conditions for a system or to determine a region of the factor space in which operating specifications are satisfied.

In most response surface methodology problems, the form of the relationship between the response and the independent variables is unknown. Thus, the first step is to find suitable approximation. If the response is well modelled by a linear function of the independent variables, then the approximating function is the first-order model. If there is a curvature in the system, then a polynomial of higher degree has to be used, such as the second-order model. The method of least squares is used to estimate the parameters in the approximating polynomials. The model parameters can be estimated most effectively if proper experimental design is used to collect the data. Designs for fitting response surfaces are called *response surface designs*. The experimental design employed in this work is called a central composite design.

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On the application of model reduction techniques for dynamic optimization of chemical plants operation

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1. Summary

The paper investigates the application of model reduction techniques in the context of dynamic optimization. A case study it is considered: the iso-butane alkylation as a dynamic optimization problem. The advantage of considering the inherent structure that exists in a chemical plant it is demonstrated. The recommended procedure is to apply model reduction to individual units of the plant, and then to couple together these reduced-order models.

Keywords: model reduction, dynamic optimization, pharmaceutical synthesis, green chemistry, green engineering, solvent selection

2. Extended Abstract

In today's competitive environment, high economical performance of chemical plants is achieved not only by cost-effective steady state integrated design, but also by continuously responding to market conditions through dynamic operation. In the first case, developing plantwide control structures to achieve stable operation is of paramount importance. In the second case, economical optimality is achieved by dynamic optimization techniques.
Both design of plantwide control structures and dynamic optimization require models of the chemical plant. The quality of these models is crucial for achieving the objective: the models must represent the plant behaviour with sufficient accuracy but the complexity must be limited because both applications require repeated solution during limited time.
Model-order reduction and model simplification might offer a solution. Several linear and nonlinear techniques have been developed and their applications to different case studies reported, showing that a significant reduction of the number of equations can be achieved. However, the benefit is sometimes partial, because the problem structure is destroyed and there is little or no decrease of the solution time.
In this contribution we investigate the application of model reduction techniques in the context of dynamic optimization. More specifically, we focus on the derivation and use of reduced-order models for the design and implementation of optimal

dynamic operation in large-scale chemical plants. A case study is considered: *iso*-butane – butene alkylation as a dynamic optimization problem (Figure 1). We demonstrate the advantage of considering the inherent structure that exists in a chemical plant. This structure arises from existence of units or groups of units that are connected by material and/or energy streams, and mirrors the decentralization of the control problem. The recommended procedure is to apply model reduction to individual units of the plant, and then to couple these reduced-order models. This procedure is flexible as the reduction accuracy can vary from unit to unit, is able to retain the nonlinearity of the original plant, and preserves the significance of model variables. The sparsity of reduced-order model has a beneficial effect on the solution time. Moreover, the modularity of the reduced-order model can become very useful in case of future plant changes.
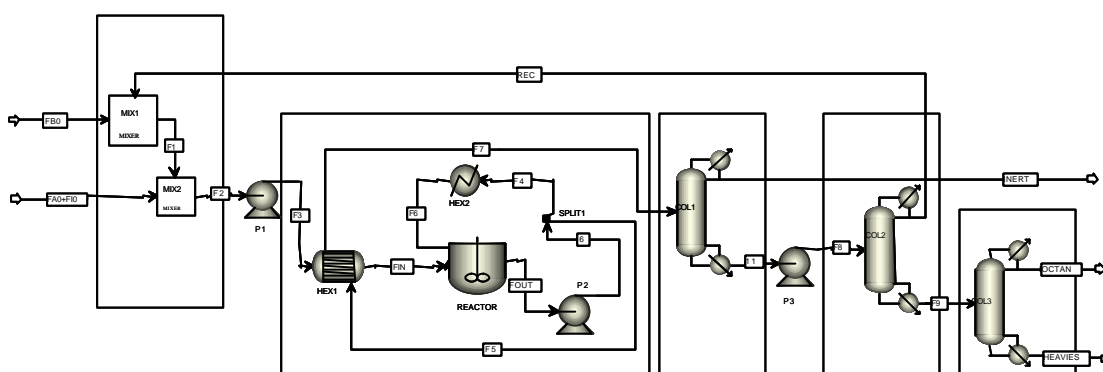

Figure 1: The proposed structure for the *iso*-butane – butene alkylation plant

In contrast, applying the reduction techniques to the overall model of the plant does not work, because numerical difficulties when dealing with large unstable systems. Even after stabilizing the plant (after decomposition and analysis of individual units) and model reduction, no decrease of solution time is observed. Additionally, the reduced-order model contains variables that no longer represent physical quantities from the real plant and the nonlinearity of the real plant is not captured, even when nonlinear techniques are applied.

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Modeling and optimization of single and multi-layer pressure swing adsorption systems

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1. Summary

This work presents a generic modeling framework for separations of gas mixtures using multibed pressure swing adsorption systems. The effects of several design and operating characteristics in a separation of hydrogen from steam-methane reforming off gas have been investigated and the formal optimization approach has been employed to address two typical industrial problems: (i) to optimize operating conditions in order to minimize the energy consumption per product unit for a given adsorbent columns design characteristics; (ii) to find the optimal distribution of activated carbon to zeolite adsorbents in order to maximize product purity and recovery for a given operating characteristics of the process.

Keywords: gas separations, multibed pressure swing adsorption

2. Extended Abstract

A generic modelling and optimization framework for separations of gas mixtures using multibed pressure swing adsorption systems is presented. The framework relies on a systematic approach for the automatic generation of the underlying flowsheet (all feasible bed interconnections and their topology) and complex operating procedure for a given number of beds. Important features of the framework also include four different mass balance theories, three thermal operating modes, single or multiple layers of adsorbents and complex, gas valve controlled bed interactions. All models have been implemented in PSE's gPROMS modelling environment.

The framework has been employed in a separation of hydrogen from steam-methane reforming off gas using single and multi-layered adsorbents. The impact of single and multilayer activated carbon and zeolite adsorbents on the process separation

efficiency has been investigated. The effect of number of beds on the product quality (purity and recover) has been analysed and trade-offs between capital and operating costs are revealed. Furthermore the effect of operating conditions as well as the design characteristics of the adsorption column on the overall efficiency of the PSA flowsheet have been critically discussed (such are duration of operating steps, feed pressure, particle radius, feed and purge gas flowrates, column length and diameter, and carbon-to-zeolite ratio). Then, a formal optimization approach has been employed to optimize the design and operating conditions of the underlying PSA systems. Two different problems have been addressed: (i) to minimize the energy consumption per product unit for a given adsorbent productivity and minimum requirements in product purity and recovery; (ii) to maximize product purity and recovery for a given adsorbent productivity and column geometry while optimizing the operating characteristics of the process and the distribution of activated carbon to zeolite adsorbents in the bed(s).

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CAPE-OPEN – Aspen based mathematical modelling for integrated simulation of an entrained bed gasifier

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1. Summary

In this work a mathematical model of an entrained bed gasifier unit has been developed for enhanced synthesis gas production. The gasification model is divided into five stages: pyrolysis, volatiles combustion, char combustion, gasification and a final gas equilibrium zone. Energy integration within the reactor section has been carried out by accounting all the energy consumed and generated by the process. Furthermore, this model is envisaged to evaluate energy losses as well as external heat supplies or refrigeration requirements in order to keep a steady reaction operation. Three different temperature zones have been considered, and the whole residence time has been estimated with pneumatic transport equations. Aspen Hysys (AH) is the chosen platform for the process simulation. The user models have been developed using Visual Basic and integrated into the global simulation by means of the CAPE-OPEN (CO) interface standards.

Keywords: Process simulation, coal gasification; CAPE-OPEN; Software Components, Interoperability

2. Extended Abstract

The produced gas in gasification of coal and solid waste is utilized in gas turbines of Integrated Gasification Combined Cycle (IGCC) systems for power production. Such systems are quite complex to model and usually lack of detailed integrated models which could improve their flexibility and performance. Within the different types of gasifiers contemplated in IGCC systems, entrained bed reactors achieve the highest gasification rates. Aspen Hysys (AH) is chosen as the platform for the overall process simulation of the entrained bed gasifier because of its capability for developing custom unit operation models as extensions, which become part of the simulation as any other AH object. Available AH models have been used for conventional process operations, while custom models have been developed for more

specific stages within the gasification process, as pyrolysis, char combustion and gasification reactions. These user models have been developed using Visual Basic and integrated into the global simulation by means of the CAPE-OPEN (CO) interface standards. CO standards provide a suitable environment for this purpose, since they allow the creation of completely custom modules which are easy to plug and use thus facilitating the handling of complex models ready to interact with any compliant commercial simulation platform [1]. These last features allow the models to be portable, thus facilitating their straightforward integration to different simulation schemes [2] and enhancing the potential of simulation to deal with complex systems modelling, validation, operation and optimization. Figure 1 depicts the basic connectivity between the different members involved. Integration of different models is accomplished in AH, which acts as the CO simulation environment (COSE) providing the basic connectivity within models components and the thermodynamic framework needed. Custom model extension communicates with AH by means of the CO interface standards.
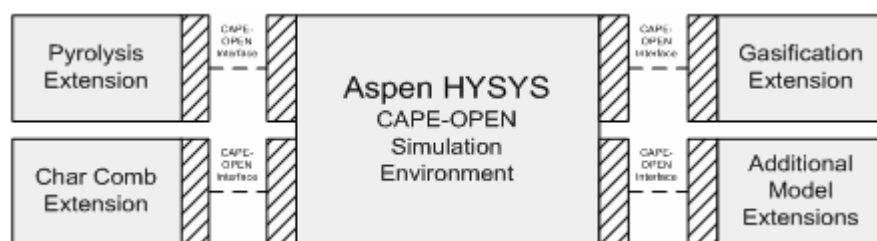

Figure 1: Simulation environment

Mathematical simulations are necessary to help finding out feasible operating conditions of the process to achieve better process performance. The solution adopted is able to predict the composition of the produced gas under various operating conditions (temperature, fuel/carburant ratio, etc.) and different fuels mixtures (coal, wastes mainly, and biomass in limited proportions) characteristics. ELCOGAS data has been used in the platform testing and validation studies. The proposed gasification model improves the understanding of the process and can be used as an accurate predictive tool at the optimization stage.

Acknowledgements

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Making value with order management for agent based systems

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1. Summary

Today the technical and business management in the process industry is linked to the workflow within Intranets and Internet, passing through the electronic mail for commerce and business promotion. The companies must be turned in make-to-order operation linking the actual or forecasted orders instantly to the plant floor. The available solutions to this scheduling problem are not always appropriate for practical issues. Heuristic approaches are needed in order to operatively manage the firm's plans in agent based systems. It is proposed an algorithm to emulate the exact mathematical models reducing the computational effort.

Keywords: Order management, agent based system, supply chain planning, budgeting, liquidity control.

2. Extended Abstract

Efficient evaluation and updating of plant's logistics, inventory control, production, finances, sales, gross margins, quality, investment/retrofitting, maintenance & other functions are now more necessary. Interactive on line schedulers tracking the production events and the financial resources can guarantee the solvency with the overall enterprise management optimization.

During last decades the operative optimization modelling practitioners included objective functions that used regular measures of system performance. Measures of schedule performance were function of the set of completion times in a schedule or of the sum of the tardiness of all orders. In fact, scheduling production tools were developed over these principles to solve the difficulties arisen during the production planning at plants. While engineers used powerful tools to optimally manage interactions between batches during production, financial and business managers

lacked a similar tool. The development of business planning guidelines considering both facts and also the supply chain in unison was absent.

The interaction between batches during processing is caused by the overlapping time. If the overlapping time is override to a cost/profit function, the whole problem can be treated in unison. When profit is the objective, if a highest contribution to profit is done at a least completion time, the value of the objective function is improved. If the makespan is used as the objective, unfortunately profit has no place to be directly the target. Instead of the commonly used cost-related measures of system performance, financial managers need measures of system value to develop the business planning guidelines of the decision makers of the firm. In our case study we use a time-value bi-criteria to sequence scheduling orders. For each binary schedule considered, it is calculated the "density" of profit per hour of completion time, which obviously is schedule dependent. This density Dii' is calculated as the profit contribution per hour of the batches considered (HPR), divided by its real processing time (ti; ti') considering overlaps (TOii') as: Dii'=(HPRi .ti+HPRi' .ti')/(ti+ti'-TOii').

	Dii'			
	1	2	3	4
1	23,16	25,78	29,13	27,82
2	28,59	29,66	32,27	31,3
3	33,5	37,77	36	35,08
4	32,21	33,86	35,08	34,09

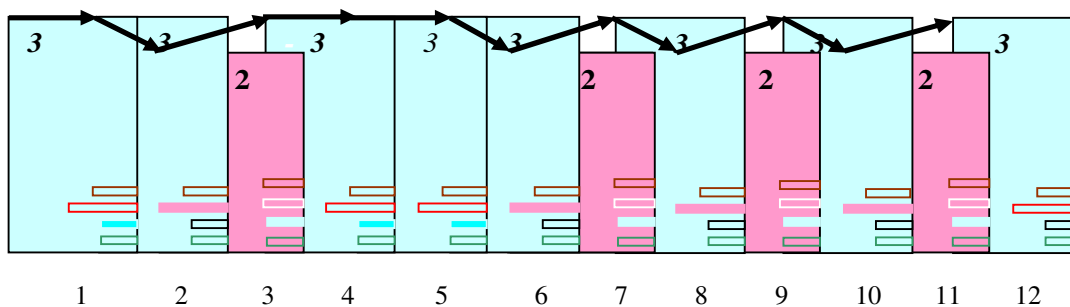Table 1. Density of profit of the binary schedules

Fig 1. Batches of products sequenced by the bi-criteria formulation.

The case study shows the possibilities of simulation with a time-value criteria when integrating financial and operative scheduling.

Acknowledgements

Comparison of liquid discharge from a tank through circular and irregular shape orifices

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1. Summary

Results of experiments concerning discharge of Newtonian and non-Newtonian liquids from a tank through circular and irregular shape orifices have been presented. The dependence of flooding constants on vessel to orifice ratio *D/d* were determined experimentally and presented graphically.

Keywords: flooding constant, tank, discharge of liquid, Newtonian liquid, non-Newtonian liquid

2. Extended Abstract

A dynamic development of industry contributed to a significant growth of the number and variety of technological processes. The processes have often been accompanied by the risk of accidents due to which substances might be released to the environment in an uncontrolled way and bring to environmental pollution, fires or even human losses.

According to the literature, mechanism of liquids discharge from a closed tank can be compare to process of bottle emptying [1,2]. The emptying process is characterize by flooding. The flooding is a limiting form of discharge, in which gas-phase flow-upwards and liquid phase flow in the opposite direction The flooding process can be describe by a correlation equation introduced by Wallis [1]:

$$U_G^{*1/2} + U_L^{*1/2} = C \tag{1}$$

where *C* is a dimensionless parameter or flooding constant. The value of the flooding constant *C* for discharge of water from a tank, is ca. 0,8 [1].

Discharge of Newtonian and non-Newtonian liquids from a tank through circular and irregular shape orifices at various pressures, and for a wide range of the ratio of the tank to discharge orifice diameters D_V/d is discussed in this paper.

The orifices of different geometries represent real orifices formed during an accidental discharge. Discharge orifices were situated in the bottom of the tank. In a case of circular orifices they had the diameters 5 8, 12.5 and 17 mm, while equivalent diameters of irregular orifices were 5, 8 and 12.5 mm. To determine precisely the mass of discharged liquid, laboratory scales were used. The experimental Newtonian liquids were water and triethylene glycol , while the non-Newtonian liquids were water solutions of carboxymethylcellulose CMC at the concentrations 1.6, 2 and 2.5% by wt.

The investigations of discharge of liquids from a tank at overpressure was realized for 30, 50 and 80kPa initial pressure in the tank. The flooding constant C for discharge of all liquids through circular orifices were determited using the following correlation

$$C = \frac{\left(r_G^{1/4} + r_L^{1/4}\right)}{\left[(r_L - r_G)gd\right]^{1/4}}\left(\frac{4V}{pd^2 t}\right) \tag{2}$$

For the discharge of liquids through irregular shape orifices, the value of equivalent flooding constant C_Z was calculated from analogical correlation

$$C_Z = \frac{\left(r_G^{1/4} + r_L^{1/4}\right)}{\left[(r_L - r_G)g\,d_z\right]^{1/4}}\left(\frac{4V}{p\,d_z^{\,2} t}\right) \tag{3}$$

As a result, a broad range of experimental data concerning a "bottleneck" discharge of liquid from a tank were obtained. The obtained data, depending on the initial pressure were lying in a range of vessel to orifice D/d ratio from 11,8 to 40,5, and considerably enlarge the range of experimental data which have been published in the literature. The flooding constants C were determined for different media and discharge geometry and were presented in a form of dependence on vessel to orifice ratio $C = f(D/d)$.

Extensive experimental investigation not available in literature so far, were performed and analysed. The experiments covered over 1200 experimental points. The values of flooding constants concerning "bottleneck" discharge of all liquids were lower than constants for the discharge at sub-atmospheric and overpressure in whole range of geometries of the applied orifices. The highest values of flooding constants were obtained in the case of liquid discharge at overpressure.

References

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