Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Session T6-K: Theme-6 Keynote Lecture

Abstract Number	Paper Title & Authors	Included
4161	Towards the European Higher Education Area: Curricula and Methods in Chemical Engineering S. Feyo de Azevedo	Yes

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Towards the European Higher Education Area: Curricula and Methods in Chemical Engineering

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1. Summary

Winds of changes have been blowing in the European Higher Education Area (EHEA) over the past years, with visible effects. In these notes and in the lecture I shall identify and examine both some of the ‘high pressures sources’ that are responsible for such ‘winds’ and the changes that are occurring. I shall also comment and give my views on some of the main tasks ahead for the building of the European Higher Education Area and on some specific implications in methods and curricula in the chemical engineering area.

Keywords: Bologna Process, qualifications framework, quality assurance; paradigms of chemical engineering.

2. Extended abstract

The Bologna Process has to be understood as one of the major components of a model for European development, in the historical background of progress in science and technology, of societal and political changes that took place on the last quarter of the 20th Century. The commitment is to develop a competitive economy based on a knowledge society, a model for growth and jobs. This requires increasing mobility and trans-national co-operation. Such can only be based on TRUST, which is only achieved with readable national qualification frameworks and degree systems and with transparent quality assurance systems. The Bologna Process should thus be seen on a dual environment of related, but different, academic and political issues. The objective is to develop cohesion and increase the European

A tremendous effort is being made by academia and professional societies to respond to these challenge of reform: (i) the degree system is being harmonised; (ii) a new directive of professional recognition has been approved in close agreement with the proposed degree system; (iii) the BFUG is committed to promote decisively national qualifications frameworks in the period up to 2009; (iv) the Register for quality assurance has been approved in the London meeting of May 2007; (v) the EUR-ACE quality label was launched in November 2006; (vi) The initiatives of the E4 and of the CDIO groups propose sets of competences related to contents in all engineering areas, including Chemical Engineering; (vii) The European project CHEMEPASS – Chemical Engineering Mobility Tools, in progress, represents a serious effort towards this goal of mutual improved understanding of qualifications; (viii) in chemical engineering, the WPE-EFCE proposed in 2005 a set of recommendations for a core curriculum, both for first and second cycles

We can question whether we are going through a change of paradigm that should influence the design and offer of new chemical engineering programs? Or, are we just facing an extension of the second paradigm? In practical terms, the objective of the exercise is to finally choose (decide) the (appropriate) answers to two main questions: (i) what role and distinction of education at the tertiary stage (University education)? (ii) what should be the structure and the core content of chemical engineering curricula for a first degree? What, what depth, when, how, which teaching aids?

Still, and finally, about this new paradigm, there are not yet enough documents to make this shift of mindset completely clear or as clear as what we have discussed about Unit Operations and Chemical Engineering Science. Prospectively, for sure that in 2020 such shift will be crystal clear.

Fuzzy as the shape may still be we recognize a number of major lines of reference:

- Our individual and local universe is larger and larger.
- Time and space concepts and dimensions have changed dramatically.
- The reference of whatever (quality, competition, etc.) is now Europe and the World, not our City or our Country.
- Standards must be high, inflexibly high, attitude holistic, mind flexible.
- The Chemical Engineering discipline on its own merits, much due to life during the 2nd paradigm, has enlarged significantly its universe of influence.
- The need is clear for a reference qualifications framework and for international recognition of quality assurance standards and procedures,
- A core group of disciplines, concerning basics and engineering, and of skills and competencies, should be recognized by consensus and implemented.
- A complementary group of elective advanced curricular modules should lead the student to work on frontier topics of chemical engineering.
- External training, more practical ‘hands-on’ training is required for first-degree level. If possible in another Country.
- There must be an understanding that it is essential that Academia and Industry, in the European Space, co-operate offering each other aided-value, by accepting students for training (the Industry), by jointly designing pilot case studies, by providing theoretical background through courses (the Academia).
- Lifelong learning is the key concept to have the edge.

If this is not a paradigm shift, it is at least an extension of the concepts of the second paradigm that, as fifty years ago, will help in pushing the frontiers of chemical engineering beyond its present limits.

Session T6-1: Chemical Engineering Education - New Directions

Abstract Number	Paper Title & Authors	Included
110	Chemical Engineering Education, where to now? - A global view D Wood	Yes
2276	Features of chemical engineer to education in Ukraine and Bologna process M Zgurovskiy, I Astrelin, G Statyukha, T Bojko	Yes
2297	CHEMEPASS - Chemical Engineering Passport S Gagneur	Yes

Session T6-1

Chemical Engineering Education, where to now? – A global view

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1. Summary

This paper summarises the recent comments of some of the critics of chemical engineering undergraduate programs and looks at where in the World such comments might be justly applied. Whilst concluding that the comments of Armstrong (Armstrong, 2006) are valid the paper suggests that the rapid changes in China might lead to that country setting the example for change for the second decade of the 21st Century.

Keywords:

2. Extended Abstract

At the 6th World Congress of Chemical Engineering held in Glasgow in 2005 some key challenges for the future emerged. The challenge relating to education was *"Educating the next generation of chemical engineers – what should we teach and how?"*

At the Congress Ed Cussler gave a keynote address where he levied some significant criticisms about current curricula as at 2005. My observations around the World since that time suggest that there have been very few curricula modifications to date.

A steady stream of comments about chemical engineering curricula has been published since the 5th World Congress of chemical engineering held in 1996. One of the most recent challenges to chemical engineering educators is from Bob Armstrong (Armstrong, 2006) where he asks "Why has the curricula & program structure remained significantly unchanged over the years?" He was discussing programs in the USA, however his comments are applicable to many other countries. Armstrong suggests that the strong emphasis on research including the enormous growth in doctoral research programs has led the neglect of the curricula content in undergraduate programs.

In the USA with a population of approximately 300m there are about 155 departments of chemical engineering producing about 5,000 first degree graduates each year. This is a significant proportion of the World's new chemical engineering graduates each year (~12.5%) and if curricula has been neglected as Armstrong suggests these graduates may be lacking in some of the major new developments in chemical engineering especially those referred to in "Beyond the Molecular Frontier" (National Research Council, 2003)

There are approximately 40,000 new chemical engineering graduates produced each year, half coming from China. There is little doubt that the curricula in Chinese universities closely resemble that in the USA with some European influence. There are between 4,000 and 5,000 new chemical engineering graduates emerging each year from Europe and a glance at some of the curricula suggests that criticisms by Cussler, Armstrong and others also apply to the European programs.

In Asia not including China the curricula and program structure for chemical engineering programs strongly follows either the American or British systems and it would be fanciful to imagine that these programs are more advanced than those from which they were derived.

Within the countries of the InterAmerican Confederation of Chemical Engineering, not including the USA chemical engineering programs are less developed in terms of satisfying modern changes in the Discipline. It might be argued that Canada (in the IACChE) and Australia (in the APCChE) have somewhat different undergraduate programs particularly in terms of relevance to chemical engineering developments in those countries. Nevertheless their fundamental curricula are also subject to the comments of Cussler, Armstrong and others.

With the exception of South Africa, countries in the African and Middle East region offer chemical engineering undergraduate programs that are somewhat historical in terms of curricula. South Africa is no further advanced in curricula reform than Australia or the UK.

Most of the graduates from the regions mentioned above come from undergraduate programs that are fully accredited from professional institutions, many from the Washington Accord countries. Such accreditation has not helped the concept of curriculum and program structure reform.

To date there has been no external professional accreditation of chemical engineering programs in China and yet the applications of chemical engineering in research and in Industry in China are rapidly evolving. With 174 university departments of chemical engineering, China is leading the World in the production of professional chemical engineers and many of the graduates continue with graduate education. The top 9 chemical engineering departments in China are about to undergo a professional accreditation program with the Institution of Chemical Engineers. Observing the undergraduate programs within these departments suggests that change and development is ongoing and in producing chemical engineers appropriate for the rapid changes in the Chinese Chemical Industry, China may well soon lead the World in undergraduate curricula developments.

Whilst Europe plans to implement the Bologna Agreement it should really ask is this the best way forward to meet the challenges of the second decade of the 21st Century. Maybe more attention might be given to curricula and designing a suitable program which will incorporate the essentials of a modern chemical engineering program as espoused by Armstrong.

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Armstrong, Chemical Engineering Education , February 2006

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Features of chemical engineer to education in Ukraine and Bologna process

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1. Summary

The Ukrainian scientific and educational community efficiently works with important increase of competitiveness of the native system of a science and higher education, and also with the increase of this system role in public transformations last years. Bologna process is such instrument by means of which Ukraine hopes to enter into the European community and to raise quality of education in the country. In the relation of matching the programs of chemical engineer preparation with the international norms the considerable help gives European Federation of Chemical Engineering (EFCE). This paper is the result of teamwork. The purpose of this paper was a comparative analysis of bachelors and masters education in NTUU "KPI" in accordance with recommendations of EFCE and the search of conversion ways of chemical engineer education in Ukraine in a whole. Recommendations of EFCE on realization of master cycle have the general nature, because it answers a major principle of expert training as variety, which reflects the needs of the market and opportunities of higher educational universities. Nevertheless, it is necessary to pay attention to some features.
Keywords: Bologna process, chemical engineer, master cycle

2. Extended Abstract

The Ukrainian scientific and educational community efficiently works with important increase of competitiveness of the native system of a science and higher education, and also with the increase of this system role in public transformations last years. Bologna process is such instrument by means of which Ukraine hopes to enter into the European community and to raise quality of education in the country. The leading educational establishment in introduction of concepts, methods and purposes of Bologna process is National Technical University of Ukraine "Kiev Polytechnic Institute" (NTUU "KPI") and in a direction of chemical engineer education the chemical-engineering department is the best one.

In the relation of matching the programs of chemical engineer preparation with the international norms the considerable help gives European Federation of Chemical Engineering (EFCE). This paper is the result of teamwork. The purpose of this paper was a comparative analysis of bachelors and masters education in NTUU "KPI" in accordance with recommendations of EFCE and the search of conversion ways of chemical engineer education in Ukraine in a whole. The analysis of first education cycle (bachelor) enables to define the following. First of all, the curriculums, which are compared, are differ considerably by a less volume of knowledge from non-technical disciplines (humanitarian, social, and economic). In recommendations of EFCE, it is 6 % against 17 % in NTUU "KPI" (in hours this difference is especially visible: 360 hours against 1296 hours). The second feature is a much greater volume of the recommended educational employment from natural-science training: 25 % against 18 % in the curriculum of KPI. The third feature of recommendations is a much greater volume professional training: 36 % against 27 % in KPI. However, this difference is partially compensated by more powerful training in a cycle of knowledge deepening (selected disciplines): in NTUU "KPI" is 38 % against recommended 33 %. The fourth feature is the basic difference between normative forms of certification: in recommendations, the project in chemical engineering is taken almost 19 % of total professional training against certification test in NTUU "KPI". Thus, the significant reduction in first cycle training in socially-humanitarian and economic directions would allow to pass from four annual cycles of education to three annual. Obviously, it can be made only in a case when in high school, there is allocated enough time for socially-humanitarian teaching. We do not think, that it approaches for us. The recommendation on intensification of natural-science education of students it is necessary to consider as expedient, mainly, through strengthening of mathematical training (especially of statistics) and training in information technologies. It is necessary to recognize of most relevant in professional training of bachelors in chemical engineering. First of all, it concerns of new tendencies in chemical engineering such as product engineering, new concepts of sustainable development of a society and new tools like optimal experiment use of the modern software, etc.

Recommendations of EFCE on realization of master cycle have the general nature, because it answers a major principle of expert training as variety, which reflects the needs of the market and opportunities of higher educational universities. Nevertheless, it is necessary to pay attention to some features. Much more hours is taken for improvement of engineering-chemical disciplines with recommendations of EFCE (70 % against 46 % in NTUU "KPI"). The hours practically coincide in studying of general scientific disciplines and mathematics. Less time is recommended to give scientific master's degree study: 17 % against 30 % in NTUU "KPI".

The other recommendations, which were presented in the document of EFCE (teaching and mastering, industrial experience, estimation of process of education, estimation of educational process by students), are generally accepted and realized in our curriculum and educational process.

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CHEM*E*PASS - Chemical Engineering Passport

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1. Summary

The **CHEM*E*PASS** project, carried out by a consortium of 13 higher education institutions and financed by the European Commission for 3 years, aims at developing innovative tools to promote international mobility and attractiveness in the European Chemical Engineering Higher Education. These tools will be of two kinds: one will improve the evaluation and the recognition of competences, through a better transparency of educational programme's learning outcomes, and the other will provide new pedagogical activities for training and evaluating the basic knowledge. Ultimately the project will initiate a new thematic network focusing on higher education issues in the area of Chemical Engineering.

Keywords: mobility; evaluation; learning outcomes; competences; basics

2. Extended Abstract

The **CHEM*E*PASS** project is financed by the European Commission within the Erasmus Mundus Programme – Action 4: "Enhancing Attractiveness of the European Higher Education Area". It started on November 2006 and the E.U. grant is allocated for 3 years. The consortium carrying out this project is composed of 13 Higher Education Institutions of 9 European countries and 1 of South Africa: **CPE Lyon** (France) (Coordinator), **Institut Quimic de Sarrià** (Spain), **Universidade do Porto** (Portugal), **Politecnico di Torino** (Italy), **INPL-ENSIC Nancy** (France), **INPT-ENSIACET Toulouse** (France), **Technische Universiteit Delft** (The Netherlands), **University College Dublin** (Ireland), **Technische Universität München** (Germany), **UCTM Sofia** (Bulgaria), **Jagiellonian University** (Poland), **Lappeenranta University of Technology** (Finland), **Durban University of Technology** (South Africa).

Objectives

The **CHEM*E*PASS** project aims at promoting Mobility(1) and Attractivity(2) in European Chemical Engineering Higher Education through:

- **Evaluation and recognition of competences**: Development of tools to improve the transparency of programmes and the evaluation of competences*

- **Knowledge pedagogy**: Development of tests of knowledge for training and evaluating the basics

(1) *Mobility within Europe and between Europe and Third countries (non-European countries).* (2) *Attractivity of European Higher Education versus Third countries Higher Education.*

The consortium proposes to develop Europe-wide and beyond these tools whose feasibility and interest have been demonstrated by CPE Lyon within a 2-year study financially supported by the French Ministry of Education. This project was inspired by the works of the **EFCE** (European Federation of Chemical Engineering) on recommendations for Chemical Engineering Education and of the **ECTN** (European Chemistry Thematic Network) on chemistry tests (EChemTest) and outcomes-based reference frameworks (for the Chemistry Eurobachelor label).

Target groups

The **CHEMEPASS** tools will be for the use of:

- **Students, young graduates and professionals** (in Life Long Learning), specialized in Chemical Engineering
  To express their competences, to diagnose their needs for training, to identify the appropriate institution, to self-evaluate;
- **Higher Education Institutions involved with Chemical Engineering** :
  To better assess the training needs of candidates and their previous educational programmes' outcomes; to better express the outcomes of their own educational programmes and requirements for applications;
- **Industries hiring chemical engineers around the world**:
  To better assess the abilities of individuals, to diagnose the needs for continuing education of their employees and better identify the appropriate training institution.

Main activities (Work Packages)

- WP1: defining **frameworks** for the use of HEI's to express the specificities of their educational programmes in terms of **Learning Outcomes**,
- WP2: conceiving tools and methods to help the **evaluation of competences** of an individual person especially competences other than knowledge,
- WP3: developing **electronic tests on knowledge** of core areas of Chemical Engineering for self-evaluation, diagnosis, and integration,
- WP4: initiating a **new thematic network**, the **ECEEN** (European Chemical Engineering Education Network), which will disseminate and manage the **CHEMEPASS** tools, and work on other higher education related issues in the field of Chemical Engineering.

Internet links

Project: http://www.cpe.fr/chemepass/CPELyon-CHEMEPASS.htm
European Commission Erasmus Mundus Action 4 projects:
http://ec.europa.eu/education/programmes/mundus/projects4_en.html
Contact: gagneur@cpe.fr

Session T6-2: Teaching Methods, Techniques & Modules

Abstract Number	**Paper Title & Authors**	**Included**
298	Creating Effective e-Learning Presentations Quickly D T Wu	Yes
1378	Computer Based Training in Biochemical Engineering V C Hass , K-M Schoop , R Pörtner	Yes
1672	Changing a Culture – A Project Centred Curriculum for Chemical Engineering Education I T Cameron, C A Crosthwaite	Yes
2708	A Flexible Experimental Learning Environment for Contemporary Chemical Engineering Education J Orelana	No
2818	Teaching Sustainability to Chemical Engineers: Pedagogical and Practical Aspects J Petrie, L Basson	Yes
3557	Teaching Logic Control Systems to Chemical Engineering Students Ruben Morales-Menendez,aLuis E. Garza Castañon, Ricardo A R Mendoza , I Y S Chávez, F G Elizalde	Yes

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Creating Effective e-Learning Presentations Quickly

D. T. Wu, Sc.D.

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1. Summary

This talk is to introduce a new audio-visual presentation authoring software application, LivePresent™. The uniqueness of this authoring application is that for the first time, an author can add not only audio, but also pointer movements to the presentation. It has extensive editing functionalities for audio and pointer movements, simply by dragging with a mouse. It is now possible to develop a "professional" presentation at your own pace, one slide at a time, at an affordable price without the expensive audio-visual recording and editing equipment. The resulting presentation rivals class room learning or face to face presentation. The presentations can be viewed with a PC or a Mac. The user has extensive control during playback, such as pause, fast forward, rewind, and jump to any slides. Links can be created to Q & A Forum or to Web sites for upload or download of announcements and exams.

Keywords: e-learning, distance learning, presentation authoring, audio-visual presentation.

2. Extended Abstract

In class room learning, the instructor uses lectures to present overviews, and elaborate and explain the more complex aspects of the topics. Pointing during presentation is essential to focus the participants' attention to certain topics on a slide. Students are free to ask questions to further clarify the topics. Most presentation authoring applications now available are cumbersome to use, expensive, and lack the interactivity and pointing during presentation. The slides of the presentation often lack resolution and clarity. LivePresent™, a PC application, was designed specifically for asynchronous e-presentations and provides the essential features, such as audio, pointer movements, and links to question and answer forum. The presentations can be viewed using a PC or a Mac. During viewing of the presentations, you can jump to any slide, pause, fast forward and rewind

To create a slide presentation, you simply capture images or slides directly from your PC monitor or import from Microsoft Power Point®, in any frame size your select. Afterwards, you may add audio and/or pointer movements to the slide. The slides of a presentation can be ordered simply by dragging the slides up or down the list.

Furthermore, slides with audio and pointer movements from any presentations can be reused simply by cut and paste to a new or another presentation.

The unique features of the software are its capabilities for recording and editing audio and pointer movements. For audio recording, it can be carried out similar to recording using regular office type recording equipment. The user can pause during a recording and automatically rewind for a short segment to listen to what has been recorded and then continue. For audio editing, you can erase, copy, cut, insert, increase volume, and add echo effects. These audio editing functionalities greatly save your time in creating an effective professional audio-visual presentation.

Pointer movements can be recorded when you record audio or when you listen to the playback of a previously recorded segment. To record pointer movements, you simply move the pointer to the spots on your monitor after you activate the Pointer Recording button. You can edit both the position of the pointer and the time when the pointer appears on the slide. To edit, you simply drag the pointer 'anchor" marker to any position you desire or drag the time marker along the time line.

LivePresent™ also allows the authors to introduce shapes (e.g., arrows, squares, etc.) during a presentation at pre determined time, or to introduce Call Out notes at pre determined time to elaborate further on the more complicated topics on a slide without switching to another slide. In addition, video segments can be embedded without having to switch to another video playback application.

When you prepare a presentation for viewing at a later time, you will always find that you may have spoken incorrectly for a few sentences or a few words or pointing to the wrong places. The unique audio and pointer movement editing capabilities of LivePresent™ greatly simplifies and minimizes the time for the recoding tasks since you do not have to re-record the whole presentation. The editing can be carried out without the expensive audio visual editing equipment.

LivePresent™ allows the author to create question and answer forum with links from any slide. This feature allows asynchronous question and answer interactivity often missing in many e-Learning presentations. LivePresent™ has its own internal FTP client for uploading and downloading files, such as tests and announcements, to and from the server. Access to viewing the presentations can be controlled using the licensing features which are available in customized versions of LivePresent™.

LivePresent™ can also be used to record a live presentations during conference presentations so that both audio and pointer movements of the presentation can be captured. While it is possible to capture audio and pointer movements and the slide using regular video recording equipment, the resolution of the recorded presentation is usually poor and it is often not possible to see the slide clearly. With the presentation recorded with LivePresent™, the resolution of the slide is usually of high quality. This recording feature of LivePresent™ can allow conference organizers to offer presentations with audio and pointer movements to those who can not attend the conferences, instead of just written materials as is commonly done at present.

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Computer Based Training in Biochemical Engineering

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1. Summary

As the requirements on the education of chemical and biochemical engineers with respect to process dynamics and control are increasing a new didactic concept has been developed by the Technical University Hamburg-Harburg and the University of Applied Sciences Bremen using interactive simulators. The use of interactive simulators enables students to actively apply their knowledge in the control of biotechnological processes without the risk of hazardous plant states.

Keywords: Biochemical Engineering, Control, Process dynamics, Education, e-Learning

2. Extended Abstract

The requirements on the education of chemical and biochemical engineers with respect to process dynamics and control are increasing. However, the classical methods of teaching (lectures, seminars, practical experiments) are of limited value, in particular if the rapidly increasing number of students in the field of biochemical engineering and biotechnology is considered.

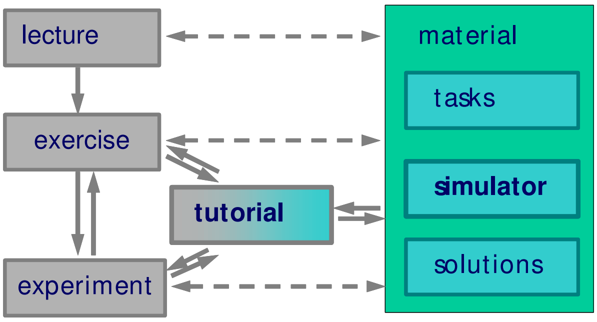

Figure 1 : Simulator Based Education

In the project “e-LearnBioTec” a new didactic concept has been developed by the Technical University Hamburg-Harburg and the University of Applied Sciences Bremen. In this concept, students are encouraged to actively apply their new knowledge in control and system dynamics using interactive process simulators for cultivation processes (training simulators). An important advantage of this "guided learning by doing" using interactive simulators is that the complexity of the required decisions and actions of the students may be increased stepwise. Thus, the initially required didactic reduction may be minimized step by step without increasing the risk of accidents or dangerous failures in plant operation.

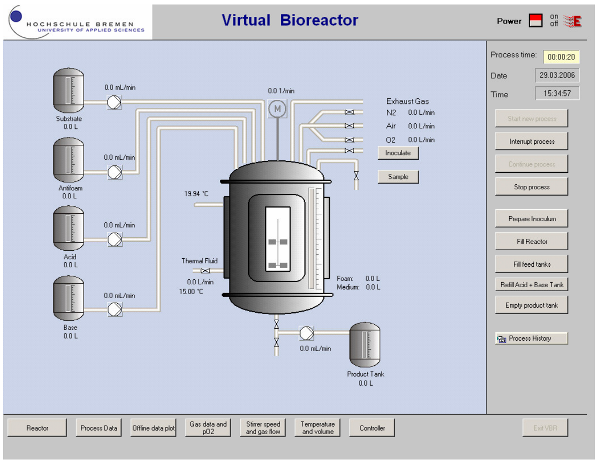

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Figure 2: Virtual Bioreactor realized with WinErs [3]

The interactive simulators are programmed on the basis of the commercial process control system WinErs, developed and distributed by the Ingenieurbüro Dr.-Ing. Schoop GmbH, Hamburg [1]. The combination of complex dynamic process models with a modern and flexible process control system leads to a powerful tool for the education of biochemical engineers [2]. Using the industrial style process control system for controlling the real time simulation of a cultivation process, students are able to recognize the consequences of their decisions and actions immediately. The practical experiences with this new form of teaching at the University of Applied Sciences Bremen and the TU Hamburg-Harburg illustrate the benefits of this method for students as well as for educational staff.

As part of the project „e-LearnBioTec“ the developed training simulators for cultivation processes have been included into a wider concept for the education of biochemical engineers. This enables us to present a "blended-learning" concept for the education of biochemical engineers that combines the advantages of classical teaching methods with those of e-Learning and training simulators.

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Acknowledgement

Financial support by the e-learning consortium Hamburg (ELCH-project D0001) is gratefully acknowledged.

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Changing a Culture – A Project Centred Curriculum for Chemical Engineering Education

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1. Summary

Like no other period in the last 50 years, engineering is in rapid transformation. Engineering education is likewise in a period of reassessment and realignment, driven by a wide range of factors that drive specialisation, globalization and engagement with disparate disciplines. Curriculum innovation is now essential to meet the newly emerging environment. Cultural change in engineering curricula is difficult to achieve but there are significant examples. This paper shows a complete top-down design of a new curriculum which directly addresses a wide range of graduate attributes within a strong systems approach to engineering education. The paper overviews the achievements and the challenges inherent in designing, delivering and sustaining a project centred curriculum. Critical factors are ownership, assessment and evaluation of change and dissemination of its success.

Keywords: project centred learning, engineering education, cultural change, curriculum innovation

2. Extended Abstract

One approach to major curriculum change to meet the modern challenges of chemical engineering education is the Project Centred Curriculum (PCC) within Chemical Engineering at The University of Queensland, where there is now greater emphasis on creative problem solving through the inclusion of a continuous core of increasingly open-ended project work as seen in Figure 1. PCC is driven by a desire to significantly improve the undergraduate experience and in particular to align the education of engineers with industry practices and requirements. Students in chemical and environmental engineering are now being challenged and engaged with relevant learning experiences that better prepare and equip them for an increasingly diverse and demanding work place. Team work, and partnerships: with peers, mentors, and industry are embedded into the learning activities associated with the projects. There are greatly enhanced student-staff interactions and a sense of belonging to a community of learning and a profession. A number of strategies are used, including student team work, team teaching, industry participation and sponsorship of projects, and industry site learning placements. The recurrent themes are: reality and relevance of the project work; and the relationships and networks that support professional development and connect the students to the profession. This impacts strongly and positively on teaching approaches and the learning outcomes of the program. The justification for developing the curriculum around the backbone of project courses is:

- project based courses embody the best educational practices of active, collaborative, student-centred learning, i.e. the students learn by doing and must achieve this through collaboration with and accountability to others.
- projects contextualize 'real world' industrial applications and professional practices for the students, and offer them meaningful and relevant opportunities to develop technical and generic knowledge and skills.
- communities of learning including students, teachers, industry partners and graduates are initiated through the team project work and these are a model of future professional engagements and networks.

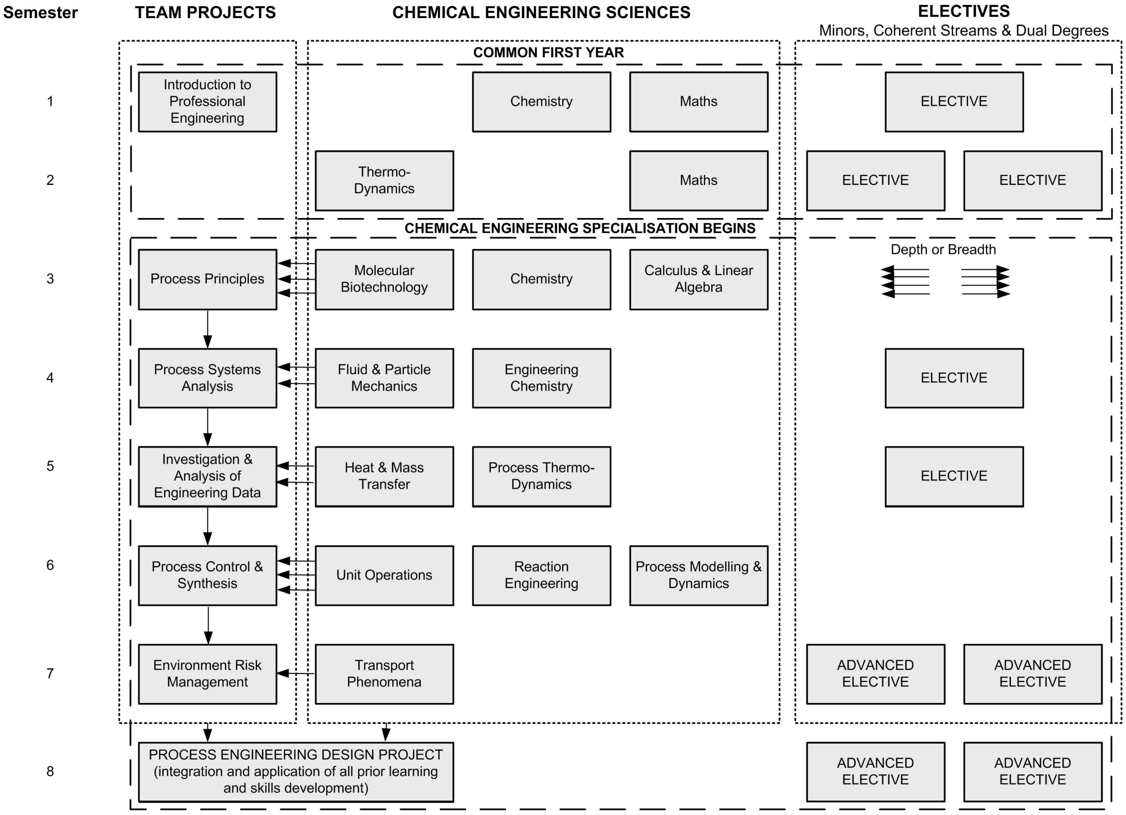

Figure 1 The project centred curriculum (PCC) structure

PCC has met with student acceptance and enthusiasm, accolades by industry, professional engineering societies and adoption by other Australian engineering schools and discipline areas. It has been recognised nationally with a number of awards culminating in a 2005 Australian Award for University Teaching, and it has been acclaimed internationally as an exemplar in engineering education. This is a transformation that has taken 10 years.

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Teaching Sustainability to Chemical Engineers: pedagogical and practical aspects

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1. Summary

This paper considers the development and implementation of course materials for teaching “engineering for sustainability” to chemical engineering undergraduates. Emphasis is given to both pedagogical and practical aspects, wherein sustainability is viewed from the standpoint of the analysis of complex systems, and the role of engineers is to facilitate improved decision making practices. The experience is informed by some 10 years of course development at the Universities of Sydney and Surrey.

Keywords: engineering education, sustainability, complex systems, life cycle thinking, decision making

2. Extended Abstract

The practice of teaching Sustainability to chemical engineers requires a fundamental shift in thinking, which takes us beyond technical and deterministic perspectives, and reductionist approaches to decision making. Rather, we require a mindset which embraces complexity, and challenges us to engage with the uncertain behaviour of physical systems, and the (often) irrational behaviour and conflicting responses of social systems, across a multitude of scales, and over extended time periods. At the same time, we are required to do so within an undergraduate curriculum which has not changed substantially since the advent of the “unit operations” approach to process problems, despite its bourgeoning content.

This paper draws together a range of perspectives from our collected teaching experience of “engineering for sustainability” courses over some 10 years, both at the University of Sydney, and the University of Surrey.

From a pedagogical perspective, we draw analogies between natural systems and their underlying thermodynamics, and the sustainability of industrial systems. This enables us to critique the plethora of so called "frameworks" and "tools" for sustainability assessment. Thereafter, having characterised industrial systems from a life-cycle perspective in terms of their drivers, constraints and behaviour, we develop tools and approaches for their management. These address decision making across a range of spatial and temporal scales, and allow a focus on discrete industries, or networks of industries. Here, we seek to convey an understanding of the practice of decision making in terms of its problem structuring and problem analysis elements, with due regard to the philosophical and psychological / cognitive dimensions of problem framing; their impact on preference elicitation and valuation; and management science / process engineering approaches to information management, including uncertainty.

At a practical level, we have endeavoured to entrench such thinking across the undergraduate curriculum. At the University of Sydney, this means core courses in the formative second and third years of a four year curriculum, with significant broadening courses offered as elective units of study in the final year. This structure serves to reinforce key concepts and provide a consistent context within which other aspects of the curriculum are developed. In general, all the material is offered in a problem-based mode of delivery, with significant opportunity for students to engage in both oral and written debate. Students elect (in significant numbers) to pursue this material through their honours-level theses, in research mode.

In our view, the approach detailed in this paper sets out a trans-disciplinary approach to the teaching of sustainability, which builds on the formative elements of Chemical Engineering, but extends these by robust consideration of the social dimensions of complex systems. In practice, this amounts to a more participatory, case-study driven, and action oriented curriculum content, with more positive learning outcomes.

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Teaching Logic Control Systems to Chemical Engineering Students

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1. Summary

Logic control systems was incorporated into the academic program of Chemical Engineering students at *Tecnológico de Monterrey*. Exploiting Active Learning (*AL*) techniques and own educational technology, a new experimental course was implemented. Experiences show that students had deep learning as result of the activity performed. Also, several abilities and skills are promoted and the gap between theory and practice is avoided through the experimental hands-on sessions.

Keywords: Logic Control Systems, Education, Active Learning, Batch Manufacturing

2. Extended Abstract

Leaders in the US chemical industry found four disciplines as crucial to the future of this field: new chemical science and engineering technology, supply chain management, information systems, and manufacturing operations. Manufacturing operations require advances in six areas where information and process control have needs and challenges such as open systems and integrated applications, process control, equipment and monitoring, supervisory systems, etc [1].

A review of the automation courses is mandatory at universities in respond to these trends. Typical process control courses for Chemical Engineering (*ChE*) students are only focused in continuous processing. Since combinatorial and sequential control systems are primarily present in batch manufacturing, they have been ignored [2].

Logic control systems was incorporated into the academic program of *ChE* students at *Tecnológico de Monterrey*. Exploiting Active Learning (*AL*) techniques and own educational technology [3], a new experimental course was implemented.

AL techniques are based on the fundamental idea that a natural and deep learning happens as a result of the activity performed [4]. Using *AL* techniques, students are engaged in more activities than just listening [5]: self development, learning by doing, hands-on practice, group work, etc. Three *AL* techniques were considered: Problem-based Learning (*PBL*), Cooperative Learning (*CL*) and Project Oriented Learning (*POL*). A tailored combination of these techniques was implemented.

A logic control station was designed by *Tecnológico de Monterrey's* professors. The station includes a set of industrial actuators and sensors grouped in a power section and three control sections: pneumatic, electrical and electronic. The power section includes pneumatic cylinders with the corresponding electro-pneumatic distributing valves. Power section can receive electric or pneumatic signals; it also includes sets of sensors that provide feedback to the control sections.

This experimental course is organized in two modules: continuous and logic control systems. The logic control system module is designed to teach students how to analyze, design and implement control logic systems. Each week considers 2 hr-laboratory session and 2-hr for complementary activities.

During the laboratory session there are 3 parts. In the first part, students are taught how to operate the station and they are asked to implement basic logic functions. In the second part, complex logic systems are asked for implementation using *CL* technique. In the last part, *PBL* or *POL* are exploited where students face a situation in the context of a chemical industry process. The implemented solution in the station allow students analyze and evaluate several alternatives.

Additionally, students can exploit an important issue: the sensory awareness of the solution. An electrical system example show how students apply their seeing and hearing senses in the process of proposing a logic control system (see [6] for an example using PLC's and [7] for an example using pneumatic systems).

Students learn and enjoy making things happen with pneumatic, electrical and electronic control systems. Several abilities and skills are promoted and the gap between theory and practice is avoided through the experimental hands-on sessions.

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Session T6-3: Teaching Chemical Product Design & Engineering

Abstract Number	**Paper Title & Authors**	**Included**
1173	Chemical product engineering teaching: opportunities and challenges R Costa, P M Saraiva, E L Cussler, G D Moggridge	Yes
1469	Transport Phenomena in Product Engineering J A Wesselingh, H W Frijlink, T Johannessen	Yes
1560	Computer-Aided Chemical Product Design - an M.Sc. Course J Abildskov, R Gani	Yes
2321	Teaching Chemical Product Design and Engineering A A Broekhuis	Yes

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Chemical product engineering teaching: opportunities and challenges

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1. Summary

This work addresses the emergence of chemical product engineering and design from the educational perspective. Some obstacles to the incorporation of these topics into chemical engineering curricula and challenges faced by those involved in teaching are first discussed. Then a possible framework for structuring chemical product engineering is presented. Finally, the explicit teaching of chemical product design is addressed by proposing a course programme and presenting a web resource of sample problems, recently developed in collaboration with the Engineering Subject Centre (UK). The main aim of this work is to stimulate discussion and promote the exchange of experiences in chemical product engineering teaching.

Keywords: chemical product engineering, chemical product design, chemical engineering teaching

2. Extended Abstract

In recent years, the need to update chemical engineering curricula in order to guarantee the competitiveness of the profession in an increasingly aggressive and diverse industrial environment has been acknowledged.

The emergence of chemical product engineering as a well-established academic field has been an enduring trend in this context (Costa e*t al.*, 2006; Cussler and Wei, 2003; Gani, 2004; Moggridge e*t al.*, 2006; Voncken e*t al.*, 2004). Many leading chemical engineering departments all around the world have started to offer chemical product design courses; the number of references related to chemical product engineering available in the open literature has grown exponentially since 1997; and this has been a very popular topic in recent important scientific conferences and meetings.

However, chemical product engineering is still often seen as a marginal area. At a time when much work remains before this discipline is widely seen as an educational and research priority, the exchange of ideas, opinions and experiences is of crucial importance.

In this work, some obstacles to the emergence of chemical product engineering are discussed. The frequently assumed incompatibility between process engineering and chemical product engineering perspectives is challenged. The major challenges faced by those involved in chemical product engineering teaching are also reviewed.

A possible framework for structuring chemical product engineering is then discussed. Such a framework is useful to systematise thinking, communicate ideas, teach concepts, guide research and organise the development of knowledge in the field.

The explicit teaching of chemical product design is addressed.

A possible syllabus for chemical product design courses incorporating chemical engineering core concepts, key marketing ideas and quality management approaches is proposed. This syllabus has been developed taking into account that flexibility, willingness to get involved in non-traditional areas and aptitude for multidisciplinary teamwork are now as essential for professional success as are the traditional core skills of chemical engineering.

Finally, a web resource of sample problems for chemical product engineering teaching, recently developed in collaboration with the Engineering Subject Centre (UK), is presented. Finding plausible examples to illustrate chemical product engineering concepts is often a major difficulty, partly because industrial innovation practices are largely undisclosed. Thus this web resource may be helpful for those involved in teaching in this area providing supporting materials. It also intends to promote the exchange of new case studies – it is open to receive contributions from academics and practitioners in order to become an increasingly richer platform of accumulated chemical product engineering and design knowledge.

The goal of this work is to stimulate discussion and promote the exchange of experiences in chemical product engineering teaching reinforcing the importance of incorporating this subject into chemical engineering curricula.

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Transport Phenomena in Product Engineering

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1. Summary

The engineers in product development teams have to answer 'how much' questions in design and development [1]. One of the techniques used is modelling of the product and its manufacturing, using mathematics and transport phenomena. This paper discusses what is required, using the example of a pharmaceutical tablet, and how students can be helped to learn to model their own problems.

Keywords: product engineering, modelling, transport phenomena, pharmaceutical tablets, mass transfer

2. Extended Abstract

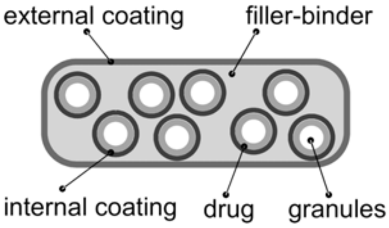

Figure 1 Construction of Nexium tablets

The tablet we consider is of the type used for Nexium, a drug for reducing acid secretion in the stomach. Its construction is shown in Figure 1. Going from the inside to the outside, we see inert granules, which are coated with the drug (esomeprazol). This is covered by an internal coating: an anionic polymer to protect the drug from the acid conditions of the stomach. This coating does dissolve in the neutral conditions in the intestines, so that the drug is rapidly released there. The matrix of the tablet consists of fine particles of a filler binder, in which a disintegrant (swelling polymer) is embedded. The whole tablet has a water-soluble external coating. The external coating and the matrix dissappear rapidly when the tablet is swallowed. In the working of the tablet we must consider different types of materials: the solute (drug), the solvent (water), the porous matrix and several types of soluble or swelling polymers.

The very simple Bateman model of the body [2] (Figure 2) gives a surprising amount of insight of what is required for the tablet content, release time and elimination time

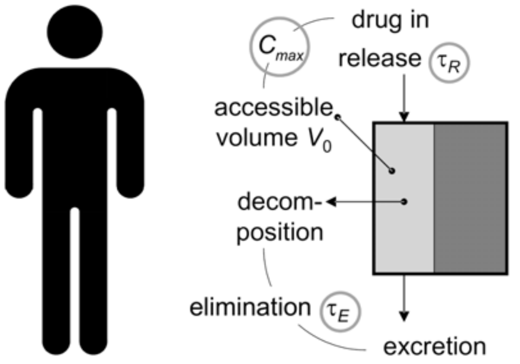

Figure 2 Bateman model of the body

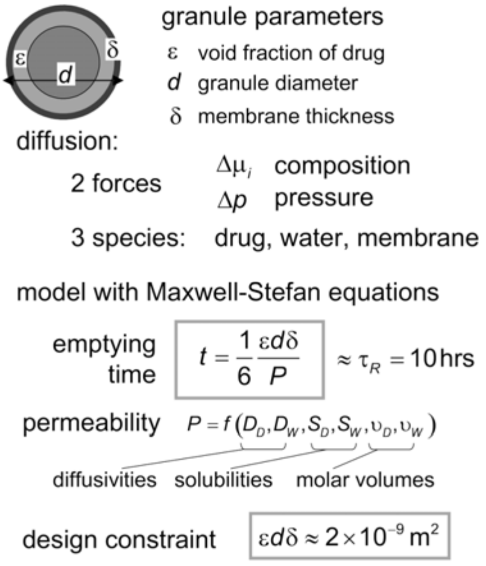

Figure 3 Design constraint on the granules

of the drug. Its derivation only requires a simple mass balance, but understanding the model does require elementary knowledge of anatomy.

In the third part of the lecture (Figure 3) we consider how the desired characteristics can be obtained, both for a rapid release tablet (Nexium), and for other drugs where a constant release rate is required. In the last case we must consider mass transfer through the granule membrane. There are three species involved: the drug, water and the membrane. Water permeates more rapidly than the drug; this causes large pressure effects which can influence diffusion. This requires multi-component modelling, for example using the Maxwell-Stefan equations [3]. The model leads to a simple design constraint, which shows why the granules have to be chosen quite small.

The last part of the lecture discusses how we have helped young students to apply modelling to their own problems, by letting them do experiments *at home*, which they were then to model [4].

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Computer-Aided Product Design – An Msc Course

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1. Summary

The paper presents a graduate course – at the M.Sc. level - developed in recent years. The talk provides the background of the course and describes its connection to existing research programs. We will give an overview of the course structure and the contents of the course. We also share some responses from course participants, based on 3 trial runs of the course.

Keywords: computer-aided design, chemical products, solvent selection

2. Extended Abstract

Many of today's products, solvents, lubricants, heat transfer fluids, and coatings will be replaced within the next 25 years. New generations of chemical products with superior performance and lesser or zero environmental impact will take their place. Specialty chemicals tailored for specific applications will be produced in small quantities and have market lives of only few years. One factor driving this vision into reality is the continuing advances made in the computer-aided design of molecules (Achenie et al., 2003). Most of these software tools assist the chemist in designing chemicals with desired structural properties. New tools are becoming available to assist chemical engineers in designing chemicals with desired physical properties. This paper describes a new course on computer-aided chemical product development. The course aims towards modernizing the foundation of the chemical product engineering subject area to be based upon novel computer-aided methods and knowledge within the molecular level perception of chemical products and processes. Traditionally, process systems engineering is concerned with the computer-aided design of processes, and the operation and control of these processes throughout their lifecycle. As the materials of interest to the modern chemical industry become ever more complex, engineers rely on increasingly sophisticated computer-aided techniques and integrated viewpoints for the characterization of product properties, product behaviour and product economy. During the past fifteen years, theoretical and algorithmic advances along with the revolution in computing technology have made it possible for design questions of practical importance to be addressed by CAMD and other computer-aided methods. The advances offered by these methods will continue to make inroads in the chemical and related industries in the coming decade. All course modules have tutorials involving hands-on computer sessions where participants formulate and solve CAMD problems, evaluate solution and method/tool performances, learn about method/tool deficiencies, learn about modelling inconsistencies and application of estimation techniques to practical problem solving. Industrial guest lectures are given.

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Teaching Chemical Product Design and Engineering

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1. Summary

Between this bulk chemical industry and the market for consumer products there is a large chemical products sector that designs, formulates, shapes and produces structured products that are used to fulfill consumer needs and, at the end of their functional life, these products are recycled or discarded.

More and more chemical engineers become involved in the design and manufacture of such structured products and the need for broadening their curriculum is being recognized by the industry and academia.

The lecture will give an overview of a new curriculum and the way in which it currently is being offered to product engineering students at the University of Groningen.

Keywords: product technology, product engineering, education, design

2. Extended Abstract

On an annual basis, the bulk chemical-industry produces millions of tons of “specified” intermediate products (solvents, polymers, pharmaceutical intermediates, etc.) and this industry employs classically trained chemical engineers to design, operate and maintain chemical plants. In general these engineers are trained in classic chemical engineering disciplines like unit operations, thermodynamics, transport phenomena and design projects.

At the same time industry statistics indicate that in the industrialized countries some 60-70 % of the turnover in the chemical sectors is realized by the manufacture and sales of complex products. Typical examples of products from this industry are adhesives, coatings, detergents, cosmetics, pharmaceuticals, fertilizers, and agricultural formulations. Besides these products, a similar list of products can be collected from processing sectors like the food, ceramics and metals industry.

Thus, between the bulk chemical industry and the market for consumer products there is a large products sector that designs, formulates, shapes and produces structured products that are used to fulfill consumer needs and, at the end of their functional life, are recycled or discarded.

More and more chemical engineers become involved in the design and manufacture of such structured products and the need for broadening their curriculum is being recognized by the industry and academia.

At the University of Groningen a new bachelor-master program has been initiated to educate chemical engineering students in the technical and managerial disciplines required for a future career in this chemical products sector.

The curriculum builds on the classic chemical engineering program mentioned above with additional courses that are centered on the following principles:

- complex formulated products are produced from low and high molecular weight inorganic and organic materials that in the range of the applied processing and application conditions behave as solids, liquids or gases.
- chemical and physical properties of individual components in a complex formulated product determine the choice of processing technology, the interaction between the components, and the final product performance properties
- processing technology may affect the chemical and physical properties of the individual components, and, as a result, may influence the final product properties

From these principles it can be concluded that the design, formulation, production and application of complex structured products requires training in:

- the managerial aspects of product design with idea generation, design methodology, project management, marketing, and, production and product economics as the main themes
- structure – performance relationships with respect to processing and final application properties
- physical technology and interfacial phenomena that play a role in the manufacture of products
- collaborating in multifunctional teams

The lecture will give some examples of product design to illustrate the competencies required for positions in this industry, resulting in an overview of the curriculum and the way in which it currently is being offered to product engineering students.

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Session T6-P: Chemical Engineering Education -Poster Session

Abstract Number	Paper Title & Authors	Included
338	Problem-based Learning For A Chemical Engineering Subject R Aldaco, F San Roman, I Ortiz, A Irabien	Yes
429	A new education model in the FCQEI – UAEM V León-Hernández, R M Melgoza–Alemán, L O Osornio-Alcaraz, M L Domínguez-Patiño	Yes
1395	Implementation Of A Virtual Course With Moodle Applied To A Case Study Methodology In Chemical Engineering Degree S L Yagüe, Mª T G Cubero, S B Rodríguez, P A G Encina, G G Benito, M Á U Alonso D Álvarez	Yes
1015	E-learning in Process Control Education M Bakosova, M Fikar, L Cirka	Yes
1684	Attracting High Potential Students taking Environmental Engineering as an Example A Blesgen, V C Hass	Yes
1934	A Structured Immersive Learning Environment for Process Engineering Based on Real VR I T Cameron, C Norton	Yes
2493	Simulation based Optimization of the Control of a Waste Heat Boiler during an In-House Control Seminar V C Hassa, A Schauenburg , K-M Schoop, D Ringel, A van Schooten	Yes
2671	Materials Science In Chemical Engineering Education I Zvereva, A Toikka, I Murin	Yes

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Problem-based learning for a Chemical Engineering subject

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1. Summary

The aim of this work is to put into practice the new teaching-learning methodology (Problem-based learning (PBL)) designed in the context of the European Higher Education Area (EHEA) for the a optional course in the Chemical Engineer degree of the Cantabria University.
Results show a high involvement of the students in all tasks commended, and a high level of agreement with this new learning methodology.

Keywords: Problem-based learning (PBL), chemical engineering, European Higher Education Area (EHEA)

2. Extended Abstract

The aim of the European Higher Education Area (EHEA) is to provide citizens with choices from a wide and transparent range of high quality courses and benefit from smooth recognition procedures. In order to adapt the Chemical Engineering degree to the EHEA, it is necessary to modify not only the objectives and contents of the different subjects but also the teaching-learning methods. The application of new methodologies involves a different way of working, considering both the knowledge and the skills reached by the students and their contribution to their capacities. Problem-based learning (PBL) is assumed as an efficient alternative to traditional teacher-centered methods (Dochy et al., 2003).

PBL requires students to work in small groups to identify and solve case studies through self-directed learning. Lectures are “tutors” that assist the group to identify their learning needs and critically appraise the applicability of new information to a given case. PBL is thought to foster critical thinking attributes, problem-solving skills, group communication skills, and a commitment to long-life learning.

The aim of this work is to put into practice the new teaching-learning methodology designed in the context of the EHEA for the “Tutorized Work” course. The selected course is optional in the Chemical Engineer degree of the Cantabria University. The purpose of the 16 week course was to provide students with an understanding of integrated design of chemical processes, using the knowledge acquired during degree courses in Chemical Engineering studies. Emphasis is put on the combination of the experimental methodology together with the analysis of the results. Process simulation techniques are also used for the final project design. PBL applied to the "Tutorized work" is a process involving several steps, which are shown in Figure 1.

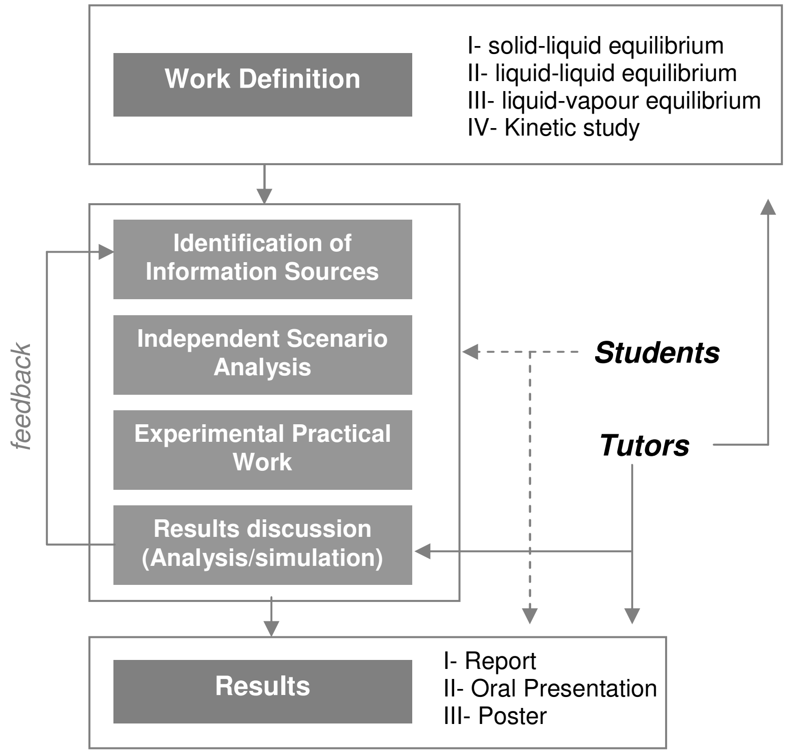

Figure 1. Steps of the Problem-based Learning.

Four PBL learning scenarios were developed: I- Analysis of solid-liquid equilibrium. II- Analysis of liquid-liquid equilibrium. III- Analysis of liquid-vapour equilibrium. IV- Kinetic study of homogeneous and heterogeneous reactions. The guideline of the course is as follows: I- Context of the work, including bibliography, analytical techniques and experimental design, II- Experimental work, III- Results discussion, including analysis and process simulation, IV- Reports, and oral and panel presentation of the results. A course Portfolio has been developed in order to include course materials to help students learning.

The majority of students show a positive attitude toward the new methodology. In addition, students improve the sense of autonomy, the responsibility of their own learning, and their ability to oral and write communication.

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New education model in the FCQeI – UAEM

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1. Summary

In September of 2005 the “continuous improvement of processes” academic corps (AC- CIP) began a project of intervention exploratory tutorship in the Chemical Sciences and Engineering Faculty (FCQeI) of the Morelos State Autonomous University (UAEM), with the purpose of take advance in the knowledge of the existent conditions and to extend the vision of students, teachers and authorities in communication with the activities of the individual and group tutorship program. The conclusion corroborates that in the FCQeI, there are enough conditions to create a formal tutorship program. With this basis the CA decides to formulate a tutorship program and to propose it to authorities of the FCQeI – UAEM to try to obtain its institutionalization and set it in a formal way, for to get on the benefit effects in the educational, administrative, labor and budget parts. The program has been designed in three stages a) adaptation stage, b) transition stage, and c) consolidation stage. The scheduled activities are: The permanent formation of tutor teachers, the design of the activities with base in the axes of 1) academic orientation and adaptation to the UAEM institution, 2) development of abilities for the learning and the self teaching and 3) development for the student's integral formation. This paper shows the main results of the tutorship program in the FCQeI – UAEM for the establishment of a new educational model into the chemical engineers program with the participation of the teachers and assessor with a new roll outside the classroom.

Keywords: Tutoring Program, Education Model, intervention exploratory, individual and group tutoring, outside classroom

2. Extended Abstract

Before the new world order, the society of the knowledge and the use of the new technologies of the information and the communication (NTIC), new currìcula of chemical engineering they demand designs focused in the emergent paradigm of the learning centred in the student, development of professional competitions, the abilities of self-learning and the formation throughout the life. Under this context, el AC-CIP of the FCQeI-UAEM, to aim to contribute to elevate the quality of teaching by means of the improvement of the circumstances of the learning, to diminish the scholastic desertion and to increase the terminal efficiency, elaborated the Tutoring Program like a support for the students in the development of professional competitions, the construction of values, attitudes and habits, as well as, direction in the disciplinary fields, offering greater opportunities to them at its integral formation

Tutoring Program was designed proposing two modalities of tutorial intervention: a) Individual tutoring - that consists of the customized attention to a student on the part of the tutor who will accompany it during his academic trajectory, and b) Group tutoring - the one that offers attention to a group of students, developing collective activities in a reasonable time once to the week.

The tutorial actions for the development of the program considered in three stages: **First stage: *Adaptation***. This stage settles down for the students of first entrance to the FCQI. Its objective is to allow the adaptation of the student to the Institution and the Faculty, as well as of the development of competitions to generate and to administer its own plan of learning. This stage also contemplates a permanent program of formation for the academic ones that makes the tutorial activities. **Second stage: *Transition***. This stage was established for students of intermediate semesters of the Faculty. The tutorial action emphasizes activities that support and fortify the integral formation of the student and its integration to the sport programs, cultural, participation in professional societies and of student mobility. **Third stage: *Consolidation*.** The activities of this stage settle down for students of the last year of the degree. The tutorial action emphasizes the development of social competitions and employment ability of the student for its integration to the productive sector or to a post degree.

Tutoring Program in the FCQI, has contributed elements to contribute in: the pursuit in the academic trajectories of the students, to give answer to the real and immediate necessities of the students and the necessities of formation of professors, the knowledge of the educational performance of the professors of the Faculty, the knowledge of the difficulties of the learning of the students and the processes of entrance and adaptation from the students to the university.

To a year of the implantation of Tutoring Program in the FCQI the results have been successful since besides to focus in the students, it has allowed to focus the attention in the development of a new educative model in where the tutoring is a main axis of the education. The implantation of a tutoring program has several dimensions, but in the middle of the definition of those dimensions one is the integral formation of the students and its expectations like well educate persons.

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E-learning in Process Control Education

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1. Summary

The paper presents some new features that have been introduced in the last years to the course Automatic Control Fundamentals at the FCFT STU in Bratislava. These involve intensive use of information and communication technologies and reduction of repetitive pedagogic work using e-learning techniques. The work also shows how to employ MATLAB as a scripting engine coupled with XML technology to generate multiple outputs using single input source.

Keywords: e-learning, LMS, education, process control, information technologies

2. Extended Abstract

The course Automatic Control Fundamentals is compulsory for all undergraduate students at the FCFT. The textbook by Bakosova et al. (2003) is used in the course. Several versions are available: paper, interactive PDF, and lecture notes PDF. The main topics of the course are modelling of chemical processes, closed-loop, stability, PID controller design and control of chemical processes. Virtual animated processes are used in simulations and their number will increase in the future. The new self-learning package covering all topics of the course has been established on the Internet. It can be found in a freely accessible web page at http://www.kirp.chtf.stuba.sk/lcza (in Slovak). The Internet suite has several components: study materials, files for download, information about the course, basic operations, Internet version of all course topic problems, on-line quizzes and preparation for written tests, Moodle e-learning portal for grade books, attendances, quizzes, etc.

Almost all tasks in the laboratory exercises of the course are based on MATLAB/Simulink. To enable the students to use the same or similar working environment individually on their home computers, or even using an Internet connection, the MATLAB Web Server (MWS) is used. MWS is a cgi-bin application that enables to launch MATLAB script files (m-files) remotely. With MWS, almost all built-in and self-written MATLAB functions can be called from the m-file, including functions that produce plots to be shown to the user. The MWS allows solving problems as e.g. solution of a matrix equation $\boldsymbol{Ax} = \boldsymbol{b}$, polynomial mathematical operations, polynomial roots finding, step responses of LTI models, process model simulations, closed-loop simulations, etc.

It has been decided that each student should have an individual assignment and that all students have assignments of a similar difficulty. Therefore, an Internet e-learning module has been built. The module consists of two parts. The first one connects individual student assignments and solutions for teacher with Open Source project Moodle (Dougiamas, 2005). The second part of the module is scientific and deals with assignment generation for all students. MATLAB scripts and functions generate random numbers for a particular problem, solve it, and generate the result as a HTML file suitable to be included in the first part of the module. The procedure consists of several parts: a function that generates random input values for one student, a function that takes the assignment and calculates not only its solution but also some intermediary results to aid the teacher with the evaluation of the student, a script that calls both preceding functions for the total number of students and stores the data in a file, a script that reads the input file from the preceding step and outputs two series of HTML files - one for students and one for teachers.

Quizzes are needed in various parts of the course. Some of them are used in Moodle at the beginning of each laboratory exercise to check whether students are prepared. There are free questions for each topic of the course that help students in self-study. Finally, there are questions that are parts of quizzes for the course examination. Examination of the course is divided into written and oral parts. The written part consists of a series of computational questions. The questions can either be multiple-choice questions with five choices where each student marks one correct choice or short answers where no choices are given. The advantage of the multiple-choice approach is that quizzes can be graded automatically. On the other hand, short answer types of quizzes have to be graded manually, but make the quiz a little harder. Preparation of all these questions has been automated. MATLAB is used as the computational engine, XML/XSLT as the transformation engine, and LATEX, HTML, and Moodle as formatting tools.

All mentioned changes have been introduced in order to bring the course in line with current trends in education and to increase its rating and attraction among students.

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Implementation of a virtual course with Moodle applied to a case study methodology in Chemical Engineering Degree

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1. Summary

An integrated learning methodology based on a Case Study has been developed and implemented in 4th course of Chemical Engineering degree during 2005-2006 academic year. This methodology was based on problems and projects, with the special characteristic that every activity was programmed about the same industrial process.

Taking as reference the previous experience and in order to promote the "active learning" based on Internet technology, the Case Study was implemented as a Moodle course in combination with conventional face-to-face sessions. In this sense, the proposed virtual course includes forums, textual resources (general information related to educational methodology, chemical engineers abilities and evaluation criteria; textbooks and exercise books), home-learning resources (video recordings, audio recordings), demonstration resources (laboratory experiments, simulators…), quizzes (partial evaluations), calendar (global, group and user events) and other activities (technical visits, conferences, upcoming events). The combination of technology-based materials and face-to-face sessions, allow developing innovative ways to motivate people to learn, provide greater access to information, help students learn conceptual matters and allow developing interpersonal skills.

Keywords: Virtual course, Moodle, Case Study, Chemical Engineering

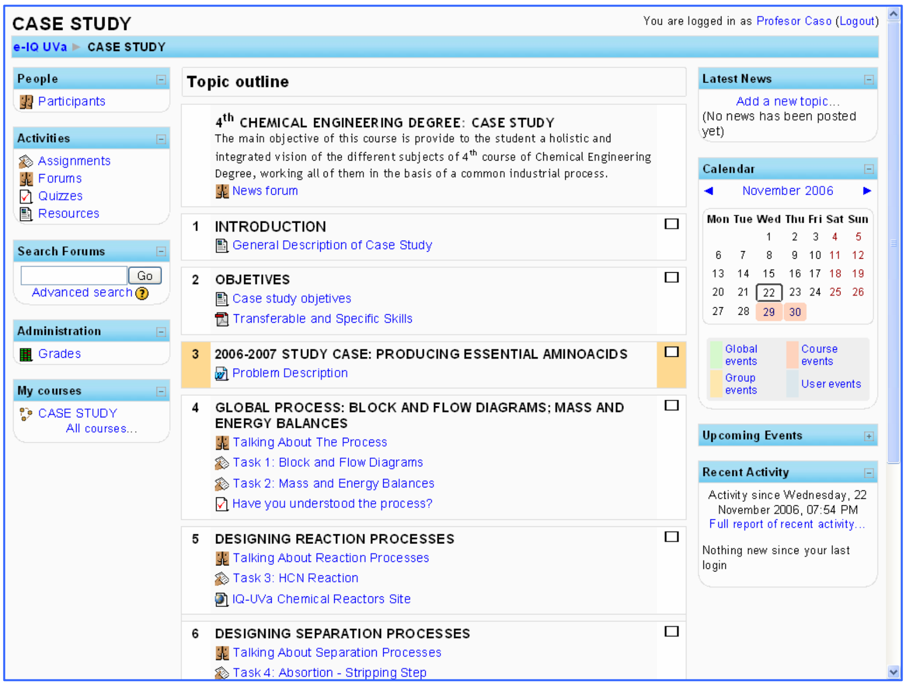
2. Extended Abstract

The main objectives of the proposed Case Study Strategy were provide to the student an integrated vision of the different subjects, working all of them in the basis of a common industrial process along with developing student's abilities that are difficult to acquire with the traditional learning system. This educational methodology was based on problems and projects, with the special characteristic that every activity was programmed about the same industrial process. The chemical process proposed was initially analyzed as a whole and later defined in different blocks. For each subject, different block aspects were detailed: selection of alternatives, operation mode, equipment scale-up, system analysis, etc. All the subjects considered are involved in the obligatory disciplines of the 4th course. Moreover, it was necessary to configure a calendar that includes all activities to carry out for the student (lectures, problem sessions, seminars, technical visits, conferences…) [1].

Taking as reference the previous experience and keeping in mind the need to promote the "active learning" based on Internet technology, the previous proposed educational methodology has been implemented using Moodle as e-learning platform in combination with conventional face-to-face sessions [2]. This arrangement combines an electronic learning component with some form of human intervention, including the concept of e-tutor or e-mentor. This effective combination of different modes of delivery, models of teaching and styles of learning, founded on transparent communication amongst all parties involved with a course is known as "Blended-learning or B-learning" [3].

The proposed virtual course implemented with Moodle includes several resources and activities as it is shown in Figure 1.

Figure 1. General view of proposed "Case Study course" implemented with Moodle.



CASE STUDY

You are logged in as Profesor Caso (Logout)

e-IQ UVa ▶ CASE STUDY

Topic outline

4th CHEMICAL ENGINEERING DEGREE: CASE STUDY

The main objective of this course is provide to the student a holistic and integrated vision of the different subjects of 4th course of Chemical Engineering Degree, working all of them in the basis of a common industrial process.

News forum

1 INTRODUCTION ☐
- General Description of Case Study

2 OBJETIVES ☐
- Case study objetives
- Transferable and Specific Skills

3 2006-2007 STUDY CASE: PRODUCING ESSENTIAL AMINOACIDS ☐
- Problem Description

4 GLOBAL PROCESS: BLOCK AND FLOW DIAGRAMS; MASS AND ENERGY BALANCES ☐
- Talking About The Process
- Task 1: Block and Flow Diagrams
- Task 2: Mass and Energy Balances
- Have you understood the process?

5 DESIGNING REACTION PROCESSES ☐
- Talking About Reaction Processes
- Task 3: HCN Reaction
- IQ-UVa Chemical Reactors Site

6 DESIGNING SEPARATION PROCESSES ☐
- Talking About Separation Processes
- Task 4: Absortion - Stripping Step

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Calendar

◀ November 2006 ▶

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27	28	29	30			

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Attracting High Potential Students taking Environmental Engineering as an Example

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1. Summary

A general and major problem for many if not all engineering degree courses is attracting those students, with the highest potential for a successful study. Engineering is perceived as difficult and complicated. Despite the fact that – at least at the moment – industry is seeking engineers from a broad spectrum of disciplines, numbers of applications and enrolled students are decreasing. This is a problem that has to be addressed adequately in order to not only fully use university's capacities but also to meet industry's current and future requirements concerning qualified human resources. This Paper describes several counter-measures aiming at (1) attracting high potential students and (2) reducing numbers of students prematurely terminating their studies at the University of Applied Sciences Bremen. These actions can be of exemplary nature for other (engineering) degree courses.

Keywords: environmental engineering, successful studies, increase of study quality

2. Extended Abstract

Taking the situation in Germany as an example, the number of high-school graduates (legitimate for enrolling at universities or polytechnics) is increasing since the late 1970's. The percentage of these young graduates actually enrolling at a university is fluctuating between 60 % in 1985 and 92 % in 1990/ 91 (just after reunification of East and West Germany). In 2004 a fraction of 19 % enrolled in engineering sciences (figure 1). In view of the high contribution of engineers to the value chain, this percentage is relatively

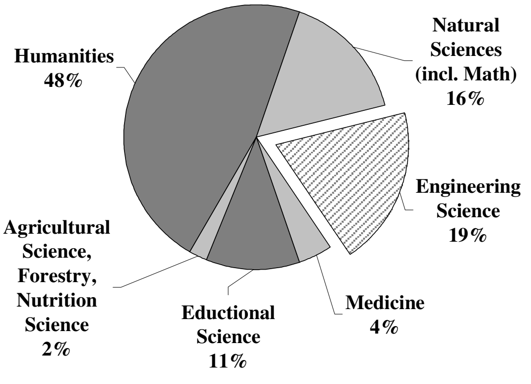

Figure 1: Enrolment at German universities and polytechnics broken down by discipline in 2004. [Heine et al., 2005]

low. Additionally, the number of engineering students prematurely terminating their studies is quite high (up to 50 %, depending on discipline) [Heine et al., 2005]. The international B.Sc. course on Environmental Engineering at the University of Applied Sciences Bremen has to deal with these problems as many other engineering courses as well. In 2005, these problems were addressed by initiating a program aiming at increasing study quality and application numbers as well as at decreasing study abortions. To reach this aim, the program includes various counter-measures of which a selection is being described below.

Every year, students of the fourth semester organise an excursion for students of the second semester. During this three-day field trip, students visit various companies that are either working in the field of environmental engineering or that have particular facilities relevant from an environmental point of view. By conducting the excursion at such an early stage (first year of studies) students become acquainted with their future working environments and typical tasks of engineers. Another example for teaching complex engineering skills at a very early stage is the "Environmental Engineering Project" (EEP). Here, teams of students of the third and fourth semester work on realistic engineering tasks, often in co-operation with industry. Examples for projects carried out so far are the conceptual design of a pilot-scale adsorption column or the optimisation of energy consumption of an agricultural enterprise. Although the required abilities for successfully managing these tasks are very demanding for second year students, the EEP is generally perceived very positively resulting in increased study motivation.

During the project it became obvious that many students lacked knowledge about study contents and about the working field of engineers. In order to rectify this lack of knowledge, various measures were implemented. These include an improved internet presence (since our experience shows that the internet is the most preferred source of information for applicants), several information events and various training courses prior to the first semester. Another extensive project aims at transferring scientific and engineering methods to high-school students. In this context, a variety of experiments is being prepared, tested and documented. Teachers are being provided with detailed instructions of these experiments and they will have the possibility of borrowing the required equipment. [www.nemab.hs-bremen.de]

By applying these and other measures in the international B.Sc. course on Environmental Engineering, the percentage of students terminating their studies prematurely, could be lowered to fewer than 30 %, with most current retention rates of up to 90 %. Furthermore, an increase in application numbers could be observed.

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European Congress of Chemical Engineering (ECCE-6)
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A Structured Immersive Learning Environment for Process Engineering based on Real VR

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1. Summary

This work presents a new development in process engineering learning environments through the use of spherical photography of a process plant coupled to an interactive learning system. The immersive environment provides a vehicle for novice, intermediate and advanced learning of process engineering principles for students and process operators. It brings the real process plant to the learner whereby the learning activities are immersed in a 3D environment. The learning system is hierarchically structured from whole plant concepts down to the equipment level. A range of learning modes is embedded in the system based on sound pedagogical principles. The structure is such that the environment is easily extensible across various domains of process knowledge and depth of enquiry. The development is being done in collaboration with major industrial organizations within Australia, with the system being progressively deployed at universities and within organizations as an advanced training tool.

Keywords: virtual reality, immersive environment, process systems, interactive learning

2. Extended Abstract

Opportunities for providing visual context for process theory in real operating systems are increasingly less accessible to students. Costs, litigation concerns as well as logistic constraints make both plant operators and university staff hesitant to conduct large scale plant tours.

This project directly addresses parallel learning needs of university and industry. For university students, the real plant is brought to the learner, through a set of virtual reality (VR) immersive environments. These environments enhance insight and understanding by providing:

- A real engineering context within the different plants
- Relevant activities and information pieces embedded within the VR imagery

- An exploratory platform to discover and investigate at the individual’s own pace.

This framework:
- creates an interface which supports self-directed learning; hence it has a web of learning paths through which concepts and conceptual difficulty build.
- frame information and activities in a system that is engaging and entertaining, so learning is enhanced
- an interface that can be used within an internet browser platform
- use of terminology and language that is general
- supports a simple means of assessing the success of the learning tool against its stated learning outcomes
- develops a platform that has a low dependency on both specific hardware and software.

For example, Figure 1 shows a user activity related to finding specific items of equipment in a crude distillation unit of a petroleum refinery. “Walk through” facilities aid learning. Figure 2 shows part of a complex pump and drive isolation exercise driven by a GRAFCET sequenced control diagram. Other learning activities that benefit from the use of VR environments are currently under development as well as the expansion of the suite of process operations into alumina, dairy and methanol processes.

Navigation aid:
Click on the green dots in the mini-map to the left to take shortcuts into the virtual environment. The red figure shows your current location. Click and drag your cursor to move around in the virtual reality environment. Use the SHIFT and CONTROL keys to zoom in and out. You can also use the controls on the grey status bar below to navigate the virtual environment. The SHOW HOT SPOTS control will reveal navigation hot spots (square shaped).

Figure 1 VR immersive environment

Discharge valve closed tightly

2 Open check valve bypass if installed

Figure 2 Pump isolation learning exercise

The current environment is deployed at 5 university sites within Australia and is being used in a range of chemical engineering and related courses across 2nd, 3rd and 4th years of the curriculum. Further deployment will take place and formal assessment of the expected learning outcomes for students and plant operators is also taking place.

The authors acknowledge the collaboration with colleagues at The Universities of Sydney, Melbourne, Monash and Curtin University of Technology. We gratefully acknowledge the financial, material and staff support from BP Refinery Bulwer Island, Australia. We also thank the Carrick Institute for Learning and Teaching in Higher Education, Australia for a major competitive grant to part fund development.

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Simulation based Optimization of the Control of a Waste Heat Boiler during an In-House Control Seminar

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1. Summary

In a joint project the Hochschule Bremen and the Arcelor Bremen GmbH developed a new concept of an in-house training for the continuing education of control and chemical engineers. During a workshop control and chemical engineers from different departments within Arcelor Bremen designed a new control strategy for the operation of a waste heat boiler. In order to assist the controller design an interactive process simulator has been developed during the workshop using the process control software WinErs. The developed controller was realized in a Siemens PLC (S7). Before installation of the PLC to the real process it was tested extensively using the interactive simulator. During the workshop under the guidance of an external moderator team the engineers learned new techniques for an efficient interdisciplinary system analysis using modern modelling techniques. This type of in-house training shall be implemented into the Arcelor Bremen programme of continuing education on a permanent basis.

Keywords: Waste heat boiler, Control, Process dynamics, In-house Training

2. Extended Abstract

Many control loops in the process industry are not operated in an optimal manner. Their optimization requires an interdisciplinary system analysis in which process engineering and control engineering knowledge must be combined.

Due to the education of staff, the required engineering knowledge is distributed amongst several persons. Thus, intensive and efficient communication is needed. However, the communication may be hindered, if qualified staff is working in several different departments.

In a joint project the Hochschule Bremen and the Arcelor Bremen GmbH developed a new concept of an in-house training for the continuing education of control and chemical engineers. The aim of the course in the form of a workshop was to develop the skills for a systematic process analysis by the efficient use of the in-house competences in control and process technology.

During the workshop under the leadership of an external moderator team a group of six engineers from different departments worked on the optimization of the control of a waste heat boiler as a case study. In the modern steelwork of the Arcelor Bremen GmbH waste heat boilers are needed to make efficient use of waste heat for vapour production. A major technical problem is the complex dynamic of the process.

The system analysis was guided by the moderators and performed in parallel to the development of a mathematical process model, that enabled a real time simulation of the process. Thus, the model reflected the process and control engineering knowledge about the boiler to the participants in form of a real time simulator [1]. The simulator was realized using the simulation and process control software WinErs of the Ingenieurbüro Dr.-Ing. Schoop GmbH, Hamburg [2]. The verification of the process model and the simulator behaviour was based on real data.

Subsequently, a controller design was performed in the group, again guided by the moderators. The developed control strategy was tested and implemented in three steps. First, it was applied to the simulator using the process control functionality of WinErs. In the second step a Siemens PLC (S7) was programmed and again tested using the real-time simulator. In the third step the PL-controller was coupled to the real process. It is now working on the process since several months with very good success.

The trainees in the workshop learned to communicate efficiently about interdisciplinary control problems. They also learned to develop control strategies systematically on the basis of a system analysis by using mathematical modelling and simulation.

Eventually, an important control loop was optimized during the in-house training. It is planned to implement this type of in-house training into the Arcelor Bremen programme of continuing education on a permanent basis.

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Materials Science in Chemical Engineering Education

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Summary

The new education program in Saint-Petersburg State University, Russia – should combine the teaching in chemistry, physics and mechanics for the study materials properties. Since 2006 this direction of education in classical universities was included in the list of official programs of Russian Ministry of Science and Education. In comparison with the similar programs of technical universities the teaching in classical universities should be oriented on the fundamental study in the area of materials science. Side by side with the topics on materials properties the objects of student's programs should be main aspects of chemical engineering. The main goals of our lecture are: i. to present the most significant elements of the education program in Saint-Petersburg State University; ii. to consider the optimal ways to combine education in material science and chemical engineering: iii. to discuss the teaching in the similar area in Russian and foreign classical universities in comparison.

Keywords: material science, chemical engineering, education

The teaching of students in material science covers large areas of chemistry, physics and other sciences. The main directions of material science education usually concern basic aspects of the synthesis and characterization of materials. The study of the processes in materials, especially for the purposes of the industrial application and other applied topics often are out of the main teaching activities. On the other side the study of materials often is out of the frame of chemical engineering education also. Moreover materials science continues to be one of the most expensive fields of the education. Such situation is typical both for technical and classical universities.

This report is focuses on the innovative process to introduce Materials Science in Saint-Petersburg State University in the frame of Russian National Project "Education". Our program "Chemistry, physics and mechanics of materials" had been organized to develop the education in material science on the base of multidisciplinary approach. One of the peculiarities of such approach is the combination of basic and applied subjects. Creation of experimental base for complex teaching and mechanism of combining in the same educational program different components - chemistry, physics and mechanics of materials – is considered as the way to grow up a generation able to solve many problems in Chemical Engineering, Applied Science and Technology. We consider the knowledge in material science as a necessary and integral part of Chemical Engineering education. An important aspect of Materials Science in Chemical Engineering education reflects the partnership with business structures and industry. It is important for the level of future bachelors and masters is their activity in the research during the study. The success of the introducing new way and new educational program is connected to international collaboration and common efforts for Materials Science in Chemical Engineering education.

One of the significant aspects of the program should be the teaching in the area of novel processes that are realized with the use of modern materials. Such studies require both the lecture courses on general topics (e.g. thermodynamics and kinetics of materials) and lectures and practical courses in specific areas (e.g. solid state ionics, magnetochemistry, membrane technology, chemistry and physics of semiconductors, etc.). In spite that many of the courses and other parts of the education program could seem like traditional ones it would be a lot of innovative elements that are important for modern specialists in fundamental material science. For example a big attention in the courses on thermodynamics should be paid on nonequilibrium processes that are the real processes in industry. Other aspects of modern science and technology (e.g. nanotechnology, catalysis, membrane processes, laser research, etc.) should be also included in classical courses.

The other peculiarities of our new program and future development of multidisciplinary education in material science and chemical engineering in classical university will be also presented in the lecture.

Acknowledgements Authors are grateful for the financial support of the Federal Education Agency of Russia. The present contribution was developed within the framework of the project "Innovative educational environment in the classical university" by the Saint-Petersburg State University.

Session S-1: Invited Session on MultiScale Modelling

Abstract Number	Paper Title & Authors	Included
4075	From molecular simulation to thermophysical properties : can we bridge the gap between the nanoscale and process scale? P Ungerer	Yes
4084	Powders, Particles and Processes: Multiscale Approaches for Improved Performance I Cameron	Yes
4156	The necessary multi-scale and multidisciplinary approach of a modern chemical engineering for product design and engineering in the frame of globalization, sustainability and technical innovation J-C Charpentier	Yes
4160	Industrial application of modeling for different processes M Wolf, A Juppke, H-J Leimkühler	Yes

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The necessary multi-scale and multidisciplinary approach of a modern chemical engineering for product design and engineering in the frame of globalization, sustainability and technical innovation

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1. Summary

To respond to the changing needs of the chemical and related industries in order both to meet the today's economy demands and to remain competitive in global trade, a modern chemical engineering is vital to satisfy both the market requirements for specific nano and-micro scale end-use properties of products, and the social and environmental constraints of industrial meso and-macro scale processes. Thus an integrated system approach of complex multidisciplinary, non-linear, non-equilibrium processes and phenomena occurring on different length and time scales of the supply chain, from molecular-scale to the production-scales is required: the «triplet molecular Process-Product-Process Engineering (3PE)"approach. A modern chemical engineering can be summarized by four main objectives: (1) Increase productivity and selectivity through intensification of intelligent operations and a multi scale approach to processes control: nano and micro-tailoring of materials with controlled structure; (2) Design novel equipment based on scientific principles and new production methods: process intensification using multifunctional reactors and micro-engineering for micro structured equipment; (3) Extend chemical engineering methodology to product design and engineering using the " (3PE)" approach; (4) Implement multiscale application of computational chemical engineering modeling and simulation to real-life situations from the molecular scale to the production scale, e.g., in order to understand how phenomena at a smaller length scale relate to properties and behavior at a longer length scale. The present publication shall emphasis the multidisciplinary and multiscale modeling and simulation approach.

Keywords: modern chemical engineering, multidisciplinary and length multiscale approach, product design and engineering

2. Extended Abstract

The purpose of teaching and basic research in chemical engineering is still the development of concepts, methods and techniques to better understand conceive and design processes to transform raw material and energy into useful products. But actual developments require increasingly specialized materials, active compound and special effects chemicals which are in fact much more complex in terms of molecular structure than traditional high bulk volume industrial chemicals. Thus the modern chemical engineering is also concerned with understanding and developing systematic procedures for the design and optimal operation of chemical process systems, ranging from the nano-and micro systems used for product analysis, tests or production to industrial-scale continuous and batch processes, all within the concept of the chemical supply chain. In this supply chain, it should be emphasized that product quality is determined at the nano-and micro scales and that a product with a desired property must be investigated for both structure and function. So a thorough understanding of the structure/property relationship at both the molecular scale (e.g., surface physics and chemistry) and the microscopic scale (e.g., coupling reaction mechanisms and fluid mechanics) is of primary importance to be able to design production processes. This will help to make the leap from the nano scale to the production process scales that ensure the customer quality requirements. Moreover most of chemical processes are non-linear and non-equilibrium, belonging to the so-called complex systems for which multiscale structure is the common nature. This requires an integrated system approach for a multidisciplinary and multiscale modelling of complex, simultaneous and often coupled momentum, heat and mass transfer phenomena and kinetic processes taking place on different time scales (10^{-15} to10^{8}s) and on different length scales (10^{-9} to10^{6}m). So organizing scales and complexity levels in process engineering is necessary in order to understand and describe the events at the nano and micro scales and to better convert molecules into useful and required products at the process scale, e.g., organizing levels of complexity, by translating molecular processes into phenomenological macroscopic laws to create and control the required end-use properties and functionality of products manufactured by continuous or batch processes (transforming molecules into money). This integrated system approach is used in order to understand how physical-bio-chemical phenomena at a smaller length-scale relate to properties and behaviour at a longer length-scale.

So in addition to the basic and irreplaceable notions of unit operations, coupled heat, mass and momentum transfer, and the traditional tools of chemical engineering (separation engineering, catalysis, thermodynamics, process control), this integrated multidisciplinary and multiscale approach is a considerable advantage for the development and success of this engineering science in terms of concept and paradigms for process design and engineering.

In this framework, computers have opened the way for the modeling of molecular and physical properties at the nano-and microscopic scales. Computer-aided molecular/mixture design (CAMD) is a promising topic in this area. And through the interplay of molecular theory, simulation, and the experimental measurements a better quantitative understanding of structure-property relationships evolves, which, when coupled with microscopic chemical engineering science forms the basis for the today required materials and process design. Turning to the macroscopic scale, to be competitive in the production of targeted products, just in time for delivery to the consumer whose needs are constantly evolving, requires dynamic process modelling and process syntheses. Event-driven simulation tools help solve these problems by simulating both material flows and states within the individual pieces of equipment, and by showing which alternative plant and storage strategies provide the greatest cost benefit. But it should be emphasized that in order to help for product design and engineering at any scale, modeling and simulation should be oriented towards the understanding of the physics, chemistry and biology of interactions rather than the refinement of numerical codes whose sophistication is not at all concerned with real life problems met in chemical pilot and production plants in industrial practice. Indeed never forget that in chemical engineering investigations on/in modeling and simulation, what is needed in models is less anatomy and more physiology!

Industrial application of modeling for different processes

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Summary

The presentation will give an overview of how process modeling and simulation is applied at Bayer. The Bayer group with its three core businesses Materials Science, Crop Science and Health Care has a large variety of plant operations. There are plants with capacities larger than 200 000 t/year producing commodity type of products. Other plants based on biological processes produce very small amounts of high value products under GMP conditions. Sewage treatment plants clean large amounts of a combination of municipal and industrial waste waters. Obviously, these plants operate in different environments and are driven by different business and technical factors. This determines the kind of problems where process modeling is applied and also how it is applied. In particular the level of detail in a process model strongly depends on the nature of the problem to be solved. Some models require details like particle size distributions or fermentation kinetics e.g. for the development and optimization of feeding strategies. The generation of consistent mass and energy balances as a basis for the workflow of plant and equipment design requires the coverage of all process and utility streams in a single model. It is a challenge to integrate such different scales of modeling and ensure information consistency in the models. This challenge can be approached with the idea of Lifecycle Modeling, where a common modeling approach is applied to support process development, plant engineering, optimization of plant operation and debottlenecking projects. The tools and methods as well as the workflow that are used in industry will be described in the presentation. We will also give an assessment from our perspective on current issues. The focus of the presentation will be on examples and applications to illustrate the different approaches and scales of modeling that are applied.

Keywords: process modelling, particle size distribution, fermentation kinetics, life cycle modelling

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

From molecular simulation to thermophysical properties : can we bridge the gap between the nanoscale and process scale ?

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Summary

From a chemical engineering standpoint, predicting macroscopic properties of any system on the basis of its microscopic description is a Holy Grail. Many chemists have dreamt of models that could predict the properties of fancy mixtures before they are prepared, many polymer engineers would like to know precisely how mechanical properties are related to structure of a polymer material, many process engineers still expect a general method to model multiphase fluid flow. Is there a chance that some of these dreams turn to reality ? This talk aims at answering on the basis of recently published work.

In a first part, we consider "simple" cases, i.e. cases where the system is sufficiently homogeneous that a very small system sample (a few nanometers large), containing a few hundreds to a few thousands atoms, is statistically representative. Then the behaviour of the small size sample may be determined by molecular simulation, i.e. as the result of the microscopic interactions between its atomic components. Macroscopic properties can be obtained by suitable averages : time averages provide transport properties like diffusion coefficients or viscosity, statistical averages provide equilibrium properties like density, saturation pressure, etc. Three advances have helped to reach this stage : the continuous increase of computer capacity, the development of dedicated intermolecular energy models, and the availability of versatile models. Various examples are given for the cases that can be solved in this way, which are in fact not so uncommon : fluids (with the exception of the near-critical region), crystalline adsorbents (zeolites), and liquid-vapour interfacial tension. In a second part, we consider cases where the quest is more difficult, i.e. the system is heterogeneous or the size of individual molecules is too large. Then alternative, system-specific strategies must be used to extrapolate from the microscopic to the macroscopic level. A first example is provided by near-critical behaviour of fluids, characterized by density fluctuations at a much larger scale than a few nanometers. Thanks to an appropriate scaling, it is possible to use small size molecular simulations to determine reliably the critical locus of pure components and binary mixtures. A second, more prospective example is provided by the solubility of gases in semi-crystalline polymers, which can be investigated by a detailed account of the amorphous fraction, coupled with an approximate description of the crystalline fraction of the material. When the mechanical behaviour of polymer materials is desired, it becomes necessary to lump several monomers in a blob, the properties of which can be obtained from atom-level simulations.

In a last part, we discuss the fields where heterogeneities are still preventing from extrapolating from microscopic to macroscopic behaviour. The computational fluid mechanics of dense suspensions of small solid particles is selected to illustrate which stages could be involved in such extrapolations. Other possible applications are outlined in conclusion.

Keywords: macroscopic properties, microscopic description, nanoscale, process scale

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Powders, Particles and Processes: Multiscale Approaches for Improved Performance

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1. Summary

Particulate products permeate all major commodity and specialty markets. The importance of powder processing and particle formation is hard to overstate, given the ubiquitous nature of these products and the challenges in designing, operating and optimizing process systems for commercial purposes. This presentation, discusses some recent multiscale particle modeling work across a variety of application areas that include different granulation processes. It is shown that a multiscale approach provides a helpful systems framework to resolve issues at varying time-length-detail (τ-L-D) scales in addressing processing issues. The complex linking of scale information is crucial in developing innovative approaches to improved processing methods. This “scale integration” problem has a number of approaches yet is still a major challenge to resolving integrated methods to particle, product and process design. Insights are drawn from a selection of industrially relevant examples.

Keywords: multiscale, particles, discrete element method, granulation, scale linking

2. Extended Abstract

Particle systems naturally constitute multiscale systems where those particles are generated by a range of processes including such techniques as high shear or drum granulation. Figure 1 shows a typical scale map related to granulation systems that applies to many major production facilities. In this work, we investigate a range of activities including:

- The fundamental physical and chemical understanding of particle-particle interactions at the microscale level and the modeling of the phenomena.
- The intermediate or macroscale level of the particle assembly or granule and how the growth, layering and breakage mechanisms are utilized in predictive models.
- The macroscale or plant scale involving the whole of the process system, its design, operation and control.

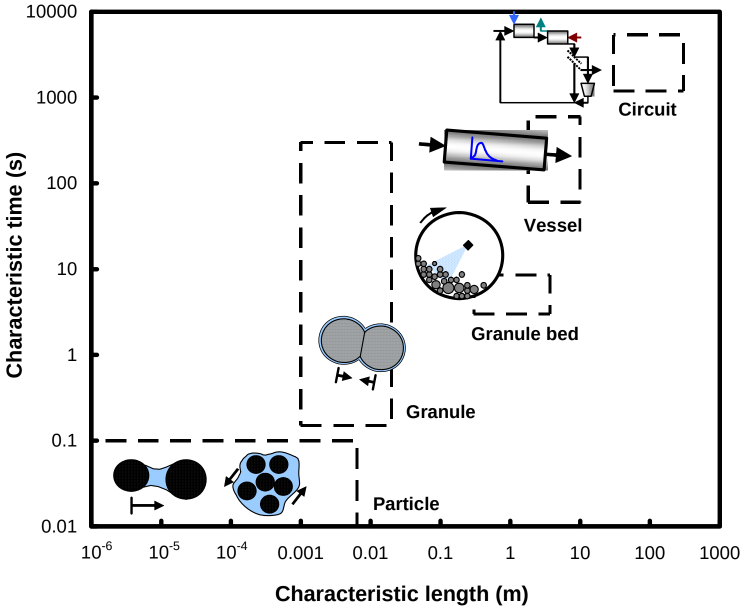

Figure 1 A scale map of granulation processes

Permeating all these issues are aspects of mathematical modeling and the application of those models for decision making purposes. This approach of fundamental sciences and modeling stands in stark contrast to the long-term historical approach of empiricism.

Issues of appropriate modeling and the validation of models for the various scales are discussed, in relation to a wide range of modelling techniques and validation methods. These include both empirical approaches and the growing use of phenomenological methods based on particle physics and population balances. The coupling of these partial models within and across scales requires careful consideration driven mainly by end-use considerations. Interesting approaches can be proposed depending on the chosen application of the modelling.

Within all this, it is important to appreciate the current advances in the modeling of these systems: where the successes have occurred and where there still exists major hurdles to overcome. This will guide outcomes that can be used in the design, operation and control of the next generation of particle design and production facilities.

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Session S-2: Invited Session on Energy Issues

Abstract Number	**Paper Title & Authors**	**Included**
2653	Mimizing the energy demand of CO2-capture in conventional power stations W Arlt, J Rolker	No
2748	Multi criteria decision making within energy networks for electricity production in emerging markets J Petrie, R Kempener, J Beck, B Cohen, L Basson	Yes
3109	A technological comparison between PEFC and SOFC systems for residential CHP applications B P Ladewig, F Lapicque	Yes
4180	An Oil and Gas Company’s Perspective on Energy Supply and CO2 Capture & Storage G de Koeijer	Yes

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Multi criteria decision making within energy networks for electricity production in emerging markets

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1. Summary

This paper explores a synthesis of modeling tools, including the use of agent-based approaches and dynamic optimisation, for the design and evolution of electricity production networks in emerging markets. Attention is given to the decision making practices of the individual agents which comprise the network, how these are informed by both quantitative and qualitative information, and how they give rise to emergent behaviour within the network. Case studies of bio-energy and coal-based networks are used to demonstrate the approach, and to draw out some general observations which relate to the challenges of modeling complex social systems.

Keywords: energy networks; multi-scale modelling, complex systems; decision making; optimisation

2. Extended Abstract

The development of sustainable energy networks for electricity production poses many challenges. These include uncertainty in demand, diversity of primary energy feedstocks, the acute pressure of climate change impacts, and, in emerging economies, the vital role which such networks can play in stimulating social development. Any structured approach to decision making relating to such networks requires due consideration of multiple objectives, stakeholder diversity, system dynamics and key uncertainties.

This paper addresses the design and evolution of energy networks to promote the production of electricity in emerging markets, using examples from South Africa as case studies. In particular, attention is given to the expansion of an existing coal mine-power station network, and to the development of a new bio-energy network using sugar-cane residues as feedstock. Our primary focus is on the decision-making capability of the individual agents which comprise these networks, as well as the institutional behaviour which evolves within the network over time.

The bio-energy study is used to demonstrate the inclusion of multi-criteria decision making routines within a hybrid agent-based model whose structure is informed by underlying system dynamics. Consideration is given to centralised and distributed power generation networks, and to various regulatory and policy interventions which could help stimulate the network(s). The coal study is used to demonstrate dynamic optimisation of an agent-based model over an extended time period, and informed by real data on infrastructure planning. Some consideration of key uncertainties is covered in both cases, including growth in electricity demand.

This work draws together relevant expertise in process modelling, optimisation, and decision making, and, as such, is informed by perspectives from both management and behavioural sciences, particularly with regards to consideration of qualitative features of decisions made by individual agents, such as trust and loyalty.

Some observations are made with respect to the general relevance of this approach to complex societal problems, with which Chemical Engineers are beginning to engage in a meaningful manner – particularly where Sustainable Development is a key driver.

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A technological comparison between PEFC and SOFC systems for residential CHP applications

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1. Summary

An overview of polymer electrolyte fuel cell and solid oxide fuel cell combined heat and power systems is presented, summarizing the current state of the art in installed and demonstrated systems. The specific features of these systems that make them suitable for CHP applications, in particular their high overall energy efficiency, are discussed. Dynamic mathematical models of the two different systems are derived and implemented using MATLAB-Simulink®, and used to examine in detail the transient response to changes in thermal demand.

Keywords: polymer electrolyte fuel cell, solid oxide fuel cell, combined heat and power

2. Extended Abstract

Fuel cell systems are gaining considerable attention for the production of electricity at high efficiency from a range of different fuel sources. A significant potential application of fuel cell systems is to produce electricity for residential applications in a decentralised manner. In these applications it is also possible to utilise some of the waste heat from the fuel cell system for domestic use, increasing the overall system energy efficiency.

In this study, two different fuel cell technologies are considered for application in small combined heat and power (CHP) systems. Firstly, the polymer electrolyte fuel cell (PEFC), which operates at around 70 °C and requires high purity hydrogen as the anode feed. The second technology is the solid oxide fuel cell (SOFC), which operates at much higher temperatures, around 700 – 800 °C, and may utilise hydrogen or methane as the anode feed.

There is currently limited distribution infrastructure for hydrogen, particularly to residential sites, however in many regions of the developed world there are extensive natural gas distribution networks. This study therefore, will examine the use of natural gas (here approximated by methane, the predominant component of natural gas, although the composition of natural gas varies significantly both spatially and temporally). In the PEFC system, this necessitates the use of a steam reformer, in conjunction with a water gas shift (WGS) reactor and a preferential oxidation (PROX) reactor to produce a hydrogen rich reformate stream with less than 10 ppm CO, the tolerance limit of the Pt anode catalyst. The SOFC system utilises a smaller pre-reformer that partially reforms the methane/steam mixture. Simplified schematics of both the PEFC and SOFC CHP units are shown in Figure 1.

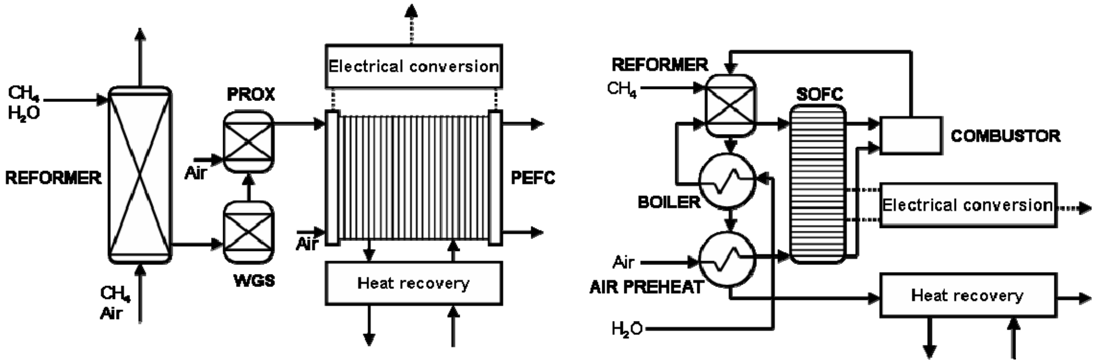

Figure 1. Simplified process flowsheets for the PEFC (left) and SOFC (right) combined heat and power systems considered in this study.

Assuming that the units are connected to the electrical grid, any excess electricity they produce can be returned to the grid, and similarly any shortfall can be met using grid supplies. This means that CHP units are often operated in a thermal load following mode. An important aspect of their performance is the dynamic response to changes in demand, for example the change in heating demand through daily and seasonal fluctuations.

To compare these two simple systems, dynamic mathematical models have been developed and implemented in MATLAB-Simulink®. This allowed detailed simulation of the transient behaviour, at both short time scales (such as a change in stack voltage in response to a change in the external load), and longer time periods (such as the change in the temperature of the stack or the heat exchangers). Although other studies have looked at the economic evaluation of fuel cell CHP systems, this study is devoted exclusively to the technical comparison between the two systems, and in particular their transient response characteristics.

An Oil and Gas Company's Perspective on Energy Supply and CO_2 Capture & Storage

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Summary

The oil & gas industry is a significant consumer of power and heat through oil and gas production facilities (upstream) and the transportation of raw materials (crude, condensate etc) and final products (refined products, LNG etc). As important are the downstream facilities such as refineries, LNG plants and chemical and petro-chemistry plants using large amounts of heat, power and other utilities such as hydrogen. Heat and power producing technologies that are applicable for these facilities are of foremost interest for the oil and gas industry. The demand for oil and gas products is increasing worldwide, but there are important drivers that may change today's market. Two of these are the security of supply and the growing environmental concerns, in particular the CO_2 emissions. These two drivers may change the demand for oil and gas in the long run, but the development will also depend heavily on how strong these concerns are, and how much taxes and incentives are used to push this development forward. In the short to medium term, this means that the oil and gas industry needs to ‘‘go green’’.

Increasing energy efficiency, fuel switching, use of renewable energy supply and CO_2 Capture and Storage (CCS) are currently pursued. Statoil operates currently two commercial CCS projects: one at the Sleipner gas field in the North Sea, and one in the Algerian dessert at In Salah together with BP and Sonatrach. Soon the Snøhvit LNG project in Northern Norway with CCS will start up. Common for these three projects is that CO_2 is captured from natural gas and stored in saline aquifers. Statoil is currently partner in two more ambitious projects, in which CCS for power plants are being investigated. The first is the Halten CO_2 project, together with Shell. A new gas fired power plant is considered with post-combustion CO_2 capture at Tjeldbergodden in Mid Norway. The second project considers a post-combustion CO_2 capture plant at a combined heat and power plant (CHP) at the Mongstad refinery in Western Norway. This project is split into two parts. The first part is the European CO_2 Test Centre Mongstad (TCM) with a total capacity of 100 ktonnes CO_2/yr with DONG Energy, Hydro, Shell, Vattenfall and the Norwegian authorities as partners. The second stage, where only Statoil and the Norwegian authorities are parties, is a full-scale CO_2 capture plant for the CHP plant and possibly other sources at the refinery.

These and many other proposed CCS projects are not only driven by climate change driven political ambitions. An important driver has been the technical or customer driven natural gas quality demands, e.g. at Snøhvit the CO_2 in the natural gas must be removed prior to

liquefaction. Also at In Salah and Sleipner there are sales quality requirements on the CO_2 content. Secondly, in some countries or regions CO_2 taxes and quota are imposed, which can make CCS more attractive. For example, the Norwegian Continental Shelf has a CO_2 tax between 300 and 400 NOK/tonne, which made CO_2 storage the preferred option at Sleipner instead of venting. Enhanced oil recovery (EOR) with CO_2 can create additional incomes. This third driver is currently active in the USA and Canada. Increased need for power and heat in certain regions can be a fourth driver for employing CCS commercially. This is partially the case for the Mongstad and Halten CO_2 projects. Building additional power plants with CO_2 capture can even decrease CO_2 emissions of the whole energy supply chain. The Mongstad project is a good example, where integrating the CHP plant into the refinery can improve the overall energy efficiency significantly and provide more flexibility for future refinery development. Another example is the supply of onshore generated electricity to offshore platforms, which can avoid the use of relatively inefficient single cycle gas turbines. The Mongstad CHP plant will provide electricity for the increasing compression needed at the already electrified Troll gas platform and for the future Gjøa oil platform.

It is acknowledged that CCS requires a large research & development (R&D) effort before it is fully accepted and commercially attractive. Good results from 10 years of CO_2 storage at Sleipner shows that it can be done safely. But for full acceptance more commercial projects are needed in various geological structures. Moreover monitoring, verification and well integrity can be improved and optimized by R&D. Another important aim of R&D on CO_2 capture is to reduce the costs significantly. Both radical new chemistry and concepts (e.g. Alstom's Chilled Ammonia and oxyfuel) or incremental improvements of existing technology (amine, gasification, reforming) are pursued. For being considered in the R&D portfolio Statoil has developed the following criteria:

- Zero harm to humans and environment
- Electric energy efficiency of natural gas fired power plant must exceed 50%
- At least 85% of the produced CO_2 must be captured
- The cost should be lower than 200 NOK/tonne CO_2

Such criteria are needed to focus the R&D and may vary significantly over the world. CO_2 transport can be done by pipeline or ship. Both are available, and need large-scale demonstrations and specialised R&D to show their potential. A fourth R&D topic is the fundamental properties of CO_2 across the value chain. CO_2 has an unusual triple and critical point relative to natural gas, oil and water, and may require its own dedicated thermodynamic models, e.g. for multi-phase transient pipeline flow. Especially knowledge of the effect of impurities on capture, transport and storage/EOR may reduce costs and increase safety.

It can be concluded that technology development for CCS is ongoing with increased pace in a co-operation between operators, technology suppliers, R&D institutes, academia and authorities. The technology development is supported by a few operating commercial projects, while many new CCS projects are announced all over the world. This development is an important contribution to securing future energy supply with zero harm to the environment.

Session S-2: Invited Session on Biotechnology: Honoring Prof. John Villadsen

Abstract Number	**Paper Title & Authors**	**Included**
1389	1389 - Process Integration onto Biochip Utilizing Novel Materials T Kanamori	Yes
1513	The role of chemical engineering in modern biotechnology J Nielsen	No
3595	Kinetic phenomena in the enzymatic hydrolysis of wheat arabinoxylan A S Meyer, A Amous	No
4071	A structured-segregated approach for modeling the dynamics of microbial populations in the three-dimensional turbulent field of a stirred-tank bioreactor M Reuss	No
4073	Bioreaction Engineering: A discipline striving for independence J Villadsen	Yes

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Process Integration onto Biochip Utilizing Novel Materials

Toshiyuki Kanamori

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1. Summary

Recently, “Proteome” following “Genome” has attracted a great deal of attention in the fields of bioscience and biotechnology. Single molecular analysis has been also feasible in the fields such as the detections of SNPs and specially-functionalized proteins. Taking this situation into account, next we should develop a method and/or device to manipulate and analyze a single cell. To handle a single cell, whose order of magnitude is micro meter, microchip is quite suitable.

We have paid attention to the advantages to use light as a controlling stimulus and are developing novel technologies utilizing photoresponsive materials. At first, I introduce the two-dimensional on-demand cell manipulation technology by light irradiation1)2). Cell selection and precious co-culture of cells are feasible using this technology.

The second topic is about photoresponsive microvalve applied to the remote control of fluids in a microchip. We have already developed the photoresponsive micro valve utilizing a photo- and thermo-responsive hydrogel3). Each valve opened within 30 seconds after light irradiation and all valves opened immediately after a temperature rise from 26°C to 46°C.

Finally, we will develop biochips, named “Taylor-made cell array chip”, where cells can be processed, to integrate the above mentioned technologies. We have been already successful to prepare a single channel based on this idea.

Keywords: microbiochip, tissuomics, photoresponsive polymer, cell manipulation

2. Extended Abstract

Recently, “Proteome” following “Genome” has attracted a great deal of attention in the fields of bioscience and biotechnology. Single molecular analysis has been also feasible in the fields such as the detection of SNPs and specially-functionalized proteins. Taking this situation into account, next we should develop a method and/or device to manipulate and analyze a single cell. To handle a single cell, whose order of magnitude is micro meter, microchip is quite suitable.

We have paid attention to the advantages to use light as a controlling stimulus and are developing novel technologies utilizing photoresponsive materials. At first, I introduce the two-dimensional on-demand cell manipulation technology by light irradiation as shown in Figure 1[1)2)]. Cell selection and precious co-culture of cells are feasible using this technology as shown in Figure 2.

The second topic is about photoresponsive micro valve applied to the remote control of fluids in a microchip. We have already developed the photoresponsive micro valve utilizing a photo- and thermoresponsive hydrogel. As can be seen in Figure 3, each valve opened within 30 seconds after light irradiation and all valves opened immediately after a temperature rise from 26°C to 46°C.

Finally, we will develop biochips, where cells can be processed, to integrate the above mentioned technologies. Figure 4 shows one of the concrete ideas for the biochips, which we call “Taylor-made cell array chip”.

We have been already successful to prepare a single channel based on this idea as shown in Figure 5.

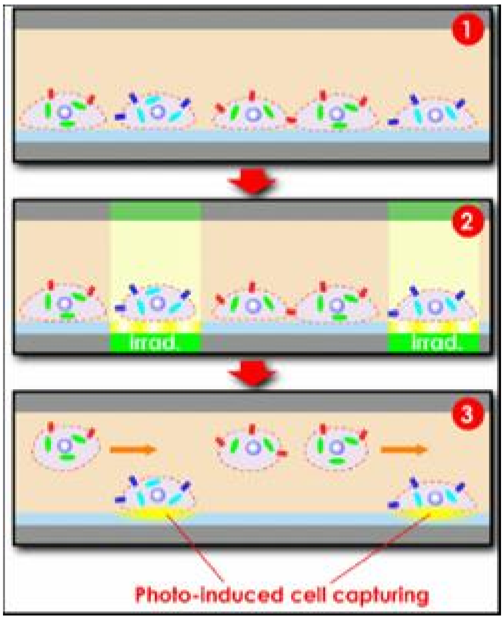

Figure 1 Scheme of Light-induced Cell-adhesion Enhancement

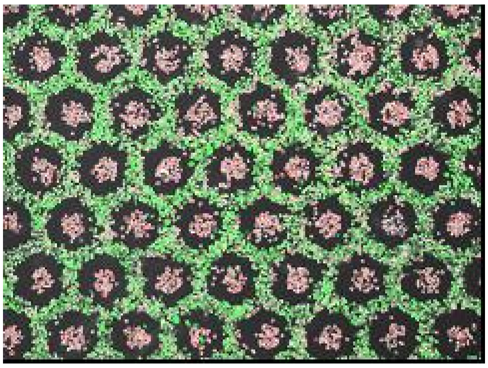

Figure 2 Precious Co-culture of Cells by Two-dimensional On-demand Cell Manipulation Technology

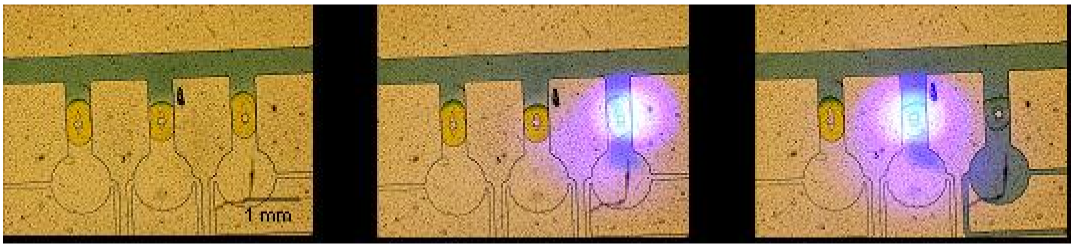

Figure 3 Photocontrol Microvalve

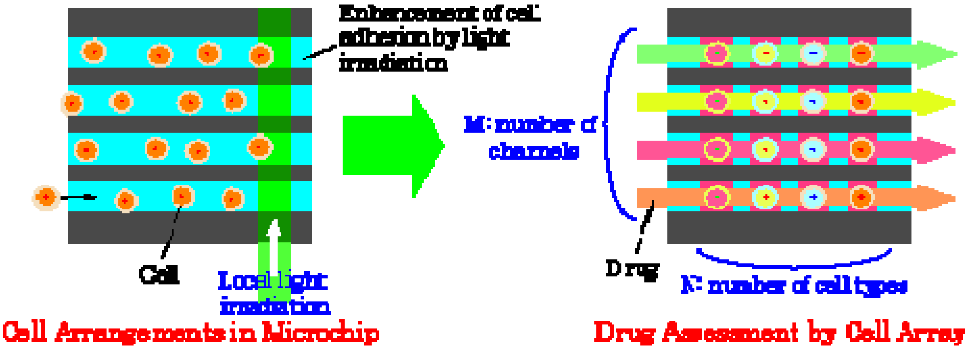

Figure 4 Concept of “Taylor-made Cell Array Chip”

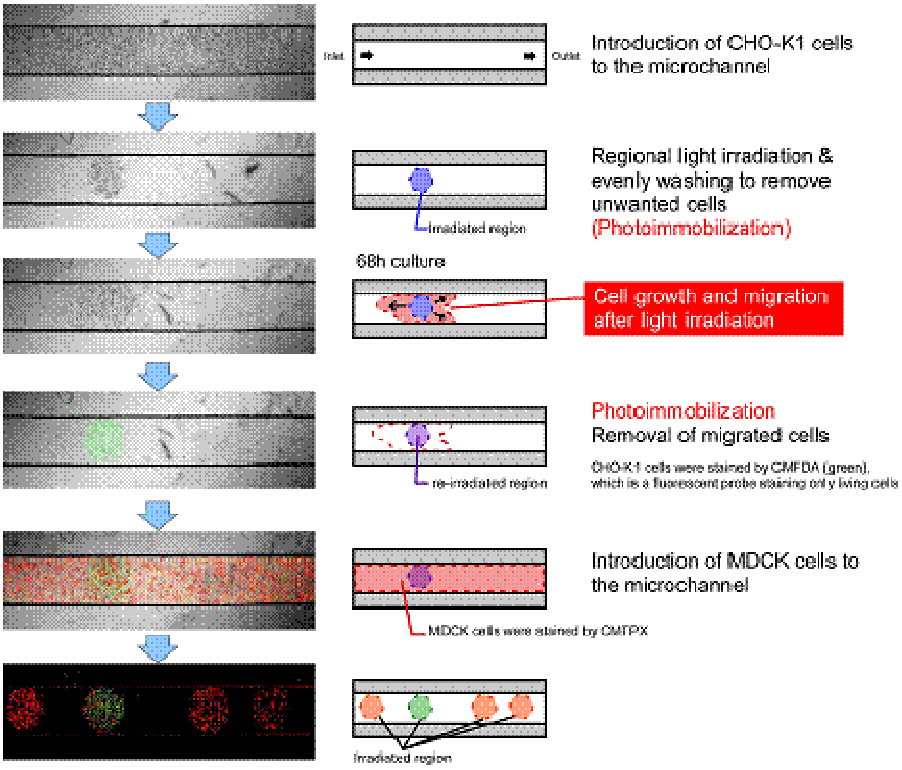

Figure 5 Cell Pattern Formation in Microchannel

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Bioreaction Engineering: A discipline striving for independence

John Villadsen

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Summary

The bioreactor will always have a place at center-stage in any bio-industrial production. This can confidently be stated despite the fact that much of the economy of the process lies in the downstream processes (recombinant protein production) or in the preparation of the feed for the reaction (2nd generation ethanol production). Consequently the teaching of bioreaction engineering has the same central role in the education of Biochemical Engineers as Chemical Reaction Engineering has in the education of “traditional” Chemical Engineers.

In Denmark, as indeed in most countries, the curriculum of the chemical engineering education is changing towards an education of Chemical and Biochemical Engineers, but within the same time frame (3 + 2 years) as was previously used in an education of either a chemical engineer or a bioscientist (biochemist or biologist).

Since the bioindustry cries out for more employees with a bio-engineering background (claiming, perhaps unjustly, that there are “enough” classical bioscientists around) the Technical University of Denmark expects to have a substantial input of BSc candidates from other universities who want to supplement a traditional bioscience education with “the right” courses offered by the leading appplied science university of the country.

This puts a great deal of responsibility on the faculty of the DTU, and especially on the faculties of the two very large departments of Biotechnology (“BioCenter-DTU”) and Chemical Engineering. Surely, Bioreaction Engineering cannot be taught in an extended sequence of courses (a generation ago one would hardly notice “bio-reaction” in comparison with “chemical reaction” as applied in the whole of the chemical industry).

But we see things differently today: The discipline of bio-reaction engineering encompasses topics as far removed as the kinetics of drug uptake by tissue, identification and manipulation of cellular pathways to steer the carbon flux towards the right product, and the liquefaction of agricultural waste as a preliminary step in the bio-refinery. Biochemistry, some biology, and a large portion of engineering (more “good sense” than heavy math) must work together to produce the desired result: A candidate who can help industry understand what takes place in the 400 m3 bioreactor and to design the whole industrial process in an optimal way.

Based on the experience of the author who has taught Chemical Reaction Engineering as well as Bioreaction Engineering for a good many years one really wants to sit down with colleagues, not only from Danish universities, but from universities in Europe as well as from countries across the oceans-to discuss the proper use of one or two 60 hour courses in Bioreaction Engineering. The industrial scene as well as the “culture” of the education may vary from country to country, but certain topics will inevitably have to be included, since they are common to all applications, and also because they will be recognized as “classical” chemical engineering disciplines” and therefore readily accepted as also amplifiying the subjects taught in “reaction engineeering for the petro-chemical industry”.

The lecture will attempt to classify the first priority topics of a Bioreaction Engineering course, and the lecture will be illustrated by some examples used by the author to catch the attention of students from both chemical engineering and from biochemistry/biology, and to convince them that quantitative treatment of bioreactions leads to fascinating results-often of direct interest to industrial production.

Session S-4A: EPIC-1 keynote Lecture 1

Abstract Number	Paper Title & Authors	Included
4155	Chemical and biological microsystems for discovery and scaling to production K V Jensen	Yes

Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Chemical and biological microsystems for discovery and scaling to production

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1. Summary

Microfabrication techniques and scale-up by replication have fueled spectacular advances in the electronics and telecommunications industries, and more recently, in microanalysis chips for chemical and biological applications. These systems transform classical batch wise laboratory procedures into integrated systems capable of providing new understanding of fundamental chemical and biological processes as well as rapid, continuous discovery and development of new products with less use of resources and waste generation. Chemical microsystems combine microfluidic channels, chemical-synthesis-on-a chip, and microscale separation to enable multiple synthesis and separation steps. Synthesis applications are enhanced by chemical and biological information gained from integrating microfluidic components with sensors and actuators. Cases studies are drawn from chemical synthesis relevant to fine chemicals and pharmaceuticals, synthesis of colloidal nanoparticles and quantum dots, and bioprocessing with cellular analysis. Emphasis is placed on process intensification applications enabled by integrated microsystems.

Keywords: microfluidics, integrated reaction and separation, organic synthesis, nanoparticle synthesis, microbioreactors

2. Extended Abstract

Integrated micro chemical systems enable rapid, continuous discovery and development of new products with less environmental impact. In particular, the systems use fewer resources, generate less waste, require less space, are potentially safer, and use fewer utilities than conventional approaches. Moreover, by integrating sensors for flow, temperature, and chemical composition it is possible to use the sensor information in on-line optimization and control for identification of optimum operating conditions – a task that otherwise can be laborious and resource consuming.

Organic synthesis reactions, such as diazotization, carbonylation, and fluorination are examples of reaction steps, which can be difficult to practice in standard laboratories. Specialized facilities are often needed to mitigate explosion and toxic exposure concerns. The reaction rate is significantly influenced by the transport of reagents within and across phases. By using microfabrication, it is possible to create microreactors that provide a hundredfold or more improvement in mass transfer and can be run safely at the benchtop at elevated pressures, including supercritical conditions. Advances in methods for monitoring and control of multiphase flow regimes make it feasible to scale microreactors while maintaining the resource and safety advantages of microreaction technology. Chemical synthesis in microreactors will perhaps have the greatest impact for conditions requiring challenging operating conditions (high pressures and temperatures) and for on-demand, on-site production. Microscale operations have been limited to one-step reactions or to a sequence of reactions not requiring purification of intermediates or products. Integration of reaction of separation elements is demonstrated by combining reaction modules into a single production line that incorporates modules for liquid-liquid and gas-liquid phase separation of reaction intermediates. The production of carbamates from organic azides serves a case study.

Engineering nanoparticles (e.g., oxides and quantum dots) by manipulating composition and structure provides opportunities for realizing properties for a wide range of applications relevant to catalysis, optics, electronics, and biomolecular sensing. Microreactors allow for rapid mixing of the precursors, controlled nanoparticle growth, and on-chip quenching of the reaction as well as precise tailoring of overcoats. The small reaction volumes combined with the high heat and mass transfer rates enable reactions to be performed under more aggressive conditions (high pressures and temperatures) with higher yields than can typically be achieved with laborious use of pressurized batch systems.

Platforms for bioprocess discovery and development are also presented, specifically microbioreactors, each with integrated bioanalytical devices, and operating in parallel. Such systems address the continuing demand in bioprocess science and engineering for fast and accurate analytical information that can be used to rapidly evaluate the interactions between biological systems and bioprocess operations. Experiments carried out in microliter volumes are analogous to results obtained in 500 mℓ bench-scale bioreactors in terms of gene expression, growth kinetics, dissolved oxygen, pH, final number of cells, and cell morphology. Moreover, the microbioreactors provide the platforms for efficiently incorporating modern tools of biology to improve bioprocess screening and development.

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Acknowledgements

The author thanks the members of the group who have contributed to this summary (N. De Mas, A. Günther, T.Inoue, S.A. Kahn, J. Kralj, S. Marre, J. McMullen, E. Murphy, H. Sahoo, N. Szita, N. Zaborenko, A. Zanzotto, and Z. Zhang,) as well as his colleagues Professors M.G. Bawendi, S. Buchwald, M.A. Schmidt, and A.J. Sinskey.

Session S-4B: EPIC-1: Alternative Energy Forms & Transfer Mechanisms (AE)

Abstract Number	**Paper Title & Authors**	**Included**
811	Intensification of photocatalytic processes T V Gerven, G Mul, J A Moulijn, A Stankiewicz	Yes
1834	Enhancement of Solid Dissolution by Ultrasound H Grénman, E Murzina, M Rönnholm, K Eränen	No
2027	Intensification of desorption processes by use of microwaves – an overview of possible applications and industrial perspectives R Cherbański, E Molga	Yes
3192	A study of free-radical copolymerisation of styrene with butyl acrylate using photo-initiation in an intensified spinning disc reactor C G Dobie, K V K Boodhoo	Yes

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Copenhagen, 16-20 September 2007

A review of intensification of photocatalytic processes

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1. Summary

Although photocatalysis is an attractive technology, industrial implementation remains limited due to scale up problems in the design of photoreactors. An overview is presented of recent advances in the design and application of novel reactors and devices. Two issues are essential: photon transfer limitations and mass transfer limitations (in the case of liquid phase reactions). In the field of mass transfer optimisation, spinning disc reactors, monolithic reactors and microreactors have been investigated for their use in photocatalysis. Significant advances are reported compared to conventional reactors. Studies focusing on performance improvement by optimising photon transfer, however, remain limited. While optical fibers and LEDs have been explored, major breakthroughs are still lacking. More focus on the introduction of a multitude of micro- or even nanoscale light emitting sources close to the catalyst particles is likely to be the way forward.

Keywords: photocatalysis, intensification, photoreactors, LEDs, microreactors

2. Extended Abstract

The current lack of industrial applications of photocatalysis is mainly due to 1) the low photocatalytic efficiency, and 2) the absence of examples where the laboratory photocatalysis set-up successfully has been scaled up to an industrially relevant scale. Two issues are important with respect to scale-up (Van Gerven et al., 2007, and references therein).

2.1. Overcoming photon transfer limitations

The main development in improving the illumination efficiency is the introduction of *optical fibers*. In these optical fibers light is propagated along the fiber length by reflection on the fiber wall. Depending on the refractive index of the fiber wall, a portion of the light intensity is not reflected but refracted. In an optical fiber reactor the catalyst is typically coated on the stripped fibers. The refracted light will then be absorbed by the catalyst which is subsequently activated. Although this development is an interesting route, a huge problem with optical fibers is that the light intensity decays exponentially along the axial direction of the coated fiber. Research on the specific area of *micro- or nanoscale illumination* in photocatalysis is rather scarce, with recent publications on the use of commercially available UV emitting LED devices. The use of microscale illumination in microreactors provides both a large catalyst surface area per unit or reactor volume and a high illumination efficiency. Nanoscale illumination opens the potential of physical integration of light source and catalyst surface. The introduction of doped titania nanostructures into the pores of porous silicon (PS) has been suggested in order to develop a device to produce visible light by electroluminescence of PS thus activating the photocatalyst particles.

2.2. Overcoming mass transfer limitations

Several intensified reactor types have been proposed to overcome the mass transfer limitations in fluid systems. *Slurry systems* are by far the most used in photocatalysis research. An obvious advantage of these systems is the good contact between reactants and catalyst. However, scaling up such a device implies a separation step of the catalyst from the reaction products. Also, it is difficult to uniformly irradiate suspended particles. A *spinning disc reactor* has attractive features such as limited mass transfer limitations due to the combination of thin film and turbulent flow with subsequent high mass transfer coefficient, increase of conversion, and better and more reliable product quality. A high catalyst surface area per reaction liquid volume can potentially be attained. The *monolithic photoreactor* provides a high surface-to-volume ratio although it appears less attractive than spinning disc reactors or microreactors. It allows high flow rates with low pressure drop, and is easy to scale-up, but exhibits a low illumination efficiency. Only very recently *microreactors* have been investigated as photoreactors. The main advantage of microreactors is the high surface-to-volume ratio. The small size of the channel also provides greater control over variables such as temperature control and flow rates, due to the fast heat and mass transfer, and the presence of laminar flow. The light source itself can also be UV-LED, thus miniaturizing the whole photocatalytic set-up.

2.3. 5. Conclusions

The most important developments in the last 10 years in the area of photoreactors were the novel configurations for maximizing the reactant-catalyst contact. Overall it appears that the microreactor, the spinning disc reactor, and the (optical fiber) monolith reactor are the most promising configurations. Less successful results were achieved with respect to the maximization of the illumination efficiency. Use of fibers is the main improvement to date, but suffers from obvious drawbacks. Availability of a multitude of low-intensity light emitting sources on the micro- or even nanoscale near the catalyst particles appears to be a novel and promising approach to achieve uniform and maximized illumination.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Intensification of desorption processes by use of microwaves – an overview of possible applications and industrial perspectives

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1. Summary

Based on an extensive literature review, the microwave regeneration method of adsorbents seems to be a reasonable and effective alternative for the conventional temperature swing adsorption (TSA) method. The most important advantages of the microwave swing adsorption (MSA) are: an intensive and remote heat transfer to the irradiated matter, leading to efficient desorption as well as better preserving of the original adsorption capacity and surface area of the adsorbent than the conventional heating method by convection. With regard to short penetration depth of microwaves, fluidized bed adsorbers and adsorptive reactors should be rather considered in industrial applications of the MSA method. For fixed beds special bed geometry should be applied to overcome this disadvantage e.g. annular beds or activated carbon fiber cloth (ACFC) adsorbents.

Keywords: adsorption, microwave desorption, regeneration of adsorbents, VOC

2. Extended Abstract

Desorption is a significant part of numerous integrated or complex processes e.g. such as: reactions carried out in adsorptive reactors, removal of volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) or soil remediation. A selective and efficient desorption influences significantly a final efficiency of the above mentioned entire processes.

The conventional regeneration methods of adsorbents, i.e.: pressure swing adsorption, temperature swing adsorption and reactive regeneration have their known drawbacks. Therefore, alternative regeneration methods are considered and tested. This work is focused on application of microwaves for rapid and effective heating up of the adsorbent bed.

Based on an extensive literature review, which reports recent contributions to intensification of desorption processes by use of microwaves, some conclusions and indications are formulated (**Table 1**).

Table 1. Remarks and conclusions regarding microwave desorption.

	General conclusions	**Literature**
1.	An effective microwave desorption of polar and non-polar solvents as well as their mixtures is possible. Dielectric properties of the system (adsorbent and adsorbates) are the key factor when consider microwave desorption. Hence, proper adsorbent have to be chosen regarding the dielectric properties of the adsorbates.	Reuß *et* al. (2002), Bathen (2003)
2.	A change in desorption selectivity under microwave irradiation when compared to the conventional methods is possible.	Turner *et* al. (2000)
3.	Due to presence of hydroxyl groups on surfaces of oxides (e.g. silica zeolites) the surface temperature is effectively greater than the measured solid (bulk) and gas temperatures under microwave irradiation. This phenomenon would be responsible for the reported for other researchers the so-called microwave effect.	Vallee *et* al. (2006)
4.	Microwave regeneration preserves the porous structure of the activated carbon adsorbents more efficiently than the conventional thermal heating.	Ania *et* al. (2005)
5.	Commercial installation for adsorption of a broad range of VOCs on polymeric adsorbents was designed as a fixed-bed for flow rates up to 8.5 (m^3/min) and as a fluid bed for higher flow rates starting from 708 (m^3/min).	Opperman *et* al. (1999)
6.	Some factors favor the microwave regeneration systems: an application - the solvent must be expensive enough and used in sufficient quantity to balance the microwave recovery costs; the solvent properties - the microwave regeneration is more attractive for water-soluble solvents; the emission stream concentration - the microwave regeneration is the best choice for low-concentrated emissions.	Price *et* al. (1998)

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Acknowledgment

This study has been performed with a financial support of the Ministry of Science and Higher Education (Poland) within a frame of the scientific Grant No. N208 003 32/0611.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Intensified free-radical photo copolymerisation of styrene with butyl acrylate in continuous flow reactors

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1. Summary

The bulk method of copolymer synthesis is potentially a greener, cheaper method of production, while UV initiation is propitious for a host of reasons. Unfortunately, owing to the production methods typically practised coupled with the increasingly viscous nature of the reaction media, the bulk method is unsound for producing high quality, high conversion products. Further, effective UV initiation is greatly hindered as a result of the reactor geometries.
The present work reports on the preliminary experimental findings from the application of intensified reactor technologies, namely, a narrow channel reactor, for bulk synthesis of styrene/butyl acrylate (S-BA) copolymers using photo-initiation methods. Such copolymers are industrially important adhesives and as binders in many paints and coatings. The initiator used was 2,2-dimethoxyacetophenone (DMPA) and free radicals were generated through 366 nm wavelength UV irradiation. Future work will concentrate on the use of a spinning disc reactor for such copolymerisation systems.

Keywords: Spinning disc reactor, thin films, narrow channel reactor, bulk free-radical photo-copolymerisation, styrene, butyl acrylate

2. Extended Abstract

The focus of the present investigation is on the use of a narrow channel reactor in the form of a glass coil of 3mm internal diameter (Figure 1) for the styrene/butyl acrylate (S-BA) copolymerisation system. This equipment promotes a certain degree of mixing of the reactants, whilst allowing for efficient UV penetration through the thin glass surface, thus giving acute rates of photo-initiation. Throughout the experiments, the effects of initiator concentration (1, 2, 3.5 and 5 wt%) and residence time (40, 72 and 137 seconds) upon conversion were investigated via the use of FTIR spectroscopy.

The narrow channel reactor results were benchmarked against static film copolymerisation of the S-BA system using a newly designed static cell (Figure 1). Manufactured from aluminium, the static film cell had provisions for (i) maintaining near isothermal conditions, (ii) varying film thickness, (iii) maintaining an inert nitrogen atmosphere and (iv) in-line FTIR analysis of the reaction. The effects of initiator concentration (2, 3.5 and 5 wt %), exposure time (1 minute intervals in the range 1-30 minutes), film thickness (509, 764, 1018 and 1274 microns), temperature (14, 30, 51 and 70°C) and UV intensity (120 and 85 mWcm^{-2}) on conversion were investigated. Other properties of interest (sequence distribution and molecular weights) for both sets of experiments were also investigated using ^{13}C-NMR spectroscopy and gel permeation chromatography (GPC), respectively.

Figure 1 the narrow channel glass reactor (left) and the static film cell (right).

Results from the narrow channel reactor experiments demonstrated an influence on both photoinitiator concentration ([PI]) and residence time on overall conversion and molecular weights as shown in figure 2. Similarly, figure 3 demonstrates the dependency of film thickness, [PI] and temperature upon overall conversion in the static film tests.

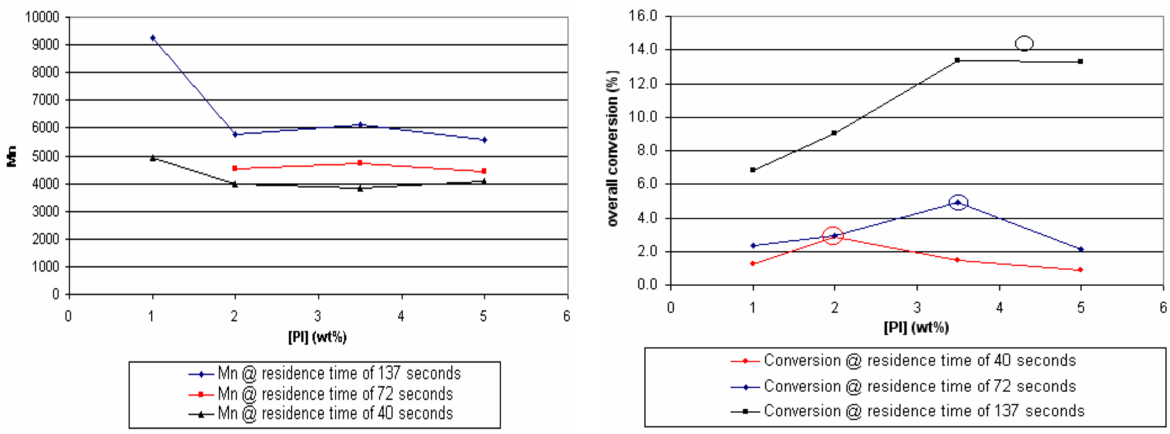

Figure 2 Effects of [PI] and residence time on molecular weight and overall conversion within the glass narrow channel reactor.

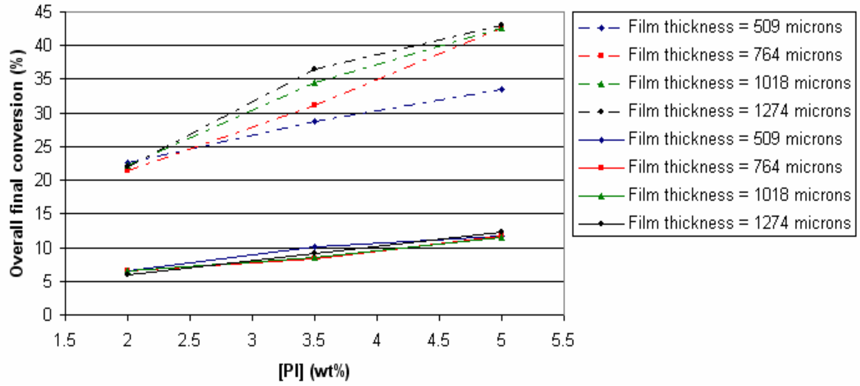

Figure 3 Effect of [PI] on final conversion in static film cell at a range of film thicknesses. (Broken lines represent reactions performed at higher temperature).

We intend to investigate the merits of employing a spinning disc reactor (SDR) for S-BA and other comonomer systems such as vinyl acetate – BA. It is envisaged that the intense mixing characteristics of the SDR will enable higher rates of copolymerisation to be achieved together with a copolymer possessing improved properties.

Session S-4C: EPIC-1: Intensified Hydrodynamics & Structured Environments (IHSE-1)

Abstract Number	**Paper Title & Authors**	**Included**
477	PI in process development and production through micro process systems O Lade, T Bayer, M Kinzl	Yes
2047	Experimental and numerical study of the use of nanofluids in compact heat exchangers M N Pantzali, A G Kanaris, A A Mouza, M J Assael, S V Paras	Yes
2166	Small Scale Continuous Reactors in Process Development M. Wernersson	Yes
3410	Advanced Separations, Including Distillation, Using Microchannel Architecture for Process Intensification L Silva, R Arora, A Tonkovich, A Glass, D Weidert, M Fanelli, D Qiu, R Litt	Yes

Session S-4C

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Copenhagen, 16-20 September 2007

Process intensification in process development and production through micro process systems

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1. Summary

The batch-to-conti-approach and its subset micro process technology are technologies with great potential for process intensification. Conventional continuous processes are established in large-scale production plants, because various advantages for application in chemical synthesis are well-known. The new micro process technology provides the chemist new possibilities in mixing and heat-transfer, which in lab-scale for many examples have already brought to use by now. Still, process development for conti-processes - with or without micro structured components - has been considered to be complex in set-up and use. Therefore, the absolute number of conti-processes is limited and only few production plants use micro process technology. SIPROCESS successfully meets the challenge. Siemens designed SIPROCESS for chemical syntheses in process development laboratories. In addition it can be used to produce initial quantities of a definite substance.

Keywords: process intensification, continuous process, process control system, automation, operation

2. Extended Abstract

Convincing features include modular set-up and integrated automation. Single modules may be exchanged easily and rapidly. Electronics are integrated in each module and are connected to the process control system SIMATIC PCS 7 (DCS) providing operating and configuration functions easily handled by the user. The benefit in using SIPROCESS is a remarkable reduction of process development time.
In general, the sequence in SIPROCESS is controlled and monitored by the DCS. For control, the user has only to select the desired function. The individual modules are then coordinated over time and logically by the DCS, i.e., for automatic startup of the system, sampling, and subsequent powering down of the system including rinsing of the chemicals channels. Closed-loop and open-loop control of the module-internal functions is carried out in a distributed configuration in the relevant modules in accordance with the setpoints specified by the DCS. The modules are equipped with sensors and actuators for this purpose. The modules communicate with the automation software by means of a communication bus. The DCS hardware and software is located in the control cabinet along with the power supply.
For safety reasons all functions are monitored by the DCS. All module-internal fuctions and limit values are monitored by the module electronics. Deviations from the desired behavior can manifest themselves in faults and warnings.

Warnings occur, for example, when warning limits for pressure and temperature are violated. Warning limits can be defined and must be within the associated alarm limits.

Faults occur, for example, when alarm limits for pressure or temperature are violated. The alarm limits can be defined and must always be within the defined limits. The consequence of a fault depends on the current state of the system. For instance, if a fault occurs during steady state the system attempts to start the Rinse function in order to rinse residual chemicals from the chemicals channels and then to approach the defined safe values of temperature and pressure.

SIPROCESS can be operated in three different modes in which the operator must intervene in the sequencer in different ways:

- Experiment series
- Single experiment
- Test

Experiment series mode is used for parameter screening, that is, an experiment series consisting of previously defined experiments with individual experiment parameters runs automatically. For each individual experiment, an experiment parameter set is started up, a sample is drawn, and the product is conveyed to the "Product" outlet for the defined duration of the experiment. After completion of the experiment series, the system is rinsed and powered down again (cf. Fig. 1).

A single parameter set is used in single experiment mode. For this purpose, a single experiment, whose parameters are to be used, is selected from the list of experiments. After loading and starting the experiment, the system is started up. When startup has been completed, the system is in the steady state. In this state, the user can carry out modifications to the experiment parameters.

Test mode

In test mode, the behaviour of the individual modules and their chronological and logical coordination are specified by the user. The experiment parameters are entered manually via the operator interface for each individual module. The distributed module functions such as the temperature or pressure control continue to run automatically.

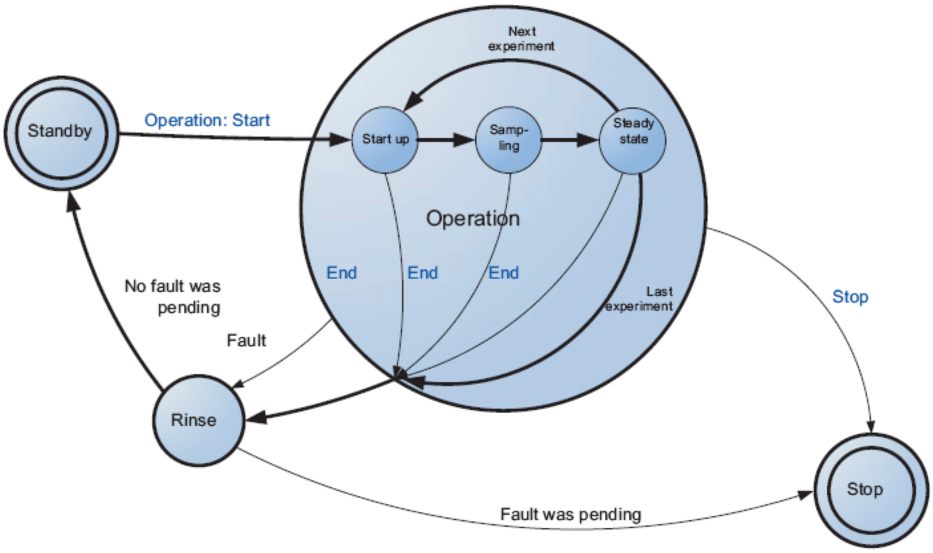

Fig.1: Operation in experiment series mode

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Experimental and numerical study of the use of nanofluids in compact heat exchangers

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1. Summary

The study of nanofluids, i.e., conventional working fluids where solid particles in the nanometer scale are suspended, has lately gained scientific interest, due to their enhanced thermal conductivity, which would significantly improve the performance of heat transfer equipment. The aim of the present work is to study experimentally and numerically the effect of the use of such fluids in a compact heat exchanger and to evaluate their performance in comparison with conventional fluids.

Keywords: compact heat exchanger, nanofluid, nanotubes, nanoparticles

2. Extended Abstract

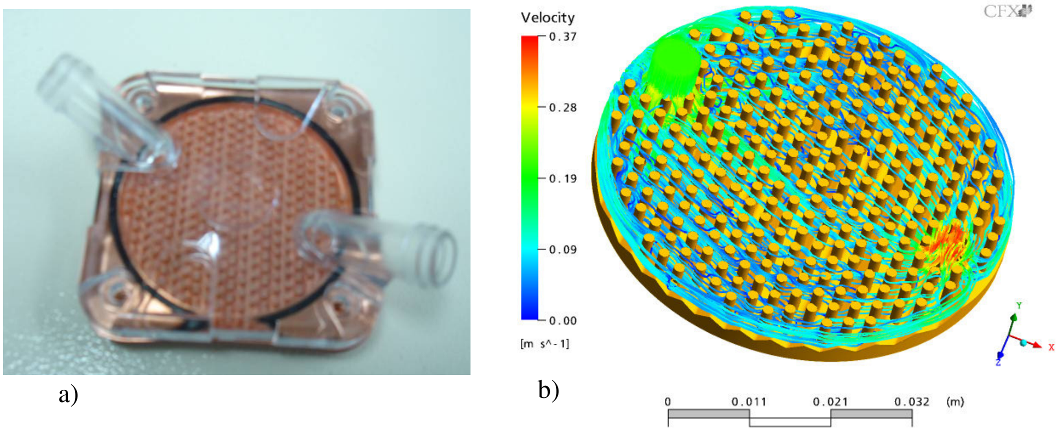
The need for efficient yet small in size heat transfer equipment has led to the development of compact heat exchangers (*CHE*) with modulated surface, as well as to an increased research interest concerning the enhancement of the thermal capability of the working fluids. In this frame, regardless of the failure of employing suspensions of millimeter- or micrometer-sized particles in conventional liquids in order to enhance their thermal conductivity, during the last decade nanometer-sized solid particles are being considered. It seems that these suspensions, called nanofluids, exhibit a significant increase in the thermal conductivity of the base fluid, while they can probably overcome problems of sedimentation as the particles are ultra-fine and at low concentrations (Trisaksri & Wongwises, 2007). Most of the recent work is mainly focused on the preparation methods and the thermal conductivity of the suspensions, rather than their heat transfer characteristics and flow behavior (Wang & Mujumdar, 2007). Experimental work in the convective heat transfer of nanofluids is still quite scarce, so further investigation is needed (Das et al., 2006).
In the present work, the performance of a nanofluid in a *CHE* is studied experimentally and numerically and it is compared with that of conventional working fluids (e.g. water, ethylene glycol etc). The nanofluids are prepared using commercially available carbon multi-wall nanotubes, *C-MWNT*, or metal oxide nanoparticles, such as Al_2O_3 or *CuO*, which are dispersed in water in the presence of a suitable surfactant and stabilized with ultrasonic vibration. Careful preparation of the nanofluids and selection of dispersants is very crucial, since their stability and enhanced thermal properties depend strongly on this process. Their physical properties are well defined, among

which the thermal conductivity, measured using the transient hot-wire method, exhibits in the case of *C-MWNT* an increase of about 20% in comparison with pure water, for an 1% w/w suspension (Assael et al., 2004).

A commercial liquid cooling system is employed and suitably adapted for the needs of the study. The main apparatus is a miniature *CHE* (Figure 1a), comprised of a small square copper plate, with rods on one side, and is covered with a plastic case, creating the flow path for the cooling liquid (Figure 1b). The other side of the copper plate is flat and is placed in contact with a cell, where hot water flows. The cooling liquid flows with the help of a small pump and after passing through an air-cooled heat exchanger is recirculated. The setup is thermally insulated, in order to eliminate heat losses. Temperatures are registered by a *PC*.

A previous experimental and numerical study by Kanaris et al. (2006) of a typical *CHE* have proved that *CFD* is a reliable tool to predict flow characteristics and heat transfer rates, as well as pressure losses, in this type of process equipment. Thus, a commercial *CFD* code (i.e., *CFX*$^{®}$ *10.0*) is employed and validated for the numerical evaluation of the performance of the above system with the use of nanofluids.

Preliminary results are encouraging, showing that heat transfer capability can be enhanced by about 5-10% by employing small amounts of nanoparticles. However, some sedimentation is observed and efforts are made to eliminate such problems and increase heat transfer rates. Information provided by this study, which is currently in progress, is expected to help the efforts to optimize the design of such *CHE*.



a)

b)

Figure 1: a) Photo of the miniature CHE, b) flow pattern inside CHE as calculated by CFD code.

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Abstract - small scale continuous reactors in process development

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1. Summary

Over the last few years AstraZeneca PR&D has evaluated the use of continuous reactors in pharmaceutical process development. This work has involved the construction of simple small scale continuous stirred tank reactors (CSTR) and tubular reactors as well as a more thorough evaluation of the Alfa Laval Plate reactor (PR-Lab).

The PR-Lab unit, the smallest model in a range of continuous reactors that is claimed to allow easy scale up from laboratory to production, has been evaluated in terms of; heat transfer capacity, mixing capacity, flow characteristics and ease of operation.

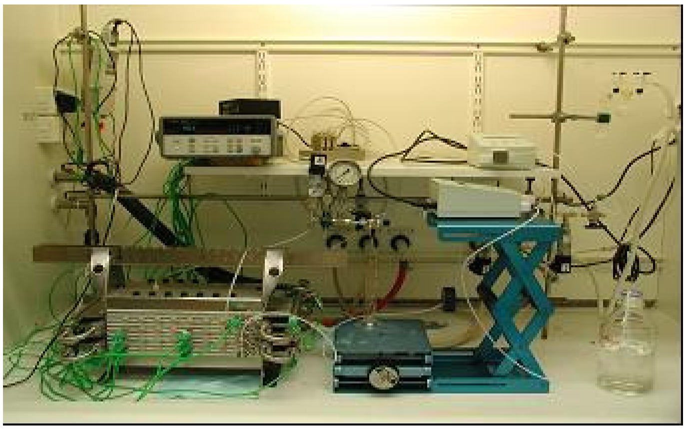
Results from different reactions run in the PR-Lab reactor will be presented along with some results from other reactor types. Conclusions are drawn regarding the benefits of continuous reactors and their application in process development and process intensification.

Key words: Continuous reactors, process intensification, heat transfer, mixing, Alfa Laval

2. Extended Abstract

Traditionally most pharmaceuticals have been manufactured in batch or semi batch equipment. This is mainly the result of relatively low production volumes, a large percentage of solid/liquid reactions and the often complex synthetic routes requiring a large number of sequential reactions and purification steps. Also, the availability of small scale continuous equipment has been limited. However, there are also some key drivers to use continuous technology (both for individual operations and for processes). For continuous reactors, these can be summarized as an increased operational and parameter envelope that allows operation, optimization and scale up outside the boundaries set by the conventional equipment.

Within AZ PR&D, tests have been made on small scale CSTR and tubular reactors and also on a micro reactor. The main body of work presented was carried out on the Alfa Laval PR-Lab reactor, see picture below.



2.1 Alfa Laval PR-Lab evaluation

2.1.1. Heat transfer capacity

Batch and plug flow reactors (to which PR-lab can be compared) ideally give the same conversion and yield. However, for fast exothermic reactions, semi batch operation is often utilized and this can lead to scale up issues. However, semi batch operation can be avoided by using a plug flow reactor with high heat transfer capacity.

2.1.2. Mixing capacity

For so called mixing sensitive reactions the initial mixing of reactants is often vital. The mixing is studied at varying flows and with and without an injection nozzle. The results are compared with results from an agitated batch reactor.

2.1.3. Flow characteristics

The deviation from ideal plug flow was tested using retention time distribution (RTD) methods. Results from both step and pulse experiments showed that the reactor was close to ideal even at half the recommended minimum flow.

2.1.4. Application to actual pharmaceutical synthesis

Results from two different tests are presented:

- A liquid/liquid reaction where an alcohol is oxidized to an aldehyde using sodium hypochlorite. The results showed a considerably higher yield compare to batch operation.
- A ring closure reaction that is carried out at a temperature above the normal boiling point of the solvent. This test also gave a considerably higher yield compare to batch operation.

2.2. Other continuous reactors

Similar performance tests have also been carried out on a micro reactor. The small channel diameters contribute to a very high heat transfer capacity. Outside the area of heat transfer, a direct comparison between Alfa Laval and micro reactor technology is seldom relevant due to different areas of application. Some tests have also been performed on, very simple, lab scale tubular and CSTR reactors. The CSTR, as opposed to batch and plug flow reactors, operates at the final conversion. For some reactions this is beneficial in terms of yield and selectivity.

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European Congress of Chemical Engineering (ECCE-6)
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Advanced separations, including distillation, using microchannel architecture for process intensification

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1. Summary

The technology for separating liquid-liquid mixtures via distillation has been practiced for literally thousands of years, yet it remains a highly energy-intensive, although ubiquitous unit operation for performing chemical separations. Over the past several decades, new distillation column, tray, and packing designs have yielded incrementally improved efficiency, while larger improvements have remained elusive. Microchannel architecture permits a radically new approach to distillation; one that has the potential to provide a step change improvement in energy consumption as well as lower capital costs and other process advantages. An example of a close-boiling separation, for hexane and cyclohexane, with an HETP less than 1 cm was demonstrated. The exciting experimental results were also validated theoretically.

Keywords: separations, microchannel, process intensification, distillation

2. Extended Abstract

Microchannel reactors and heat exchangers have been demonstrated to bring significant processing advantages, including reduced capital and operating costs, increased product purity, reduced environmental impact, and improved safety. The enhanced heat and mass transfer demonstrated for microreactors may also be exploited for chemical separations. Intensification of both reaction and product purification steps may provide significant benefit for the overall chemical process flowsheet. Since the 1990s, laboratory development in microchannel separation systems has included absorption, adsorption, liquid-liquid extraction, distillation and phase separation (TeGrotenhuis et al. 1999, Palo et al. 2006). This paper will focus on the development of a microchannel multistage distillation process.

Microchannel distillation technology enhances mass transfer by contacting thin vapor and liquid films in very small channels, dramatically reducing the Height-to-an-Equivalent Theoretical Plate (HETP), from more than 25 cm to less than 5 cm. Microchannel architecture also allows temperature profiles to be tightly controlled along the length of the channels using adjacent heat exchange channels integrated in the separation hardware. Enhancements in both mass transfer and heat integration enable dramatically improved performance and new process flow sheet options which were previously seen as commercially unattractive. Microchannel technology is scaled to commercial plant capacities by increasing the numbers of parallel channels conducting identical processes. Techniques for design and fabrication of scaled-up microchannel processing hardware have been developed for a range of large-scale microchannel processing applications.

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Session S-4D: EPIC-1: Intensified Hydrodynamics & Structured Environments (IHSE-2)

Abstract Number	Paper Title & Authors	Included
64	Process Intensification, a tool for Innovative Products: achievements and prospects J Jenck, P Burille	Yes
702	Process intensification of electro-organic synthesis by microstructuration A Attour, S Rode, F Lapicque, A Ziogas, M Matlosz	Yes
3183	Viscous Mixing Process Intensification: Innovations and Trends P A Tanguy, K Takenaka	Yes
3295	Break-up of nano-particle clusters in high-shear devices J Bałdyga, W Orciuch, Ł Makowski, M Malski-Brodzicki, K Malik	Yes
3729	Mobile Micro Reactor Technology For Industrial Production J T Harmsel, S Pissavini, P Caze	Yes

Process intensification, a tool for innovative products: achievements and prospects.

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Keywords: process intensification, product engineering, usage quality, formulation.

Abstract:

Process intensification, where the motivation is “doing more with less”, is a design methodology aiming to minimize diffusion phenomena (mass and/or energy transfer). Its first goal is to build smaller, safer and cheaper production plants. An additional goal is to operate in currently difficult if not impossible conditions. Novel equipment and innovative processing methods allow a re-engineering of our chemical plants, relying on eco-efficient processes.

Precision product engineering is a new emerging goal of process intensification. Properties of products can be closely controlled by strictly mastering the production process. By precision engineering of products, highly reproducible end-user value (usage quality) can be guaranteed. Operation in continuous mode, in equipment with low axial dispersion, opens new opportunities by sharpening property distributions (molecular weight, particle size, form factor, etc.)

We will try to assess the potential development of technologies such as micro-processing, gravitational fields, etc. and present some real cases in synthesis and formulation of liquids but also solids, where progress will probably be most noticeable.

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Process intensification of electro-organic synthesis by microstructuration

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1. Summary

This work concerns the realization and the validation of a microstructured reactor for organic electrosynthesis. The electrochemical reaction is the oxidation of 4-methylanisole to 4-methoxy-benzaldehyde (anisaldehyde) under its diacetal form.
The experimental tests carried out on high conversion thin-gap flow reactor showed the influence of the supporting electrolyte (KF) concentration on the reaction yield.

Keywords: microreactor, Process intensification, supporting electrolyte, aldehyde electrosynthesis.

2. Extended Abstract

Electroorganic synthesis is a domain in which microstructured devices are especially promising, with potential improvement of both production rates and selectivity. This study deals with design and build-up of a new microreactor for organic electrosynthesis together with its validation tests. The present communication describes experiments carried out in a segmented microstructured device constructed by IMM, shown in Figure 1. The miniaturised cell is characterized by a 100 µm electrode gap leading to a reduced ohmic drop even with low-conducting organic electrolytic media. The anode is composed by 10 glassy carbon elements, each with an area of 1x1 cm^2. The cathode facing the segmented anode is a 10x1 cm^2 stainless steel plate. The reactor was designed in order to obtain high conversion of the substrate in continuous operation without recirculation of the liquid. The reactor was constructed by Institute of Microtechnics of Mainz (IMM). The model reaction was the anodic oxidation of the 4-methoxytoluene to 4-methoxy-benzaldehyde-dimethylacetal in methanol, and, after hydrolysis, to anisaldehyde. The reaction route is shown in Figure 2. The counter-electrode reaction was hydrogen evolution. The reaction is industrially performed by BASF.

We used here the cell without segmentation of the anode, each element being connected to the same potential: optimal conversion and selectivity were searched by selecting the nature of supporting electrolyte and its concentration as well as the flow rate and the applied current. Moreover, in order to increase the cell productivity, with conditions closer to industrial practice, the reagent concentration was increased to

0.1M – higher concentrations could not be used because of significant overheating of the cell due essentially to the high ohmic drop leading to heat dissipation by Joule effect. The concentration of the supporting electrolyte, KF, exerts an influence on the reaction selectivity: decreasing the KF concentration to 0.01 M increases noticeably the acetal production. For optimal conditions (0.2 ml/min, 0.1 M methoxytoluene and 0.01 M KF), selectivity up to 86 % (figure 3 b) was attained with the single-pass microreactor allowing 95% conversion (figure 3 a). The selectivity value is higher than that obtained in industrial practice (68%).

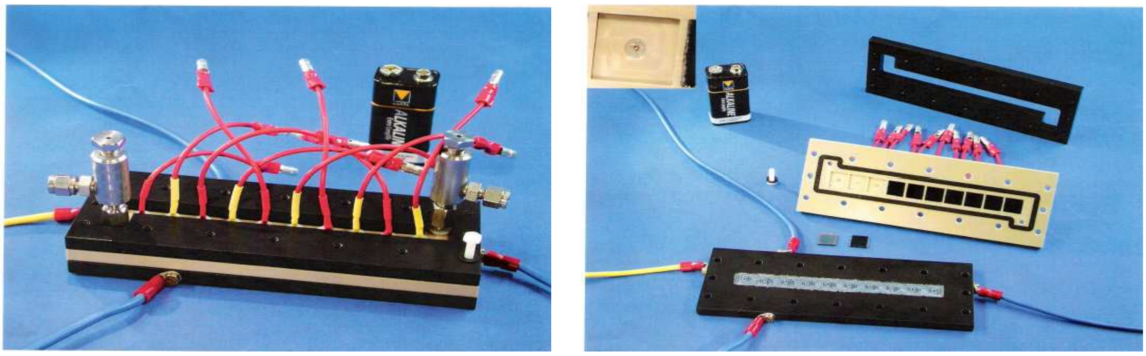


Figure 1: Photographs of the microstructured device constructed by IMM: 10 independent anodic segments with dimensions : 10x10 mm; insulation length : 1 mm; electrode gap : 0.1 mm.

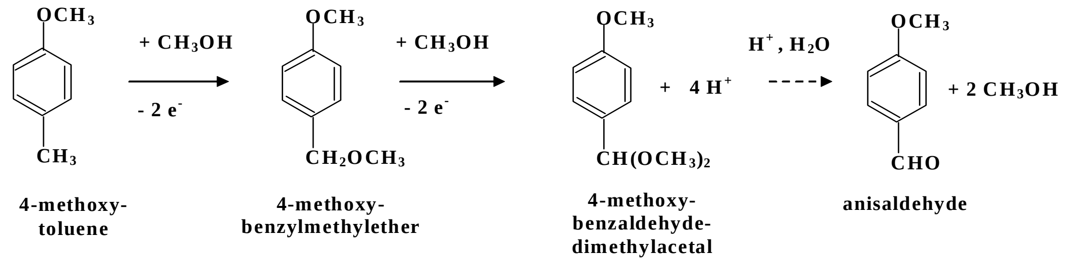
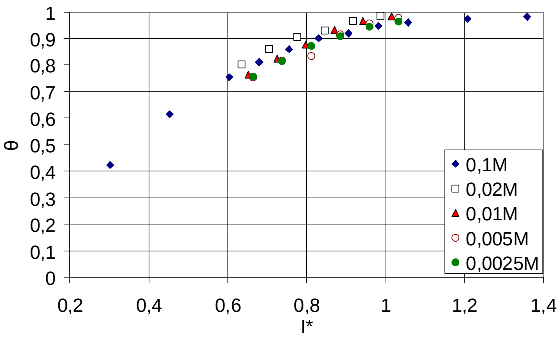


Figure 2: Reaction system: the oxidation of 4-methoxytoluene in methanol



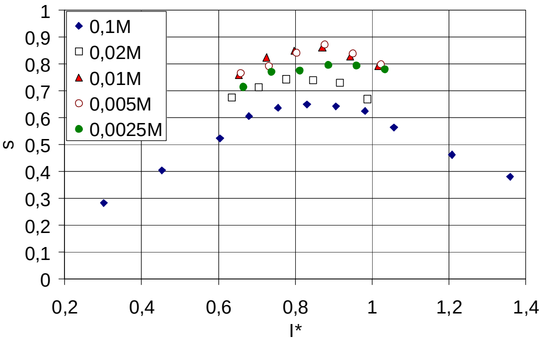


Figure 3a: Conversion versus the dimensionless current I^* for 0.1 M rmethoxytoluene, flow rate at 0.2 ml/min and various KF concentrations from 0.0025 to 0.1 M.

Figure 3b: Selectivity versus the dimensionless current I^* for 0.1 M rmethoxytoluene, flow rate at 0.2 ml/min and various KF concentrations from 0.0025 to 0.1 M.

I^*: ratio between applied current and the current necessary to convert all reagents.

Acknowledgments

The investigation is part of the IMPULSE project funded by the EU (contract n°: 011816-2)

Viscous mixing process intensification: innovations and trends

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Abstract

Process intensification is a new paradigm that describes the use of more cost-effective and leaner industrial operations characterized by reliable, simpler, safer and faster processes, resulting in lower energy consumption, reduced emissions, and higher quality end-products. Mixing is a ubiquitous operation in chemical engineering and it is considered as a major candidate for process intensification. Mixing is a core technology in many production processes. In the case of complex formulated products involving non-Newtonian rheology, mixing problems generate significant mixing inefficiencies that cost every year, billions of dollars of losses in out-of-spec products, undesirable by-products, and poorly selective chemical reactions to name a few.

The general objective of this presentation is to present new innovations and trends in intensified mixing processes involving rheologically complex media. Three technologies will be presented, namely two Multi-Shaft Mixer technologies, i.e. the dual shaft concentric coaxial mixer and the dual shaft eccentric mixer and one example of a Single-shaft Multifunctional Impeller Mixer, namely the Sumitomo Maxblend. A review of the performance of these mixers will be given in the context of the processing of viscous non-Newtonian media as well as information regarding their design. Examples of their utilization in industry where they have replaced more traditional mixer systems will also be presented along with the benefits that have been obtained. New mixing processing trends will also be discussed in the light of further progress in process intensification involving complex rheology.

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European Congress of Chemical Engineering (ECCE-6)
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Break-up of nano-particle clusters in high-shear devices

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1. Summary

Formulation of stable nano-suspensions by breaking-up nano-particle clusters is considered. The rotor-stator mixer and the high pressure nozzle disintegrator are investigated. The main part of the work is related to simulation of the processes of disintegration of agglomerates in both systems. The population balance modelling is applied to account for effects of breakage and restructuring of aggregates on their size distribution. Effects of resulting structure of aggregated suspension on its rheology and details of the flow are simulated as well. Effects of the flow on creation of local stresses include hydrodynamic stresses and stresses generated by cavitation. Population balances are solved using the QMOM that is linked to the CFD code FLUENT. Results of numerical simulations show that the high pressure system is more efficient than the rotor-stator device; one pass through the high pressure system gives better disintegration than several passes through the rotor-stator.

Keywords: agglomerates, high-shear-device, nanoparticles, suspension, shear flow.

2. Extended Abstract

The high shear flows of suspensions consisting of breaking up clusters of nano-particles occur in a broad range of technological applications, which explains interest in high shear flows observed in many engineering disciplines. In this work we are interested in formulation of stable suspensions of nano-particles by breaking up nano-particle clusters (agglomerates). In technical applications disintegration processes are very often carried out in high shear devices; two devices of practical importance are considered in this paper: the Silverson 150/250MS rotor-stator mixer and the high pressure nozzle disintegrator. The rotor–stator system consists of a rotor equipped with four inner blades, eight outer blades, and a stator equipped with a disintegrating head and a square hole disintegration screen. The high pressure system is equipped with a nozzle of diameter equal to 80 µm and the working pressure is as high as 2400 bar. In both devices very high stresses are generated; in the case of rotor-stator device only hydrodynamic stresses participate in aggregate disintegration, whereas in the high pressure system disintegration results from both the hydrodynamic stresses and effects of cavitation. The stresses generated by fluid deformation, inertia and cavitation depend on the structure of the flow field. Rheological properties of the suspension depend on suspension structure (Buyevich and Kabpsov, 1999). To describe these phenomena and to simulate the process a complex model based on the population balance equation is applied. The population balance supplemented with breakage and restructuring terms is solved in the CFD environment using the Quadrature Method of Moments (McGrow, 1997). As a model material for investigation of agglomerate breakage in high-shear systems in the EU funded project PROFORM an Aerosil 200V has been chosen. Structure of this material is characterised using a cluster-fractal model proposed by Logan (1999).

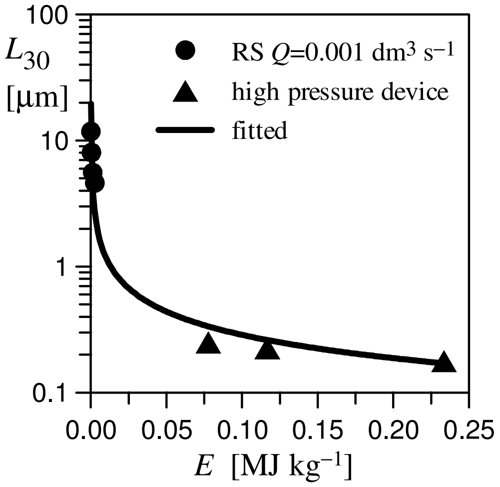

Figure 1: Effect of specific energy input on the mean particle size L_{30}.

Presented results of numerical simulations based on experimentally validated modelling show that the high pressure system is more efficient than the rotor-stator device; one pass through the high pressure nozzle gives better disintegration than several passes through the rotor-stator. This may result in part from the fact that in the high pressure system disintegration results from both: the hydrodynamic stresses and effects of cavitation, whereas in the case of the rotor-stator mixer only the hydrodynamic stresses are active. Effects of process conditions on particle breakage are often presented in terms of specific energy input per one kilogram of suspension E. Finally Figure 1 shows results for both: the rotor-stator system (RS) at a small flow rate and the high pressure device. The conclusion is rather simple: energetic costs of decreasing particle size by disintegration increase nonlinearly with decreasing the particle size. The model has rather universal character and can be used to interpret disintegration processes in systems of complex geometry and practical importance.

Acknowledgements

This study was carried out within the project PROFORM („*Transforming Nano-particles into Sustainable Consumer Products Through Advanced Product and Process Formulation*” EC Reference NMP4-CT-2004-505645) which was partially funded by the 6th Framework Programme of EC. The contents of this paper reflects only the authors’ view. The authors gratefully acknowledge the useful discussions held with other partners of the Consortium: BHR Group Limited; Karlsruhe University, Institute of Food Process Engineering; Bayer Technology Services GmbH; University of Loughborough; Unilever UK Central Resources Limited; Birmingham University School of Engineering; Poznan University of Technology, Institute of Chemical Technology and Engineering; Rockfield Software Limited; C3M d.o.o. Ljubljana.

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Mobile micro reactor for industrial production

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1. Summary

The integrated Corning Micro Reactor Technology, used in pharmaceutical and fine chemical industry, will be presented. As an example the Mobile Micro Reaction Technology Plant based on Corning's Micro reactor design and Zeton's plant engineering technologies, will demonstrate the flexibility of one combined plant for either testing on pilot scale or production on industrial scale.

Keywords: micro reactor, pharma, fine chemical, pilot plant, continuous processing

Currently many new developments are related to micro reaction technologies. However, many of these technologies are still in the development phases and have been applied only on laboratory scale.

The presented Mobile Micro Reaction Technology Plant based on Corning's Micro reactor design and Zeton's plant engineering technologies, will demonstrate the flexibility of one combined plant for either testing on pilot scale or production on industrial scale.

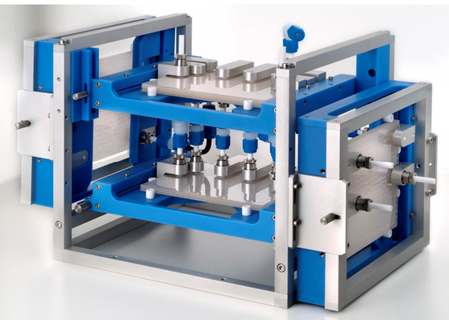
Figure 1: An example of a Corning Glass Micro Reactor

The core of the system is based on Corning's proprietary micro processing technology which brings an unique level of integration in mixing, reaction time and heat management. The Corning technology is based on an engineered reactor approach which enables to fit specific chemistry-needs into modularised building blocks.

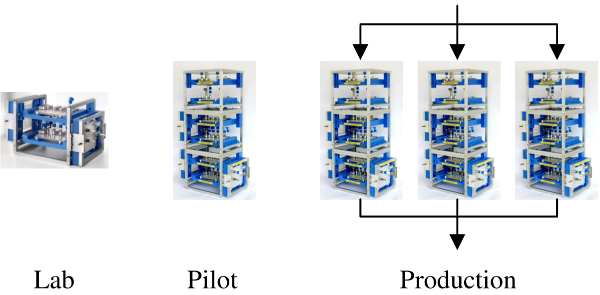

Figure 2: Reactor setups for testing in the different phases of process development up to production

Minimising the development and scale-up time of new synthesis routes is a very important step in the constant battle of being "first-to-market". A variety of special designed micro reaction building blocks will allow to quickly develop a customised reactor concept which can be used for both the development stage and production scale. The combination of Corning's micro reaction technology together with Zeton's modular plant design concept is an excellent basis for a functional and efficient mobile micro reactor plant design.

Figure 3: The industrial mobile multi-purpose micro reactor unit

The demonstrated Mobile Reaction Unit is the first result of this cooperation. The Mobile Reaction Unit is suitable for operation with liquids and gases, for pressures up to 40 bar, and for the temperature range of – 80 °C up till + 200 °C. It is suitable for operation in EEX div II areas and with its own PLC controller it will be operated as a true plug-and-play unit. It is suitable for use in development (pilot) environments, but also in production as output volumes with one single unit can be as high as 40 tonnes/year. The built Mobile Reaction Unit allows for three different continuous reactions in series and thus replacing the cascade of equivalent batch operations. It could also operate in parallel to increase single step reaction capacity.

The ample design of various building blocks allows for flexible use of the unit and, with minor adjustments only, the Mobile unit is a flexible unit for many multi-purpose applications.

This presentation will demonstrate a micro reaction technology beyond the development phase and ready for use in the chain of research, development and production of fine chemicals and pharma intermediates.

Session S-4E: EPIC-1: Intensified Plants & Process Integration (IPPI)

Abstract Number	**Paper Title & Authors**	**Included**
469	Energy-Saving Process Intensification of an Oil Refinery Distillation Plant by an Internal Heat Integration Method K Kataoka, H Noda, T Mukaida, M Kaneda, H Yamaji, K Horiuchi, M Nakaiwa	No
1026	Production of leather under the influence of compressed carbon dioxide E Weidnera, M Rennera, H Geihslerb, G Brandina	Yes
1446	Integrated production of biodiesel from palm oil using in situ produced bioethanol L F Gutiérrez, O J Sánchez, C A Cardonaa	Yes
2565	Integrating fermentation and crystallization: a case study on the production of L-phenylalanine M C Cuellar, A J J Straathof, J J Heijnen, L A M van der Wielen	Yes
3148	Intensification of probiotics drying. Spray-drying of bifidobacteria biosuspension N Menshutina, M Gordienko, A Avanesova, A Voinovskiy	Yes
3738	Functional Design of Integrated Reaction and Separation Processes G Schembecker, M Tylko	Yes

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Production of leather under the influence of compressed carbon dioxide

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1. Summary

The leather producing industry transformes untreated hides that may rot under wet conditions and are brittle under dry conditions into durable, imperishable leather by processes which incorporate tanning agents into the hides. Several steps can be enhanced by high pressure technology. For the tanning of skins compressed carbon dioxide can be used to shorten tanning times, to reduce water pollution and to save leather-finishing-fats. This presentation focuses on the time retrenchment of the tanning-step. Typically, about 30 h are used to tan skins with chrome. At increased pressures between 30 and 100 bar it could be shown that time can be saved by a factor of 6 to 5 h. The presentation will demonstrate the process principle, the acceleration of the tanning process and a quantitative analytical method for monitoring the tanning success via the ion content in the tanning liquid.

Keywords: compressed carbon dioxide, tanning, high pressure, process intensification

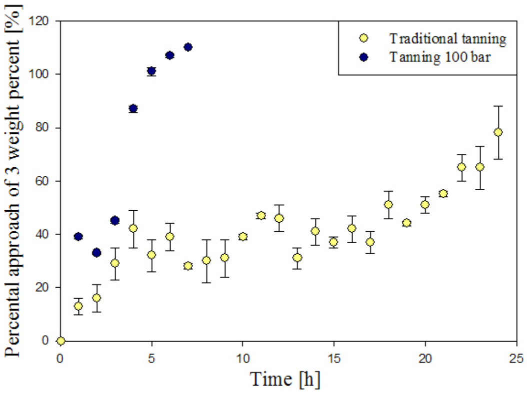
Extended Abstract

The traditional tanning processes comprise a multitude of different steps (up to 70) and are time-consuming and water intensive. A consumption of 20 to 40 t of wastewater per tonne of hides is typical. About 75% of the wastewater contains less critical compounds like salts and tensides, while 25% of the wastewater may contain metal cations and/or organic tanning agents. A value of 3 weight percent of chrome in leather has to be reached for reaching high quality leather. The problem tackled in this investigation was the identification of these 3% and the knowledge of the point in time when these 3% are achieved using traditional tanning methods as well as using traditional tanning methods plus compressed carbon dioxide.

In literature a time corridor of up to 24 h was given for industrially produced raw chrome tanned leather. In the industry, whole skins are put into large rotating barrels which include the tanning solution. After about 24 h the skins turn into leather. Then they are taken out of the barrel and have to be finished.

In order to have conditions similar to real leather production the ratio of masses used was the same, but in small scale For the experiments pieces of goat skin (Ø 2 cm) were put into closed tanning bins. The samples lay in a chrome solution and were slowly stirred by a magnetic stir bar. The mass ratio between solution and skin mass was kept as in industry scale (10/1). For covering the corridor of 24 h two skin samples were tanned per hour. 48 samples with 48 tanning solutions were produced. The basic idea was to analyze the leached solutions accordingly with an ICP. With the knowledge of the lost chrome in the solution, it is possible to figure the chrome content of the leather. For the measurement in the ICP each leached solution was depleted twice (1/500 and 1/1000). 4 results were achieved per hour.

For the comparison of the time savings using compressed carbon dioxide a high pressure cell was used. The cell has a volume of 63 ml, can be heated to 150°C and is built for a pressure of 450 bar. The ratios were exactly the same as before. For the experiments a piece of goat skin (Ø 2 cm) was put into the cell. Accordingly, the tanning solution was pumped into the cell (10/1). The skin lay in the solution and then carbon dioxide was pumped into the cell up to a pressure of 100 bar. All along a stirrer alloyed the solution for an optimal mass transfer. To reduce the time considerably a tanning time of 7 h under CO_2 influence should not be exceeded. After the given tanning time the leather was taken out of the cell. Again, 2 samples were made per hour and the leached solutions were depleted twice for the measurement in the ICP. The results of the comparison are presented in the figure.



The figure demonstrates the time needed for producing high quality chrome tanned leather. On the x-axis the tanning time is shown and on the y-axis there is the weight percent of chrome that has to be reached for high quality. 100% means that 3 weight percent of chrome are reached in the leather. The light-coloured points were measured by using traditional tanning methods and the dark-coloured points were measured by using traditional tanning methods plus compressed carbon dioxide. As mentioned above, each point shows the results of two leather samples that were measured twice. So each point is the result of 4 measurements. The bars show the standard deviation. It becomes apparent that the tanning under compressed CO_2 is much faster. Using traditional methods 24 h do not suffice to reach good leather quality. Using CO_2 as co-solvent 5 h suffice to reach 3 weight percent of chrome in the tanned leather. With the knowledge of the chrome content of the leather it is obvious that time can be saved by a factor of approximately 6.

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Integrated production of biodiesel from palm oil using in situ produced bioethanol

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1. Summary

Liquid biofuels as a source of renewable energy represents an important alternative to the fossil fuels. Currently, these biofuels (mainly biodiesel and bioethanol) are produced from oilseed crops and from sugar and starch containing materials. The integration of the production of these two biofuels using a single source of biomass as a raw material may allow the intensification of liquid biofuels production offering attractive alternatives for lowering production costs. In this work and using process simulation tools, the integrated production of biodiesel from palm oil including the *in situ* production of bioethanol is explored. Lignocellulosic residues obtained during the extraction of crude palm oil are utilized for ethanol production. For this, an integrated process involving the pretreatment of biomass by dilute acid and simultaneous saccharification and co-fermentation is simulated. The oil extracted from Fresh Fruit Bunches was considered as the feedstock for biodiesel production taking into account an integrated process of extractive reaction using the ethyl alcohol produced from the lignocellulosic residues for the transesterification reaction. Overall process was simulated employing Aspen Plus. The integration of material flows between these two production lines allowed a 4.7% reduction in energy costs, whereas the material and energetic integration leaded to 21.3% decrease in these costs. This kind of integrated configuration will become an important option when the technology for ethanol production from biomass reaches such a degree of maturity that its production costs be comparable with those of the process from starch or sugars.

Keywords: biodiesel, bioethanol, process integration, extractive reaction, simultaneous saccharification and co-fermentation

2. Extended Abstract

The utilization of liquid biofuels as a source of renewable energy represents an important alternative to the fossil fuels. The main liquid biofuels are biodiesel produced from oilseed crops, and bioethanol produced from sugar and starch containing materials. In mid-term, the most perspective feedstock for producing ethanol is the lignocellulosic biomass due to its low cost and big availability. Process integration has the potential for intensifying the production of these biofuels offering attractive alternatives for lowering production costs. The integration of the production of these two biofuels has not been studied from the viewpoint of process engineering using a single source of biomass as a raw material.

In this work, process simulation tools were utilized for the design of an integrated process for producing biodiesel from palm oil including the *in situ* production of bioethanol. The process is integrated in the sense that the lignocellulosic residues generated during the extraction of crude palm oil are utilized for the production of ethanol. In addition, energy integration was considered. Empty Fruit Bunches (EFB) and Palm Press Fiber (PPF) are pretreated using dilute acid; the liquid fraction from the pretreatment step is detoxified and combined with the solid fraction for the biological transformation. Through simultaneous saccharification and co-fermentation (SSCF) (a process of the reaction-reaction integration type), the pretreated and detoxified biomass is converted into ethanol, which is concentrated by distillation and dehydrated employing molecular sieves. Ethanol production was simulated as described in Cardona and Sánchez (2006). The anhydrous ethanol is sent to the reactor-extractor where it is added to the oil extracted from Fresh Fruit Bunches. In this unit, an extractive reaction process (reaction-separation integration) is considered. During this process, the produced ethyl esters of palm oil (biodiesel) migrate to one of the two formed liquid phases; this phase is continuously removed from the reactor-extractor in order to separate the biodiesel and recirculate the ethanol. Glycerol, the by-product of the transesterification reaction, remains in the other phase, which is also removed from the reactor-extractor for recovering the ethanol that is recycled to the distillation step.

Overall process was simulated employing *Aspen Plus*. The integration of material flows between the production line for ethanol production and the line for biodiesel production allowed a 4.7% reduction in energy costs, whereas the material and energetic integration leaded to 21.3% decrease in these costs (see Table 1). This kind of integrated configuration will become an important option when the technology for ethanol production from biomass reaches such a degree of maturity that its production costs be comparable with those of the process from starch or sugars.

Table 1: Energy consumption of several technological configurations for biodiesel production

Process	*Energy consumption,* MJ/h	*Unit energy cost of biodiesel,* MJ/L
Non-integrated production of biodiesel	1,210	-
Ethanol production from EFB and PPF	3,821	-
Base case (non-integrated process)	5,031	16.77
Material integration for biodiesel production	4,791	15.99
Material and energy integr. for biodiesel prdn.	3,962	13.21

References

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Integrating fermentation and crystallization: a case study on the production of L-phenylalanine

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1. Summary

In this work we discuss the application of product recovery by crystallization during fermentation to the production of the amino acid L-phenylalanine. The objective is twofold: to improve the fermentation productivity by removing the inhibiting product and to reduce the downstream processing steps by obtaining the product already in crystal form. Based on the fermentation and crystallization characteristics of the system, different process configurations where evaluated by modeling. A process configuration consisting of an external crystallization loop resulted in improved process performance. This configuration is currently under experimental study.

Keywords: bioprocess integration, industrial fermentation, crystallization, phenylalanine, product inhibition.

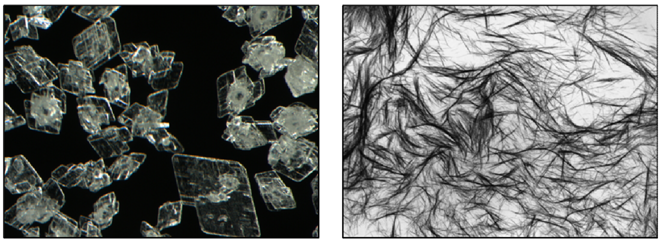
2. Extended Abstract

Industrial fermentation processes often suffer from low productivity. Factors such as product toxicity to the micro-organism or product degradation result in a low product concentration, which in turn leads to a more complex or inefficient product recovery. One way of circumventing these issues consists on removing the product from the fermentation medium as soon as it is being formed. This approach, known as *in situ* product removal or *in situ* product recovery (ISPR), has been described in literature with techniques such as adsorption, extraction and membrane technology [Stark and von Stockar (2003)]. In this work, we evaluate product recovery by crystallization, since most chemicals produced by fermentation are commercialized as solids. In this way, the resulting integrated process should lead to higher fermentation productivities (by removing product toxicity and/or degradation) and reduced downstream operations (by recovering the product already in crystal form), without requiring the use of auxiliary materials.

2.1. Case Study: production of L-phenylalanine

L-phenylalanine (Phe) is one of the most important commercially produced amino acids, being a precursor for the production of the artificial sweetener aspartame. Phe is produced by chemo-enzymatic methods or by fermentation, the latter being however limited by the metabolic pathway of the micro-organisms, which is highly regulated. The key enzymes in the microbial synthesis of Phe suffer from feedback inhibition.

For this case study, an engineered *Escherichia coli* strain as described in Takors (2004) is considered. This strain had been modified to eliminate some of the sources of inhibition resulting in a feedback inhibition concentration of 20 $g \cdot L^{-1}$. In a fermentation without product recovery Phe concentration can reach 30 $g \cdot L^{-1}$ after 50 hours. Regarding the crystallization, Phe is known to crystallize in two forms: anhydrate and monohydrate (see Figure 1). The anhydrate is usually preferred due to its easier to handle flake-like structure. In water, anhydrate is thermodynamically stable above 37°C, while monohydrate is thermodynamically stable below this temperature.



anhydrate monohydrate

Figure 1: Crystal forms of L-phenylalanine.

Based on this information, the process configuration for product recovery by crystallization should aim at:
- Maintaining a low product concentration in the fermenter, preferably below the inhibition concentration in order to obtain maximal productivities.
- Obtaining anhydrate crystals at high crystallization yield.

From modeling calculations different process configurations were evaluated in terms of major process indicators such as productivity, product yield on substrate and crystal yield. A configuration consisting on product crystallization in a external loop resulted in better performance and was chosen for further experimental study. The experimental study is currently in process and focuses on:

- Fermentation implementation with cell retention
- Selection of crystallization method and operating conditions for producing anhydrate crystals
- Integration of fermentation and product recovery

References

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Intensification of probiotics drying. Spray-drying of bifidobacteria biosuspension

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1. Summary

Spray drying has been offered as an alternative method for dry B.bifidum biomass obtaining for production of solid dosage forms. To create the generalized mathematical model according to the proposed strategy the complex of experimental and analytical researches of B.bifidum biosuspension has been carried out. These researches have been directed to study drying kinetics, kinetics of cells death because of heat shock and growth of osmotic pressure, to define the influence of process parameters to the dry product quality and their limitations during drying. On the basis of experimental data and modeling results, the recommendations have been given for the industrial process organization.

Keywords: process intensification, mathematic modelling, spray-dying, Bifidobacteria biosuspention

2. Extended Abstract

The innovation spray-drying of probiotics considered by the example of Bifidobacteria biosuspension drying has been proposed. The spray-drying can be used as an alternative for vacuum freeze-drying because it allows to intensify heat and mass transfer, to organize continuous process, to produce fine powders with high quality, to delete the powdering stage and as result to increase the sterility of product and reduce operation costs [1].

The complex of analytical and experimental investigations was carried out:

- Investigation of Bifidobacteria biosuspension as drying object which included the following steps: the heat sensitive analyze, drying kinetics, investigations of biosuspension physical and chemical properties.
- Laboratory scale spray-drying of Bifidobacteria biosuspension with the complex analysis of basic dry powder properties in order to indicate influence of the operation parameters on product quality.

The mathematical model based on heterogeneous media mechanics and non-equilibrium thermodynamics had been developed to choose the optimal operation parameters and to intensify spray-drying. The mathematical model consists of the mass, momentum and energy conservation equations written for gaseous and dispersed phases; equations described drying kinetics of biosuspensions, kinetics of bacteria survival under the high temperatures and osmotic pressure influences; some additional correlations, initial and boundary conditions. The system of equations was written in cylindrical coordinates. The numerical solution of the system allowed to investigate the drying process and to found the distributions of basic phases parameters in dryer. The mathematical model was verified by using of experimental data (maltodextrin water solution) in the pilot spray-drying. It was found the model is adequate to the experiment.

The mathematical model has been used to scale-up the spray-dryer for dry biomass production. The main dryer sizes were found by calculation. Figure 1 shows the calculated distribution of basic phases parameters for industry spray-dryer.

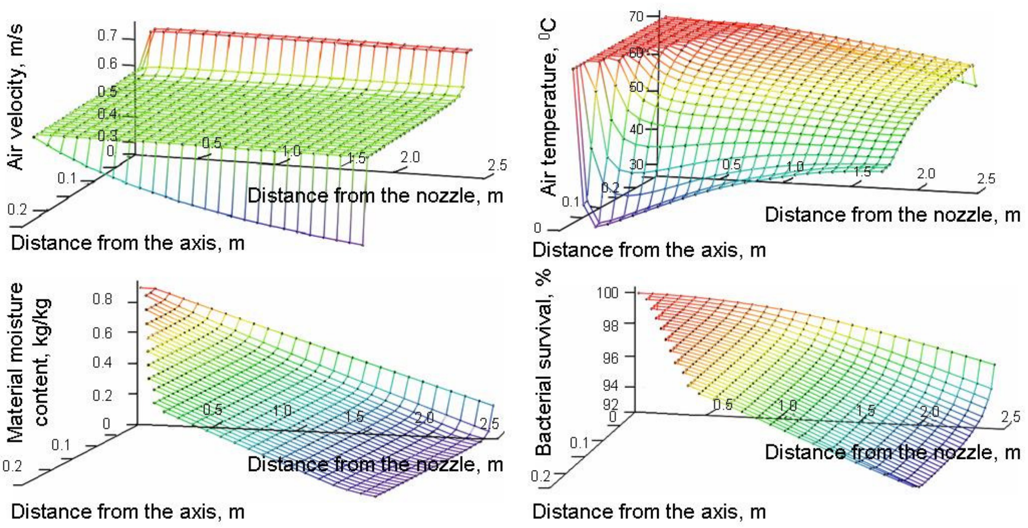

Figure 1. Distribution of basic phases parameters for industry spray-dryer

The energy analysis based on the dynamic coefficients of energy consumption had been done for this apparatus [*Menshutina N.V. et al., 2004*]. It was showed that inlet energy is used in spray-drying more efficiency then in vacuum freeze-dryer.

Thus, the application of spray-drying for probiotics production allowed to intensify the process, to reduce the drying time and to organize continuous process.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Functional Design of Integrated Reaction and Separation Processes

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1. Summary

The presentation will introduce to a synthesis method applying a generic view on integrated reaction and separation processes. Any integrated process can be described by using the four building blocks representing the four basic functions in such processes: reaction, separation, reactive separation and mixing. Based on key chemical and physical properties these functions are arranged such that their overall spatial distribution in the process leads to an optimal process design.

Keywords: process synthesis, process intensification, process integration, conceptual design

2. Extended Abstract

The integration of reaction and separation into one process unit offers huge potential for material and energy saving in chemical industry. In principle, a chemical reaction can be integrated with any separation process. However, besides some very successful reactive distillation processes (e.g. Eastman’s methyl acetate production) not a lot of applications have found their way into industrial application. This can partly be explained by the reduction of degrees of freedom in the design variables which comes intrinsically along with process integration (*Schembecker and Tlatlik 2003*). But another major hurdle for industrial application of integrated reaction and separation systems seams to be posted by just overlooking promising integration options during the synthesis of a new process. Methods like the one described by *Gadewar et al. 2006* do not consider integrated processes as essential part of process synthesis. Therefore, this contribution will present a comprehensive process synthesis procedure, which focuses on the conceptual design of integrating reaction and separation and which covers a combination of a reaction step with any separation technology.

The backbone of the synthesis method is a generic view on integrated reaction and separation processes using four building blocks representing basic functions in such processes: reaction, separation, reactive separation and mixing. Based on key chemical and physical properties these functions are arranged such that their overall spatial distribution in the process leads to an optimal process design. The flexibility of the approach is demonstrated in Figure 1. Any integration concept of reactors and columns can be represented, starting from fully integrated reactive distillation columns to the sequential arrangement of the process units.

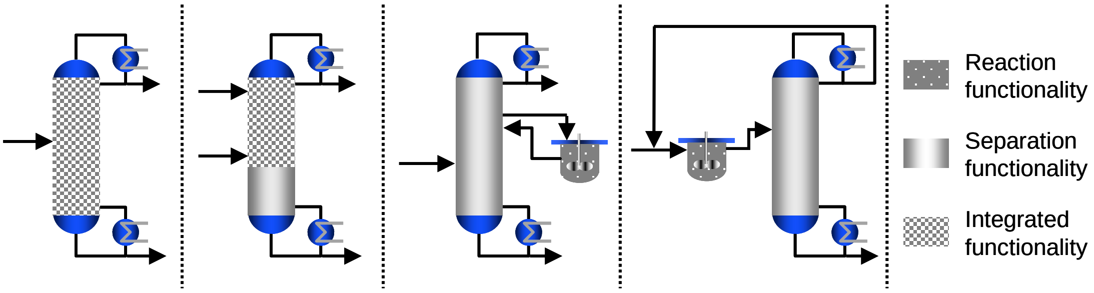

Figure 1: Representation of different levels on integration: fully reactive column, partly reactive column, external reactors, sequential arrangement of reactor and column

The method consists of 10 steps. After defining the target for the process integration project (e.g. higher selectivity, higher conversion, simpler work up) thermodynamic data have to be collected. The investigation of the reaction phase defines optimal conditions (e.g. temperature, pressure, concentration level of components) for the chemical reaction. After identifying incentives to improve the reaction promising separation technologies to be coupled with the reaction are determined. In case knock-out criteria can be found which prohibit the integration of reaction and separation the product region for full integration can be estimated. If the desired product quality does not fall into the product region additional measures like excess of a feed component, closing recycles or apparatus internal accumulation of components can be considered. The distribution of functions (like columns with external reactors) might overcome the limitations encountered during the last design step. The procedure ends with a simulation and optimization of the design options proposed.

The functional design procedure is demonstrated by applying it to combinations of chemical reactions with distillation, adsorption and extraction. In addition, its generic character will be proven by an application to bio-catalytic reactions.

References

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Session S-4F: EPIC-1 keynote Lecture 1

Abstract Number	Paper Title & Authors	Included
1434	Reactive distillation: The front-runner of industrial process intensification J Harmsen	Yes

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Reactive Distillation: The front-runner of Industrial Process Intensification: A full review of commercial applications, research, scale-up, design and operation

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1. Summary

Reactive Distillation combines multiple functions into a single unit, requiring less equipment in particular less heat exchangers, pumps and compressors. In this way energy, variable cost, capital cost and diffusive emissions are reduced. Moreover runaway behavior is less severe, hence; safety is relatively easy maintained. Scale-up is done successfully from pilot plants directly to commercial scale plants. At present reactive distillation is applied commercially in over 150 processes at very large scales, most of them in refineries and bulk chemicals. Applications included are hydrogenations, hydrodesulphurisation, alkylations, etherification and esterifications. The positive effects of reactive distillation in sustainable development terms, People, Planet and Prosperity and the collaborations between the actors, university, technology provider, engineering contractor and manufacturing company could be a successful model for other process intensification implementations in the process industry.

Keywords: Sustainable, Industrial, Reactive Distillation, Process Intensification, Scale-up

2. Extended Abstract

Most industrial scale reactive distillations (presently more than 150), in operation worldwide today at capacities of 100 - 3000 kton/y, and are reported in this paper. Most of these plants started up less than 15 years ago. The drivers, processes, systems, scale-up methods and partner collaborations for this rapid invasion of a new process intensified technique are explained in this paper.

The business drivers are a) economical (prosperity): variable cost, capital expenditure and energy requirement reduction In all cases these are reduced by 20 % or more, when compared to the classic set-up of a reactor followed by distillation.

b) Environmental (planet): lower emissions to the environment. In all cases carbon dioxide and diffusive emissions are reduced and c) social (people): improvements on safely, health and society impact are obtained by lower reactive content, lower run away sensitivity and lower space occupation.

These industrial reactive distillation systems comprise homogeneous and heterogeneous catalysed, irreversible and reversible reactions, covering large ranges of reactions, notably hydrogenations, hydrodesulphurisation, etherification and esterification. Various commercial methods for packing heterogeneous catalyst in columns are now available.

The systems comprise amongst others: multiple catalyst systems, gas and liquid internal recycle traffic over these catalyst systems, separation, mass flow, and enthalpy exchange. These are integrated optimally in a single vessel, a characteristic feature of process intensification.

The scale-up methods applied from pilot plants to commercial scale are brute force and modelling. Technology providers CDTECH and Sulzer Chemtech have used these scale-up methods successfully Barriers perceived and real have also been removed by these companies. Chemical manufacturing companies have also developed their own specific reactive distillations by their own research and development. These companies, both on their own and in consortia, also developed heuristic process synthesis rules and expert software to identify the attractiveness and technical feasibility of reactive distillation.

Academic research also produced design methods to identify the feasibility of reactive distillation, to determine the feed locations, to select packing types, to sequence columns optimally and also produced methods to design, optimise and control the columns with steady state and dynamic simulation models.

The rapid commercial scale implementation of reactive distillation by co-operation of partners in research, scale-up, design and reliable operation can be a model for rapid implementation of other process intensification techniques in the chemical industry.

Session S-4G: EPIC-1: Intensified Hydrodynamics & Structured Environments (IHSE-3)

Abstract Number	**Paper Title & Authors**	**Included**
93	Hydraulic And Thermal Study Of A Compact Heat-exchanger Reactor M A Bennani, S Elgue, C Gourdon, M Cabassud	Yes
1858	Continuous Epoxidation of oleic esters in a micro reactor D H Mueller, D Herzog, F Pontzen, S Eichholz, M A Liauw, L Greiner	Yes
3445	Refined and extended investigation of microreactor based ionic liquid synthesis for further process intensification V Hessel, P Löb, R Miszczuk, A Renken, L Kiwi-Minsker, M Uerdingen	Yes

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Hydraulic study of a compact heat-exchanger reactor

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1. Summary

Chemical industry needs to advance continually in order to satisfy the growing economic and environmental constraints. In this context, batch reactors present limitations (Read 2000), particularly because of their restricted thermal and mixing capacities compared to compact heat-exchangers reactors (Dautzenberg 2001). The hydraulic characterization of this new generation of reactors then appears as one of the primordial steps to validate their design and ensure their capacities from a process intensification viewpoint. This study will focus on the hydraulic description of an example of compact heat exchangers reactors using metallic foams. This study was carried in two main stages. The first one consists of theoretical study from a functional analysis using transfer function characterization and from dynamic simulation. This study has then been performed in two ways: using Simulink, software derived from MATLAB, and by the writing of the mass and energy balances in transient state and the resolution of the related equations system. The last approach is based on the acquisition of experimental data. The objective here is to compare the numerical results to the experimental ones and to check and validate the numerical representation of the heat-exchanger reactor from hydraulic considerations.

Keywords: Intensification, chemical reactor, RTD.

2. Extended Abstract

In this work we focus more precisely on the use of specific interns: metallic foams. Experimental pilot thus consists of two rectangular foams, with a square cross section, laid out in series and forming a loop of recirculation. This type of insert presents a great specific surface (between 900 m^2/m^3 and 2400 m^2/m^3) and the capacity to evacuate a high amount of heat. Moreover these metallic foams have a strong porosity (> 95%) which limits pressure drops.

The modelling of the reactor (Functional analysis and simulation tool) allows the prediction of its hydraulic behaviour to be carried out, assuming that the heat-exchanger reactor can be modelled as a succession of N stirred tank reactors. It was done using two specific methods. The first one deals with a functional analysis of the pilot device using Simulink a software derived from Matlab. Simulink is a platform for multidomain simulation and Model-Based Design for dynamic systems. It was used here to visualize the response of our system, in various situations of operating conditions of the loop reactor.

The second one is based on the modelling of the mass and energy balances governing the reactor behaviour. This study uses a specific simulation tool based on dynamic modelling taking into account at the same time the hydraulic, thermal and reactional aspects of the process and that aims to predict the behaviour of the reactor for different operating conditions.

From a hydraulic viewpoint, RTD experimental data was compared to the numerical ones. Figure 1 shows the experimental concentration evolution of a tracer injected in the reactor according to time and compared to the one calculated using the two numerical tools.

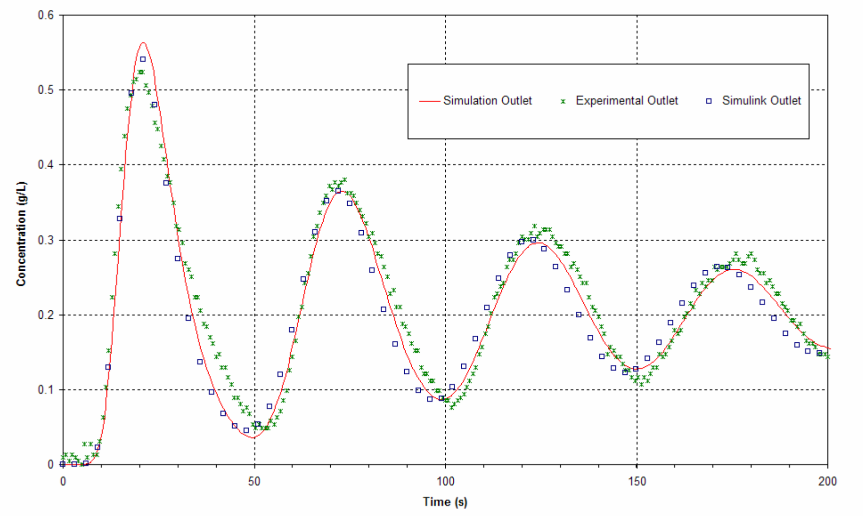

Figure.1 : Concentration at the exit according to time for the loop reactor, Flow rate=90L/h

As a conclusion to this hydraulic study, we can say that the developed numerical tools reproduce well the behaviour of the reactor. In this way, they allow a good representation of the reactor hydraulics to be carried out and therefore, the optimal operating conditions as well as the process limitations to be determined.

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Continuous epoxidation of oleic esters in a micro reactor

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1. Summary

The synthesis of environmentally friendly lubricants based on oleic acid methyl ester is studied. The lubricant is formed within two steps, epoxidation and alcoholysis. In this work, the epoxidation is studied in a microreactor.

Keywords: scale, epoxidation, lubricants, solvent free, two phase system, renewable resources

2. Extended Abstract

Aim of the collaborative research center 442 (SFB 442) is to develop environmentally friendly high performance tribosystems. Therefore, engineers, material scientists, chemists, and biologists are working closely together. Our research is focused on the development of new environmentally friendly lubricants. We use oleic acid methyl ester from renewable sources as starting material. This is processed to give a lubricant within two steps epoxidation and successive alcoholysis (Figure 1). The reaction is currently carried out routinely as a batch process on a 50L scale to satisfy the needs of the collaborators for the use in machining and property testing.

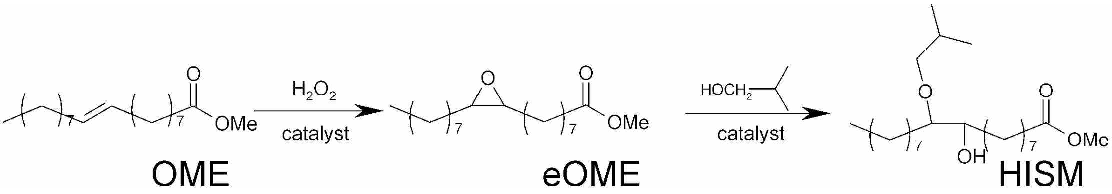

Figure 1: Two step synthesis of HISM as environmentally friendly lubricant via epoxidation of OME (Oleic acid methyl ester) to eOME and alcoholysis.

Aiming for a continuous process both chemical and enzymatic routes of synthesis are evaluated for process intensification. For the development of an environmentally friendly product, evaluation of toxicity and biodegradability has to be taken into account which could be demonstrated successfully for the batch process. Thus, besides yield and selectivity these factors are taken into account directly as the process is developed and are used to judge alterations and process intensification directly

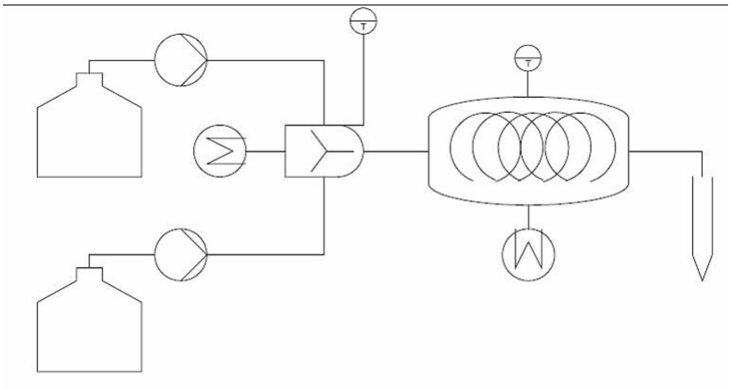

Figure 2: Flow scheme for the continuous epoxidation

Our kinetic studies by reaction calorimetry revealed that the epoxidation in the oil/water biphasic mixture is greatly influenced by temperature and mass transfer. Lower temperature is generally favorable for better selectivity but reaction rates decrease considerably making a continuous reaction unfeasable. By means of microreaction engineering the reaction can be sped up considerably by the intensification of mass transfer.

We will present the results for the epoxidation as the first step using micro reaction engineering for evaluation and production and isothermal reaction calorimetry for process intensification. The effect of a solvent free approach for reaction and down-stream processing will be evaluated. The results will be compared to the established production.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Refined and extended investigations of microreactor based ionic liquid synthesis for further process intensification

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1. Summary

The considered ionic liquid synthesis, the alkylation of 1-methyl-imidazole with diethyl sulphate, is connected with a large heat release resulting in impurity formation and colouring of the product if heat transfer is insufficient. The current in this regard insufficient batch process was transferred in a continuous microreactor process with improved heat removal. Based on experiments performed in an initial micromixer-tube set-up leading to a decrease of reaction time from the hour range to a few minutes a design for a pilot- to production-scale (about 4.0 l/h) reactor set-up has been derived. The approach has been validated now using a first prototype representing the basic element for a later numbering-up. Furthermore, kinetics and thermodynamics of the reaction has been studied based on calorimetric measurements. The obtained data have been used to simulate the process in order to optimise the process conditions for the suggested reactor set-up aiming at a further process intensification mainly by reducing reaction time and therewith reactor volume by optimal setting of the temperature in the different reactor parts. The simulation revealed a further potential of reactor volume reduction by more than a factor of 3.

Keywords: microreactor, ionic liquid synthesis, process intensification

2. Extended Abstract

Ionic liquids have gained an enormous interest over the past years because of their unique properties allowing them to replace traditional organic solvents in chemical reactions and as extraction media (Wagner, 2005). The respective synthesis often uses reaction paths which comprise at least one feature which render reactions tailored for use in microstructured reactors – large heat releases which may result in impurity formation, if heat transfer is insufficient. Microstructured reactors by their superb transfer properties principally allow overcoming such limits.

As reported already earlier (Löb et al., 2006), we have investigated in the framework of the EU project IMPULSE the limitations of conventional batch processing and the principal potential of continuous microreactor based operation for the highly exothermic alkylation of methyl imidazole by diethyl sulphate. Initial experiments in lab-scale batch vessel demonstrate impressively the occurrence of hot spot for the one-step dosing of the reactants and therewith connected the fast change of the reaction mixture from a clear colourless to a dark black-brownish solution. The process was then transferred successfully in lab-scale into a microreactor based continuous operation. The set-up thereby consisted basically of a micromixer for contacting the undiluted reactants followed by a Teflon tube (7.5 ml inner volume) as residence time section, both embedded in a thermostat bath. Based on measurements of the temperature profile over the length of the reactor, the tube dimension was finally fixed to 1/16´´ for the first part of the tube section and 1/8´´ for the following part. A temperature controlled operation sufficient for the avoidance of colouring of the product is possible up to a total flow rate of 0.2 l/h. Compared to the conventional batch processing reactor volume is reduced down to 7.5 ml and reaction time also from the hour range to a few minutes.

The set-up has now been further improved by switching from Teflon to stainless steel as tubing material leading due to the better heat transfer capability of stainless steel to even better temperature control. Based on the results obtained so far an adapted reactor concept targeting at higher, production throughput (about 4 – 8 l/h) has been developed in which a microstructured heat exchanger forms the reactor part which has to handle the largest heat release. The throughput capacity of the latter will be adjusted by internal numbering-up (Schenk et al., 2004). A first prototype of the micro heat exchanger has been realized for a total flow rate of 0.4 l/h and integrated to a complete set-up. The principal functionality was successfully proven.

Supplementary, the kinetics and thermodynamics have been studied based on calorimetric measurements. A reaction enthalphy of – 100 kJ/mol and an activation energy of 78 kJ/mol has been found. The data has been used to simulate the process using the software Berkeley Madonna. After validation against experimental data (e.g. temperature profiles in the reactor), the simulation has been used to optimise process conditions in the reactor set-up aiming at the exploration of even more intensified operation regimes. The simulation revealed that by applying different temperature zones and setting temperatures as high as possible while avoiding colorization of the product a further reduction of residence time, i.e. reduction of inner reactor volume, by a factor of 3 is possible. Corresponding experiments to validate this are currently running.

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Session S-4H: EPIC-1: Multifunctionality (MF-1)

Abstract Number	Paper Title & Authors	Included
282	Reactive dividing-wall columns – towards process Intensification A A Kiss, H Pragt, C van Strien	Yes
2433	Membrane reactors for process intensification A Brunetti, G Barbieri, A Caravella, E Drioli	Yes
3395	Autothermal catalytic reactors for hydrogen production: experimental and modelling analysis D Scognamiglio, L Salemme, L Russo, M Simeone, P L Maffettone, S Crescitelli, C Allouis, G Volpicelli	Yes

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Reactive dividing-wall columns – towards process Intensification

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1. Summary

This work presents an industrial case study within Akzo Nobel Chemicals. Due to the market demand changes, one of the by-products of an existing plant became more attractive than the main product. However, the current plant design does not allow an increase of the by-product production rate at the cost of the main product. To solve this problem we propose an integrated design based on a reactive divided-wall column. The RDWC allows 35% and 15% savings in capital and operating costs.

Keywords: reactive distillation, dividing-wall column, equilibrium reactions.

2. Extended Abstract

Distillation is the major separation process used in the chemical processing industry. However, one key drawback is its significant energy requirements. Dividing-wall column (DWC) offers a cost effective alternative to conventional distillation.

The direct sequence of two distillation columns evolved via the Petlyuk column to the concept of dividing-wall column. DWC is a very attractive design alternative as it saves the cost of building two columns and cuts operating costs by using a single condenser and reboiler. However, using DWC requires a match between the operating conditions (T, P) of the two stand-alone columns. Integrating reaction and separation into one unit, leads to reactive distillation. What about integrating a reactor and two distillation columns into one unit? The answer is the reactive dividing-wall column. This work presents an industrial case study within Akzo Nobel Chemicals. One of our processes involves a relatively complex fast equilibrium of 10 species (*A*-*J*, listed in descending order of relative volatility, *A* being the most volatile component).

1. $A + J \leftrightarrow C + H$ (main reaction)
2. $B + H \leftrightarrow C + E$
3. $D + H \leftrightarrow C + I$
4. $B + E \leftrightarrow A + F$
5. $F + J \leftrightarrow 2\,G$

After reactor, the reaction mixture is separated in a series of distillation columns. Most of the streams are recycled back to the reactor while component *H* is purified and sold as main product. Due to market demand changes and the price increase of product *C*, the focus shifts from main product *H* to component *C*. The problem is that the current plant design is not suitable for producing by-product *C* instead of *H*.

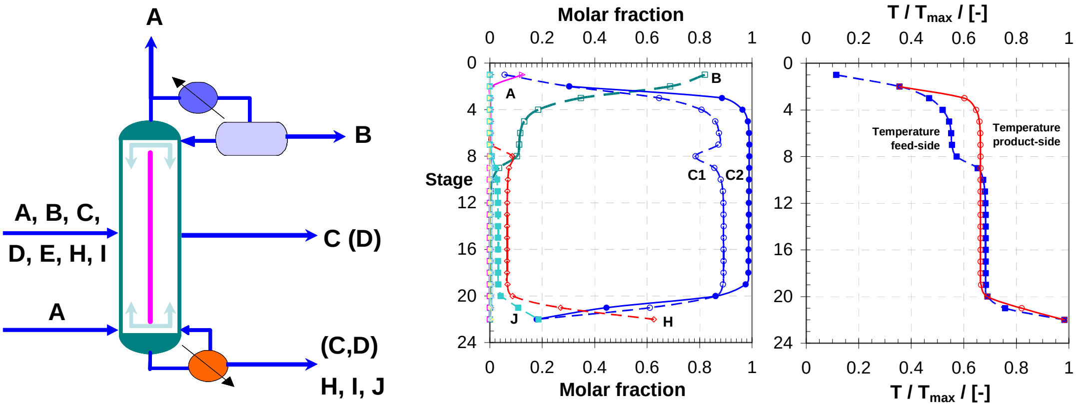

Figure 1. Reactive DWC. Composition and temperature profiles (C1/C2 – feed/product side).

To solve this problem we used a conventional design based on a reactive distillation column, followed by a regular distillation column (base case scenario). In addition, we considered a more integrated design that combines reaction and separation into one RDWC. The reactions take place only on the feed side of the column, where the light components are separated from the heavy ones. The formation of heavy components *F* and *G* – useless by-products – is avoided by adding an additional feed of light component *A*.

This study shows that equilibrium limitations can be overcomed and high purity components can be obtained by integrating reaction and separation into one unit. The key factor that allows this integration is the similar pressure and temperature conditions in the two standalone columns. Note that the column copes well with disturbances in both feed flow rate and composition.

Compared to the base case using two distillation columns (RD+DC), the RDWC based design presented in this industrial case-study allows 35% savings in capital costs and 15% savings in energy costs, respectively.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Membrane reactors for process intensification

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1. Summary

The development of innovative systems and techniques offering a drastic improvement in chemical manufacturing and processing is a fundamental issue for a sustainable growth, following the Process Intensification Strategy (Drioli et al., 2001). According to this logic, membrane reactors (MRs) are the most significant class(Stankiewicz A, 2003) of the so-called multifunctional reactors integrating reaction and separation in the same unit and, therefore, moving towards plant size reduction, better material exploitation, lower energy consumption, etc..
In this work, the advantage of the MR was demonstrated by means of new indexes, assuming the water gas shift reaction as case study:

- Volume Index, the ratio of the catalytic volume of MR to TR (Brunetti et al., 2005)
- Conversion Index, the ratio of the conversion of an MR to a traditional one.

Keywords: membrane reactors, Process Intensification, volume index, conversion index

2. Extended Abstract

A significant size reduction (volume index equal to 25%) was achieved by the MR for a final conversion of ~80% (corresponding to 90% of the traditional reactor equilibrium one) feeding an equimolecular mixture (Figure 1). Furthermore, a conversion index of 5 was reached using a typical syngas mixture (50%H_2; 10%CO_2; 20%CO; 20%H_2O) which is of particular industrial interest (Figure 2). These values were calculated by means of a 1-D non-isothermal model at 280°C and 1,500 kPa of feed pressure for a 60-micron Pd-Ag self-supported membrane. The catalyst weight and reaction volume necessary to achieve a suitable conversion drastically reduces using an MR with clear gain in terms of plant size reduction (a factor 4-5) and better catalyst utilization. This is due to hydrogen permeation through the Pd-alloy membrane shifting the reaction toward a further conversion; therefore, the MR conversion exceeds the equilibrium one of a traditional reactor.

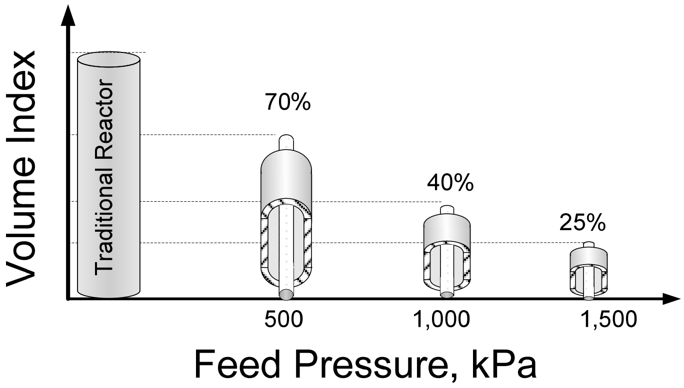

Figure 1 Volume Index as a function of Feed pressure for equimolecular mixture. Furnace temperature=280°C. Set CO Conversion 90% of the TREC

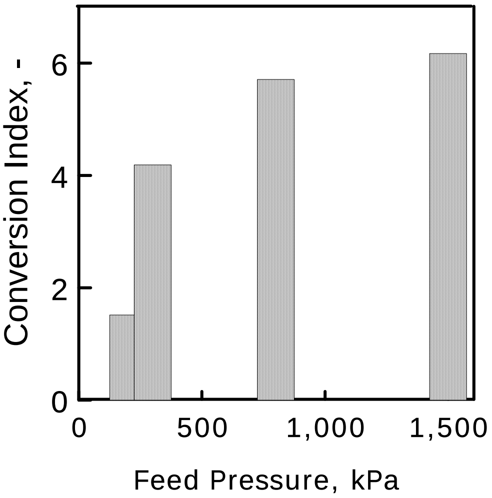

Figure 2 Conversion Index as a function of feed pressure for the syngas mixture. Furnace temperature=280°C.

In addition, the reduced hydrogen concentration (on the reaction side) reduced the reverse reaction rate, thus improving the kinetics. Around 80% of the total hydrogen produced, recovered on the permeation side as pure stream, does not require further separation and purification units before its use also in PEMFCs.

Acknowledgments

The Italian Ministry for Foreign Affairs, Direzione generale per la promozione e la Cooperazione Culturale, Rome, Italy is gratefully acknowledged for co-funding this research

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Autothermal catalytic reactors for hydrogen production: experimental and modelling analysis

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1. Summary

In this work we study from experimental and theoretical point of view the autothermal reforming of methane for hydrogen production. The process is operated in a catalytic fixed bed reactor with a commercial Ni/Al2O3 catalyst pellet. We present experimental data of products composition and temperature profiles within the reactor. Temperature profiles were measured with an IR camera (ThermaCamTM Phoenix). The reactor was operated feeding methane, air and steam, to produce syngas. To assess the impact of steam, on temperature profile and product composition, an experimental campaign feeding several steam and methane ratios was performed. Temperature profiles and products composition obtained via numerical simulation of a heterogeneous model are compared with those obtained experimentally. The effect of different operating conditions on the overall conversion and selectivity to syngas is studied.

Keywords: autothermal reforming, temperature profile, hydrogen, fixed bed

2. Extended Abstract

In recent years most of studies on hydrogen production are focusing on the development of small and medium scale technologies for a decentralized production. In this context the most promising processes are the catalytic partial oxidation (CPO) and the autothermal reforming (ATR) of methane. The main technical barrier to the application of CPO is catalyst deactivation due to the very high temperatures formed in the initial portion of the catalyst bed.

In the ATR, steam is added to the fed of CPO, thus lowering the temperatures reached in the catalytic bed and enhancing the hydrogen yield (De Groote et al. 1996).The temperature profile developed in the catalyst bed is an important aspect in catalyst and reactor design. While for the CPO several models, developed and validated with measures of the solid surface temperature, are available in the literature, no such data is available for the ATR in the open literature.

This work is devoted to model the ATR of methane in fixed bed reactors. The theoretical predictions are compared with experimental activities performed measuring the composition products and the surface temperature profiles of the catalytic bed with an IR camera (ThermaCamTM Phoenix) which operates in the short wave range 3-5 μm. Typical results are shown in Figure.The reactor consists of a cylindrical quartz tube (internal diameter is 21 mm) in which the catalyst section (14 mm) is placed between two beds of inert alumina spheres (the diameter is 1mm).

The process was modelled with a 1D dynamic heterogeneous model of a fully insulated packed bed reactor. The model includes the mass balance equations for each species (H_2, CH_4, CO, CO_2, H_2O, O_2, N_2), and the energy balance equations for both gas and solid phases. The gas phase balance equations are dispersive, whereas an effective conduction, which takes into account radiation effects, is considered for the solid phase energy balance equation. The momentum balance equation was neglected as the observed pressure drop is low. The gas phase is assumed ideal. The kinetic model is reported in Hoang, D. L.(2005). The values of the relevant parameters are reported in Table.

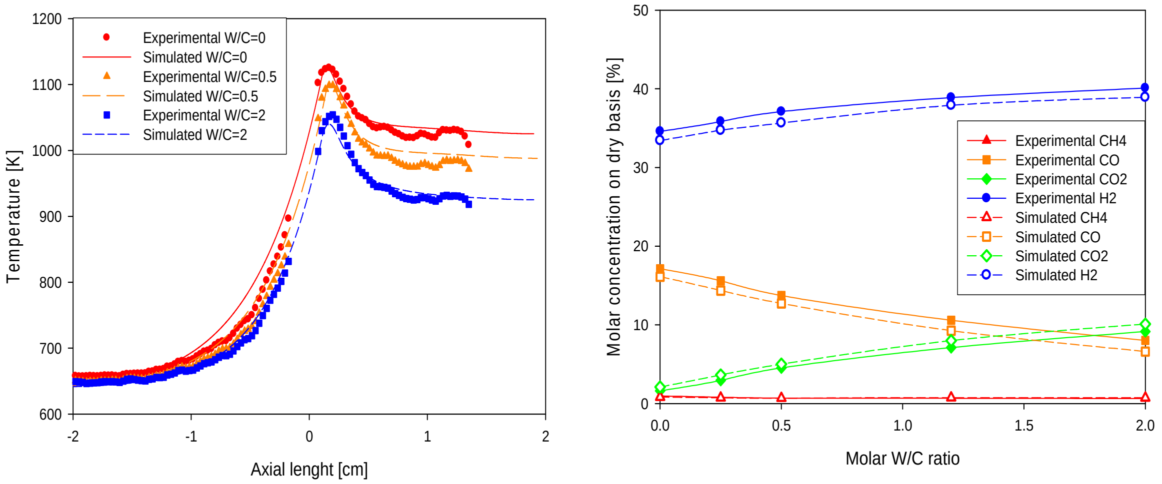

Figure : On the left: Catalyst temperature profiles: comparison between experimental and model calculations at different steam and methane ratios (W/C). On the right: comparison between experimental and theoretical exit composition. The methane and oxygen ratio is 1.6.

ρ_{cat}(kg m^{-3})	K_s (W m^{-1}K^{-1})	ε	U (W m^{-2} K^{-1})	e
1700	16	0.42	9	0.8

Table : Model parameter values: catalyst density, thermal conductivity, bed void fraction, external heat transfer coefficient and solid emissivity.

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Session S-4I: EPIC-1: Intensified Hydrodynamics & Structured Environments (IHSE-4)

Abstract Number	Paper Title & Authors	Included
839	Single Flow-Through Catalytic Membrane Microchannel Reactor for Intensified Heterogeneous Catalysis: Characterisation and Application to Hydrogenation of Ethyne T Westermann, T Melin	Yes
1006	Instabilities of Immiscible Liquid-Liquid Two-Phase Laminar Flow in a Micro Channel T Matsumoto, T Shikata, T Takigawa, N Ohmura	Yes
2937	Micro-Scale Liquid-Liquid Separation in a Plate-Type Coalescer E Kolehmainen, I Turunen	Yes
3474	Methanol Synthesis Using Microchannel Reactors for Off-Shore Applications A H Bakhtiary, B R Myrstad, C P Pfeifer, D H Venvik, E K X Phan, F K Schubert, G A Holmen	No

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Single flow-through catalytic membrane microchannel reactor for intensified heterogeneous catalysis: characterisation and application to hydrogenation of ethyne

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1. Summary

In flow-through catalytic membrane reactors (FTCMR) the reactant mixture flows convectively through a membrane which acts as a structured catalyst support and performs no separative function. The resulting intensive contact between reactants and catalyst allows for a high catalyic activity whereas the residence time inside the membrane is very small. The concept can be applied to slow reactions in a loop reactor operated in batch mode, but is especially attractive as continuous single flow-through reactor for fast reactions. In this work the unique uniform multichannel structure of anodized alumina membranes is applied as FTCMR in order to assess its advantages regarding selectivity and residence time distribution compared to conventional randomly structured membranes. A reactor model has been set up to quantify the influences of Knudsen diffusion, pore size distribution and axial dispersion on conversion, selectivity and pressure drop. The experimental setup was characterized and applied to the selective hydrogenation of ethyne as model reaction.

Keywords: Catalytic Membrane Reactor, Microchannel Reactor, Flow Through, Reactor Modelling, Knudsen Diffusion

2. Extended Abstract

Catalytic membranes without separative function have successfully been applied as microstructured reactors [Dixon2003]. If the reactant mixture is forced to flow through the pores of a membrane which has been impregnated with catalyst, the intensive contact allows for high catalytic activity without mass transport resistances. Reaction rates measured in catalytic membrane reactors have been found up to ten times higher than in conventional packed bed reactors with the same catalyst [Zaspalis1991]. In conventional membranes the void spaces between sintered particles resemble the pores, resulting in a relatively wide size distribution with remarkable tortuosity. Flow-through catalytic membrane reactors (FTCMR) for gas-liquid applications are often applied in batch mode with high recirculation ratios [Dittmeyer2004].
In this work anodized alumina membranes with very uniform pore channels are examined for their applicability as catalytic reactors for gas phase reactions. The

investigated membranes possess a regular structure of parallel open pore channels with diameters of 200 nm and a length of 60 µm. Catalytically active material (Pd) is introduced into the pores by means of impregnation methods. The reactor is operated in continuous mode without recirculation. The narrow channels intensify the contact between reactants and catalyst resulting in high conversion, while the regular channel structure leads to a narrow residence time distribution which allows for high selectivity. The concept is tested with the selective hydrogenation of ethyne catalyzed by palladium as model reaction.

As a reactor model the membrane is represented by a high number of parallel one-dimensional plug flow reactors taking into consideration the pore size distribution and axial dispersion. Higher flow-through velocity leads to lower axial dispersion but increases the pressure drop. Deviations from an ideal pore size distribution can be counteracted by flowing through several membranes in sequence. The resulting conversions and selectivities are compared to the ideal case of a single plug flow reactor without axial dispersion on the one hand and to the realistic alternative of a fixed bed reactor on the other hand.

Pressure drop measurements confirm that the flow through the membrane consists of a laminar flow contribution and a Knudsen diffusion contribution. The ratio of the contributions can be manipulated by altering the absolute pressure. Reaction experiments have been performed to measure reaction kinetics and to validate the reactor models. Advantages of the catalytic membrane microchannel reactor compared to an equivalent fixed bed reactor as well as to an unstructured catalytic membrane reactor are quantified.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Instabilities of immiscible liquid-liquid two-phase laminar flow in a micro channel

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1. Summary

The present study investigated instabilities of immiscible liquid-liquid two-phase laminar flow in micro channel systems. Four representative flow patterns, i.e. stratified flow, stratified wavy flow, stratified flow with inclined interface and annular flow, were observed due to the difference of channel dimension of the organic-phase flow and physical properties of liquids.

Keywords: immiscible liquid-liquid flow, two-phase flow, micro channel, instabilities, flow visualization

2. Extended Abstract

A micro chemical chip is one of the powerful tools currently used for process intensification technology because of its favourable characteristics such as reduction of regents, high throughput, savings on energy and materials, and so on. The immiscible liquid-liquid multi-phase flow such as aqueous-organic phase flow in a micro channel system can be used for solvent extraction, interfacial chemical reaction, and drop formation etc. (Sugiura *et al.*, 2001; Nishisako *et al.*, 2004). In order to intensify processes using liquid-liquid micro multiphase laminar flow, it is necessary to establish a precise control method. The present study investigated instabilities of immiscible liquid-liquid two-phase laminar flow in a micro channel.

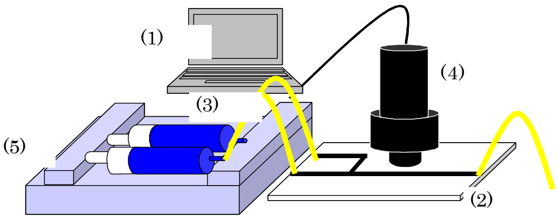

Fig. 1 Experimental setup; (1) computer, (2) micro channel, (3) syringe, (4) microscope and (5) pump

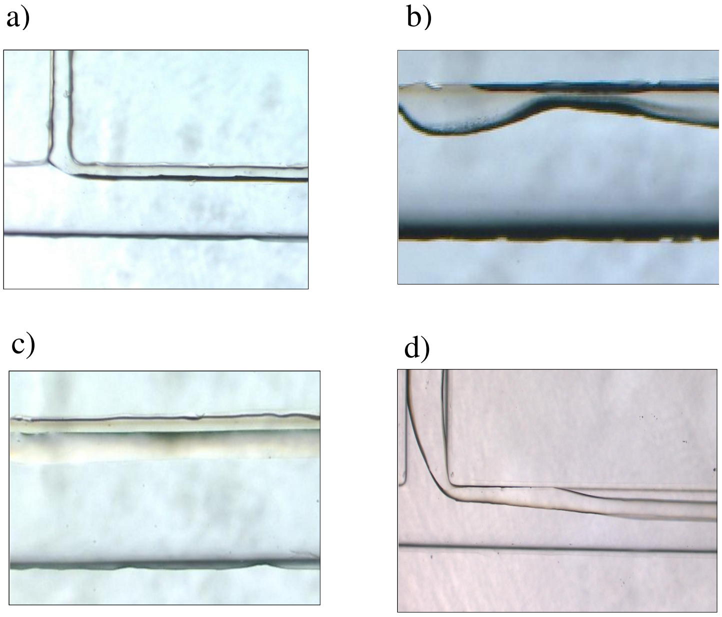

Fig. 3 Flow patterns: a) stratified flow, b) stratified wavy flow, c) stratified flow with inclined interface and d) annular flow

Figure 1 shows a schematic of the experimental setup. Two T-channels of glass fabricated by micro precision machining were used. The aqueous-phase-flow channel is 320 μm in width and 120 μm in depth in both channel systems. One of the channel systems has an organic-phase-flow channel with 100 μm in width and 120 μm in depth (Channel-1), while the other is of 320 μm in width and 120 μm in depth (Channel-2). An aqueous solution of glycerol or distilled water with or without surfactant was used as aqueous phase, while styrene monomer was used as organic phase. The two liquids were separately fed into two inlet branch channels by micro syringe pump. The interface between two liquids after T-junction is enlarged by a microscope system which also took the visual data.

Four representative flow patterns, i.e. stratified flow, stratified wavy flow, stratified flow with inclined interface and annular flow, were observed due to the difference of channel dimension of the organic-phase flow and physical properties of liquids. Stratified flows including stratified wavy flow and stratified flow with inclined interface were observed in Channel-1. Stationary waves were superimposed on the interface when using pure distilled water. On the other hand, a straight interface was formed when a small amount of surfactant (SDS) was added to distilled water. In both cases, the stratified flows formed a perpendicular interface between two phases. When the aqueous phase of glycerol solution was of relatively high viscosity, the interface was inclined. An annular flow of the aqueous solution was observed in Channel-2 under certain conditions. The aqueous phase flowed as a film around the channel wall and a core of the organic phase formed in the middle of the channel. In this flow pattern, the aqueous phase needs to be of relatively high viscosity. These results indicate that the channel dimensions, viscosity and surface tension affect flow instabilities.

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Micro-scale liquid-liquid separation in a plate-type coalescer

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1. Summary

The plate-type coalescer was constructed and tested for the continuous separation of immiscible liquids in micro-scale. Two horizontal plates formed the main structure of the coalescer. A flat and rectangular channel was located between the plates. The coalescer had two outlets, one for the aqueous phase and the other for the organic phase enabling the continuous separation and withdrawal of separated phases. The performance of the coalescer was evaluated with respect to the channel height, flow rate, residence time and plate configuration. It was observed that in suitable conditions, the plate-type coalescer enabled the efficient steady-state phase separation. The separation method utilizes the interaction between the fluids and channel surfaces. The phase separation in the coalescer occurred considerably faster than in a conventional settling tank.

Keywords: microprocess, liquid-liquid separation, extraction, coalescer

2. Extended Abstract

Introduction

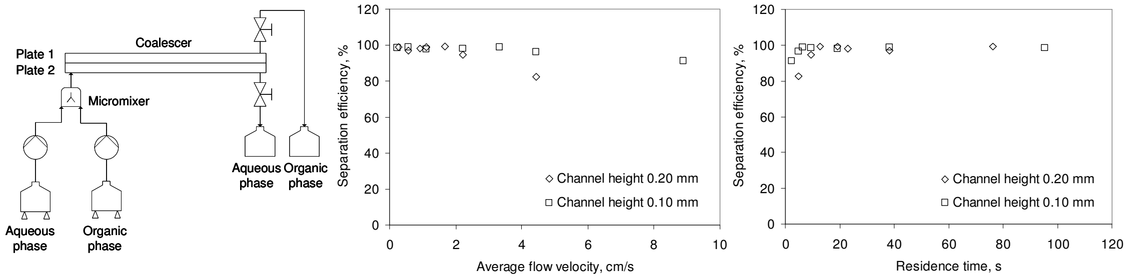
Microprocess technology represents process intensification at its extreme eliminating the extra heat and mass transfer limitations in chemical processing. Several applications of microreactors have been presented for chemical reactions, but still microprocesses for separation purposes are rare. In micro-scale extraction processes, efficient separation of immiscible liquid streams is important. The aim of this study was to test the use of the plate-type coalescer for continuous separation of immiscible liquid streams in micro-scale.

Experimental set-up

The coalescer consisted of two plates. Materials were stainless steel, PTFE and glass. A rectangular flat channel was machined on the surface of the other plate and the channel was located between the plates. The dimensions of the channel in the coalescer were as follows: width 15 mm, length 200 mm, height 100 μm and 200 μm. In the experiments, dispersion was achieved by feeding the immiscible fluids through the slit interdigital micromixer. The micromixer was connected to the coalescer, where coalescence of the liquid droplets took place. The schematic drawing of the experimental system is depicted in Figure 1a.

Results

Results showed that high separation efficiencies could be achieved in the plate-type coalescer. Separation efficiency is defined on the basis of the component concentration in the influent and the effluent. Water and Shellsol-solvent with tris(2-ethylhexyl)phosphate (TEHP) were the immiscible liquids. High separation efficiencies were obtained by using stainless steel and PTFE plates (Figure 1b).



a) b)

Figure 1: a) The schematic drawing of the experimental set-up. b) Separation efficiencies in the plate-type coalescer as the functions of the average flow velocity and residence time at different channel heights. The feed streams were water and Shellsol with 10 weight-% TEHP. The volumetric flow ratio of the aqueous feed to organic feed was 1:1.

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Session S-4J: EPIC-1: Multifunctionality (MF-2)

Abstract Number	Paper Title & Authors	Included
678	Managing impurities in an integrated crystallization system C Wibowo, Y S Cheng, K M Ng	Yes
1264	Hybrid separation process - combination of reactive distillation with membrane C Buchaly, P Kreis, A Górak	Yes
1361	Performances comparison of intensified mixers and micromixers L Falk, J-M Commenge, S Lomel	Yes
2085	Determination of the interfacial area of a continuous integrated mixer/separator (CINC) using a chemical reaction method B Schuur, W J Jansma, J G M Winkelman, H J Heeres	Yes

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Managing impurities in an integrated crystallization system

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1. Summary

This presentation discusses a workflow for managing the impurity content in the product of a crystallization process in consideration of the entire train of crystallization and post-crystallization steps. The workflow is illustrated using a case study on the purification of Vitamin C (ascorbic acid). Experiments are performed to determine the dependence of the impurity inclusion on several key factors such as growth rate, solvent concentration, and the yield of crystallization. The effect of washing and deliquoring on the amount of surface impurities are also evaluated. Semi-empirical models are then used to correlate the performance of washing and deliquoring steps to the target product purity. In this way, the specifications for a suitable solid-liquid separation unit to perform the task can be determined.

Keywords: process development, crystallization, impurity incorporation, solid-liquid separation, washing

2. Extended Abstract

Crystallization is widely used for separation as well as purification of various products, ranging from commodity chemicals such as mineral salts to specialty chemicals and active pharmaceutical ingredients. Despite the fact that it is thermodynamically possible to crystallize pure substances, impurities may still be incorporated into the final product through different mechanisms. Mother liquor that contains impurities can be trapped inside the crystals during growth, adsorbed on crystal surface, or imperfectly removed from the voids among the crystals during solid-liquid separation. The amount of impurities in the final product depends on how much is retained at the post-crystallization steps – filtration, washing, and deliquoring (Figure 1). Therefore, in order to achieve the target product purity, these post-crystallization steps must be designed properly along with the crystallization process itself as an integrated system (Chang and Ng, 1998; Wibowo et al., 2001).

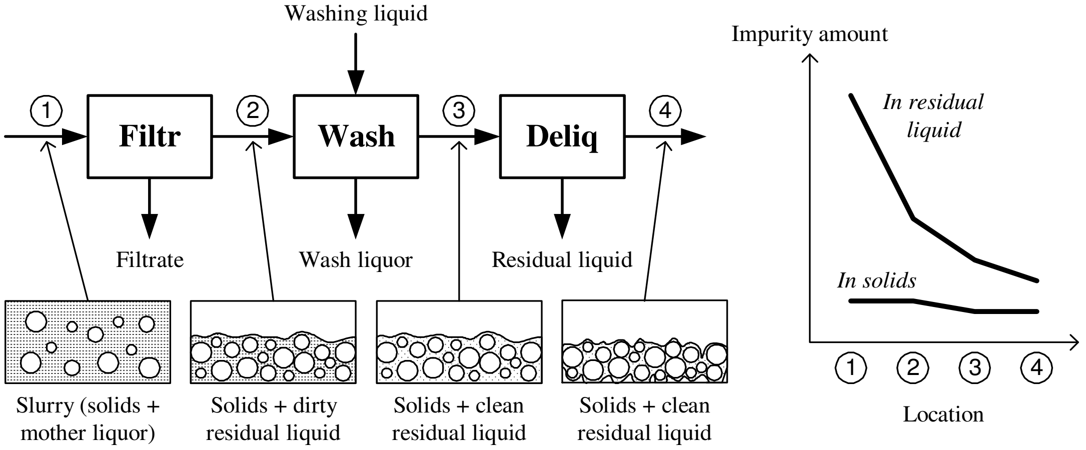

Figure 1. Impurity removal at various post-crystallization steps.

In order to manage the impurity content in the product of a crystallization process, a workflow that considers the entire train of crystallization and post-crystallization steps has to be developed. The workflow incorporates various components, including process synthesis, laboratory experiments, and analysis using models. An example of such a workflow is illustrated using a case study on the purification of Vitamin C (ascorbic acid). The dependence of the impurity inclusion on several key factors such as growth rate, solvent concentration, and the yield of crystallization is experimentally determined. The impurity concentration profile within the crystals is also investigated to find out whether the impurity content can be minimized by controlling the crystal size or by partially dissolving the crystals. The effect of washing and deliquoring on the amount of surface impurities are evaluated. Semi-empirical models based on fundamental knowledge about the physical phenomena involved are used to correlate the performance of washing and deliquoring steps to the target product purity. In this way, the specifications for a suitable solid/liquid separation unit, such as a rotary filter, a belt filter, or a centrifuge, which also performs washing and deliquoring functions in the same equipment, can be determined.

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Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Hybrid separation process - combination of reactive distillation with membrane

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1. Summary

In this presentation, the modelling, simulation and process analysis for a hybrid separation process, the combination of reactive distillation with membrane separation, is shown. The application is illustrated by the heterogeneously catalysed *n*-propyl propionate synthesis from 1-propanol and propionic acid. The membrane module is located in the distillate stream of the reactive distillation column in order to remove selectively the produced water without use of entrainers. For the stand-alone reactive separation process, the simulation results with a non-equilibrium model are in good agreement with experimental data obtained in a pilot scale column. Vapour permeation experiments using Sulzer Pervap^{TM} 2201(D) have been performed in a lab-scale membrane plant in order to determine the separation characteristics as well as in pilot-scale in order to analyse scale-up effects on the efficiency of technical membrane modules. Finally, experimental results of the reactive distillation column connected with the pilot-scale vapour permeation unit are presented. The validated process models are used for the process analysis of the combined unit operations and show the influence of structural and operational parameters on the performance of the feasible hybrid process.

Keywords: experimental investigation, hybrid process, reactive distillation, membrane separation, vapour permeation

2. Extended Abstract

Reactive separations such as reactive distillation which are combining reaction and separation in one apparatus have been established in process technology. The combination of reactive separations with other separation operations can lead to a more sustainable and economic process performance due to strong synergy effects and hence, is at present a focus of academic and industrial research. A promising example seems to be the combination of a reactive distillation column with membrane separation to a hybrid reactive separation process, since the membrane separation is selective and independent of the vapour-liquid equilibrium.

In this work, the heterogeneously catalysed esterification of propionic acid with 1-propanol to *n*-propylpropionat and water in a membrane assisted reactive distillation column is investigated. Such a hybrid process combines the specific benefits of each unit-operation: it shows higher conversions compared to the corresponding chemical equilibrium because of selective product removal from the reactive part of the column and simultaneous dewatering of the produced non-ideal aqueous-organic mixtures. Since the operation of a plant consisting of coupled reactive distillation and membrane separation is very complex, at first the independently operated units are experimentally investigated in order to prove their applicability. Reactive distillation experiments are performed within a pilot plant RD-column (DN50) equipped with Sulzer BX and Katapak-SP 11 elements. The total packing height is 5.5m. The experimental results show the influence of decisive operational parameters and column loadings on concentration and temperature profiles. Binary water/alcohol and ternary alcohol/ester/water vapour permeation experiments are performed in a multifunctional lab-scale plant equipped with a flat membrane test cell from Sulzer Chemtech to determine the separation characteristics of the used polymeric membrane Pervap^{TM} 2201(D). To analyse scale-up effects on the efficiency of technical membrane modules, results of pilot-scale experiments with a membrane area of 0.5 m² are shown.

Finally, the pilot-scale reactive distillation column connected with the vapour permeation unit has been experimentally investigated. The aim of the experiments is on the one hand to demonstrate the advantages of the advanced process concept and on the other hand to provide reliable data for the validation of rate-based models for both reactive distillation and membrane separation. The validated process model allows investigating the influence of structural and operational parameters of the hybrid process on conversion and required heat duty and exhibit the basis for a rigorous process optimisation.

Acknowledgment

We acknowledge the financial support provided by the European Commission within the 6th Framework Programme, Project "INSERT - Integrating Separation and Reaction Technologies"; Contract-No: NMP2-CT-2003-505862

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European Congress of Chemical Engineering (ECCE-6)
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Performances comparison of intensified mixers and micromixers

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1. Summary

A detailed analysis of numerous experimental results obtained on several micromixers is realized. For each mixer, we determine thanks to the IEM model (Interaction by Exchange with the Mean) the mixing time as a function of operating parameters as the power dissipation rate or the Reynolds number. We show that all the results can be well represented by a simple model which takes into account the shear rate, the molecular diffusion and the characteristic dimension of the mixer. It is also shown that the mechanical efficiency of micromixers (defined as the shear rate used for mixing / rate of the total spent shear rate) is of the order of 3 %.

Keywords: intensification, micromixers, characteristic times.

2. Extended Abstract

The production of high added values molecules in the fine chemistry and pharmaceutical industry is essentially carried out in batch and semi batch stirred tanks, which conception has in fact not changed since hundreds of years. The chemical reactions are very often fast exothermic reactions involving complex reactions schemes which may induce selectivity and yield problems because of poor mixing efficiency of the stirred tank. Besides, it is known that for reactions with multiple consecutive or parallel stoichiometry, the introduction of the co-reagent by a feeding law is synonymous of selectivity loss if the desired product is an intermediate replacement product. To prevent selectivity problems induced by mixing, batch reactors work in diluted solvent environment which fatal consequences are the important use of solvent that is necessary to separate and to recycle. For some years, there is an alternative in the use of these batch reactors, thanks to process intensification and to microreactors development. These mixers are very often characterized by chemical test reactions, whose selectivity of the products is influenced by the mixing conditions. These methods are very convenient to use but they have the drawback to give information about the mixing quality which is only the reflection of the reaction conditions: on fixed hydrodynamics conditions, i.e. mixing conditions, one have an impression, for a slow reaction, of an effective mixing while for a fast reaction, the mixing quality is lower. As a result, the comparison between the mixers is even often difficult, all the more impossible if different test reactions have been used. In spite of the numerous publications on these intensified mixers, it is still difficult to get clear information on theses mixers. Furthermore test reactions are not the reactions used industrially, and the transposition is particularly delicate.

From several published results, we compare all the devices on the same graph giving the mixing time as a function of a key parameter of the operating conditions, as the power rate dissipation per unit mass or the Reynolds number. The aimed objective is that a user can easily compare the technologies between them so as to choose the most appropriate for his process. For each mixer, we determine thanks to the IEM model (Interaction by Exchange with the Mean) the mixing time as a function of operating parameters as the power dissipation rate or the Reynolds. We show that all the results can be well represented by a simple model which takes into account the shear rate, the molecular diffusion and the characteristic dimension of the mixer. It is also shown that the mechanical efficiency of micromixers (defined as the shear rate used for mixing / rate of the total spent shear rate) is of the order of 3 %

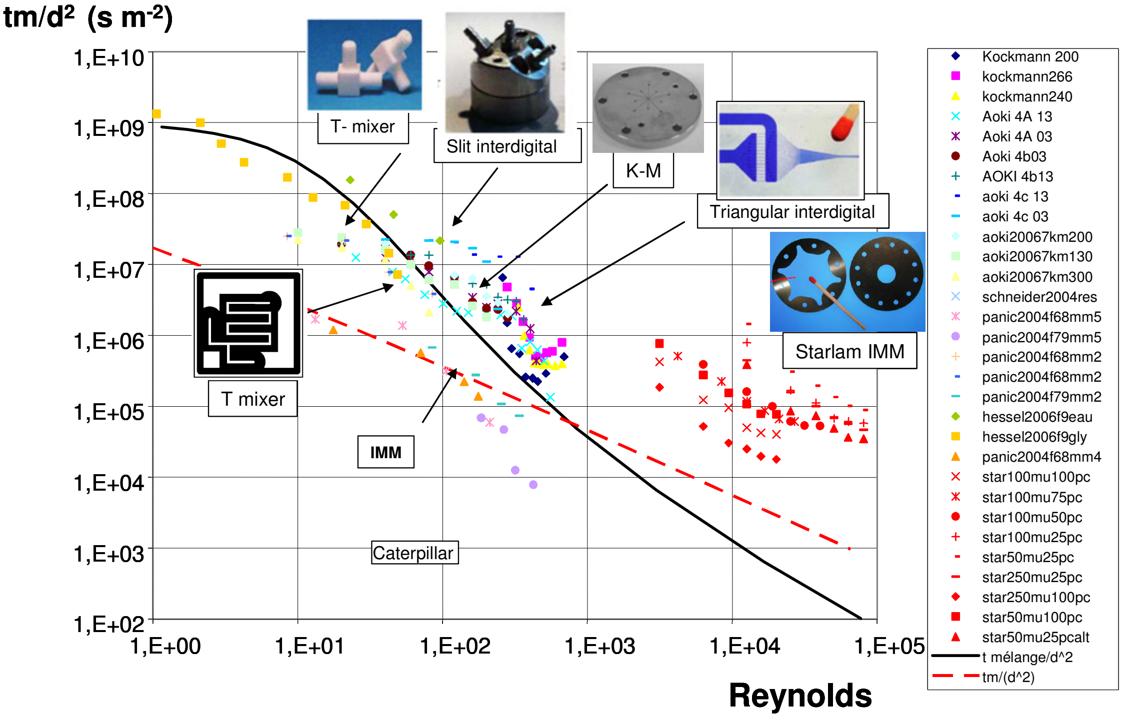

Figure1: Experimental mixing times of various micromixers divided by the square of the characteristic dimension versus the Reynolds number. The simple model proposed (continuous black line) is in good agreement with the experimental data

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Determination of the interfacial area of a continuous integrated mixer/separator (CINC) using a chemical reaction method

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1. Summary

The effect of the liquid flow rates (18 – 100 mL/min) and rotor frequency (30-60 Hz) on the interfacial area of a liquid – liquid system in a CINC-V02 continuous integrated mixer/separator have been studied using a chemical reaction method. Typical specific interfacial areas were in the range of $3.2 \cdot 10^2$ to $1.3 \cdot 10^4$ m^2 per m^3 liquid volume, which is comparable with those for a continuously stirred tank reactor (CSTR). A pronounced maximum in the interfacial area with respect to the rotor frequency was found at about 45 Hz. The interfacial area increased considerably at higher aqueous phase flow rates whereas the organic phase flow rate had no significant effect. The experimental data were modelled using a linear empirical model. Good agreement between experiments and model was observed.

Keywords: Process Intensification, CINC, Interfacial area, Chemical reaction method

2. Extended Abstract

Process intensification is a powerful concept to replace large, energy intensive equipment or processes with smaller plants that combine multiple operations in single, highly integrated devices. Examples are reactive distillation and reactive extraction [1]. For the latter, the integration of reaction and separation is not only advantageous with respect to energy and investments costs but also to the efficiency and/or the selectivity of the extraction process.

A very attractive device to integrate chemical reaction and separation is the CINC integrated mixer/separator. The CINC basically consists of a rotating hollow centrifuge in a static housing. The liquid(s) enter the device in the annular zone between the static wall and the rotating centrifuge, where they are intensely mixed. Next, they are transferred into the centrifuge to be separated.

We have recently demonstrated the application of the CINC for the continuous biphasic enzyme catalyzed (*Rhizomucor miehei* lipase) esterification of oleic acid with n-butanol in a heptane/water mixture [2] and racemate separation using solvent extraction with chiral extractants [3]. Optimization of these novel applications in the CINC require detailed scientific knowledge about the hydrodynamics in the devices like liquid flow patterns, liquid hold-ups in the various zones and the liquid-liquid interfacial area. Here we report experimental results on the interfacial area in the CINC as a function of process conditions (flow rates and rotational speed of the centrifuge). In this study, the reaction between n-butyl formate and sodium hydroxide [4] was used for determination of the total interfacial area. To quantify the effect of the process variables on the interfacial area, the total interfacial area was modeled empirically. The linear model in equation 1 was fitted to the data, where F_{aq} is the aqueous flowrate (mL min^{-1}) and N the rotational frequency (Hz). The effect of both variables on the interfacial area is visualized in fig. 1.

$$A_{\mathrm{mod}} = -11.14 + 0.612N - 0.0685F_{aq} - 6.76 \cdot 10^{-3} N^2 + 1.1 \cdot 10^{-3} F_{aq}^2 \qquad (1)$$

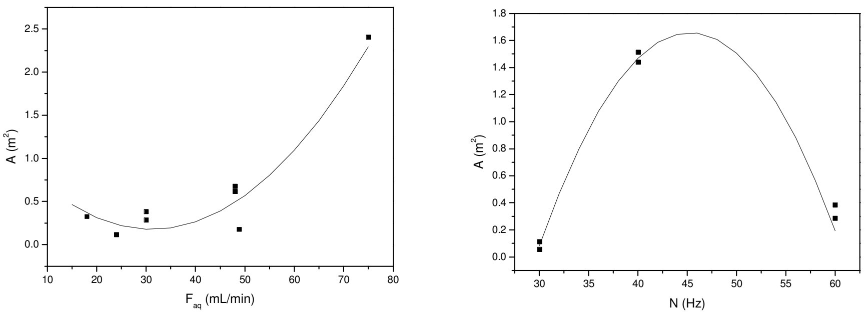

Fig. 1. Effect of variables F_{aq} (left) and N (right) on the interfacial area

The rate of rotation of the centrifuge and the flowrate of the aqueous phase both have significant effects on the interfacial area as shown in Fig. 1. However, the interfacial area was independent of the organic flow rate, suggesting that, for this solvent combination, the organic phase is the continuous phase and the aqueous phase is the dispersed phase in the CINC device. The interfacial area showed a clear maximum at intermediate rate of rotation of the centrifuge (45 Hz), which was ascribed to several opposing effects in the centrifuge and annular zone. These results will be valuable input for subsequent modeling and optimization studies for the above mentioned CINC applications.

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Session S-4K: EPIC-1: New Concepts (NC)

Abstract Number	**Paper Title & Authors**	**Included**
695	Stripping of acetone from isopropanol solutions with mesh and membrane gas-liquid contactors X Sun, A Gavriilidis	Yes
1725	Energy optimization of corn-based bio-ethanol plants A Peschel, R Karuppiah, M Martín, I E Grossmann, L Zullo, W Martinson	Yes
1726	Basic parameter study for the separation of a isopropanol-water mixture by using FricDiff technology A Selvi, B Breure, J Gross, J De Graauw, P. J. Jansens	Yes
2308	Methodology for process intensification applied to the scale-up of microreactors E Kolehmainen, B-G Rong, I urunen	Yes
2567	Selectivity enhancement of microencapsulated enzymes with permselective shells E E Barth, A Ufer, D W Agar	Yes
3463	Mass-production of miniaturised microstructured fuel processors for distributed energy generation G Kolb, Y Men, J Schürer, D Tiemann, M Wichert, R Zapf, V Hessel	Yes

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Stripping of acetone from isopropanol solutions with mesh and membrane gas-liquid contactors

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1. Summary

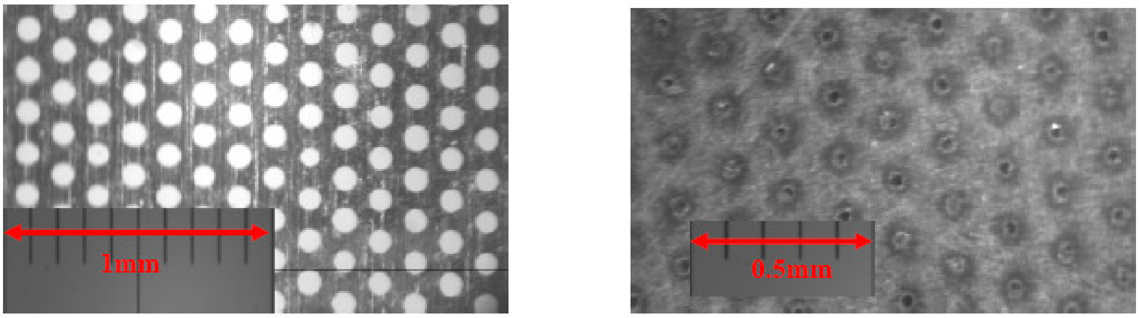
Stripping of acetone from acetone/isopropanol solutions with nitrogen was investigated in a flat membrane contactor arrangement which employed thin layers of gas and liquid separated by porous thin stainless steel or PTFE sheets. Four different contactors were investigated. The best performance was obtained for the contactor with the smallest thickness, which was a metal mesh with 76μm openings and 23% open area, 50μm thick.

Keywords: stripping, membrane contactor, mesh contactor

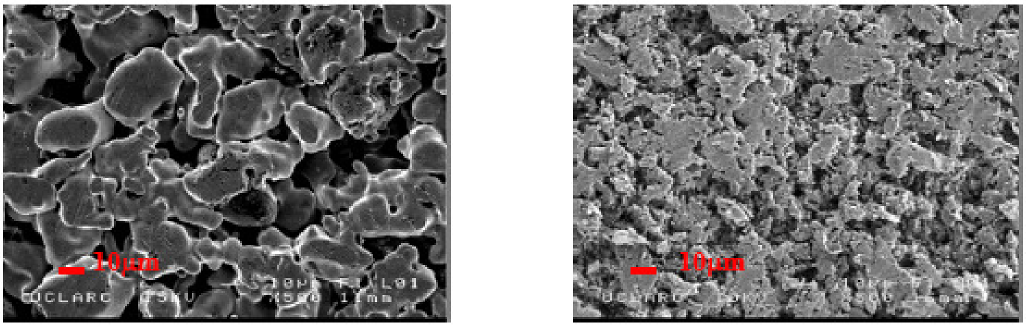
2. Extended Abstract

There has been a lot of research on membrane processes for the separation of volatile components from solutions. The membrane acts as a fixed interface and keeps the gas/liquid phases separated while the transport of volatiles can take place through the membrane. Advantages membrane contactors offer over packed columns and other conventional mass transfer equipment include relatively large interfacial area between the two phases, no fluid-fluid dispersion, while flooding, foaming, and emulsion formation can be avoided, and scale up can be facilitated. On the other hand, membrane contactors have also disadvantages: the membrane introduces an additional resistance to mass transfer, they are subject to fouling and phase breakthrough between the two phases can result to reduced performance.

In this work, the issue of mass transfer resistance that the membrane introduces is addressed. More specifically, thin metal plates with small thickness containing openings manufactured by laser machining (Laser mesh) or photochemical etching (Internet mesh) were studied. For comparison metal (Mott) and Teflon membranes (PTFE) were also employed (see Figure 1). The principal characteristics of the different contactors are given in Table 1. The contactors were used for stripping of acetone from isopropanol solutions with nitrogen at 30°C, at gas residence time 0.0035 min and liquid residence time 2.4min. For pressure difference between phases of 30mm H_2O, acetone removal with different membranes is shown in Table 2.



Internetmesh Laser mesh



Mott PTFE

Figure 1: Pictures of the contactors utilised

Table 1: Principal characteristics of the contactors utilised.

Contactor	Average pore size (µm)	Maximum pore size (µm)	Thickness (µm)	Open area	Material
Internetmesh	76	100	50	23%	Stainless steel 304
Laser mesh	30	50	200	8%	Stainless steel 316
Mott	5	10	1575	30%	Stainless steel 316
PTFE	5	10	200	20%	PTFE

Contactor	$C_{Ac,out} / C_{Ac,in}$
Internetmesh	0.35
Laser mesh	0.67
Mott	0.77
PTFE	0.75

Table 2. Acetone removal with the various contactors employed.

It can be seen that internetmesh gave the best performance on acetone stripping. About 65% of the acetone can be removed with it, while only 23~33% of acetone was removed using the other contactors. The improved mass transfer resistance was due primarily to its small thickness of 50µm. However, due to the large opening size of the internetmesh contactor of 76µm the pressure difference between phases has to be carefully controlled to avoid breakthrough of one phase into the other.

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Energy optimization of corn-based bio-ethanol plants

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1. Summary

In this work we carry out an energy optimization of a corn-based bioethanol plant. A superstructure optimization problem is formulated by modelling the different processes involved in the plant using a nonlinear programming problem. Furthermore, common techniques from the petrochemical industry such as heat integration and multieffect distillation columns are used in the plant to significantly reduce the energy consumption required to manufacture fuel grade ethanol.

Keywords: Bio-ethanol, Superstructure optimization, Heat Integration

2. Extended abstract

The supply of energy for various operations such as transportation, power generation, heating etc. is the critical concern all around the world today. Fossil fuels like crude oil that have been the traditional source of energy are non-renewable and are depleting fast. This along with increasing concerns about global warming has led to a search for alternatives to fossil fuels. As the prices of crude oil increase, cost-efficient ways to produce energy from alternative sources are being researched. Hence, the use of new sources of energy, like fuel cells, solar energy or bioethanol has become a priority. Particularly, bioethanol shares the advantage of traditional fuels in terms of storage and distribution, compared to other energy sources like hydrogen. Its production has increased all over the world in the last few years and new plants are being built and existing plants increasing their production capacity. In the United States, it is usually produced using a technology called the “dry-grind process” that utilizes corn kernels as feed to produce ethanol. As a result of the effort to substitute ethanol for gasoline as transportation fuel, the production capacity of ethanol in the United States has risen up to 4 billion gallons of ethanol per year in 2005.

In this work we address the problem of synthesizing optimized corn based bio-ethanol plants through the use of mathematical optimization techniques. The goal is to reduce the operating costs of the plant, minimize the energy usage and also maximize the yields of the plant, which is of significance given the current debate about the viability of corn based ethanol as a sustainable fuel. We propose a superstructure optimization approach, where we first construct a flowsheet including various process units and utility streams involved in ethanol production. Our objective is to optimize the structure determining the connections in the network and the flow in each stream in the network, such that we minimize the energy requirement of the overall plant while

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trying to maximize the yields. The optimization of the system is formulated as a Nonlinear Programming problem, where the model that is optimized involves mass and energy balances for all the units in the system. The results of the optimization are used in determining the hot and cold utilities required in the plant and on performing heat integration using these results, by using novel design arrangements like multieffect distillation columns, we obtain significant energy reduction in the manufacture of ethanol. We optimize an example network for such a corn to ethanol plant and present results for the optimal configuration where the steam consumption in the system is minimized.

As a result of this study, it is found that it is possible to reduce the steam consumption required in the transformation of corn into fuel grade ethanol by about 50%, which translates to a reduction of about 10% in the manufacturing cost. Finally, it is worth mentioning that the production of co-products and commodities along with bio-ethanol in a biorefinery, would definitely improve the process economics and profitability of the plant.

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Basic parameter study for the separation of a isopropanol-water mixture by using FricDiff technology

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1. Summary

In this paper simulation results are presented for the separation of IPA and H_2O mixture using CO_2 as a counter (sweep) gas by FricDiff technology. A model was developed and implemented in Aspen Custom Modeler (ACM), which was used to gain better understanding and to explore the potential of this new technology. Three key-indicators (enrichment factor, recovery and productivity) were defined and used to evaluate the performance of FricDiff technology. A parameter sensitivity analysis was executed for different operating conditions, like feed-flow and sweep-ratio, and various design variables, like pore-size and tube dimensions. The simulation results indicate that it is possible to break azeotropic mixtures using FricDiff technology.

Keywords: frictional diffusion, multi-component separation, azeotropic alcohol water mixtures, macro porous membrane

2. Extended Abstract

Frictional Diffusion, briefly FricDiff, is a novel and promising separation technology, based on the difference in diffusion rate of two components when diffusing in opposite direction to a third component - the so-called counter gas [1].
The potential of FricDiff can be found in energy consuming separations like azeotropic distillation.

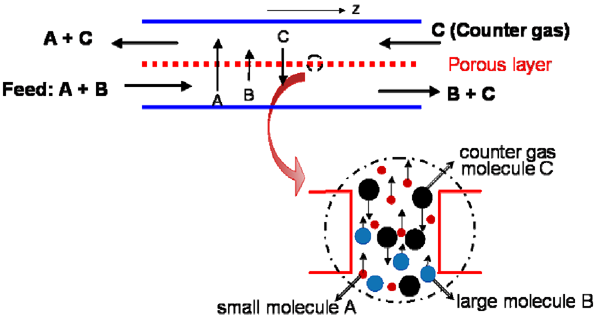

Fig.1. Principle of FricDiff separation technique

This paper presents a model which has been used to simulate the effect of design parameters and operating conditions on the performance of a single tube FricDiff module. The model is used as a design-tool for the construction of a test unit which has to demonstrate the technical viability of FricDiff technology under industrial conditions.

Modeling and simulation studies were executed with an objective to determine the sensitivity of design parameters and operating conditions such as sweep ratio, feed flow rate and tube characteristics on three performance criteria, namely enrichment factor and recovery which are defined as:

1) Enrichment Factor (-) $= \dfrac{X_{F,IPA_{out}} / X_{F,IPA_{in}}}{X_{F,H_2O_{out}} / X_{F,H_2O_{in}}} = \dfrac{X_{F,IPA_{out}}}{X_{F,H_2O_{out}}} \cdot \dfrac{X_{F,H_2O_{in}}}{X_{F,IPA_{in}}}$ where X is the mol fraction and subscript F indicates the feed side.

2) Recovery (-) $= \dfrac{F_{F,IPA_{out}}}{F_{F,IPA_{in}}}$ where F is the molar flow rate.

3) Productivity (kg/h/m^2) $= \dfrac{F_{IPA_{out}} / MW_{IPA}}{2\pi r_{in} L}$

3. Results

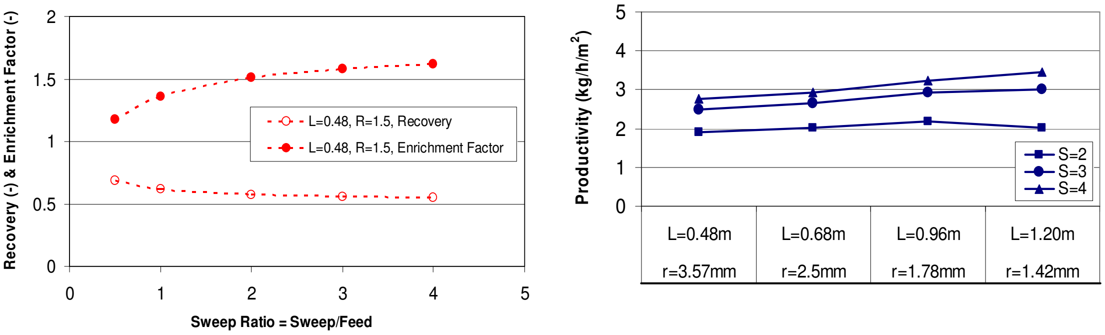

Fig. 2 **a)** Enrichment factor and recovery as a function of the sweep ratio. In these simulations sweep ratios= 0.5, 1, 2, 3, 4; lengths of the tubes= 0.48m; inner radii=1.5mm; at constant thickness of the barrier= 1.5mm; pore diameter= 5.10^{-6}m; porosity= 0.2; tortuosity= 1.307; feed flow rate= 10^{-5}m^3/s at 1bar **b)** Calculated productivity results for different tube dimensions and sweep ratios at a constant membrane area and characteristics

4. Conclusion

In one stage an enrichment factor of 2 can be obtained at a reasonable recovery of 40% with productivity up to 4 kg/m^2/h. The ratio of the flow rates of the counter gas and the feed (sweep-ratio) has a dominant effect on the performance. The simulation results support the claim that FricDiff technology has a potential for breaking azeotropic mixtures.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Methodology for process intensification applied to the scale-up of microreactors

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1. Summary

A new methodology is suggested for systematic process intensification. It is demonstrated with scale-up problem of microstructured reactors. The method can be characterized as a combination of phenomena-based reasoning with a creativity technique. For the test process, suggestions for favorable construction of microstructured reactors are obtained.

Keywords: process intensification, microreactor, scale-up, equipment design, creativity technique

2. Extended Abstract

Background
Process intensification is often considered as one of the main current trends in chemical engineering. It has even been suggested as a possible candidate for the third paradigm of the field. The development and applications of process intensification are restricted by the lack of general methodology. Descriptions and suggestions of the methodology have been given e.g. by Green [1998] and Stankiewicz & Moulijn [2000]. However, the essential element of creativity makes the systematic approach very difficult.

Description of the method
Systematic methodology for process intensification is developed and applied in this paper. Development of new equipment and processes require both deep knowledge and creativity. To fulfill this requirement, the method combines phenomena-based reasoning with a creativity technique. Moreover, knowledge from different sources, namely mechanistic knowledge from science, empirical knowledge from experimentation and subjective, experience-based knowledge, are involved in the approach.

The first step is to identify the relevant physical and chemical phenomena in the process to be developed, as well as the key variables affecting them. This stage is mainly based on scientific knowledge of chemical engineering. Next, process conditions, equipment geometry and flow conditions have to be selected in optimal way considering the main phenomena. This step is largely based on experience, subjective information, analogy, heuristic rules etc. New, creative solutions can be generated as well. Typically, several alternative or partial solutions are obtained, each of them optimal in respect of different goals (e.g. maximizing the rates of different phenomena). The final solution is looked for by combining the best of the partial solutions. This is not straightforward but several technical contradictions may appear. Solving these contradictions requires creativity and often leads to new solutions, e.g. to new type of equipment. Therefore creativity techniques are employed at this stage in the method.

Application of the method to the scale-up of microreactors

Concept such as number-up is regularly used instead of scale-up in the connection of microreactors. This means parallel installation of a large number of microchannels, Design errors may be avoided this way, but other problems appear. Uniform distribution of fluids into hundreds or thousands of channels is not easy. Also the investment cost of a microstructured reactor resulting from number-up might be high. Therefore better, innovative scale-up strategies are needed for microstructured reactors. The systematic method for process intensification is demonstrated with the scale-up problem of microreactors.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Selectivity enhancement of microencapsulated enzymes with permselective shells

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1. Summary

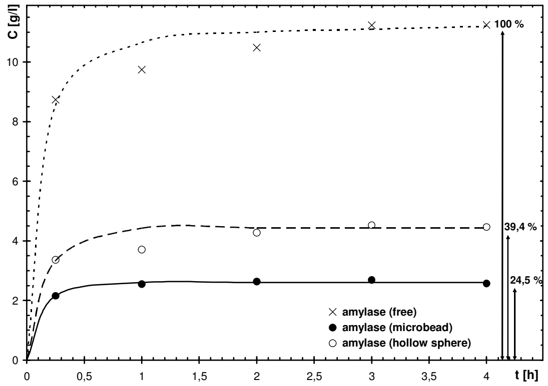
The encapsulation within a permselective shell offers the possibility to control the accessibly to a non-selective catalyst for a mixture of substrates. Applying this system at a microscale provides well-balanced harmonisation between reaction and diffusion processes.

Keywords: microencapsulation, microscale membrane reactor, selectivity improvement

2. Extended Abstract

Immobilised enzymes offer considerable advantages over dissolved enzymes: simple recovery from the reaction medium, greater stability and the lower enzyme losses in downstream processing. The retention of enzymes using membranes, which segregate the large protein enzyme molecules from the remaining reaction medium, is a well-established technique for heterogenisation of the enzymatic catalysts, circumventing the deactivation or catalyst loss associated with alternative immobilisation procedures. The additional mass transfer resistance of the membrane material represents a major disadvantage of this immobilisation technique, which can, however, be offset by employing the very high specific surface areas available in hollow fibers or microcapsules. By the use of permselective membranes can even exploit the mass transfer resistance, in order to regulate the accessibility of the enzymatic catalyst for different substrates in a mixed system. In this manner one can achieve a more effective control of the enzymatic reaction through incorporation of an additional physical separation process, analogous to zeolithic catalysis [1], in which selectivity is enhanced by the integration of diffusive molecular sieving into the catalyst architecture. Standard techniques for immobilising enzymes on or in a membrane are encapsulation using hollow fibers, porous beads or in microcapsules [2], the last two methods being somewhat simpler than the first in terms of development, production and handling.

In the work presented, the non-selective hydrolytic enzyme α-amylase and a permselective alginate membrane material were chosen as a suitable test system. Different types of hollow and solid spherical microcapsules containing α-amylase were prepared by using a specially designed nozzle with a superimposed concentric air jet and varying the composition of the alginate with respect to the two component monomers ß-D-mannuronate and α-L-guluronate, which form the skeleton of the biopolymer, and the gelation solution, comprising different alkali earth metal ions at various concentrations [3]. The microbeads and hollow microspheres produced were characterised with respect to their structure, permeability and reactive behaviour. Variation of the experimental parameters enabled the systematic manipulation of both the size of the microcapsules and the thickness of the membrane (> 120 mm) for the hollow microspheres.



Initial work demonstrated that the activity of the encapsulated biocatalyst in both types of microcapsules is inferior to that of free α−amylase, but also that the hollow spheres (40% of free enzyme value) are significantly better than comparable microbeads (25% of free enzyme value), as would be expected from the prevailing mass transfer resistances [4].

Subsequent studies revealed that the encapsulation of catalysts in microcapsules is a powerful method for improving their selectivity with help of a discriminating permeable membrane. Although the permselectivity of the alginate membranes is based the exclusion of larger molecules above a given molecular weight threshold, the principle could be extended to alternative or multiple separation criteria to further enhance selectivity. The encapsulation of catalyst within a permselective shell can also be considered to be a form of process intensification yielding a microscale membrane reactor [5], with the high specific surface areas providing excellent harmonisation between reaction and diffusion rates.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Mass-production of miniaturised microstructured fuel processors for distributed energy generation

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1. Summary

Future sustainable and distributed energy generation will rely in many cases on fuel cell technology. However, especially in case of mobile and portable devices hydrogen supply remains a critical issue owing to the limited energy density of compressed hydrogen and related technology. Fuel processing of fossil fuels addresses this issue and is sustainable in case renewable fuels are applied.
Because a fuel processor/ fuel cell system for mobile applications will be a future mass product, manufacturing technologies need to be developed, which can cope with high volume production at competitive pricing.
Complete prototype fuel processors have been developed at IMM applying microstructured plate heat-exchanger technology. All production steps required to build a fuel processor are currently addressed at IMM to meet demands of future mass production.

Keywords: mass production, fuel processor, microstructures, heat-exchanger, reactor

2. Extended Abstract

A fuel processor is a complex device composed of the reformer itself (Kolb, 2004-1, Cominos, 2005-1)and carbon monoxide clean-up (Kolb, 2005, Cominos, 2005-2) in case of proton exchange membrane fuel cell applications. Additionally balance-of-plant components are required to operate the system. The application of microstructured plate heat-exchanger reactor technology improves system integration, start-up time demand and system efficiency (Hessel, 2005, Kolb, 2004-1).
Complete fuel processors have been developed at IMM, which work with methanol, liquefied petroleum gas (LPG), octane as surrogate for gasoline and diesel. Fig.1 shows the fuel cell/ fuel processor system VEGA, which is under joint development in cooperation with TRUMA, Europe's largest manufacturer of heating systems for caravans and trailers.
The fabrication of the fuel processor starts with the introduction of microchannels into stainless steel metal foils applying cheap techniques such as wet chemical etching or embossing. Fig. 2 (left) shows a heat-exchanger, which was produced applying embossing technology.
The devices cover the wide range of operating temperature from ambient to 800°C. The next step is the coating of catalyst onto the structured metal foils applying techniques such as screen printing or spray coating.

Fig. 1 250 Wel LPG fuel cell/ fuel processor system VEGA under joint development of IMM and TRUMA GmbH

Next the reactors and heat-exchangers need to be sealed by automated procedures such as laser welding or brazing. The resulting reactors are then one-way products. The heat-exchanger shown in Fig.2(left) is sealed by laser welding.
A careful choice of production techniques is required to address the market volume of different applications. While some techniques such as wet chemical etching are well established technology and require no investment for medium series production, it may be too costly for high volume mass products in the range of millions of devices, as it is the case for lap top chargers. Fig.2(right) shows a 'screen shot' of cost distribution of the different production steps of a microstructured heat-exchanger on the basis of 100,000 devices per year. This distribution of course changes continuously during the optimization procedure.

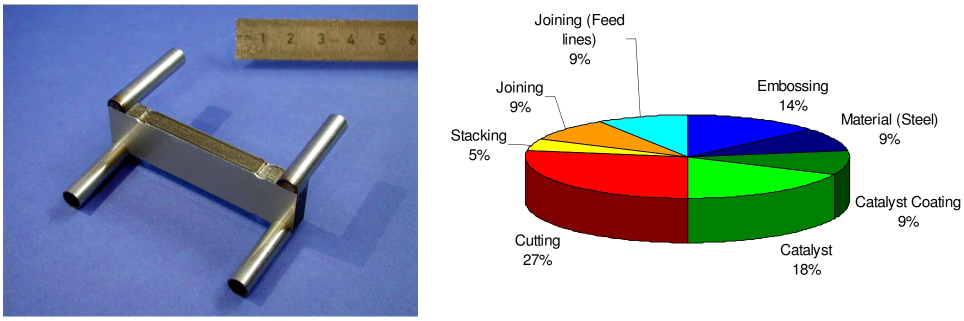

Fig. 2 Microstructured heat-exchanger produced by embossing and laser welding

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Session S-4L: EPIC-1: Multifunctionality (MF-3)

Abstract Number	Paper Title & Authors	Included
325	Fischer-Tropsch synthesis in novel monolith loop reactor R Güttel, U Kunz, T Turek	Yes
1905	Computer aided process design of affinity membrane adsorbers P van Beijeren, P Kreis, M Mutter, S Sommerfeld, W Bäcker, A Górak	Yes
2452	Assessment of coupling chromatography and crystallization for productivity enhancement G Ziomek, M P Elsner, M Kaspereit, D Antos, A Seidel-Morgenstern	Yes
2927	Continuous reactive chromatography under non-isothermal conditions T Sainio, L Zhang, M Kaspereit, A Kienle, A Seidel–Morgenstern	Yes
3744	Microreactors on production scale: A technical and economical status report for pharmaceutical applications D Kirschneck	Yes

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Fischer-Tropsch synthesis in novel monolith loop reactors

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1. Summary

The present paper presents a laboratory reactor concept that allows for comparison of structured and suspended catalysts for Fischer-Tropsch Synthesis (FTS). The setup consists of a combination of a fixed-bed reactor for the structured honeycomb catalysts and a well-mixed tank reactor. The gas and liquid phase will be recycled, to remove the heat of reaction and to obtain the desired Taylor-Flow regime inside the honeycomb catalyst. First comparing results will be shown, where similar productivities and product distributions were obtained in both reactor systems.

Keywords: Fischer-Tropsch Synthesis, Monolith Loop Reactor, Slurry Reactor

2. Extended Abstract

The Fischer-Tropsch Synthesis (FTS) is a strongly exothermic, heterogeneously catalysed reaction to convert synthesis gas into hydrocarbons. Modern reactor technologies for this reaction on industrial scale comprise slurry bubble columns and fixed bed reactors (Dry 2002). An alternative to these reactors with conventional catalyst geometries could be reactors with structured catalysts like honeycomb shaped monoliths. These structured reactors combine the advantages of slurry and fixed bed reactors, such as short diffusion distances and plug flow behaviour, and eliminate their typical drawbacks like catalyst separation and high pressure drop (Roy et al. 2004).

First experimental and theoretical investigations have shown the feasibility of using monolithic reactors for FTS. Kapteijn et al. (2005) carried out experiments in single-pass operation of synthesis gas. Furthermore, simulations of monolith reactors in the Taylor-Flow regime showed comparable or slightly better performance as in industrial slurry bubble columns. Hilmen et al. (2005) performed experiments with external oil recirculation and single-pass for the gas phase in the film flow regime inside the capillaries. As a result these authors found that with recirculation of the liquid phase the temperature in the reactor was much easier to control, while the overall rate was found to be slightly lower than using powder catalysts. Besides honeycomb shaped monoliths also foam type monoliths have been tested by Khassin et al. (2003).

This work presents a laboratory reactor concept that allows for the first time the investigation of FTS in the desirable Taylor-flow regime (Figure 1). It consists of a combination of fixed-bed reactor for the honeycomb catalyst and well-mixed tank reactor. Gas und liquid flow through the monolith can be independently adjusted by means of a compressor and a pump. Due to the high velocities of gas and liquid the conversion per pass is low, which results in entirely isothermal operation of the monolith.

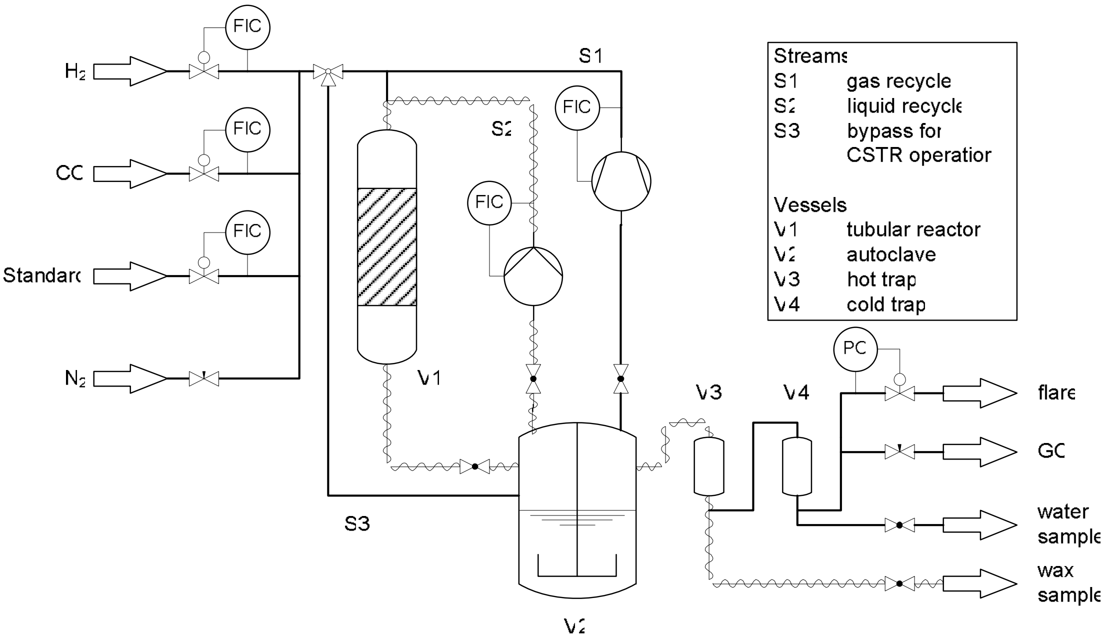

Figure 1: Reactor concept with external recirculation of gas and liquid phase

The stirred-tank reactor can also be used for experiments with powder catalysts in the slurry phase. Thus different catalyst geometries can be directly compared in the same experimental installation. In the present paper, first results comparing monolithic and powder catalysts are presented. Similar productivities and product distributions were obtained with both catalysts.

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Computer aided process design of affinity membrane adsorbers

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Keywords: membrane chromatography, affinity separation, elution, monoclonal antibodies, protein A

Abstract

A typical downstream process for antibodies consists of multiple separation steps, in which affinity chromatography is the most costly and time-consuming one. An alternative to affinity chromatography are affinity membrane adsorbers. The separation principle of both technologies is the specific interactions of antibodies with immobilized ligands. Conventional affinity chromatography operates using a packed bed of beads, where productivity is limited due to intra-particle diffusion. In membrane adsorbers the mass transport is governed by convection through the membrane pores and the antibodies can bind directly with the immobilized ligands. Membrane adsorbers offer therefore a much faster rate of separation, but have the disadvantage of a lower capacity compared to conventional chromatography.

Until now the focus of research has been set on modelling and simulation of breakthrough curves without including washing and elution stages. Several models for the loading step have been proposed, as well as design heuristics. In order to perform an overall process analysis the contribution of all the different process steps (loading, washing and elution) is required. Therefore this work has focused on the development of a complete process model, which does not only take into account the different steps, but also considers buffer vessels, dead volumes and product fractionation. The capturing of human IgG with Sartobind Protein A modules has been used as a test system, where the values of kinetic constants, capacities and dead volumes have been obtained from experimental results.

The model is applied for the optimization of important process parameters, such as flow rate and elution cut off criteria. These parameters have a strong effect on overall process performance, characterized by productivity, process yield, concentration factor, buffer consumption and processing time. Relations between process parameters and the mentioned process performance characteristics are presented in a systematic way and allows for computer aided design of affinity membrane adsorbers. The applicability of the method is illustrated by a case study based on the experimental results obtained with IgG and protein A. Additionally the output of the

detailed process model can be used as input for commercial simulation tools like SuperPro Designer® in which complete downstream processes can be designed.

Acknowledgements

This work has been performed as part of the "Advanced Interactive Materials by Design" (AIMs) project, supported by the Sixth Research Framework Programme of the European Union (NMP3-CT-2004-500160).

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Assessment of coupling chromatography and crystallization for productivity enhancement

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1. Summary

The intention of this work is the analysis and optimization of the process combination of chromatography and simultaneous preferential crystallization. Preferential crystallization processes are sometimes carried out with an initial concentration excess of the preferred enantiomer. To produce such an excess chromatographic process can be employed and properly designed. In this presentation the optimized process parameters for both unit processes as well as for the integrated process will be given. Parallel to the theoretical analysis, an experimental validation of the process will be also presented.

Keywords: preferential crystallization, chromatography, process combination, optimization

2. Extended Abstract

Among all enantioseparation methods the enantioselective preferential crystallization (Elsner et al., 2005) is an attractive and inexpensive possibility for mixtures which reveals for a conglomerate typical phase diagram i.e., a physical mixture of enantiopure crystals. In solution such systems tend to reach an equilibrium state in which the liquid phase will have racemic composition and the solid phase will consist of a mixture of crystals of both enantiomers. However, before approaching this state, it is possible to preferentially produce just one of the enantiomers after seeding with homochiral crystals

Preferential crystallization processes are sometimes carried out with an initial concentration excess of the preferred enantiomer. To produce such an excess chromatographic process can be employed. It will be shown that by integrating preferential crystallization with batch chromatography higher process productivity can be achieved. Such a complex integrated process requites proper design to be successfully conducted on an industrial scale. The objective of this work was to analyze and optimize operating parameters of chromatography and simultaneous preferential crystallization (Kaspereit, 2006).

The theoretical investigations of the crystallization process were based on a simplified mathematical model deriving under assumption of ideally mixed batch crystallizer, of size independent rate of the crystal growth and of negligible coalescence, attrition or agglomeration. The kinetic parameters of the model were determined experimentally for the system threonine-water (Elsner et al., 2007).

In order to produce the initial enantiomeric excess the chromatographic process was properly designed. To generate the mobile phase composition adequate for enantioseparation as well as for the subsequent process of crystallization the gradient elution has been selected as the operating mode. For evaluation and optimization of the dynamics of chromatographic process the equilibrium-dispersive model (Ziomek et al., 2006) was applied. The model parameters such as isotherm coefficients and kinetic parameters were determined experimentally.

In this presentation the optimized process parameters for both the unit processes as well as for the integrated process will be given. Parallel to the theoretical analysis, an experimental validation of the process will be also presented.

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European Congress of Chemical Engineering (ECCE-6)
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Continuous reactive chromatography under non-isothermal conditions

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1. Summary

Thermal effects in reactive chromatography were investigated both experimentally and by means of numerical simulations for reversible exothermic liquid phase reactions. Esterification of acetic acid with methanol and ethanol to produce methyl acetate and ethyl acetate, catalysed by acidic ion exchange resins, were used as model reactions in the single-column and simulated-moving bed chromatographic reactors.

Keywords: reactive chromatography, SMB, nonisothermal, heat of reaction, heat of adsorption

2. Extended Abstract

Reaction and separation can be integrated into a single unit operation in several ways. Selective adsorbents can be used in non-steady state fixed bed reactors to enhance the conversion of reversible reactions through separation of products, which diminishes the undesired backward reactions. This is the main idea of chromatographic reactors that are currently intensively investigated considering various liquid feed stocks (e.g. alcohol/acid mixtures or esters in water) [1,2].

In most of the studies reported up to now, the processes have been considered to proceed under isothermal conditions. Only recently, more attention was paid to the aspect that, in such periodically operated reactors, significant temperature effects can occur [3, 4]. Reliable prediction of the performance of chromatographic reactors also at large scale requires that thermal effects due to adsorption, reaction, and also mixing are properly accounted for.

In the present work, thermal effects in reactive chromatography were investigated both theoretically and experimentally for reversible exothermic liquid phase reactions. Esterification of acetic acid with methanol and ethanol to produce methyl acetate and ethyl acetate were used as model reactions in the experiments. Amberlyst 15 and Finex CS16G strong acid cation exchange resins in H+ form were chosen as the stationary phases. Adsorption enthalpies were determined from chromatographic data at various temperatures. Reactor experiments were carried out in thermally insulated (adiabatic) columns, fitted with several thermocouples, as well as under isothermal conditions.

Positive (higher temperature than in the feed) and negative thermal waves were found to develop in both reactor types. Complexity of the observed temperature profiles stems from the fact that heats of adsorption, reaction, and mixing of the liquids are all significant. The maximum temperature increase in the reactor was approximately 25 K, which is large considering the relatively low heats of reaction for these systems (less than –5 kJ/mol).

Behaviour of single column and simulated moving bed chromatographic reactors was analysed with numerical simulations. It was shown that adiabatic operation of a chromatographic reactor yields higher productivity than isothermal operation only for intermediate reaction rates. In the case of slow kinetics, the amount of heat produced is small and the increase in reaction rate due to the thermal wave insignificant. With very fast reactions, the conversion is limited by separation and a further increase in the reaction rate has no effect. Largest effects are observed when the solid phase to liquid phase heat capacity ratio, which determines the velocity of the thermal wave, is such that the thermal wave travels with the same velocity as the reaction front. Under such conditions the thermal wave has a self-amplifying nature.

It was also found that the adsorption properties of the eluent play a major role under adiabatic conditions. In the case the eluent is not adsorbed or its adsorption enthalpy is negligible, thermal effects are larger and, in fixed-bed reactors, the cycle time is always longer than under isothermal conditions.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Microreactors on production scale: A technical and economical status report for pharmaceutical applications

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1. Summary

Microreactors used on lab scale for more than ten years now. Several applications on pilot and production scale have been started up. The pharmaceutical industry is highly regulated. This reason keeps the pharmaceutical industry away from early adapting new technologies. Microreactors have proved their ability to be a reliable production tool now. Due to high needs according to process performance, this presentation demonstrates the high process intensification potential for pharmaceutical applications.

Keywords: pharmaceutical synthesis, process intensification, microreactor, production scale, API production

2. Extended Abstract

Classical pharmaceutical synthesises have usually some characteristic criteria. Pharmaceutical plants run in small or medium scale in batch production. Multi step synthesises are carried out with high value products and working with toxic substances is very common. The focus was not very strong on optimisation in the past. The focus is on clinical research and not on the production process

Micro process engineering can deliver some important advantages especially for pharmaceutical applications. The first point is development speed. It is possible to cut out the kilo-lab. It is only necessary take the labscale development plant and let it run for several days. Amounts between 100g and 1 kg can be produced. Lonza has proved this method and implemented this method.[Roberge *et al.*, 2005] The second point is yield improvement. Microinnova carried out several studies. Labscale experiments have shown a yield improvement potential of about 15 %. Economic calculations show that chemicals and solvents are dominating block in the costs of operation (more than 80%). This means that the pay back time of a complete new plant is less than two years. Microinnova can offer plants with fulfil cGMP criteria. Microinnova has just finished the basic engineering for 1 ton per hour throughput plant for a diagnostics application.
Microinnova transfers micro reaction technology into production scale. [Kirschneck & Tekautz, 2007] One Microinnova developed liquid-liquid application with a

throughput of 3 tons per hour has been started up in May 2005. Several others are in the engineering stage and will be started up soon. Scale-up experiments have already been done successfully for liquid-liquid applications as well as for liquid-gas applications. The examples have proofed technical feasibility. One of the success stories has just been published. The technical advantages lead to a strong economic impact.

Results of more than one year production experience with a 3 tons per hour plant will be presented. Achievements and problems will be discussed in detail. The economic impact of two main aims: energy savings and debottlenecking of a production application will be demonstrated. The technical concept and economic impact of a liquid-gas project will be shown. The economic figures are compared with a conventional plant solution.

An overview of activities will be given and will be summarised in a general trend description. Finally some general remarks will be given, how to transfer lab scale results into production scale. Micro reaction technology will have an impact on the way of chemical and pharmaceutical production in the future. Some considerations to new strategies will be presented. Future scenarios will be shown.

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Session S4-P-1: EPIC-1 Poster Session – I

Abstract Number	**Paper Title & Authors**	**Included**
1105	High-fidelity DEM-CFD modeling of packed bed reactors for process intensification S Ookawara, M Kuroki, D Street, K Ogawa	Yes
1151	The RAPTOR : an intensified continuous reactor for chemical synthesis F de Panthou, S Marie, L Falk	Yes
1376	Analysis to intensify the energy utilization in incineration plant M Dudeková, J Klemeš, P Stehlíka	Yes
1720	Hairy foam: towards control at the catalytic site P W A M Wenmakers, J van der Schaaf, B F.M. Kuster, J C Schouten	Yes
1984	Measurements of slug frequency and length in gas-liquid flow in a microreactor channel R Pohorecki, P Sobieszuk, K Kula, W Moniuk, F Ilnicki, F P Cyganski, P Gawinski	Yes
2188	Non-intrusive method for measuring residence time distribution in microreactors S Lohse, P S Dittrich, D Janasek, J Franzke, D W Agar	Yes
2292	Novel Syngas Production Techniques for GTL-FT Synthesis of Gasol C Dillerop, H van den Berg, A G J van der Ham	Yes
2414	Exploring a Particle Engineering Toolbox of intensified processes C P M Roelands, J G H Brouwer, J van der Meer, A E D M van der Heijden, D Verdoes	Yes
2771	Enzymatic Kinetic Resolution in water / scCO2 biphasic systems C Roosen, L Kalender, N Bieler, M Ansorge-Schumacher, T Mang, L Greiner, W Leitner	Yes
2863	An Investigation into the Micromixing Characteristics in a Spinning Disc Reactor S R Al-hengari and K V K Boodhoo	No
2874	ATR-IR spectroscopy for process monitoring in microstructured reactors C Minnich, L Küpper, M Kaever, L Greiner, M Liauw	Yes
2929	Lipase-catalysed transesterification in ionic liquid/supercritical carbon dioxide biphasic systems using a recirculating enzymatic membrane reactor	Yes

	F J Hernández-Fernández, A P de los Ríos, D Gómez, F Tomás-Alonso, M Rubio and G Víllora	
2945	Membrane-based oxidation processes for the remediation of polluted groundwaters with As (III) E Bringas, A Criuscuoli, M F S Román, I Ortiz, E Drioli	Yes
2952	Optimization of integrated reaction/separation processes for the kinetic resolution of rac-1-phenylethanol using supported liquid membranes based on ionic liquids A P de los Ríos, F J Hernández-Fernández, F Tomás-Alonso, D Gómez, M Rubio and G Víllora	Yes
3162	Pilot Plant Analysis Of An Integrated Process For The Treatment Of Landfill Leachates Ó Primo, A Rueda, M J Rivero, I Ortiz	Yes
3220	Kinetic resolution of rac-1-phenylethanol in a stirred tank bioreactor in ionic liquid/supercritical carbon dioxide biphasic systems A P de los Ríos, F.J. Hernández-Fernández, D Gómez, F Tomás-Alonso, M Rubio and G Víllora	Yes
3308	Structured Catalysts Based On Sintered Metal Fibers For 3-phase Hydrogenation: The Design Of Compact Reactor L Kiwi-Minsker, M Grasemann, N Semagina, A Renken	Yes
3412	Simulation study of membrane supported oxidation C Hamel, H Wang, J Caro, E Tsotsas, A Seidel-Morgenstern	Yes
3545	Reactor model for the selective catalytic reduction of NO over Ag/Al2O3 in a gas-phase microreactor J R Hernández Carucci, J Sosa Pieroni, K Eränen, J Wärna, T Salmi, and D Yu Murzin	Yes
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High-fidelity DEM-CFD modeling of packed bed reactors for process intensification

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1. Summary

A novel high-fidelity DEM-CFD approach is proposed for process intensification of packed bed reactors. The model enabled random packing of 880 particles in a tube with a reasonable accuracy regarding voidage and pressure loss. The model capability is demonstrated by examining the effect of blending manner of hot and cold particles on temperature distribution.

Keywords: high-fidelity DEM-CFD model, packed bed, process intensification

2. Extended Abstract

Blending catalytic with absorbent and/or inert particles is one of process intensifications for packed bed reactors. The former would be for sorption-enhanced reactors and the latter for the control of temperature distribution. The mixture fraction and blending manner are to be significant factors to enhance the blending effect. A recent high-fidelity CFD model, which represents the bed by gaps between many particles each shaped without geometrical simplification, would be a potential tool to optimize the factors. The precise reality and large scale of packing is crucial for its practical and reliable utilization. In this study the frame of novel numerical approach for such demands is presented and the capability is conceptually demonstrated.

Packed beds are modeled by allowing 220 to 880 spherical particles to fall randomly under gravity into a cylinder whose diameter is 4 to 8 times larger than the particle diameter as shown in Fig. 1. A commercial code EDEM (DEM Solutions Ltd) is employed for simulating the packing. It is shown that the discrete element method can constitute appropriate random packing whose voidage agrees with the literature (Leva and Grummer, 1947). The particles in (nearly) contact are cylindrically bridged to eliminate the fine computational cells around the contact point and then to avoid large mesh size, which cannot be handled easily. It should be mentioned that the novel bridging model has attained the packing about 10 times larger than previous hi-fi models described by others (Nijemeisland and Dixon, 2004; Guardo et al., 2006) regarding the number of particles. The method also enables automatic mesh generation for such complex geometries.

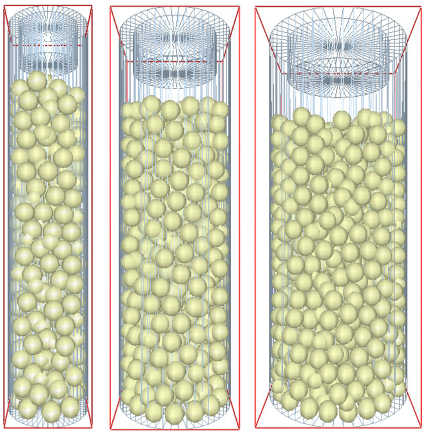

Fig. 1 Random packing of 220 to 880 spheres in tubes with diameter of 4 to 8 times larger than particle.

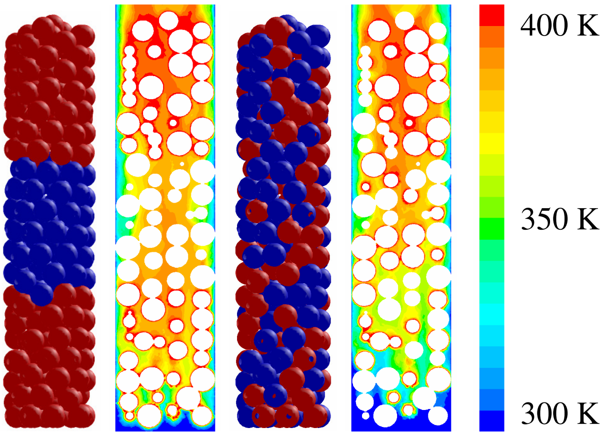

Fig. 2 Temperature distributions in packed beds of laminar and random arrangements of hot (in red) and cold (in blue) spheres. (*Re* = 510)

In this study the novel hi-fi DEM-CFD model is further verified in terms of pressure loss compared with a correlation taking into consideration particle to tube diameter ratio (Eisfeld and Schnitzlein, 2001). The accuracy of particle-to-fluid heat transfer was thoroughly examined elsewhere (Kuroki et al., 2007). A commercial code FLUENT6 (Fluent Inc.) is employed to perform all the CFD processes. As seen in Fig. 2, laminar and random blending of hot catalytic and cold inert particles are conceptually simulated by specifying surface boundary conditions as 400 K and zero heat flux on the hot and cold particles respectively. Inlet velocity of air with 300 K is specified so that particle *Re* becomes 510. Wall temperature is specified as 300 K. It can be seen that the blending manner influences temperature distribution despite almost same fraction of cold particles. In future, subsequently, reaction and mass transfer will be incorporated into the model for the process intensification in practice.

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The RAPTOR : an intensified continuous reactor for chemical synthesis

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1. Summary

The objective of this paper is to present the performance of a new continuous reactor for process intensification: the RAPTOR (french acronym for Polyvalent Rectilinear Stirred Reactor with Optimized Transfer). As a proof of concept, an exothermic gas-liquid reaction has been chosen: the catalytic reduction of a phenol into cyclohexanone with hydrogen. The study compares the performance of the Raptor with a conventional batch vessel in terms of thermal exchange, mass transfer and from the industrial point of view. We demonstrate the reason why this reactor, intrinsically safe, can be considered as an optimum between industrial capacity and thermal performance.

Keywords: intensification, green chemistry, sustainable chemistry, batch to continuous, characteristic times.

2. Extended Abstract

Stirred tanks have low surface to volume ratio and their heat exchange capacity is limited. To handle fast highly exothermic reactions, it is often necessary to degrade the reactions conditions by working with diluted reagent with a high amount of solvent or with co-reagent addition limited in time. The kinetics are considerably slowed down resulting in long durations of synthesis (achieving several hours) while, when intensified and operated in continuous mode, operation times can be reduced to several minutes. The Raptor reactor is a novel continuous reactor proposed by AET which combines both advantages of efficient stirring (1500 rpm) and the possibility to support pressure up to 250 bars and temperature up to 300 °C. In continuous operation, chemistry can be performed under safe environment. Small quantities of reactants, a high exchange surface ratio for a higher thermal performance and no accumulation of unstable intermediate are the main reason of intrinsic safety advantages of this new technology. Several hydrogenation reactions have been performed in this new device and the paper presents, as a proof of concept, the hydrogenation of pure o-cresol into the corresponding cyclohexanol.

The heat of reaction is about -210 kJ/mol. The comparison between experimental results obtained in a classical batch process and in the Raptor is described in the following table:

	Batch process	RAPTOR
Amount of catalyst	4%	0.4 %
Solvent	3 vol. of Solvent for 1 vol. of reactant	No solvent
Operation time	4 to 5 hours	Less than 3 min.
Adiabatic temperature rise	100 °C	925 °C
Yield	95 %	> 99 %

It can been noticed that for the o-cresol reduction performed in the Raptor, the amount of catalyst was reduced ten times, solvent was totally suppressed and almost 100% conversion was obtained in less than 3 minutes instead a few hours in a batch vessel.
This shows that the Raptor is a technological break offering interesting perspective for sustainable chemistry: energy saving for separation, environment friendly by solvent consumption reduction, economic benefits (OPEX with solvent and energy, CAPEX with small reactor size).
The experimental results are analyzed and explained thanks to a characteristic times analysis which shows how it is possible to intensify such a hydrogenation reaction. Figure 1 presents internal temperature increase versus characteristic times ratio of thermal transfer and G/L mass transfer for different dilution factors F. In order to prevent thermal runaway of the reactor, semi-batch reactor need to work with high dilution, what considerably decrease rate of reactions, while Raptor is safe independently from dilution.

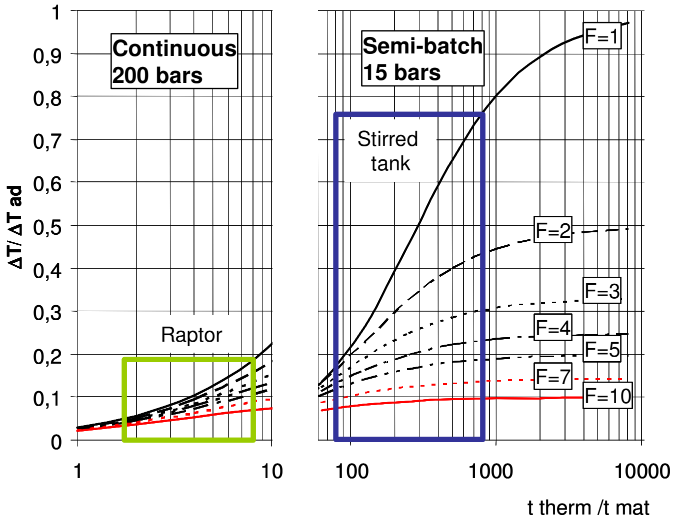

Figure1: Comparative operation diagram of the semi-batch stirred reactor and the Raptor. Internal temperature increase versus characteristic times ratio of thermal transfer and G/L mass transfer for different dilution factors F.

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Analysis to intensify the energy utilization in incineration plant

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1. Summary

Thermal processing of waste represents not only waste disposal including reducing its volume but also waste to energy (WTE) process. This is the case in most up to date municipal solid waste (MSW) incinerators. Results from analysis of energy utilization in one of this type of MSW incinerators are presented in this paper. The aim of the analysis was to identify the potential energy saving within the plant. *Plant efficiency factor* and *Energy utilization rate* are considered as the criteria used for assessment of plant performance from the view of energy utilization. Simulations based on industrial data acquired by monitoring system were carried out and obtained results are analyzed. It was found out, that the potential energy savings are available in the area of low-potential heat. The possible improvements were proposed and consulted with the specialist. Moreover, the elementary economic analysis is mentioned.

Keywords: intensification of energy utilisation, incineration plant, waste to energy

2. Extended Abstract

Thermal treatment of waste (municipal, hazardous, biological) is used as an integral part of integrated waste management throughout Europe because it is a safe and clean technology superior to landfill and is compatible with high levels of recycling. Using municipal solid waste (MSW) to produce energy (waste to energy system – WTE) is not only an important waste treatment option but it also cuts down the use of fossil fuels and hence can help to meet renewable energy targets. Thermal treatment processes recover the energy in MSW incineration plants and convert it into heat and power (electricity, steam, gas etc). Thus thermal processing of MSW can be considered as certain form of recycling energy. It is necessary to analyze all feasible ways how to utilize this energy as much as possible.

The work focuses on one of the up to date MSW incinerators with capacity of 12 t/h, which belongs to WTE category. The energy released during thermal oxidation of waste is utilized for generation of high pressure process steam and subsequently for co-generation. The majority of produced steam is exported and sold outside the plant.

The remaining amount is used inside the plant for covering the heat requirements e.g. preheating the primary air, heating the boiler feed water. Therefore decrease of the in-house energy provides an additional potential to export the steam and to improve overall economy of the plant.

The effectiveness of utilization energy in incineration plant was evaluated by two criteria proposed by The Confederation of European Waste-to-Energy Plants (CEWEP): *Plant efficiency factor* and *Energy utilization rate*. The calculations were based on the industrial data from the incineration plant monitoring system. First, the individual process streams, heat flows and utilities were identified. Then, these data were used for mathematical model creation. Newly developed WTE software for simulation of waste to energy systems (a product of UPEI-VUT Brno) was used for this purpose. Influence of different factors on plant performance has been investigated and several general recommendations stated. An alternative approach considering heat integration and utility system was investigated by using software code SPRINT for process integration (a product of CPI UoM). From the results of performed simulations it is quite obvious that the potential energy saving could be reached in the area of low potential energy. The suggestions for the improvement acceptable by the plant are the key deliverables of this paper.

The support from an EC Marie Currie Research Training Network “Towards Knowledge-Based Processing Systems (PRISM)” Contract No: MRTN-CT-2004-512233 is gratefully acknowledged.

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Hairy foam: towards control at the catalytic site

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1. Summary

Carbon nanofibers (CNFs) have been grown on reticulated vitreous carbon (RVC) by decomposition of ethylene and methane. Methane does not show any activity towards CNF growth. Ethylene yields a thick (up to 60 μm) layer of CNFs on the surface of the RVC. The fibers can be made catalytically active for gas-liquid-solid reactions.

Keywords: carbon nanofibers, reticulated vitreous carbon, gas-liquid structured reactors, solid foam, reticulated vitreous carbon

2. Extended Abstract

Modern catalytic (multiphase) reactors most often use structured catalyst supports, instead of the familiar randomly packed beds. An example of such a structured support material is solid foam. Solid foam is an open-celled structured material with a voidage of 92% to 97% (Figure 1a). The advantages of using solid foams are the large hydrodynamic operating window (including counter-current operation), a low pressure drop, a low degree of back mixing, high gas-liquid mass transfer rates and a high liquid hold-up (Stemmet et al., 2005, 2006). A disadvantage is the relatively low solids holdup. The surface area available for deposition of a large amount of catalyst is insufficient. The foam surface area can be increased by growing a layer of CNFs (**Figure 1** b,c) on the solid foam, resulting in Hairy Foam.

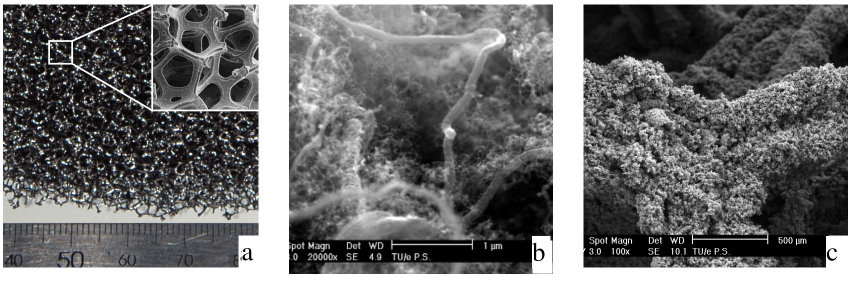

Figure 1: Images of a) Carbon foam; b) Carbon nanofibers; c) CNFs grown on solid foam

Hairy Foam can be seen as the inverse image of a porous packed bed, i.e. the void space is the foam structure and the CNFs are the micropores (Figure 2).

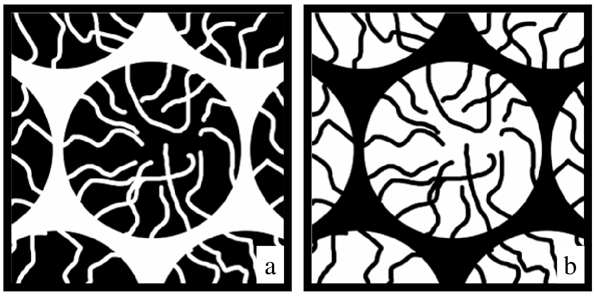

Figure 2: graphical representation of a) packed bed with porous catalyst particles; b) Solid foam with a layer of CNF's (black is solid, white is void space)

With Hairy Foam the catalyst is deposited on the CNFs instead of in the micropores or on the surface of the support. Pore diffusion limitations are virtually absent, allowing for a higher reactivity and selectivity. The CNFs are protruding into the gas-liquid stream, which makes the catalyst hydrodynamically accessible. Consequently, the liquid-solid mass transfer is increased with respect to a usual washcoat applied on a structured support with diffusion limitations.

Nickel coated RVC samples, placed in a quartz reactor with a sintered porous quartz plate at the bottom, were reduced in a 20% H_2, 80% N_2 flow (flowrate 100 ml/min) at 500 °C for 2 hours. After reduction the reactor was brought to the desired reaction temperature (500°C or 600 °C). The inlet gas was changed to 20% CH_4 or 20% C_2H_4, 7% H_2 balanced with nitrogen with a total flow rate of 100 ml/min (Toebes et al., 2004). The reaction was left to continue for 10 hours after which only nitrogen was passed to the reactor and the reactor was allowed to cool down to room temperature.

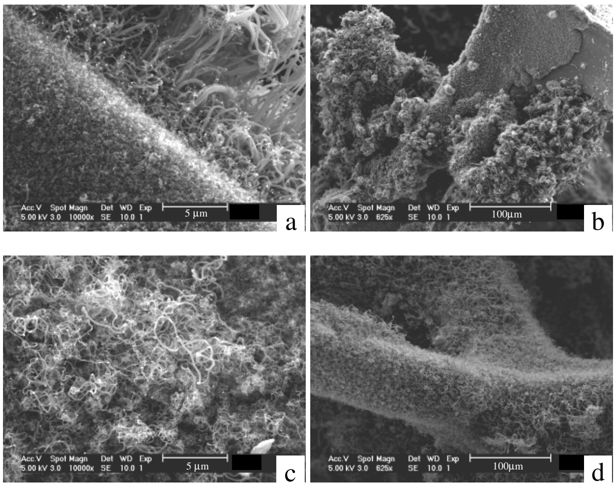

Figure 3: CNFs on RVC grown at a,b)500°C; c,d) 600°C

Using CH_4 as a carbon source does not show any activity towards CNF growth for both 500°C and 600°C. Using C_2H_4 as carbon source yields a thick layer (up to 60 µm) of CNFs.

The CNFs grown at 500°C (Figure 3 a,b) show a large spread in the fiber diameter (26 nm to 470 nm). The thickness of the CNF layer is varies significantly (2 µm - 60 m). A reaction temperature of 600°C results in thinner more uniform fibers (26 nm to 128 nm, Figure 3c,d). The layer thickness is more uniform than for 500°C (~13 µm).

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European Congress of Chemical Engineering (ECCE-6)
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Measurements of bubble and slug frequency and length in gas-liquid flow in a microreactor channel

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1. Summary

According to earlier investigations carried out to determine the character of the gas/liquid flow in microchannels ("regime maps") (Vaillancourt et al., Waelchli and von Rohr, Pohorecki et al.,), the most common regime of two phase flow in microchannels is the slug regime. In this regime slugs of one phase flow through the microchannel alternately with slugs of the other phase (gas bubbles and liquid slugs in the case of a gas-liquid system). In the case of a liquid wetting the microreactor wall material, the microreactor wall is covered by a thin liquid layer, and the gas bubbles are sliding over this "lubricating" layer. The "lateral" part of the interfacial area may be many times greater than the "perpendicular" part. To be able to apply the criterion for the activity for mass transfer of the lateral part of the interfacial area (Pohorecki et al.), one has to know the frequency and bubble length involved.

Keywords: microreactor, interfacial area, gas absorption

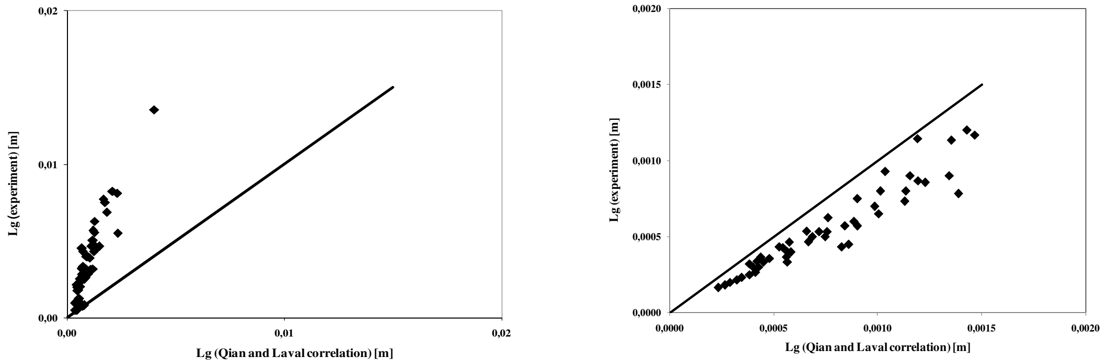
2. Extended Abstract

The bubble and slug frequency and lengths in gas-liquid flow in a microreactor channel have been measured, using three different liquids and two microreactors using nitrogen as an inert gas. The microreactors were Y shaped, with the following main channel dimensions:

Microreactor 1:	
material	PETg (polyethylene terephthalate with glycol)
width/ height/ length	0.2/0.55/55 mm
Microreactor 2:	
material	PDMS (polydimethyloxosilane)
width/ height/ length	0.15/0.15/25 mm

The slug and bubble lengths and frequencies were measured using high speed camera CCD (PCI 8000S).
In the numerical experiments performed by Qian and Laval, these authors determined the length of the bubbles and slugs by CFD methods. Fig 1 – 2 presents, as an

example, a comparison of our experimental results with those calculated from the Qian and Laval correlation.



A B

Fig. 1: Comparison of bubble length calculating from Qian and Laval correlation with experiment, etanol-nitrogen system; A – microreactor 1, B – microreactor 2.

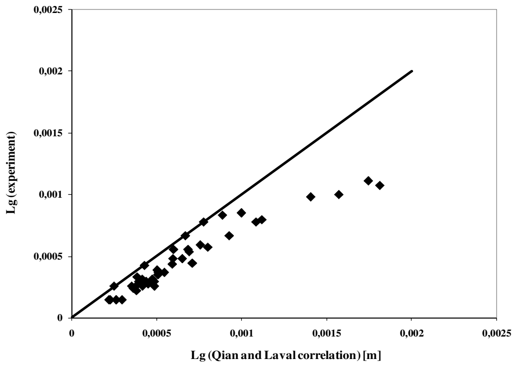


Fig. 2. Comparison of bubble length calculating from Qian and Laval correlation with experiment, heptan-nitrogen system (microreactor 2)

As can be seen, there is reasonable agreement for the narrow channel (0.15 mm), whereas for the wider channel the correlation underpredicts the bubble lengths.

Acknowledgements

This work has been supported by 6th Framework EU under Grant IMPULSE No: NMP2-CT-2005-011816

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Non-intrusive method for measuring residence time distribution in microreactors

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1. Summary

Characterisation of flow through microreactors is an essential prerequisite for their design and optimal performance. An accurate method for the determination of residence time distribution in microreactors as an effective method for describing the real behaviour of chemical reactors is presented. To overcome the shortcomings of conventionally used techniques a caged dye has been used as tracer species. The residence time distribution is determined by simply exposing the inlet section of the transparent microreactor to a laser beam. The tracer 'injection' is well-defined, non-intrusive and applicable to arbitrary geometries without need for signal deconvolution. Furthermore, the significance of the prevailing laminar flow regime for the data measured is demonstrated.

Keywords: microreactor, residence time distribution, reaction engineering, microfluidics

2. Extended Abstract

Miniaturisation is a powerful technique for enhancing the yield and selectivity of chemical syntheses [1]. In addition to the advantages of increased heat and mass transfer, miniaturised systems offer the realisation of chemical processes with a virtually identical processing history for each converted molecule. A crucial requirement for exploiting the full potential of process intensification using miniaturisation is the availability of accurate methods for the characterisation of microreactors. The residence time distribution of chemical reactors is a crucial 'parameter' for describing their true behaviour. The main objective of this work is to develop and evaluate an appropriate experimental method for the purposes of microreactor design and performance assessment.

Conventionally, injective methods are widely used for the determination of residence time distribution (RTD) in chemical reactors: an easily detectable tracer is introduced into a steady-state flow in the reactor inlet and the distortion of the signal determined in the reactor outlet. The residence time distribution is then calculated by deconvolution of the inlet and outlet signals. Previous research [2, 3] has shown that the main challenge in measuring microreactor RTD is to obtain a well-defined signal at the re-

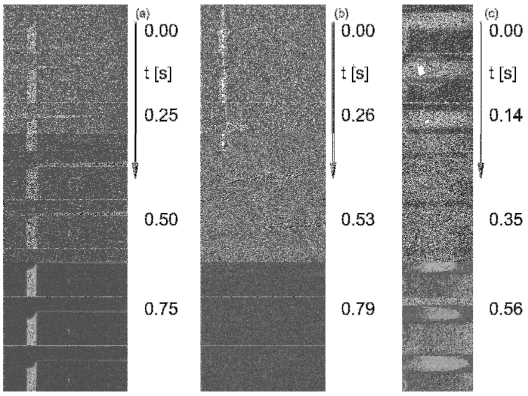

Figure 1: Comparison of different injection methods into a straight channel (150 μm width)
a) pressure induced injection, b) injection into stationary fluid, c) 'optical injection'

actor inlet, which is independent of the actual flow rate, without disturbing the flow. To avoid the shortcomings of conventional methods in microreactors, a novel technique for RTD determination has been evaluated. The underlying idea is the continuous introduction of a caged fluorescent dye dissolved in the aqueous flowing medium. This procedure has already been used for visualisation of velocity fields in microchannels [4]. By exposing a defined section of the inlet channel to a pulse of UV-light, a certain amount of tracer is activated or 'de-caged' and thus becomes fluorescent. This kind of optical 'injection' is non-intrusive and disturbs the flow in no way. Due to the possibility of locating the 'injection' site directly at any position within a transparent device, artefacts from peripheral equipment can be eliminated. The method generates almost ideal input signals, which simplifies the numerical treatment of experimental data. A comparison demonstrating the superiority of this new approach over various traditional injection methods has been presented recently [5].

To obtain the RTD, the activated fluorophores are detected at a given cross-section in the outlet of the structure being studied by using an EMCCD-camera mounted on an inverse research microscope. For complex structures, this kind of detection corresponds to a closed/closed system, i.e. the measured data yield the RTD directly. For simple straight or meandering channels (open/open boundaries) the velocity profile of the fluid in the detection sections has to be considered. This is feasible by virtue of the spatially resolved measurement provided by the EMCCD. Initial experiments to show the feasibility of this procedure for determining the RTD in complex microreactor structures have been carried out. With the experimental data obtained using this technique one can reliably validate mathematical models describing mass transfer behaviour in (micro)structures with extremely unfavourable aspect ratios.

Acknowledgements: to DFG for financial support of the project AG26/9-1

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Novel syngas production techniques for GTL-FT synthesis of gasoline

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1. Summary

Syngas production plays an key role in gas to liquid (GTL) technology. In this feasibility study existing and new syngas production techniques are compared. As the conventional autothermal reforming reactors always consist of extensive heat exchange equipment and air separation units, alternatives are based on integrating these within the reactor design. Reverse flow reactors make it possible to perform heat integration within the reactor; integrated air separation is accomplished by O_2 selective membranes within the reactor. The alternatives show a higher economic potential than the conventional technique. The second part of the study consists of an extended conceptual design of both the conventional design as well as the reactor with integrated heat transfer. The feasibility of the reversed flow reactor is shown by a reduced methane and oxygen consumption.

Keywords: Gas-to-liquid, synthesis gas, reverse flow reactor, air separation, process design, heat integration

2. Extended Abstract

Gas To Liquids (GTL) technology is becoming an increasingly lucrative technique to exploit stranded and/or abundant natural gas resources. A GTL plant consists of syngas production and Fischer-Tropsch (FT) units. A feasibility study has been performed on the syngas production techniques available, both conventional as well as those in development.

The design process is conducted in a systematic way from black box to conceptual design to index flowsheet and finally the PFD level. It included all tools such as working diagrams, alternatives and decision trees, and appeared to be robust and flexible at the same time.

Following process types were assessed both technically and economically: Auto Thermal Reforming (ATR), Reverse Flow Catalytic Membrane Reactor (RFCMR) with porous membranes, Catalytic Membrane Reactor (CMR) with O_2 selective membranes, Reverse Flow Catalytic Membrane Reactor (RFCMR) with O_2 selective membranes.

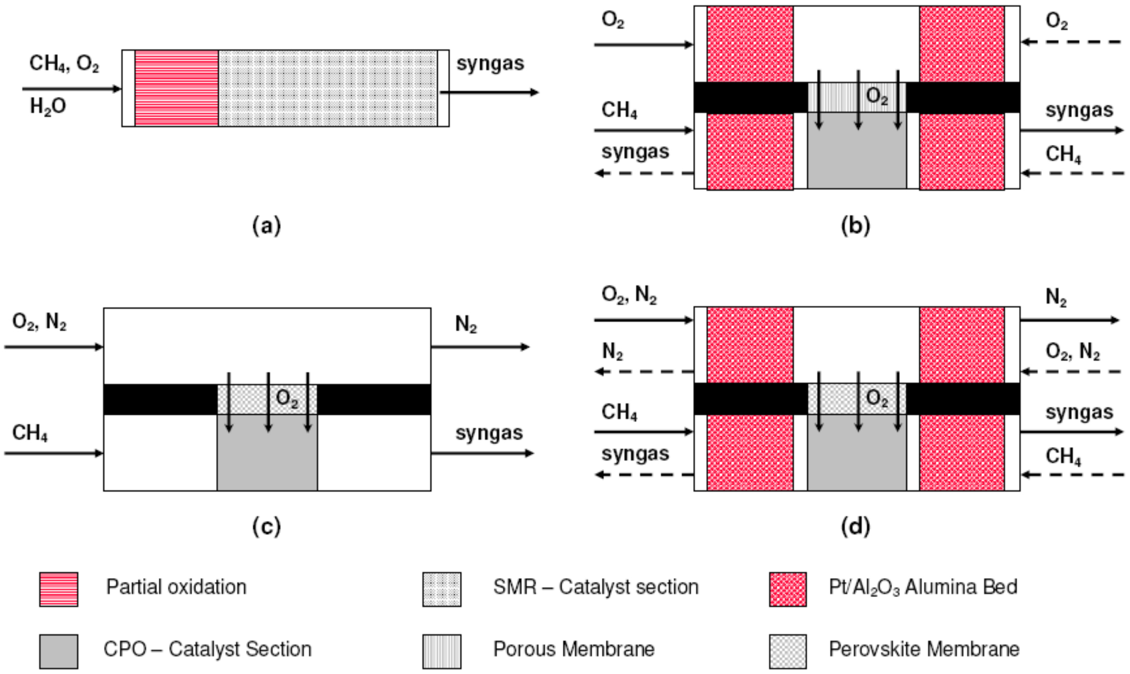

Figure 1. Schematic overview syngas reactors: (a) ATR reactor; (b) RFCMR reactor with porous membranes; (c) CMR reactor with O_2 selective membranes; (d) RFCMR reactor with O_2 selective membranes. Dashed lines give flow direction after flow reversal

ATR combines partial oxidation with catalytic steam reforming, it is considered to be the more conventional technique. The reverse flow reactors consist of an integrated recuperative heat exchange design and, therefore, have a lower required O_2/CH_4 ratio in the feed. In case of the membrane reactors with O_2 selective membranes, the air separation is integrated within the reactor design and an air separation unit (ASU) is not required. For more information on the RFCMR see the work of J. Smit et al.

The economic feasibility was evaluated with OPEX and CAPEX calculations for given boundary conditions. The RFCMR with O_2 selective membranes was the most economically feasible option due to the lower O_2 feed costs and higher efficiency resulting in a 15% improvement in economic potential related to the ATR process.

As the reactors with O_2 selective membranes are still in development, it was decided to do an extended conceptual design of the ATR and RFCR with porous (non selective) membranes (option b). Mass and energy balances and a preliminary design of reactor systems were prepared. Results show that the RFCR has a higher potential than an ATR for an optimum syngas production process. For example, the carbon efficiency improved from 77 to 85%.

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European Congress of Chemical Engineering (ECCE-6)
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Enzymatic reactions in water / $scCO_2$ biphasic systems

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1. Summary

We present a holistic approach for a dynamic kinetic resolution with supercritical carbon dioxide ($scCO_2$) as vector in the biphasic system H_2O / CO_2. Issues of catalyst and enzyme activity and stability and their immobilisation will be presented. Furthermore we present our results for pH measurement and control for this promising media combination.

Keywords: green chemistry, supercritical carbon dioxide, aquous pH, lipase,

2. Extended Abstract

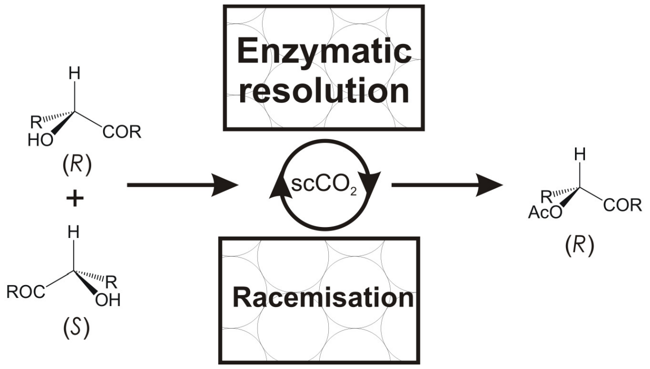

Figure 1: $ScCO_2$ as a vector for Dynamic kinetic resolution (DKR)

Enantiopure chemicals are important intermediates and products for pharmaceuticals, food industry, agrochemicals, and cosmetics. Kinetic resolution of racemates is still the most widely used method in industrial applications because of its general applicability. It is the main field of application for enzymatic catalysis.

The main disadvantage of limited conversion and sometimes down stream processing can be overcome by dynamic kinetic resolution. The combination of enzymatic kinetic resolution and transition metal catalysed racemisation, as introduced recently by Bäckvall and co-workers [1], is a powerful tool in the synthesis of enantiopure chemicals and allows racemisation and kinetic resolution under mild conditions. However, remaining problems of this approach are the removal and/or recycling of the precious metal catalyst and the need for reaction conditions to be compatible.

We aim to overcome these issues by compartimentisation of the catalyst by immobilisation and the use of supercritical carbon dioxide as transporting vector between the catalyst system and for successive extraction (Figure 1). Within this work a way to use enzymes in a continuous process with water as reaction medium for kinetic resolution in combination with $scCO_2$ is presented.

The control of pH is generally important for all aqueous reactions and especially for enzyme catalysed reactions since most enzymes exhibit their optimum of activity at pH values near neutrality and tend to be unstable at low pH. Within these studies we investigated pH-measurements with dyes and a modified electrode at reaction conditions. Furthermore, an easy way to shift the pH to a desired value and an equation to predict the pH could be established (equation 1). The results of this study allow to optimize reactions carried out in the biphasic system $scCO_2$ / water and pave the way for reactions to be performed in the presence of $scCO_2$ (Figure 2).

$$pH = 2 \cdot pH_{unbuffered} + \log(c(HCO_3^-))_{added} - \frac{\sqrt{I}}{1+\sqrt{I}} \cdot (A + 0.5) + 0.1 \cdot I \qquad (1)$$

Beside the pH, both the interface between the water phase and the $scCO_2$ phase and the solvent power of the $scCO_2$ is important for lipase catalysed biphasic reactions, since most lipases are activated at the interface and high product solubility in the non-aquous phase is required. Within this work we found a way to run the desired reaction in the biphasic system water - supercritical carbon dioxid by tuning the $scCO_2$ in means of solvent properties and interface.

To overcome the remaining reaction engineering problems in this specific biphasic system, not only the lipase needs to be immobilised, but the whole aquous phase needs to be stabilized. One way to stabilize the waterphase for biphasic reactions is presented (Figure 3).

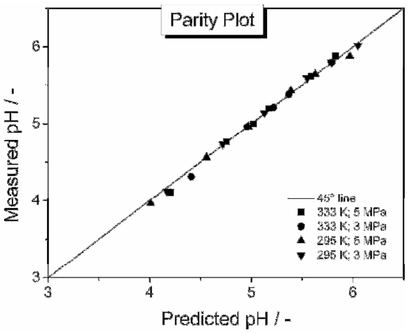

Figure 2: Parity Plot of predicted and measured pH

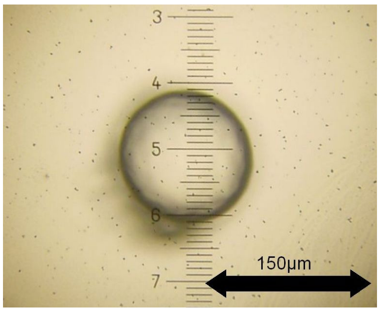

Figure 3: Stabilised aqueous phase

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Realisation of a process control strategy for micro reaction plants based on ATR-IR spectroscopy and chemometric models

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1. Summary

Beyond the established analytical tools for the measurement of physical process parameters (pressure, temperature) there is an increasing interest in the inline or online recording of chemical process information (reactant concentrations etc.). In the emerging field of Micro Reaction Technology (µRT), optical spectroscopy faces additional restrictions concerning the size of optical elements. We aim at an adaptation of spectroscopic tools to the micro scale and at its integration into process control systems.

Keywords: process monitoring, micro reaction technology, fiber optics

2. Extended Abstract

Easy-to-handle methods for process monitoring and control in Micro Reaction Technology are an important prerequisite for establishing it as a standard tool for process development. Due to its good time resolution and the extensive information available, infrared spectroscopy in the spectral mid-range ($4000 - 400\ \mathrm{cm}^{-1}$) is a valuable source of chemical information, e.g. concentration profiles of reactants. For its application in small volumes, the use of fibre optical sensors that adapt the geometries of the reactor spaces and avoid large dead-volume bypasses has proven powerful.

The synthesis of the Ionic Liquid 1-ethyl-3-methyl-imidazolium ethylsulfate $[EMIM]EtSO_4$ by *N*-alkylation of 1-methylimidazole with diethylsulfate is an outstanding example for a reaction that benefits from being performed in microstructured equipment. As reaction calorimetric experiments show, reaction enthalpy is $-123\ \mathrm{kJ\ mol}^{-1}$ and maximum heat output reaches $400\ \mathrm{W\ L}^{-1}$ [1] , so that in consequence sophisticated heat removal is required in order to keep isothermal conditions. Experience from the traditional batch synthesis shows that hot spots affect the product in an unacceptable way causing formation of coloured by-products.

For these reasons, the reaction has been chosen as a process example for reaction monitoring and control in a compact continuous flow setup with microstructured components. Flow cells for fibre optical IR sensors (which have been employed in reaction monitoring before[2]) have been developed providing minimised hold-up volume and optimised fluid geometry[3] for inline measurements of reactant concentrations. Efforts have been made to integrate the signal into control loops for the automation of the process.

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Copenhagen, 16-20 September 2007

Lipase-catalysed transesterification in ionic liquid/supercritical carbon dioxide biphasic systems using a recirculating enzymatic membrane reactor

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1. Summary

This work presents a synthetic biocatalytic process combining supercritical carbon dioxide, ionic liquids and membrane technology. The use of membrane reactors represent an attempt to integrate catalytic conversion, product separation and catalyst recovery into a single operation. Butyl propionate synthesis from vinyl propionate and 1-butanol catalyzed by *Candida antarctica* lipase B (CALB) has been chosen as reaction model. Firstly, the synthetic activity of CALB, covalently attached to a polymer layer previously adsorbed on α-alumina tubular membranes, in supercritical carbon dioxide, was tested into a tangential-flow reactor. According to the initial rates, a model based on the Ping Pong Bi-Bi mechanism with competitive alcohol inhibition was proposed. Then, the immobilized enzyme was coated with three different ionic liquids (i) [bmim$^+$][PF$_6^-$]), (ii) [bdimim$^+$][PF$_6^-$] and (iii) [omim$^+$][PF$_6^-$], in order to study the influence of these media on both the activity and selectivity of CALB.

Keywords: enzymatic membrane reactor, ionic liquids, supercritical carbon dioxide, lipase, transesterification reaction

2. Extended Abstract

Supercritical carbon dioxide (scCO$_2$) and room temperature ionic liquids (RTILs) have recently been revealed as interesting clean alternatives to classical organic solvents [1] to be used in biocatalysis. Recent researches have demonstrated the possibility of carrying out integral green biocatalytic processes by combining these two different neoteric solvents [2]. The success of this biphasic system is based on the high solubility of the scCO$_2$ in the RTIL phase, while the same RTIL shows non-detectable solubility in the scCO$_2$ phase. Moreover, it was found that scCO$_2$ can be used to extract organic substances from RTILs without any cross-contamination of the extract with the RTILs [3].

In this work, dynamic membranes with immobilized *Candida antarctica* lipase B (CALB) were successfully applied for butyl propionate synthesis in a recirculating bioreactor in supercritical carbon dioxide medium and in room temperature ionic liquid/supercritical carbon dioxide biphasic systems at 50ºC and 80 bar. Figure 1 shows the synthetic activity and selectivity of immobilized CALB in $scCO_2$ medium and in three assayed RTIL/$scCO_2$ biphasic systems. As can be seen, an increase in the selectivity of the process was achieved in RTIL/ $scCO_2$ biphasic systems compared with supercritical carbon dioxide assayed alone, although the synthetic activity was lower.

Additionally, a model based on the Ping Pong Bi-Bi mechanism with competitive alcohol inhibition is proposed to describe the kinetics of the transesterification reaction in supercritical carbon dioxide (Figure 2).

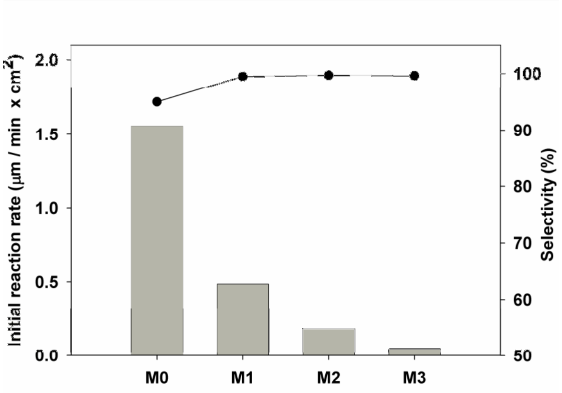

Figure 1. Initial reaction rate (bars) and selectivity (•) of immobilized CALB in $scCO_2$ media (M0) and in three different RTIL/$scCO_2$ biphasic systems: [$OMIM^+$] [PF_6^-] (M1), [$BMIM^+$][PF_6^-] (M2), and [$BDiMIM^+$] [PF_6^-] (M3). The reaction conditions were T = 50ºC, P =80 bar, vinyl

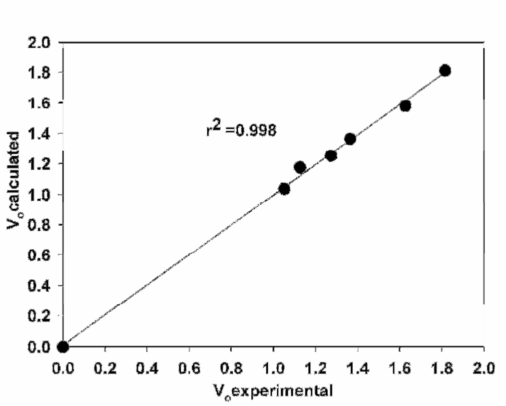

Figure 2. Comparison of experimental rate data and the rate data calculated by the kinetic model (µmol · min^{-1} · cm^{-2}).

Acknowledgment

This work was partially supported by the CICYT CTQ2005-09238/PPQ grant. F.J. Hernández-Fernández and A. P. de los Ríos have fellowships from the University of Murcia and the Spanish Ministry of Education and Science, respectively

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Membrane-based oxidation processes for the remediation of polluted groundwaters with As(III)

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1. Summary

This work aims at the viability of replacing traditional oxidation processes by membrane-based oxidation technologies. In particular, it is focused on the oxidation of As(III) contained in polluted groundwaters as pre-treatment step to the reverse osmosis process used in the removal of arsenic. The viability of the As(III) oxidation with ozone using hollow fiber modules as gas-liquid contactors has been analysed by means of process simulation.

Keywords: arsenic, groundwater, membrane contactor, oxidation, ozone

2. Extended Abstract

The presence of arsenic in groundwater reservoirs is an environmental problem of big concern; the situation has special relevance in those developing countries with slender hydrological resources. It is generally caused by the filtration of polluted waters that incorporated dissolved natural arsenic initially contained in minerals and sediments (Emeet and Khoe, 2001). In surface waters arsenic is mainly present as As(V), while in groundwaters As(III) species represent the major contribution to the total arsenic content due to the absence of oxygen (Ning, 2002).

Different technologies can be used in the treatment of groundwater containing arsenic but membrane technologies such as reverse osmosis and nanofiltration can be considered promising alternatives to reduce the level of metallic pollutants in groundwaters (Shih, 2005). Research efforts show that the rejection percentage of As(V) using membrane technologies is greater than the one for the reduced species. Therefore, it is convenient to oxidise As(III) to As(V) to improve the removal process efficiency (Moore, 2005).

The arsenic oxidation has been traditionally performed using different oxidizing agents (ozone, chlorine, hydrogen peroxide, manganese oxides, etc.) and different contact equipments (spray towers, packed columns, etc.) (Kim and Nriagu, 2000).

This work proposes a pre-treatment step for oxidizing arsenic with a gaseous oxidant using membrane contactors. Figure 1 shows the process setup.

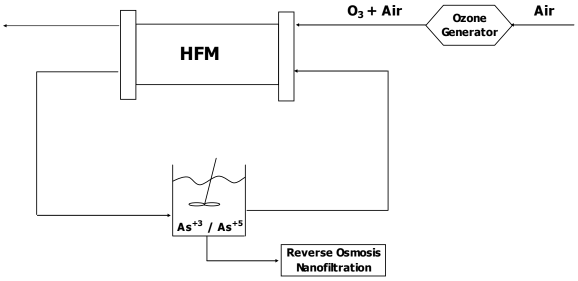

Fig 1. Process setup

To analyse the process viability, a mathematical model that describes the process behaviour has been developed to simulate the kinetics of the oxidation of As(III) to As(V). The influence of the operation variables in the oxidation kinetics has been analyzed by means of process simulation using Aspen Custom Modeler 11.1.

The work aims at the development of process intensification and integration strategies analysing the replacement of traditional processes by innovative alternatives able to bring substantially decrease of equipment size, energy consumption, or waste generation increasing at the same time the process flexibility and modularity (Bringas et al., 2006).

3. Acknowledgements

Financial support from projects CTQ2005-02583/PPQ and CTQ2006-14360/PPQ (MEC, Spain) and the SOCRATES-ERASMUS program is gratefully acknowledged.

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Optimization of integrated reaction/separation processes for the kinetic resolution of rac-1-phenylethanol using supported liquid membranes based on ionic liquids

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1. Summary

In the present study, a lipase-catalysed reaction has been combined with a supported liquid membrane based on ionic liquids to achieve the selective separation of a racemic mixture. The performance of the membrane bioreactor containing an SLM based on ionic liquids for the kinetic resolution of racemic 1-phenylethanol by transesterification with a vinyl ester catalysed by a commercial immobilized *Candida antarctica* lipase B (CALB) was analysed. More specifically, the effect of various process variables including the nature of the liquid membrane phase, the enzyme concentration in the feed compartment and the nature of the vinyl esters used as acyl-donor on the separation efficiency were investigated.

Keywords: integrated reaction/separation processes, supported liquid membranes, kinetic resolution, rac-1-phenylethanol, ionic liquids.

2. Extended Abstract

Enantiopure compounds have undoubtedly gained a vital role in the develop of modern chemical technology. From among many methods for obtaining such enantiomerically pure compounds, the processes performed in the enzymatic membrane reactors are considered as especially useful [1]. These reactors integrate the enantioselective catalytic action of the enzyme and the selective permeability of the compounds. The use of room temperature ionic liquids (ILs) as an immobilized phase in a supporting membrane is particularly interesting due to the non-volatile character of the ILs and their solubility properties in the surrounding phases, which makes it possible to obtain very stable supported liquid membranes without any observable loss of the IL to the atmosphere or the contacting phases [2].

In this work, the kinetic resolution of (rac)-1-phenylethanol by transesterification with vinyl esters catalysed by a commercial immobilized *Candida antarctica* lipase B was succesfully carried out in a membrane bioreactor containing an SLM based on ionic liquids. This system integrated the enantioselective catalytic action of the enzyme and the selective permeability of the compounds through the SLM. Various process variables were investigated in order to optimize the integrated reaction/separation process. After testing six different ILs for use as liquid membrane phase, the SLM based on [bmim$^+$][BF$_4^-$] was seen to be the most suitable SLM for the selective separation of the compounds involved in the transesterification reaction. The effect of enzyme concentration in the feed compartment on the efficiency of the process was also analyzed, and an increase in the efficiency was observed with increasing concentrations of the enzyme (Figure 1). Our results also showed that the greatest efficiency in the process was achieved with the longest vinyl esters, vinyl laurate. With this ester, after 24 h of operation, the (S)-phenylethanol is nearly completely separated in the receiving phase (Figure 2).

In conclusion, our investigations demonstrate that the coupling of lipases with an SLM based on IL provides a promising basis for the development of environmentally friendly methodologies for practical production of enantiomerically pure or enriched compounds.

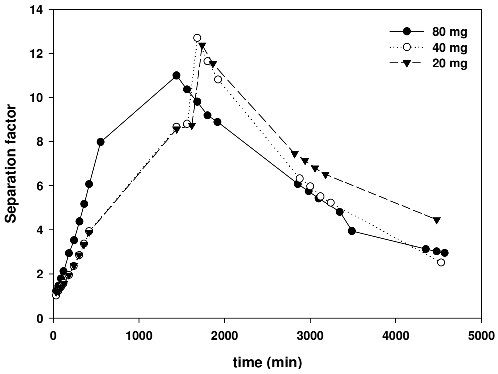

Figure 1. Evolution of the separation factor ($\alpha_{S/R}$) with time for different concentrations of enzyme in the feed compartment.

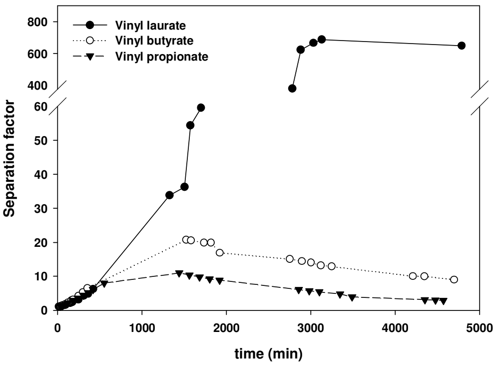

Figure 2. Evolution of the separation factor ($\alpha_{S/R}$) with time for different vinyl esters used as acyl donors in the transesterification

Acknowledgment

This work was partially supported by the CICYT CTQ2005-09238/PPQ grant. A. P. de los Ríos and F.J. Hernández-Fernández have fellowships from the Spanish Ministry of Education and Science and the University of Murcia, respectively.

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Copenhagen, 16-20 September 2007

Pilot plant analysis of an integrated process for the treatment of landfill leachates

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1. Summary

The treatment of a biologically stabilized landfill leachate, collected from a municipal landfill located in northern Spain (Cantabria), by an integrated system (Fenton + neutralization + ultrafiltration) was carried out in a pilot plant scale. The influence in Fenton reaction of different parameters such as H_2O_2/COD and H_2O_2/Fe(II) mass ratios, reaction time and the effect of the neutralization and ultrafiltration (UF) processes was investigated. The Fenton's stage was the most important to degrade organic compounds whereas neutralization and UF processes resulted in a further removal of residual COD due to precipitation and separation phenomena. The COD removal efficiency after this treatment was up to 75 %. Colour (>90 %), suspended solids (>95 %) and iron removal were achieved in the final effluent.

Keywords: advanced oxidation processes, Fenton's reagent, landfill leachate, membrane ultrafiltration

2. Extended Abstract

Landfill is one of the most widely employed methods of disposing of municipal solid wastes (MSW). About 57 % of the total MSW generated in the USA in 2000 was disposed of in landfills (Kurniawan et al., 2006). One of the most serious environmental problems related to landfill is the generation of leachates. These aqueous effluents contain large amounts of organic compounds, heavy metals, ammonium and inorganic salts. Consequently, landfill leachates need to be treated to meet the quality standards before discharge.

The use of Advanced Oxidation Processes (AOPs) is a promising alternative for wastewater remediation, mainly due to the capacity to improve the removal of recalcitrant organic compounds or to transform them into more easily biodegradable substances (Wang et al., 2003). Fenton´s reagent (Fe^{2+}/H_2O_2) is one of the most common AOPs. To complete the treatment, neutralization and sludge separation are required. However, when compared with bench scale research, the reported applications on pilot plant scale are scarce (Zhang et al., 2006).

The aim of this work is to analyse and operate a pilot plant of an integrated process for the treatment of landfill leachates that combines Fenton oxidation and ultrafiltration with submerged membranes evaluating the efficiency in the reduction of organic matter expressed as COD.

The leachate came from a municipal landfill site located in northern Spain (Cantabria). It generated 800 m^3 app. leachate/day. After biological treatment, the average COD concentration was 900 - 1500 mg/L. The plant consisted of a 100 L Fenton reactor, a 250 L neutralization tank and a ZeeWeed 10 ultrafiltration unit (Zenon) equipped with an immersed hollow-fiber membrane module of 0.93 m^2 surface area (*Figure 1*). Fenton oxidation was carried out during 60 minutes of reaction time at pH = 3 and different reagents dosages were studied (*Figure 2*). Neutralization at pH = 7 was performed either with NaOH or $Ca(OH)_2$. Submerged membranes worked with a permeate flow up to 50 L/h without fouling problems with an amount of total solids in the tank higher than 3.5 g/L. Reductions up to 75% COD and total colour removal were achieved. Organic acids were identified as main refractory compounds after the treatment.

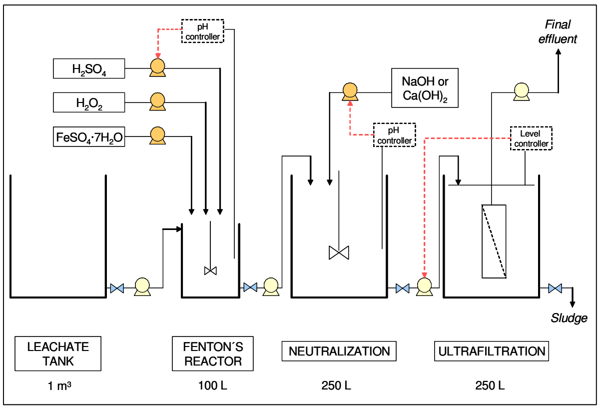

Figure 1. Pilot plant scheme.

The results obtained in the operation of the pilot plant show the efficiency of the integrated process, Fenton´s oxidation in combination with submerged ultrafiltration membranes, in the remediation of landfill leachates.

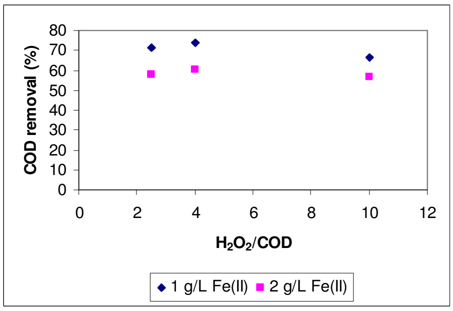

Figure 2. Influence of reagents doses in Fenton reaction.

Acknowledgments Financial support from the Spanish Ministry of Environment (project 546/2006/2.2-5) is gratefully acknowledged.

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Copenhagen, 16-20 September 2007

Kinetic resolution of rac-1-phenylethanol in a stirred tank bioreactor in ionic liquid/supercritical carbon dioxide biphasic systems

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1. Summary

In this work, the kinetic resolution of rac-1-phenylethanol in a stirred tank bioreactor in ionic liquid/supercritical carbon dioxide biphasic systems at 70ºC and 100 bar was studied. In these systems, a commercially immobilized *Candida antarctica* lipase B (Novozyme 435) was coated with two different ionic liquids: (i) $[bmim^+][PF_6^-]$ and (ii) $[bmim^+][BF_4^-]$ and then introduced into the tank. The efficiency of the catalytic action was analyzed by means of three parameters: the synthetic rate, the selectivity (ratio between the synthetic rate and the hydrolytic rate) and the enantioselectivity. Furthermore, in order to get a better understanding of the mass transfer phenomena involved in this process, the solubility, the diffusion rate and the liquid-liquid equilibrium data of the substrates and products were analysed.

Keywords: kinetic resolution, rac-1-phenylethanol, ionic liquids, supercritical carbon dioxide, lipase.

2. Extended Abstract

There is a continuing interest in developing new concepts for biphasic or phase-separable catalysis where a catalyst is immobilized in one liquid phase and the reactants and/or products reside largely in another liquid phase. One example is the combination of ionic liquids (ILs) and supercritical carbon dioxide ($scCO_2$). The different miscibilities of $scCO_2$ and ILs lead to two-phase systems that have found application in several areas [1,2]. The success of this two-phase system is based on solubility of $scCO_2$ in the IL but insolubility of the IL in the $scCO_2$.

This work studies the kinetic resolution of rac-1-phenylethanol in a stirred tank bioreactor in ionic liquid/supercritical carbon dioxide biphasic systems at 70ºC and 100 bar. A commercially immobilized *Candida antarctica* lipase B (Novozyme 435) coated with two different ionic liquids $[bmim^+][PF_6^-]$ and (ii) $[bmim^+][BF_4^-]$) was introduced into the tank reactor which was filled with $scCO_2$.

When room temperature ionic liquid/supercritical carbon dioxide biphasic systems were used the enantioselectivity of the process was > 99.9% and the selectivity about 90% in both cases. However, the synthetic activity decreased compared with supercritical carbon dioxide assayed in absence of ILs, probably due to the mass-transfer limitations across the IL-layer around the biocatalyst, being much smaller for the water-miscible ionic liquid, $[\text{bmim}^+][\text{BF}_4^-]$.

The solubility, the diffusion rate and the liquid-liquid equilibrium data of the substrates and products (rac-1-phenylethanol, rac-1-phenylethyl propionate, propionic acid, vinyl propionate) were also studied in order to get a better understanding of the mass transfer phenomena involved in this process. Liquid-liquid equilibrium data has been obtained for mixtures of IL+n-hexane+solute, where hexane has been used as reference solvent because its solvent capability may be comparable to that in supercritical carbon dioxide in mild operating conditions. This study also could allows us to design integrated reaction-separation processes using ionic liquids as reaction media and supercritical carbon dioxide as extractor solvent.

Acknowledgment

This work was partially supported by the CICYT CTQ2005-09238/PPQ grant. A. P. de los Ríos and F.J. Hernández-Fernández have fellowships from the Spanish Ministry of Education and Science and the University of Murcia, respectively.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Structured catalyst based on sintered metal gibres for 3-phase hydrogenation: design of compact reactor

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1. Summary

We report herein an innovative design of staged bubble column reactor (SBCR) with structured catalyst based on sintered metal fibers (SMF) applied for 3-phase hydrogenation. The SMF catalysts are used as thin (0.4 mm) porous sheets where each metallic fiber is coated by a thin ZnO layer. As the diameter of a single metal fiber is in a micrometer range (10-20 μm), mass transport limitations are avoided. The open SMF structure possesses a high porosity >80% allowing easy passage of reactants without high pressure drop. Each SMF catalytic stage acts also as micro-mixer enhancing bubble redistribution and facilitating H_2 transport. Furthermore, the high thermal conductivity of metallic SMF ensures isothermal conditions on the catalyst surface for highly exothermic hydrogenation reactions. Due to the efficient heat management, a high ratio of catalyst to substrate is admitted leading to the process intensification.

The hydrodynamic characteristics of the SBCR, like the pressure drop and residence time distribution, were investigated varying superficial liquid and gas velocities for different gas/liquid systems. A semi-empirical model has been developed for describing the influence of superficial fluid velocities as well as gas and liquid physical properties on the pressure drop during the SBCR operation and was found consistent with experiments.

Keywords: staged bubble column reactor, three phase hydrogenation, sintered metal fibers, structured catalyst

2. Extended Abstract

A novel approach in the three phase reactor engineering is based on the use of structured catalytic materials. Recently we suggested fiber catalysts in the form of woven cloths for the staged bubble column reactors (SBCR) [1]. Glass and activated carbon fiber cloths have shown promising results in SBCR, but their low rigidity complicates their use. Another problem for the reactor design is related to the heat removal since hydrogenations are highly exothermic reactions. Precise temperature control is required to achieve high selectivity and to prevent run-away.

We report herein an innovative design of staged bubble column reactor (SBCR) with structured catalyst based on sintered metal fibers (SMF) coated by a thin ZnO layer. The liquid phase hydrogenation of C-C triple bond of acetylenic alcohol was taken as a model reaction. The high thermal conductivity of metallic SMF ensures isothermal conditions on the catalyst surface during the reaction.

To explore the potential of the SMF-based catalyst for 3-phase reactions, we address a study of the hydrodynamics (pressure drop and backmixing characteristics) in a SBCR staged with SMF layers. To characterize the backmixing, the residence time distribution (RTD) was determined for various gas- and liquid superficial velocities for the system water/air. The pressure drop was measured using SMF layers both with and without ZnO coating. The influence of liquid properties (viscosity & liquid/gas surface tension) and the distance between the layers on the pressure drop is determined for various gas/liquid superficial velocities. The liquids used in this study cover a broad range of viscosities and surface tensions for both aqueous and organic reaction systems. The frictional pressure drop over SMF layers was found to depend mainly on the gas velocity, u_{G0} and the gas-liquid surface tension. The influence of liquid superficial velocity is relatively small. A semi-empirical model to predict the pressure drop over SMF layers within the SBCR was developed. The model data obtained for various liquids were consistent with experiments. A narrow residence time distribution (RTD) was obtained in the SBCR and described by a tanks-in-series model. The low pressure drop and narrow RTD suggest the SMF-based structured catalysts as suitable for SBCR applied in continuous three phase hydrogenations.

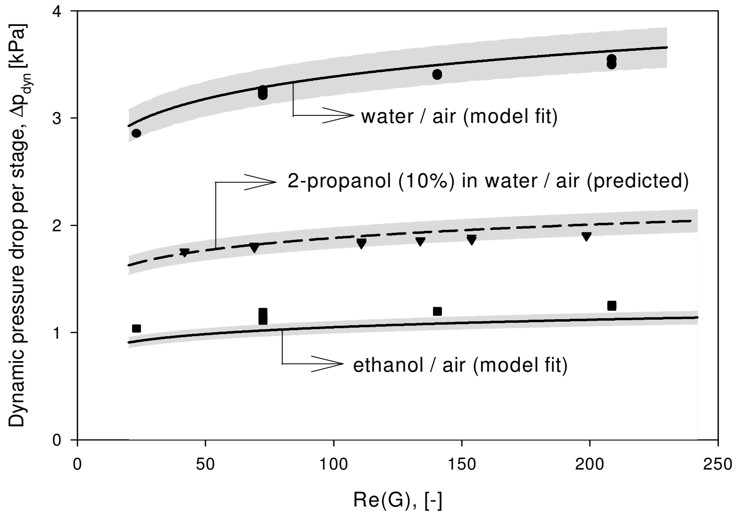

Figure: Dynamic pressure drop per SMF stage (reactor with 8 SMF layers) for different liquids

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Copenhagen, 16-20 September 2007

Simulation study of membrane supported oxidation of methane with simultaneous steam reforming using O_2-selective Perowskite hollow fibres

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1. Summary

Considering a new type of mixed conducting hollow fibre Perowskite membranes the operating behaviour of a membrane reactor integrating the process steps air separation, selective O_2 transfer in the membrane and oxidation of methane with simultaneous steam reforming was investigated theoretically. Different arrangements of the used catalyst in the membrane reactor were evaluated in a broad range of operation conditions by means of reduced 1D and detailed 2D reactor models.

Keywords: Synthesis gas, Perowskite hollow fibres, membrane reactors, modelling

2. Extended Abstract

The generation of synthesis gas from methane is currently performed by conventional steam reforming or by partial oxidation (POX) in fixed-bed reactors using nickel or noble metal based catalysts at temperatures around 900°C. In the last years several new reactor concepts were suggested to improve in particular the heat exchange, e.g. auto thermal reformers, catalytic coated wall reactors, fluidised bed or membrane reactors [1]. Improved POX of methane is currently a very promising direction for better generation of synthesis gas, in particular if oxygen is fed in a distributed manner separated from air using O_2-selective mixed conducting membranes. The industrial applicability of this concept depends on the availability of suitable selective tubular membranes characterised by thin walls to intensify the mass and heat transfer. In addition to the desired slightly exothermic partial oxidation in such reactors also the highly exothermic total oxidation can take place. The related heat generation can be exploited by coupling with conventional endothermal steam reforming to realise an auto thermal operating mode. Based on experimental results characterising a new type of mixed conducting hollow fibre membranes ($BaCo_xFe_yZr_zO_{3-\delta}$, BCFZ, produced by spinning) the operating behaviour of a membrane reactor integrating the process steps air separation, selective O_2 transfer in the BCFZ and oxidation of methane with simultaneous steam reforming was evaluated. The estimation and validation of mass transfer parameters for characterisation of the membrane was based on results of systematic experiments [2]. The derived equations describing the mass transport in the membrane as well as kinetic approaches for the rates of oxidation and steam reforming of methane coming from the literature [3,4,5] were implemented in a detailed two dimensional pseudo homogeneous reactor model. Comparing with predictions of a reduced 1D model this model was found necessary for a detailed analysis of the pronounced concentration, temperature and velocity fields. The fibre membrane is placed in a reactor housing and separates the reactor in an air providing side (tube) and synthesis gas side (shell). The following arrangements of the used catalyst in the membrane reactor were investigated: a) catalyst bed, b) catalyst coated hollow fibre, c) structured catalyst bed, d) hollow fibre and catalyst separated by an additionally Al_2O_3 membrane. Depending on the catalyst arrangement hot spot obtained can be located directly on the membrane, which leads under unfavourable operation conditions to an inactivation or melting of the hollow fibre. In figure 1 are illustrated configurations of the membrane reactor with a catalyst bed (a) and a catalyst coated hollow fibre (b). Additionally, the complex temperature fields are depicted for the considered reactor configurations as predicted with the reduced 1D (c) and detailed 2D models (d, e). It will be shown that the essential temperature effects and the performance of the investigated concept can be described only using the more detailed two dimensional reactor model.

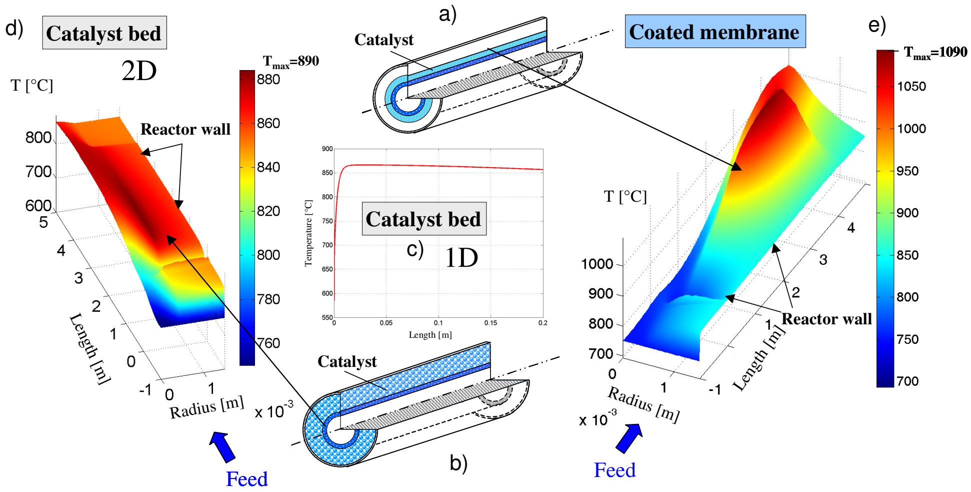

Figure 1: Membrane reactor set up investigated (a and b) and temperature profiles predicted using 1D (c) and 2D models (d,e)

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Reactor model for the selective catalytic reduction of NO over Ag/Al_2O_3 in a gas-phase microreactor

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1. Summary

A 2-D reactor model for the selective catalytic reduction of NO over a silver/alumina catalyst at atmospheric pressure and temperature range of 100-500 ºC has been developed. The model includes the dispersion before and after the microchannels, which showed to be great importance. The dispersion added by the analyzing device (Mass Spectrometer) was taken into account in the final expression and explained. CFD calculations were also carried out in order to predict the flow behavior inside the microchannels. These results were further compared to the prediction of the mathematical model. Both CFD calculations and the presented mathematical model were validated against experimental data obtained in the microreactor.

Keywords: Microreactor, reactor model, HC-SCR, Ag/Al_2O_3

2. Extended Abstract

During the last few years, microreactors and microflows have attracted a lot of interest in science. Microdevices for laboratory testing offer new opportunities for kinetic studies and new fabrication techniques and materials have been developed recently for process intensification. Due to higher mass and heat transfer capabilities, microreactors permit an improved heat transfer and control of the reaction conditions compared to those in industrial-scale reactors. In order to design and use microdevices accurately for research and later on for industrial purposes, the behaviour of the gas flow of reactants and products inside the microchannels has to be characterized and explained. New methods must be developed for predicting and describing this flow.

Recently, strong environmental policies have arisen and it has become compulsory to drastically reduce the emissions of pollutants from mobile and stationary sources.

This work presents a two-dimensional mathematical model which describes the behaviour of the gas flow inside the microchannels of a microreactor with two inlets (A and B, Figure 1) for the selective catalytic reduction of NO using octane (HC-SCR) on Ag/Al_2O_3 catalyst. The microchannels were previously coated with alumina and further impregnated with silver. The catalyst was characterized by means of Laser ablation – Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS) and Scanning Electron Microscopy (SEM). The activity of the catalyst was investigated at temperatures varying from 100-500 ºC and hydrogen-to-NO ratio from 1 to 7. These experimental results were compared to those predicted by the reactor model proposed and a good agreement was obtained. The presented model explains the performance of the gas flow in the HC-SCR reaction. It is demonstrated that most of the dispersion takes place at the inlets (A and B) and outlet of the microreactor (C), while there is almost no dispersion inside the microchannels. The dispersion effect added by the measuring device (mass spectrometer) was calculated and taking into account in the relevant term of the expression.

Finally, computational fluid dynamics (CFD) calculations were done with the actual reactor geometry and the results were compared to the offered model.

The final expression of the model allows us to mathematically describe the gas flow inside the microchannels predicting the behaviours of various reactions of industrial interest.

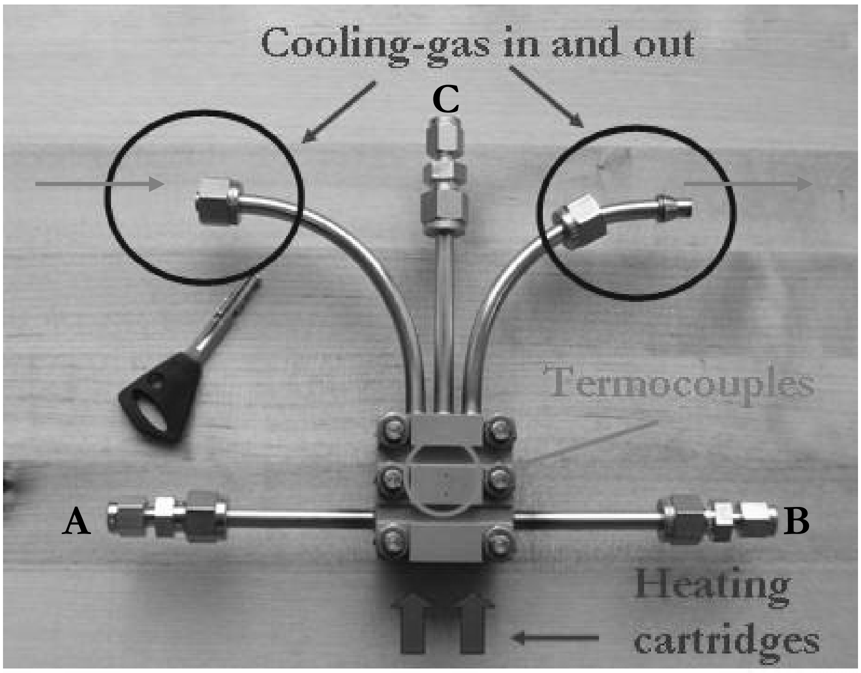

Figure 1. Upper view of the Microreactor

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Experimental analysis of the liquid hold-up contributions in catalytic packing Katapak-SP

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1. Summary

The liquid hold-up represents a key hydrodynamic parameter for a deep understanding of the reactive distillation column performances. The modular structure of the new generation catalytic packing Katapak-SP, manufactured by Sulzer Chemtech, provides an elevated flexibility in the process applications but complicates the design and the inner flows distribution. The estimation of the different liquid holdup contributions for this packing is therefore a challenging task and, in the present work, the results of this investigation are reported.

Keywords: catalytic structured packing, liquid hold-up, Katapak-SP

2. Abstract

The implementation of heterogeneous catalysis in reactive separation columns, motivated by the possibilities of numerous advantages, has however introduced a complexity in the design and the performance of internals. Catalytic internals have to satisfy the requirements of chemical reaction, separation and capacity. Among the most promising internals are the so called structured catalytic packings, which combine the advantages of a structured packing with the features of a catalyst support. Adequate knowledge and understanding of the complex hydrodynamics occurring in the internals and of their mass- and heat- transfer behaviour are needed as they are key element both for the design and reliable scale-up of reactive separation processes. This contribution presents the experimental investigation on the liquid holdup for Katapak-SP, the new generation structured catalytic packing manufactured by Sulzer Chemtech. The packing consists of MellapakPlus type sheets ("separation elements") and wire-gauze catalyst bags ("reaction elements") assembled in alternate sequence (Figure 1). This modular configuration provides a high flexibility varying the separation to reaction zones rate. Depending on the process, it is possible to enhance the distillation over the reaction working with Katapak-SP 12, which is characterised by two layers of MellapakPlus for each catalyst bag, while in Katapak-SP11 the separation to reaction rate is 1:1.

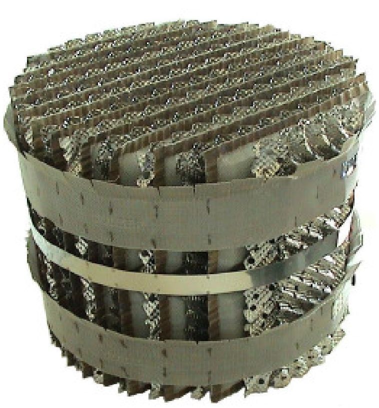

Figure 1: Structure of Katapak-SP 11manufactured by Sulzer Chemtech

The geometrical structure strongly influences the behaviour of the flows inside the column and consequently the overall column performances. The external wire gauze of the catalyst bags allows the liquid flow penetration and prevents the gas crossover, limiting the use of this catalytic packing only to applications with liquid phase reaction. The liquid hold-up inside the catalyst bags is therefore the parameter influencing the reactive performance of the internal. The liquid hold-up in the reaction zone is given by the sum of two contributions, a static fraction and a free draining part, while the liquid hold-up on the MellapakPlus layers is only dynamic. The latter part of the liquid hold-up is responsible of the interaction with the gas and of the related pressure drop in the column.

Different techniques have been used to determine the various contributions to the overall packed bed liquid hold-up and a standardized experimental procedure has been tested. The behaviour of this new generation packing has been investigated and compared with the performances of other packings reported in literature. The results of this work are useful for supporting on-going efforts to develop fundamental packing design models.

Acknowledgement

We acknowledge the financial support provided by the European Commission within the 6th Framework Programme, Project "INSERT Integrating Separation and Reaction Technologies"; Contract-No: NMP2-CT-2003-505862.

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Copenhagen, 16-20 September 2007

Simulation of a novel water gas shift reactor with CO_2-selective hollow fiber membrane module

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1. Summary

This work focuses on the simulation of a water gas shift reactor based on a CO_2-selective hollow fiber membrane with different gas flow direction (i.e., co-current and counter-current flow). A one-dimensional and non-isothermal model of the membrane reactor is used to investigate the reactor performance with respect to various operating parameters including sweep-to-feed ratio, reactor length, number of hollow fiber and feed-side pressure. The simulation results have shown that the membrane reactor can remove more CO and obtain high-purity H_2 product, compared with a conventional fixed bed reactor. It is also found that the membrane reactor with counter-current gas flow direction is more effective than that with co-current gas flow.

Keywords: water gas shift reaction, membrane reactor, hollow fiber membrane, simulation

2. Extended Abstract

The production of high-purity hydrogen from hydrocarbon fuels is essential for fuel cell applications, especially in proton exchange membrane fuel cells which require hydrogen feed with low CO level in order to avoid poisoning of the anode catalyst (Wee and Lee, 2006). In general, CO can be eliminated from the hydrogen-rich synthesis gas via a water gas shift (WGS) reaction. However, the WGS reaction of CO with H_2O is an equilibrium reaction, resulting in a limited conversion when a conventional fixed bed reactor is employed. A promising approach is the use of a membrane reactor that combines reaction and product separation through a selective membrane. Many previous researches have considered the application of Pd-based hydrogen selective membranes to enhance the efficiency of the WGS process (Basile et al., 2001; Barbieri et al., 2005). In comparison of the membrane reactors with different types of membrane, a CO_2 selective membrane reactor offers advantages in obtaining a high purity H_2 product at high pressure. However, few research works are carried out to investigate the performance of the CO_2 selective membrane reactor.

2.1. Model of CO_2 Selective Membrane Reactor

A WGS reactor based on a CO_2-selective hollow fiber membrane module with commercial Cu/ZnO as catalysts is shown in Fig. 1. By performing mass and energy balances on feed and sweep sides, the following equations are obtained.

Feed side:

$$\frac{dn_{fi}}{dz} = \frac{1}{4}\pi d_{in}^2 r_{CO} - \pi d_{in} J_i$$

$$\sum_{i=1}^{n}(n_{fi}c_{pfi})\frac{dT_f}{dz} = \frac{1}{4}\pi d_{in}^2 r_i \Delta H_r$$

$$-\pi d_{in}(U_i + c_{pCO_2}J_{CO_2} + c_{pH_2}J_{H_2})(T_f - T_s)$$

Sweep side:

$$\frac{dn_{si}}{dz} = \pm\pi d_{in} J_i$$

$$\sum_{i=1}^{n}(n_{si}c_{psi})\frac{dT_s}{dz}$$

$$= \pm\pi d_{in}(U_i + c_{pCO_2}J_{CO_2} + c_{pH_2}J_{H_2})(T_f - T_s)$$

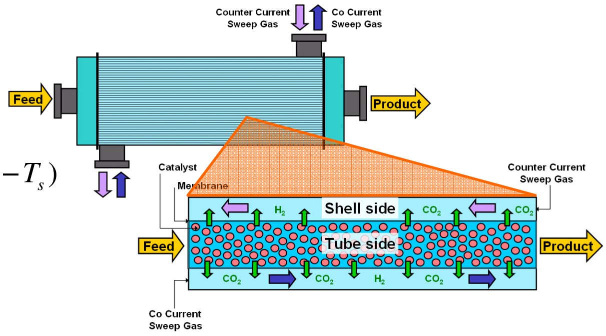

Fig. 1 Schematic diagram of a water gas shift hollow-fiber membrane reactor.

2.2. Simulation Results and Discussion

From simulation results, it is found that both a CO_2-selective WGS membrane reactor operated in both the counter-current and co-current modes can decrease more CO compared with a conventional fixed bed reactor and at the same time, remove CO_2 along the reactor length, thus obtaining the high-purity H_2 product. The performance analysis of the two configurations of the reactor with respect to operating parameters, i.e., sweep-to-feed ratio, reactor length, number of hollow fiber, and feed-side pressure, shows a similar trend, even though the reactor with the counter-current mode provides better performances. Increasing the sweep-to-feed ratio decreases CO due to the increased permeation driving force. As the reactor length or the number of hollow fiber increases, the concentration of CO decreases due to the permeation area is increased. The results also present that the operation of the reactor at high feed-side pressure decreases the exit CO concentration since CO_2 can more permeate from feed side.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Comparison of periodically forced reactor networks with different switch strategies

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1. Summary

The effect on the stability for two different switch strategies of a Loop Reactor is studied by comparing the stability range of the periodic regimes as the switch time is varied for different values of the feed temperatures. This analysis is conducted by a numerical continuation technique based on the spatio temporal symmetry of the forced system. A physical interpretation of the bifurcation analysis is given an the basis of the spatio-temporal temperature patterns.

Keywords: Loop Reactor, bifurcation analysis, periodically forced fixed bed reactors

2. Extended Abstract

Autothermal catalytic combustion in packed beds is often used to decontaminate polluted Volatile Organic Compounds (VOCs). Several studies have shown that autothermal catalytic combustion can be efficiently carried out in periodically forced reactor networks also called loop reactors (LR). Networks of two or more catalytic beds reactors are a promising alternative to overcome washout problems typical of Reverse Flow Reactors (RFRs). In such a configuration, the dynamic regime is reached by periodically varying the feed position according to a cyclic permutation of the reactor sequence. The range of stable operating conditions is here found to depend on the specific switch strategy applied. In this work the dynamics of three catalytic fixed bed reactor network where an exothermic irreversible reaction takes place is studied. Two different switch strategy are investigated. In both cases a cyclic permutation of the feed/discharge order is implemented. For the strategy 1 the permutation is 1-2-3, 2-3-1, 3-1-2; for the strategy 2 is 1-2-3, 3-1-2, 2-3-1. The effect of the switch strategy on the stability is studied by comparing the stability range of the T-periodic regimes as the switch time is varied for different values of the feed temperatures. This analysis is conducted by a numerical continuation technique based on the spatio temporal symmetry of the forced system (Russo et al. 2002).
Left and central figures show solution diagrams for both strategies with the switch time (τ) as the bifurcation parameter. In these solution diagrams the locus of T-periodic regimes is shown. For both strategies the ignited (high conversion) solutions form an isola bounded by two catastrophic saddle node bifurcation points: S_1 (at τ=1386) and S_2 (at τ=3950) for strategy-1 and S'_1 (at τ=2810) and S'_2 (at τ=7900) for

strategy-2. When the switch time is increased above τ_{S2} (or $\tau_{S'2}$), forcing is not able to sustain autothermal operation anymore, and, correspondingly, no high conversion solution is found. Conversely, for switch times lower than τ_{S1} (or $\tau_{S'1}$), T-periodic ignited solutions disappear but the system still possesses ignited solution until τ approaches to zero, which are stable multi-periodic, quasi-periodic and chaotic regimes. The most important difference of the solutions diagrams is the significantly larger stability range (almost doubled) of T-periodic ignited solutions for the strategy-2 with respect to that predicted for strategy-1. The results agree with the analytic criteria of Sheintuch and Nekhamkina (2005).

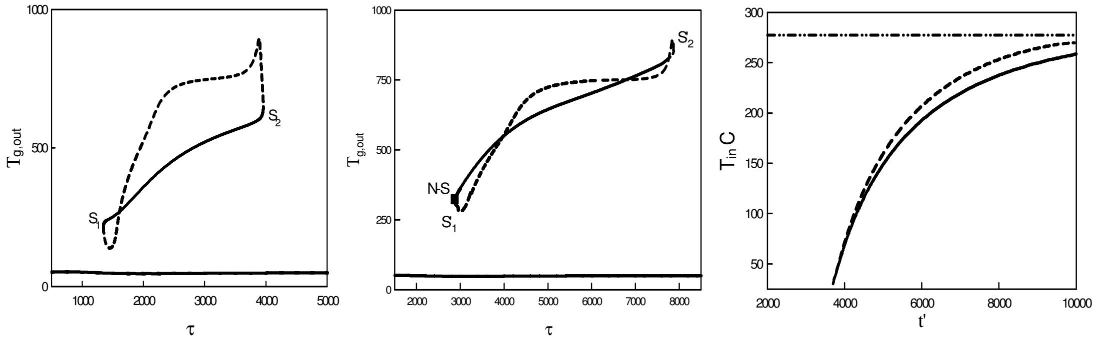

Figure. Left and Center: The symmetric T-periodic solution diagram with the switch time, t, as bifurcation parameter at Tin=60 C for strategy-1(left) and strategy-2 (center); solid lines: stable T-periodic regimes; dashed lines: unstable T-periodic regimes. Right: Bifurcation diagram, as bifurcation parameters the inlet temperature Tin and the switch time t'; the solid curve represent the locus of saddle-node bifurcation S_2, the dashed curve represent the locus of saddle-node bifurcation S_2'; the dashed-dotted line is the asymptotic behavior for the unforced network.

A mismatching with the analytic criteria of Sheintuch and Nekhamkina (2005) occurs as the inlet temperature is increased. The values at which the saddle node S_1 (and S_1') occurs is not affected by the inlet temperature, whereas the saddle-node bifurcations S_2 and S_2' (right figure) depend on T_{in}. Right figure shows the loci of the two saddle node points in the plane T_{in}-τ' for both switch strategies. Note that in order to compare more easily the two strategies we used a normalized switch time $\tau'=\tau/2$ so that its value is strategy independent. It is apparent that at low inlet temperatures the two curves in the right figure overlap, thus confirming the doubling of the limiting conditions as the strategy changes from 1 to 2. As T_{in} increases, the two curves separate, showing a reduction with respect to the factor 2. Analyzing the temperature spatio-temporal patterns in three fixed beds the results are motivated by the external heat losses.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Kilogram scale production of *trans*-1,4-cyclohexane dicarboxylic acid via continuous thermal epimerization

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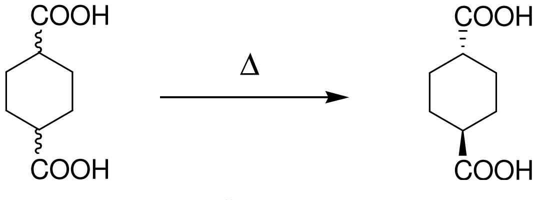
1. Summary

A simple, scaleable, continuous process for the production of *trans*-1,4-cyclohexanedicarboxylic acid using a custom thermal tube reactor system has been developed. This continuous process avoids the use of a solid-melt process using costly specialized processing equipment.

Keywords: pharmaceutical synthesis, continuous reaction, thermal epimerization

2. Extended Abstract

The process for the thermal epimerization of 1,4-cyclohexanedicarboxylic acid (CHDA) as described in the patent literature[1] involves a thermal epimerization of crude CHDA that contains primarily *cis*-1,4-cyclohexane dicarboxylic acid (*cis*-CHDA at a temperature higher that 180 °C but lower than the melting point of *trans*-1,4-cyclohexane dicarboxylic acid (*trans*-CHDA). The *trans*-CHDA is then isolated by melt-crystallization. Such melt crystallizations require expensive, specialized equipment when run on pilot plant scale.



Scheme 1

An alternative process has been developed in which a solution of crude CHDA in *N*-methyl-2-pyrrolidinone (NMP) is pumped continuously through a coiled tube reactor (Figure 1) in an oven at 300 °C and 250 psi back-pressure to affect the epimerization. Water is then added to the bulk product solution, crystallizing the desired *trans*-CHDA in high yield and purity.

While this process also uses specialized equipment, it is relatively inexpensive and no significant changes need to be made in order to increase the throughput.

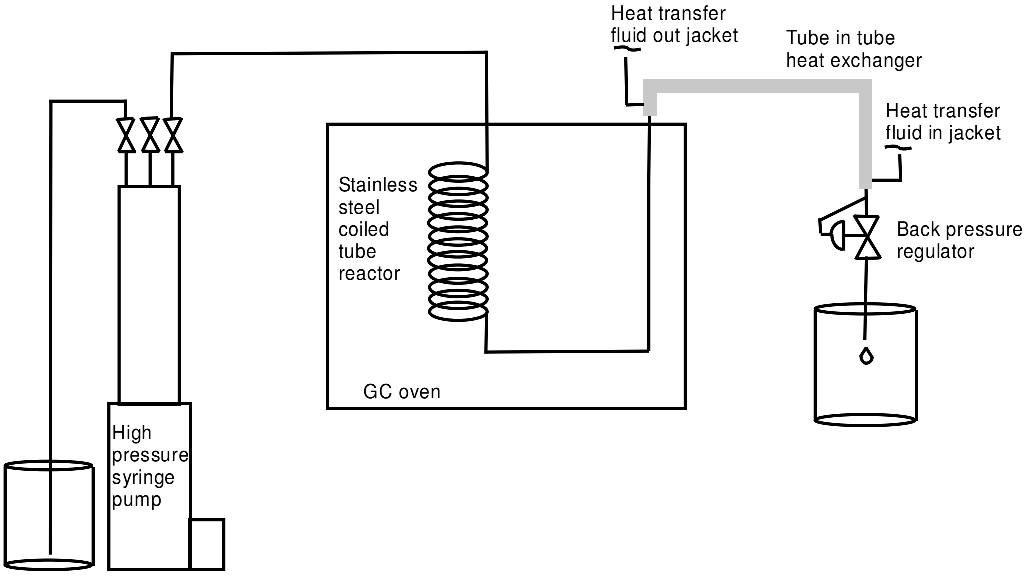


Figure 1

This poster describes the development, optimization and implementation of this continuous process, allowing the production of kilogram quantities of *trans*-CHDA.

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European Congress of Chemical Engineering (ECCE-6)
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A Continuous Newman-Kwart rearrangement reaction using supercritical glyme

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1. Summary

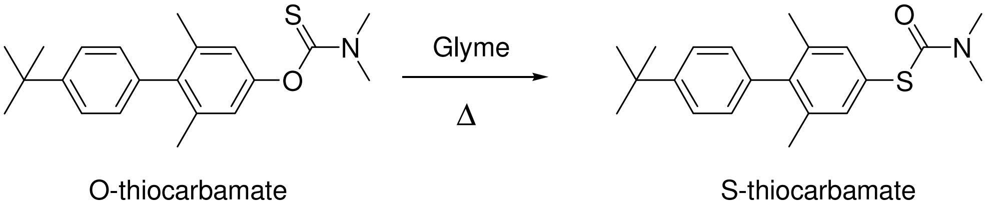
A simple, continuous Newman-Kwart[1] rearrangement reaction using a custom thermal tube reactor system has been demonstrated. On 200 gram scale the process was carried out in supercritical glyme under 280-300°C at > 70 bar to afford a 92% yield in 4 hours.

Keywords: pharmaceutical synthesis, continuous reaction, Newman Kwart rearrangement

2. Extended Abstract

A continuous process to perform a Newman-Kwart rearrangement has been reported in the literature[2]. These rearrangements were carried out at > 170°C using a high boiling solvent, tetraglyme or sulfolane. Operating at these very high reaction temperatures limits the solvent choice to generally high molecular weight solvents which can complicate the process as a result of poor solubility or difficulty with isolations. Applying pressure to the system permits the use of typical low boiling solvents which can facilitate higher throughput as a result of higher solubility and allows more flexibility with isolations.

The batch Newman-Kwart rearrangement of O-thiocarbamate to S-thiocarbamate in Scheme 1 was accomplished either neat or as a thick slurry in tetradecane at 250°C. The reaction yields were inconsistent at between 75 and 85% and the product quality was generally poor at ~ 90-95% purity.



Scheme 1

An alternative process has been developed in which a solution of O-thiocarbamate in glyme is pumped continuously through a coiled tube reactor (Figure 1) in an oven at 300°C and 70 bar back-pressure to affect the rearrangement. Critical temperature is 263 ºC and critical pressure is 570 psi [CRC Handbook]. Isolation is accomplished via solvent exchange into heptane to effect crystallization of the desired S-thiocarbamate in 92% yield and 99+% purity.

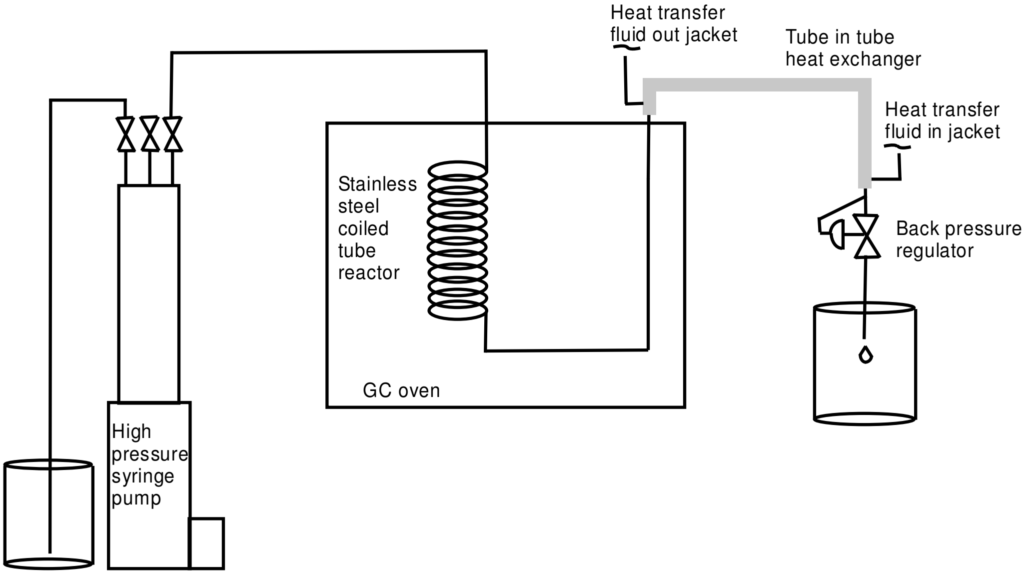


Figure 1

This poster describes the development and implementation of this continuous process, allowing the production of a Newman-Kwart product at a rate of 50 g/hour.

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Session S4-P-2: EPIC-1: Poster Session – II

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74	Intesification of the commercial run of deriving of isobutylene E Mammadov, R Kasimov, R Melikov, A Aliyev	No
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2124	Process Intensification for Optimal Retrofit of a Multicomponent Distillation Plant -A Real Industrial Case Study M Errico, B Rong, G Tola, I Turunen	Yes
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2867	Possibilities of process intensification using microwaves applied to catalytic microreactors U Kunz	No
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3294	Synthesis of heat-integrated distillation sequences in non-conventional processes F J M Neves, N M C Oliveira, F P Mendes	Yes
3444	Retrofit of Crude Distillation Unit Using Process Simulation and Process Integration M M Shanazari, F Shahraki, M Khorram	Yes

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Optimal Heat Exchanger Network Synthesis Including Heat Transfer Equipment Design

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1. Summary

This paper presents an optimisation model for the synthesis of heat exchanger networks (HEN) including the detailed design of the equipments formulated as a decomposition method. Shell and tube pressure drops and fouling are considered, as well as mechanical aspects, like shell and tube bundle diameters, internal and external diameter of tubes, number of tubes, number of baffles, number of shells, tube length, tube arrangement and the fluid allocation in the heat exchanger. The optimisation model is based on area, energy and pumping costs. The algorithm combines two distinct models, in a decomposition method, a Mixed Integer Non-Linear Programming (MINLP) superstructure simultaneous optimisation model for the heat exchanger network synthesis considering stream splitting, assuming isothermal mixing and a MINLP model for the detailed equipment design, following rigorously the standards of the TEMA. Two examples from the literature are used to test the algorithm developed, and the results confirm the achievement of the optimum HEN configuration with the detailed heat exchangers design, following the TEMA standards.

Keywords: Optimisation, heat exchanger network synthesis, heat exchanger design, Mixed Integer Non Linear Programming.

2. Extended Abstract

In this paper an algorithm for the synthesis of HEN including the detailed design of the equipments is proposed. It is based in a decomposition method that includes a MINLP model for the optimal synthesis of HEN and a MINLP model for the optimal design of a shell and tube heat exchanger design, following rigorously the standards of TEMA. The global annual cost objective function takes in account investment, utility and pumping costs. An initial HEN configuration is synthesized by using constant heat transfer coefficients, considering the possibility of stream splitting and assuming isothermal mixing. The equipments are designed and the individual stream film coefficients are calculated. With these values, a new HEN configuration is generated and its structure is compared with the first one. If it is different, the HEN equipments are designed and the global annual cost is calculated. The new heat transfer coefficients are calculated and the objective function is tested. If it is smaller than the anterior one, the procedure must continue. If not, the procedure must stop and the HEN with the smallest global annual cost is assumed as the best one.

Two examples were used to describe the algorithm applicability, comprising two different possibilities in the algorithm use. The final results obtained in this paper are more realistic than the presented in the literature, because of the TEMA standards, the use of Ft correction factor and the number of shells. In the second case, a big difference exists in the results obtained. The objective value is minor because of the large use of utilities in the solution presented in the literature. The heat exchangers most important variables in manufacturing the equipment are available. Moreover, the designed heat exchangers are rigorously in accordance with the standards of the TEMA. Certainly the tube length, jointly with the number of tubes, the number of shells and the heat exchangers configurations are the responsible for the differences in the compared results.

The algorithm presents always the best HEN configuration considering stream splitting, assuming isothermal mixing. It presents also the detailed heat exchangers design, rigorously according the Standards of TEMA.

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Biodiesel by catalytic distillation – towards sustainable fuels

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1. Summary

The properties of biodiesel as renewable fuel, as well as the problems associated with its conventional production processes are outlined. A novel sustainable process based on catalytic reactive distillation is proposed as alternative. The pros and cons of manufacturing biodiesel via fatty acid esterification using metal oxides as solid acid catalysts are investigated. The experimental findings are used for designing a continuous biodiesel production plant based on catalytic reactive distillation.

Keywords: reactive distillation, solid acids, green chemistry, sustainable fuels.

2. Extended Abstract

In the context of reduced availability of fossil fuel sources, sustainable energy management is a major concern that makes the urgent implementation of renewable fuels a crucial issue. Biodiesel is a sustainable alternative to petroleum diesel, with major environmental benefits and better performance – it is safe, renewable, non-toxic, biodegradable, sulfur-free and it is a better lubricant. Biodiesel can be produced from vegetable oils, animal fat or even recycled oil or greases from food industry. [1] It consists of fatty acid methyl esters (FAME), currently manufactured by either trans-esterification using liquid NaOH/KOH catalyst, or batch esterification of free fatty acids (FFA) using H_2SO_4 as catalyst. These catalysts are not only corrosive and toxic, but they can form unwanted soap with FFA, and require neutralization and an expensive separation of the salt by-product. The complete catalyst removal is imperative due to the EU restrictions on sulfur content in diesel fuels (< 15 ppm as of 2006). In addition, the large excess of alcohol has to be separated and recycled. All these extra operations make biodiesel an attractive but costly alternative fuel.

To solve these problems, we propose the replacement of the homogeneous acid catalyst with solid acids [2] and develop a sustainable esterification process based on catalytic reactive distillation. Solid acids can be easily separated from the biodiesel product; they need less equipment maintenance and form no polluting by-products.

The main challenge for a successful design is finding catalysts that are active, selective, water-tolerant and stable under the process conditions. In recent studies, we have screened a large number of zeolites, heteropoly-compounds, metal oxides, ion-exchange resins, and carbon-based solid acids.[3]

In this work, we focus on the application of metal oxides catalysts (based on niobia, zirconia, titania and tin oxide) in an integrated reactive-separation design that is able to shift the chemical equilibrium to completion and preserve the catalyst activity by continuously removing the products. The catalyst development was integrated in the process design at an early stage, by data mining and embedding of reaction kinetics in the process simulation. Rigorous simulations were performed using AspenONE suite.

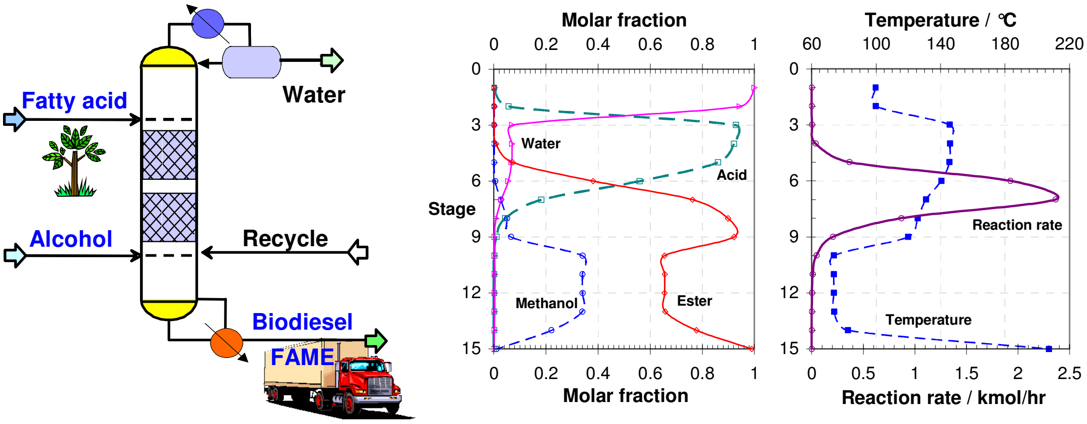

Figure 1. Catalytic reactive distillation column (RDC). Composition and temperature profiles in RDC.

The integrated design proposed in this work is based on catalytic reactive distillation, powered by metal oxides as solid acid catalysts for esterification. This alternative improves the economics and HSE benefits compared to conventional biodiesel processes, and reduces dramatically the number of downstream processing steps. The key major benefits of this approach are:

1. High conversions as chemical equilibrium is shifted towards completion.
2. Increased unit productivity (5-10 times higher than conventional processes)
3. No excess of alcohol required – stoichiometric reactants ratio at RDC inlet.
4. No catalyst neutralization step hence no salt waste streams are produced.
5. Sulfur-free fuel, since solid acids do not leach into the product.
6. Reduced capital and operating costs, due to less units and lower energy use.
7. Multifunctional plant suitable for a large range of fatty feedstocks.

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Multi-scale solids processing in Pharmaceuticals: batch to continuous

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1. Summary

Solids processing plants in pharmaceuticals face many operational problems. The need for short time to market and lack of full understanding of phenomena at particle and bulk solids scales have resulted in the domination by batch or semi batch modes of operation. The pharmaceutical industry receives intensive regulatory oversight by relevant authorities. This has increasingly focussed on process robustness and understanding. As a result of this, as well as the potential for significant performance improvements, there is a strong desire in the industry to move to continuous and more intensive manufacturing processes.

The aim of this research is to apply the concept of “multiscale design” to equipment selection and design procedures for various solids processes. This research presents a new approach to select and design the solids processing equipment as well as supporting the move from batch to continuous processing and revealing the knowledge gaps in the area.

Keywords: Multiscale processing, process intensification, solids processing, pharmaceuticals, batch to continuous

2. Extended Abstract

The IMPULSE [1] project aims at effective, targeted integration of innovative process equipment such as microreactors, compact heat exchangers, thin–film devices and other micro and/or meso-structured components, to attain radical performance enhancement for whole processes, thereby contributing to significant improvements in supply–chain sustainability for the chemical industry. Complete miniaturization or intensification of entire process systems is unrealistic and economically prohibitive, the multiscale design approach of IMPULSE provides intensification locally only in those parts of a process and on the time and length scale where it is truly needed and can produce the greatest benefit.

Relatively little has been done on the process system engineering of pharmaceutical solids processes, despite the economic significance of solid dosage forms. The approach within IMPULSE has been to bring more science into the field in order to establish useful links between various relevant length-scales, i.e. from plant size down to particle size. The focus is on matching the length scales presented by the equipment to the ideal length scales that give best process performance. This presents an alternative to the use of past experience and rule-based algorithms that are much prevalent in the field for the "design" of solids processes [2, 3]. It is also valuable in the identification of opportunities to move from batch to continuous processing.

In this work, underlying physics of solids handling and processing as well as algorithms of solids processing synthesis were studied; the IMPULSE philosophy was applied to equipment selection and design. A new methodology is proposed in which various critical decision-making issues in each unit should be identified and the relevant product specifications, operating conditions, parameters and solids properties and behaviours are linked to those steps, as illustrated in the Figure 1. A key feature of the approach is to match equipment capability for each operation to process need.

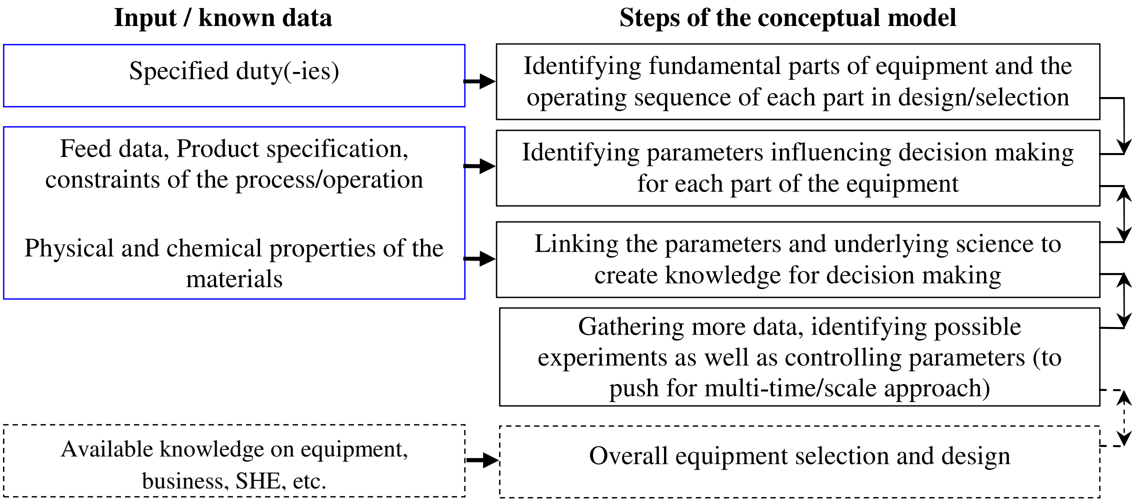

Figure 1: New model proposed for solids equipment selection and design; current research is on the boxes with solid lines; more steps may exist between dashed lines.

The conceptual model above was applied to equipment selection and design of a drying process, leading to better understanding of the process, linking various length scales, delivering more precise conditions to the materials and revealing the opportunities for process intensification, continuous operation etc.. This approach also enables a designer to specify a dryer which is not already available "off the shelf", opening the possibility of targeted innovation in the field.

The opportunity will be created to design for parameters and factors which affect the overall process as well as individual steps in various length and time scales. Major gaps in the multi-scale approach to solids processing synthesis were identified. Solids handling and flowability in equipment as well as between units are major key areas to explore, and also crucial to the move from batch to continuous operation.

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Distillation intensification by simultaneously enhancing both mass and heat transfers

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1. Summary

Process Intensification for novel distillation systems with the potential to substantially reduce both energy consumption and capital investment is a challenging task. However, it is a significant problem as distillation is widely used in process industry, and it needs both high energy consumption and large capital investment. Distillation is a typical process with simultaneous mass and heat transfers, the optimal synthesis of a distillation system must simultaneously maximum improve both the mass and the heat transfers efficiency. For a multicomponent separation, the final performance of the distillation system will depend on the optimum synergy of the multiple individual tasks for the enhancement of both mass and heat transfers within the distillation system, which is inevitably concerned with the simultaneous optimal synthesis of the mass and heat exchange networks. In this work, a method of simultaneous mass and heat exchange networks synthesis to design such novel distillation systems is presented.

Keywords: distillation intensification, mass and heat exchange network, thermal coupling, heat integration

2. Extended Abstract

For a multicomponent distillation, the traditional designs of simple column configurations use n-1 columns and 2(n-1) condensers and reboilers for an n-component separation. Each column implements one of the n-1 sharp splits for an n-component distillation. Such simple column configurations have the intrinsic separation inefficiency and suffer from both high energy consumption and large capital investment. To improve the separation efficiency, the sloppy splits can be used in the separation sequence, however, this will increase both the number of columns and the number of heat exchangers in the traditional distillation configurations. It is known that the number of columns and the number of heat exchangers (condensers and reboilers) in a distillation system represent not only the final equipment costs but also the installation costs in the final plant construction. Therefore, it is desired that the novel distillation systems could have the same or reduced number of both the columns and the heat exchangers than the traditional distillation configurations. Needless to say, if we want to improve the separation efficiency and simultaneously keep or reduce the number of columns and the number of heat exchangers, we must have the new method other than the traditional distillation configurations to coordinate the mass and heat transfers among the separation tasks.

In this work, a new method of simultaneous mass and heat exchange networks synthesis to design such novel distillation systems is presented. The mass exchange network consists of identifying the suitable separation sequences for a given separation problem. Depending on the feed conditions and product specifications, both sharp and sloppy splits are used to formulate the separation sequences for the separation problem. The total number of individual tasks in a feasible separation sequence is determined by the decisions made for the submixtures to be separated. As a consequence, different mass exchange networks can have different number of individual tasks designated for the mass transfers. The optimal number of individual tasks in a mass exchange network can not be determined by the mass exchange network itself. It will be determined by coordinating both mass exchange network and heat exchange network.

In this work, a strategy of simultaneous thermal coupling and heat integration has been used to coordinate the mass and heat transfers. We found that thermal coupling and heat integration follow two different ways to deal with the heat exchangers which are concerned with both mass and heat exchange networks synthesis for a multicomponent distillation system. In certain cases, thermal coupling can enhance both mass and heat transfers by eliminating the condensers or reboilers. In other cases, heat integration is advantageous to enhance both mass and heat transfers by reducing both the number of heat exchangers and the number of columns. However, thermal coupling and heat integration must be simultaneously used to enhance the mass and heat transfers when a large number separation tasks are involved. The key in design of such novel distillation systems is by flexibly using thermal coupling and heat integration to determine the mass and heat exchange networks for the distillation systems. This will determine the actual number of columns, as well as the actual number of heat exchangers in the final distillation system. With different separation cases, some specific mechanisms are found which can determine the situations whether the thermal coupling or heat integration alone or simultaneously both to enhance the mass and heat transfers. The number of both columns and heat exchangers has been reduced and less than traditional configurations. In certain cases, they have the potential to significantly reduce both energy and capital costs, in other cases, they have better controllability and operability compared to traditional distillation systems.

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Process intensification in the esterification of rosin and glycerol

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1. Summary

In this work, the enhancement of the esterification of rosin and glycerol through catalysis and increase of the solubility of glycerol in the rosin phase is studied. The p-toluensulfonic acid (PTSA) acts as an acid catalyst, as well as a surfactant, enhancing the solubility of the phases form by both reactants. The use of the chloride of the acid (PTSC) shows how the solubility enhancing ability is enough to intensify the process by leading to a one-phase reacting system.

Keywords: process intensification, solubility enhancement, PTSA, PTSC, esterification.

2. Extended Abstract

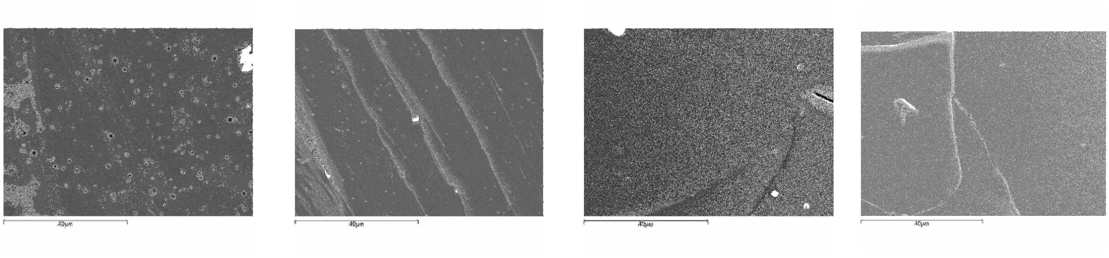
Rosin is the non-volatile fraction obtained in the distillation of pitch. The esterification of rosin with polyhydric alcohols produces several esters used in the sizing of paper, in adhesives, in the formulation of several polymers for their use in coatings and devices for the controlled release of fertilizers and drugs, etc. One of the most usual esters is the rosin-glycerol tri-ester. This product is obtained traditionally by a thermal activation of the acid, rosin, at high temperatures (260 ºC or higher) [1]. In a previous study, the statistical and physical selection among several kinetic models for the esterification between glycerol and rosin has been performed [2]. A hyperbolic kinetic model was selected as the best one to fit data at several temperatures and initial concentrations of glycerol. Esterification reaction rates are usually well described by first- or second-order kinetic models [3]; the need of the hyperbolic model was supposed to be due to the presence of two phases at the beginning of the reaction, one of them of pure glycerol. The use of SEM and optical microscopy confirmed this fact. A thorough study of the solubility of glycerol in rosin showed that the phase distribution depends much on the temperature and the quantity of glycerol. It was observed by SEM that the reaction medium proceeds from an initial two-phase medium to a one-phase one when theoretical glycerol concentration was under its solubility at the reaction temperature.

Thus, it seems that the reduction of the drop size in the two-phase system or the existence of only one phase could enhance the reaction rate (Figure 1). P-toluensulfonic acid (PTSA) and its chloride (PTSC) were added at several concentrations (from 0.01 % to 0.1 % in weight with respect to rosin). The acid is a known esterification catalyst, while the chloride, in a low water liquid, could behave as a surfactant. With both compounds, an enhancement of the initial reaction rate was observed in the parameters of the hyperbolic kinetic model used to fit data (Table 1). Observation of the samples by SEM agrees with this fact: the initial two-phase system evolved from one containing great drops of glycerol to others with smaller drops, and the evolution to the one-phase system was faster with both compounds. The solubility enhancement is obvious as it is the increase of the reaction rate, being it proportional to real glycerol concentration (as is usual with other well solved alcohols).

Table 1. Kinetic model and parameters for the esterification of glycerol and rosin at 270ºC with and without catalyst PTSA and surfactant PTSC

Runs	Kinetic parameters		Kinetic model
	k_1	k_2	
Blank	0.62 ± 0.13	1.16 ± 0.63	$r = \frac{k_1 \cdot C_G \cdot C_C}{1 + k_2 \cdot C_G}$
PTSA 0.06%	1.43 ± 0.17	0.62 ± 0.12	
PTSC 0.06%	0.74 ± 0.23	0.78 ± 0.14	

Figure 1. SEM microphotographs at 1500x at zero time and at 20 minutes



Zero time Blank With 0.06% PTSA With 0.06% PTSC

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Design of a minimum energy/CO_2 emissions distillation column for separation of close boiling mixtures

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1. Summary

The performance and design related aspects of an annular sieve tray equipped with heat transfer panels to facilitate heat transfer from hot rectification to cold stripping section in a concentric, internally heat integrated distillation column are discussed.

Keywords: energy saving, distillation, heat integration, HIDiC, carbon dioxide emissions

2. Extended Abstract

An internally heat integrated distillation column, HIDiC, offers the maximum energy saving potential for difficult and energy intensive separations, such as propylene-propane and the like, which are carried out in tray columns. Since in a propylene-propane splitter the stage requirement differs considerably for rectification and stripping sections, there are several possibilities for heat coupling, which, as experienced, strongly affect the heat transfer duty and consequently heat transfer area requirement per stage. Coupling all stripping section stages with equivalent number of stages in the upper part of rectification section appeared to be the best option in this respect (see Fig. 1a). Simulations indicate that energy requirements and CO_2 emissions generation of this stripping-rectification tray coupling configuration are respectively 25 % and 36 % lower than that of a state of the art vapor recompression column (Olujic et all, 2006). This HIDiC configuration was translated into a concentric distillation column design, with low pressure annular stripping section configured around a high pressure rectifying section, with integrated part placed above the conventionally designed part of rectification section column.

In order to ensure sufficient heat transfer area, the heat transferring panels are placed on the active area of an annular type stripping section sieve tray, which was developed and evaluated experimentally at the TU Delft (see Fig 1b). Results of total reflux experiments carried out at atmospheric pressure using cyclohexane/n-heptane system obtained in a 0.8 m diameter pilot plant were used to validate literature models for the prediction of the heat and mass transfer efficiency and pressure drop. The separation efficiency and pressure drop of this complex annular tray resemble those of a conventional cross flow sieve tray. The heat panels appeared to have a significant enhancing effect on tray efficiency, without affecting the pressure drop and/or capacity adversely.

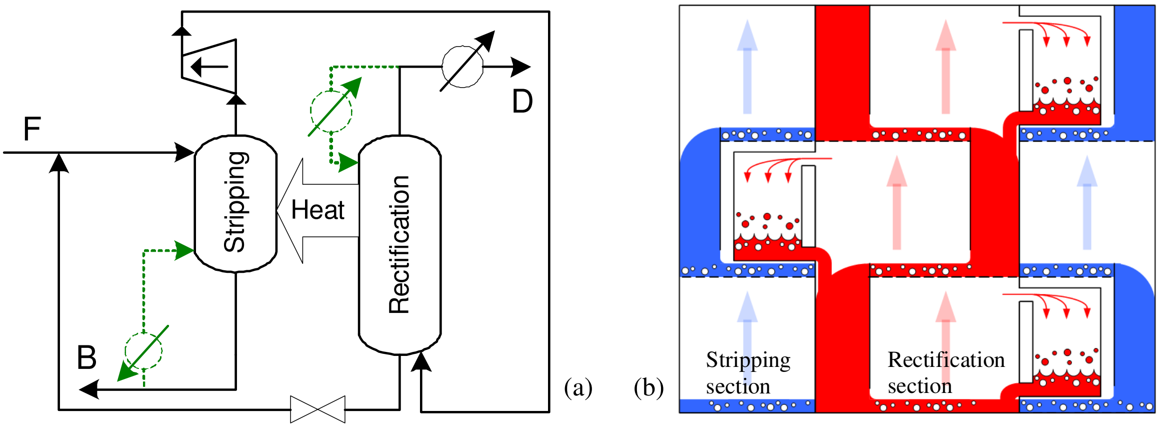

Fig. 1 (a) Principle of the HIDiC, and (b) schematic illustration of a concentric column configuration with heat panels placed above the active area of stripping section annular sieve trays

The obtained values of the overall heat transfer coefficients and mass transfer efficiency were used to design a HIDiC version of a state of the art, stand alone propylene splitter. It appears that an equivalent HIDiC PP-splitter could be realized at a 20 % lower total annualized cost. With increasing energy costs, this gain tends to increase, and with energy cost making 70 % of total annual cost the moment is not far when building such a capital intensive column will be economically justified. However further scale-up relevant research is needed to ensure certainty regarding the level of heat transfer efficiency expected under actual operation conditions.

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Process intensification for optimal retrofit of a multicomponent distillation plant – A real industrial case study

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1. Summary

Since the energy crisis of 1970s, energy conservation has been a research field of increasing interest for chemical engineers to develop new methods for improving the energy efficiency of different plants. Initially many studies were devoted in the design of heat exchanger networks and the Pinch Analysis and the Grand Composite Curve approach are the most enabling methods to allow energy targets.
Recent trends in energy saving with regards to the optimization of distillation sequences and the most significant developments in this field are the applications of thermally coupled sequences and the divided wall columns.
In particular many studies in this field have been devoted to chemical and petrochemical plants that utilize highly energy-intensive processes, mainly because distillation is by far the most widely used separation method to obtain pure components from an initial multicomponent mixture. Recent surveys indicate that about 3% of the world energy consumption is utilized in distillation plants. The possibility to lower the energy demand of the process increases plant earnings and also reduce pollution emission resulting from the less energy usage.

Keywords: Process Retrofitting, Process Intensification, Thermal Coupling, Multicomponent Distillation, Energy Saving.

2. Extended Abstract

Due to the continuous increasing of energy prices, plants where distillation is intensively used are always interested in improving their earnings with better energy utilization. One major task in plant retrofit is to identify new process alternatives which have the potential to replace or improve the existing plant. For distillation system, the new alternatives are expected to have the substantial savings on energy consumption. Moreover real plant retrofit is expected to have the minimum modification of the existing plant, and simultaneously to have the minimum investment of the capital cost. Currently Process Intensification is regarded as the main tool to improve process performance, and one of the major approach to this regard is to reduce the number of pieces of equipment in the plant. For distillation system, thermal coupling technique provides such an approach to retrofit the traditional simple columns through the elimination of the condenser and/or the reboiler.

In this work, starting from the simple columns configuration of the existing plant reported in Fig.1, two groups of new alternatives are proposed.

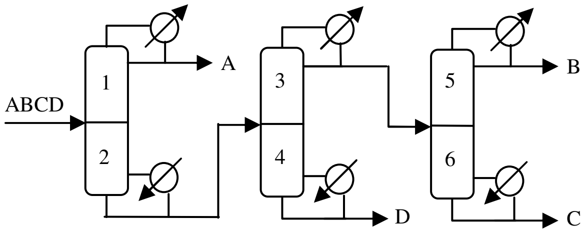

Figure 1: Plant configuration

The first group includes all the possible alternative by eliminating all of the condensers and reboilers involving the submixtures. The second group includes all the possible alternatives when a condenser or a reboiler is eliminated at one time, which then represents the minimum modification of the real plant. In addition, in order to investigate the capital investment for the modified plant, all of the obtained alternatives through the recombination of the column sections have been compared. All the possibilities were compared with respect to energy saving and to the possibility of reuse of the plant equipment like heat exchangers and column sections. Other factors are considered in qualitative way to search the best solution that matches energy savings and least plant modification. The optimal solution was found to be the alternative which has the minimum modification to the existing plant and is reported in Fig.2. At the same time, it has achieved a 23% savings on energy consumption. This configuration is obtained removing the reboiler of the first column of the plant design with a single thermal coupling and represent a really small modification of the original plant that satisfy the objective of the retrofit work for the maximum utilization of the existing plant equipments.

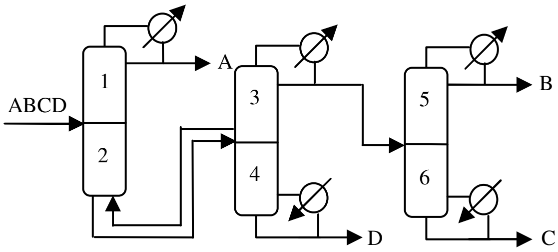

Figure 2: Selected configuration

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CO_2 removal from power plants flue gas: comparison of different membrane gas separation configurations

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1. Summary

The production of greenhouse gases (GHGs), particularly carbon dioxide affecting the global climate, is worldwide increasing causing undesired warming. As well as the recourse to less pollutant energy sources using alternative technologies, the CO_2 sequestration from flue gas is an approach in GHGs emissions reduction. In particular, it can be successful applied to big existing power plants that can meet, for instance, the specifications on CO_2 emission policy.
Current processes for CO_2 removal from flue gas are too expensive (e.g., chemical absorption requires large scale equipment and energy consumption). Therefore, new and less expensive processes are necessary: membrane technology (membrane gas separation, membrane contactors) might contribute to solve this problem.

Key Words: GHGs, membrane gas separation, pressures ratio, process intensification.

2. Extended Abstract

In this work the performance of gas separation membrane systems for carbon dioxide removal from flue gas have been theoretically analysed using a 1-D model for steady-state permeation. The membrane stage-cut, CO_2 recovery and permeate stream composition were analysed as function of feed flow rate and composition. Moreover, the effect of the feed to permeate pressures ratio, Φ, on membrane modules performance was investigated, considering in particular the variation of permeate composition versus the CO_2 recovery.
Two different membrane system configurations, the (a) flue gas stream compression and (b) the vacuum on permeate stream, were compared for a permeate stream with the same CO_2 concentration and recovery. In particular, the possibility of the vacuum is a valuable alternative instead of the more expensive compression. This happens specifically for applications in which the species to be recovered is at a low concentration (the CO_2 content in flue gas ranges around 10%) and low recoveries could be enough to meet process specifications (the Kyoto protocol indicate a CO_2 emission reduction of the 5.2% with respect than those of 1990).

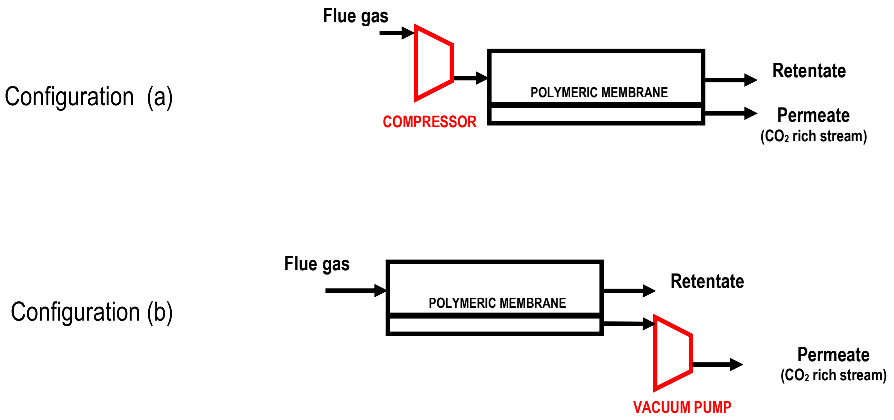

Figure. 1 : Configuration of the two systems.

At a fixed Φ the configuration (a) requires a lower installed membrane area but an higher investment and operating compression cost (the whole stream must be processed). On the contrary, in the configuration (b), even if the total installed membrane area increases considerably, the compression cost strongly reduces (only the permeate stream must be sucked). The high size compressor in the (a) configuration is substituted by a high number of modular, easy control, low investment and operating cost membrane modules. For a 20% recovery from a flue gas stream with the 13% of CO_2 and Φ=15 the vacuum system (b) reduces the compression cost at less that the 5% with respect to pressured system (a); in meantime, the required membrane area in (b) increase up to more than 10 times.

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Wastewater minimization using methods of process integration – a case study

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1. Summary

In this work, a case study on water minimization in a petroleum refinery is presented. A simplified water balance of critical water using processes was established. Re-use possibilities were identified, and water re-use network synthesised using available tools and methods, such as water-pinch.

Keywords: Process integration, wastewater minimization, petroleum refinery

2. Extended Abstract

There are many reasons why wastewater minimization is becoming more and more important to various chemical industries. Some of those reasons are increase in fresh water cost, more stringent environmental laws, discharge permit compliance and, last but not least, the public image of the company.

While previous approaches in environmental protection were mainly focused on end-of-pipe solutions, process integration approach leads to actual prevention of waste generation by modifications of the production process itself. Wang and Smith have developed a method for wastewater minimization using water pinch technology, analogue of the pinch technology developed by Linnhoff for heat exchangers network synthesis. The approach is based on the use of limiting water profile for each operation, which defines the maximum inlet and outlet concentrations of pollutants in water used in the process. By this approach, operations which are very different considering the nature of mass transfer can be easiliy compared, and treated on the same basis. Moreover, constraints for wastewater minimization, such as minimum mass transfer driving force, fouling and corrosion limitations are easily incorporated into the analysis.

If the possibility of changing the water-using operation itself, in order to reduce its water consumption, is left out, there are three possibilities to reduce wastewater generation:

1. **Reuse**. Wastewater is re-used directly in other operations providing the level of previous contamination does not interfere with the process. This may require mixing with other operation's wastewater or with freshwater
2. **Regeneration reuse**. Wastewater is regenerated with a partial treatment which decreases contamination level to a point which allows its reuse in other

operations. In this case, the wastewater is not used in the same process that produced it.

3. **Regeneration recycling**. After regeneration wastewater can re-enter process in which it has previously been used.

The applicability of the water pinch approach was tested on a petroleum refinery. There are five "kinds" of water that appear in a petroleum refinery - cooling, process, demineralized, sanitary, and surface. The water gets polluted with a variety of contaminants. In order to simplify the study, we have limited it on process water only, and only three contaminants were taken into consideration: H_2S, suspended solids and hydrocarbons. The study has 3 main phases:

1. Establishing the water balance.
2. Analysis of the existing water using network.
3. Proposal of a strategy for wastewater reduction.

The main problem in such study is actually obtaining the real plant data and establishing the water balance. The main reason for that is lack of laboratory analyses and flow data of various process water streams exiting different water-using operations and difficult sampling. Once the water balance was established, analysis based on water pinch method was carried out, and a solution for wastewater minimization proposed.

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Technologies comparison for separation of CO_2 and H_2S from oil/gas within the reservoir

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1. Summary

Crude oil and hydrocarbon gas streams may contain high levels of CO2 and/or H2S as contaminants. Opportunities for disposal of the unwanted components include subsurface sequestration of these substances. With the cheaper oil and gas reservoirs being produced, more difficult and, hence, more expensive fields are targeted for production. It is clear that sour gas gives rise to extra costs and potential environmental hazards.

It is desirable to prevent any contaminant to reach the surface, or to considerably reduce the contaminant levels reaching surface facilities. The technologies here considered for the separations are membranes, absorption/extraction, and cryogenic separation. On basis of operation conditions and volume limitations different technologies are compared with each other with their advantages and disadvantages.

Keywords: carbon dioxide, hydrogen sulphide, natural gas, oil, separation

2. Extended Abstract

Membrane materials for the separation of CO_2/CH_4 and H_2S/CH_4 are screened, which are stable under downhole conditions (100-300 bar, 50-100 °C) and moreover are stable to the natural gas impurities, for example H_2O[1], and higher hydrocarbons[2]. Zeolite membranes, for example type DD3R, were identified as potential candidates.

At the same time absorption/desorption processes for the treatment of natural gas and extraction processes for oil fields were elaborated. The distinct advantage of the fluid processes is the robustness under severe conditions of the reservoir. There are different choices for the solvent selection, strong chemical absorbents, mildly basic aqueous electrolyte solutions[3] and organic (physical) solvents[4].

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Production of sec-butyl alcohol by olefin hydration – a candidate for process intensification?

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1. Summary

The production of lower alcohols like sec-butyl alcohol (SBA) by direct hydration of olefins with acidic ion exchange resins as catalysts - an example for a liquid-liquid-solid process – is practiced in industry since many years [1]. The alcohol forms inside a well wetted resin catalyst. Superimposed to the chemical reaction is the extraction of the alcohol into the olefin phase while the low olefin solubility in the water phase determines the global rate of alcohol formation. This process is an example of applied reactive extraction [2].

Keywords: multiphase, reactive extraction, ion exchange catalyst, reaction kinetics, butyl alcohol

2. Extended Abstract

In this project a continuously stirred *Carberry* type tank reactor with baskets attached to the stirrer shaft is used. The baskets contain catalyst and rotate on the stirrer shaft stirring the multiphase reaction mixture to a grey coloured emulsion. The discharging reaction mixture is separated and each phase is sampled by two special sample injectors for online GC analyses. A second analytical system is a FTIR-ATR-spectrometer directly attached to the reactor which allows in situ measurements with high sample rates of the reaction or the mass transfer, respectively. The mass flows of the water and olefin feed streams are determined by two piston pumps, while the water exit stream is measured by a coriolis mass flow meter (Fig 1).

Mass transfer limitations were investigated in order to determine the reaction controlled kinetic regime by varying the temperature, stirring speed and the catalyst pellet size (Fig 2). Details of the kinetic experiments will be presented.

Theoretical examinations clarify that the olefin has to pass through the water phase until it reaches the active sites. Model calculations show a quasi-instantaneous consumption of the low olefin load in the water phase. The low solubility and transport of the olefin into the water phase lowers the chemical reaction rate significantly. The influence of the product extraction will be discussed.

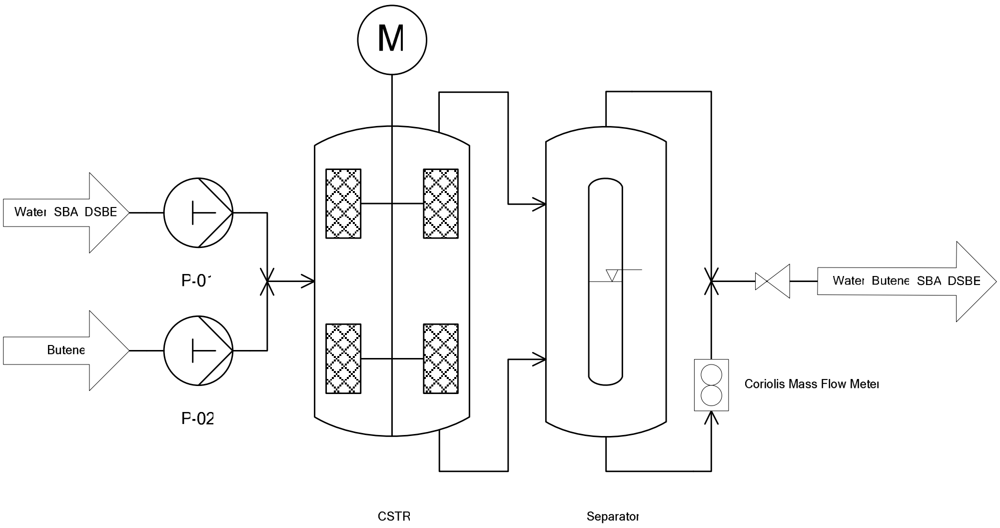

Fig. 1 Simplified flowsheet of the high pressure laboratory plant for liquid-liquid-solid reactions

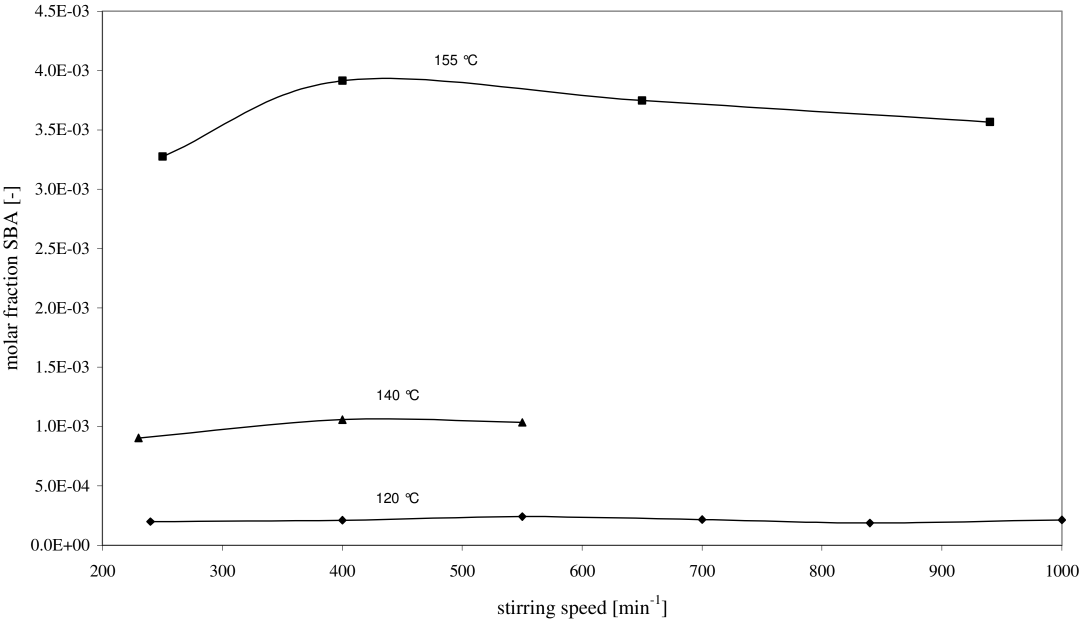

Fig. 2 SBA fraction in the organic phase for 60 barg and catalyst size fraction of 0.71mm < x < 0.8mm

Furthermore, the common multi phase operation of a fixed catalyst bed leads to strong hydrodynamic difficulties sharpening the mass and heat transfer issue. Proposals for process intensification, remedying the mentioned deficiencies, will be discussed.

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Task-based design techniques for solution crystallization processes

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1. Summary

There is a need for a more synthesis-focused design approach for industrial crystallizers. A new design approach is proposed that aims to conceptually build-up the crystallization process from fundamental building blocks called physical tasks. In the framework of such a design approach experimental results from a bubble column crystallizer are discussed. The experimental setup isolates the physical task of crystal growth. The results show that the system is dominated by growth and nucleation is minimized, which allows for more flexible operation by for example choosing proper seeding conditions in case of batch-wise operation.

Keywords: Crystallization, Task Based Design, Bubble Column, Crystal Growth,

2. Extended Abstract

Crystallisation is one of the oldest and economically most important separation technologies in chemical industry. Many interacting physical phenomena occur in industrial crystallizers. This complicates model-based optimization studies and reduces flexible operation and design. The selection of crystallisation equipment is traditionally done in an early phase of the design from a limited number of state-of-art industrial crystallizers followed by optimization of that particular type of equipment. This reduces the design space and creative input of a designer. Furthermore, optimization of each individual physical phenomena is not possible because in present industrial crystallizers these phenomena are strongly interrelated.

To improve on these drawbacks a more synthesis-focused design approach is proposed called task-based design. In the task-based design approach an attempt is made to conceptually construct the crystallization process from fundamental building blocks called physical tasks. Tasks can be connected in a network to accomplish the complete transition of a given feed into a desired product. The aim is to generate alternative ways of structuring the tasks, leading to a task superstructure that contains all possible and relevant tasks and their interconnectivity. Optimization of the task superstructure can be realized based on product quality, throughput or economic evaluation of the process and can be dependent on design constraints. The task based design approach is more flexible than traditional design approaches and allows for the optimization of each individual crystallisation task. In this way a much larger solution space is created which is needed to arrive at process intensification.

One of the key challenges of the task based design research is to control a certain crystallization task independently from the other tasks, which makes optimization of that particular task possible. In that perspective, a novel experimental crystallisation configuration that mainly facilities the task crystal growth is studied. The setup consists of a bubble column in which supersaturation is created by simultaneous cooling and evaporation of the solvent by sparging air. The crystals are kept in suspension by the upward velocity of the bubbles, eliminating the need for a stirrer or a circulation pump. In this way attrition caused by crystal-impeller collisions is absent. Moreover, the generation of supersaturation is nicely distributed along the complete length of the column. Experiments on lab-scale show the feasibility of the concept. Figure 1 shows the measured final median size of two identical seeding experiments ($L_{50,seeds}$ = 220 μm) for an ammonium sulphate water system. It can be seen that the final median size is on the ideal growth line which approximates a situation in which the total number of crystals do not change. It can therefore be concluded that nucleation is indeed minimal in the bubble column. As a reference, figure 1 also contains experimental results from Hojjati et al. (2005), indicated by the black line, who did seeding experiments on a lab scale for cooling crystallization of ammonium sulphate for seeds with two different median sizes in a stirred crystallizer. Furthermore, figure 1 contains experimental results, indicated by the dotted lines, from seeding experiments in a 75-liter draft tube crystallizer operated in evaporative fed-batch mode. The seeds that were used for those experiments were identical to the seeds that were used for the experiments with the bubble column. It can be concluded that optimization of the single task crystal growth in principle allows for more flexible operation as the final product size can be manipulated directly by adjusting the seed mass.

Experiments in which the bubble column is operated in continuous flow mode show that a device that isolates the task crystal growth can also be used to increase the median size of a slurry while maintaining the total number of particles. The aim is to connect the bubble column to devices that contain other isolated tasks. In that perspective, the use of membranes is interesting as they can be used to optimize the generation of supersaturation independently from the other tasks. Finally, the use of ultrasound is investigated for production of nuclei. In the end, the combined experimental setup is the translation of a task superstructure to real life equipment.

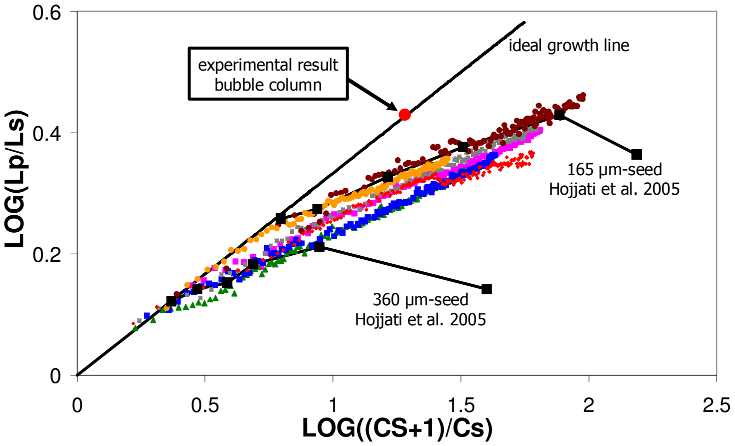

Figure 1: Seed chart.

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Copenhagen, 16-20 September 2007

Basic criteria for microreactor selection

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Abstract

Microreaction technology and microchemical engineering are fast growing disciplines in chemistry and chemical engineering. A large number of microstructured devices with different mixing principles have been developed and microreactors have been used in a wide range of labscale applications for a lot of different reactions. [1, 2]

Microstructured devices provide a more efficient heat and mass transfer due to large specific surface areas. This leads to a higher yield and selectivity for chemical reactions. They use different principles with specific advantages and disadvantages. [3]

During our work in the field of microreaction technology we have generated experience with chemical reactions in labscale microreactors and the up-scaling of these processes. In this work we present a set of criteria we found to be important in the process of choosing a microreactor for a given application. Usability, mixing quality, scalability and economic aspects are among the criteria that are discussed. Here we will mainly focus on liquid/liquid reactions. Some general guidelines reactor selection will be given and a few special cases like the mixing of liquids at different phase ratios and/or with different viscosity will be discussed.

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Synthesis of heat-integrated distillation sequences in non-conventional processes

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1. Summary

This work deals with the synthesis of heat-integrated distillation sequences in processes where the presence of a large number of important vestigial species and the scale and non-linearity of the involved mathematical models may hinder the use of classical MINLP/GDP approaches. The procedure described, which relies on a NLP/MILP decomposition, was tested on the *CUF*'s aniline process allowing the synthesis of new advantageous configurations already industrially implemented.

Keywords: Distillation, heat integration, process synthesis, nonlinear programming.

2. Extended Abstract

The optimal synthesis of heat integrated distillation sequences has received great attention in the past and, currently, is still an important research area in Process System Engineering. Several strategies have been proposed, presenting distinct ranges of applicability and requiring different numerical schemes for their solution:

- based on Mixed-Integer Linear Programming (MILP): these are suitable when all of the product streams correspond to pure components (Andrecovich and Westerberg, 1985); under these circumstances, a branch expansion of all sharp separation alternatives is considered, and simplified linear relations employed.
- based on Mixed-Integer Non-Linear Programming (MINLP); these enable the synthesis of the more general non-sharp separation problem, and consider the optimization of a superstructure where the mixing, fractioning and bypassing of streams are key aspects (Aggarwal and Floudas, 1992).
- based on Generalized Disjunctive Programming (GDP); with a similar range of applicability to MINLP strategies, they can allow a more compact problem formulation by including logical expressions that enable a given equipment to assure different tasks (Yeomans and Grossmann, 2000).

Although more general, MINLP/GDP strategies can face critical convergence difficulties when non-sharp separation models are considered, especially when these refer to highly non-ideal liquid-vapour equilibriums (LVE). Under these circumstances, the construction of approximate models is often adopted (Aggarwal and Floudas, 1992) as a way of reducing the scale and non-linearity of the original formulations. However, since these simplified models are obtained through regression exercises, they also exhibit some limitations, and assumptions must be made concerning the non-distribution of non-key components.

The current work focus on the difficulties that classical strategies may exhibit, when addressing complex processes of non-conventional nature, for instance:

- in the presence of highly non-linear separation models, as a consequence of complex LVE and of the necessary distribution on non-key components.
- the feed stream is characterized by a great number of byproducts in vestigial concentrations, but with crucial importance for a set of purity constraints.

In both of these cases, the use of discrete numerical schemes and the construction of approximate models can be hindered. In order to allow the optimization of such processes, a new strategy is introduced that includes three main aspects:

- considers a problem reformulation, with the purpose of enabling a more simplified approach, by grouping sets of real species into pseudo-components.
- deals with non-sharp separations, using mathematical approaches easy to implement, initially developed for more simple and less general problems.
- exploits the capacity of optimizing large-scale non-ideal models, through continuous formulations, to reduce the risks involved in the previous aspect.

In order to illustrate the robustness of this procedure, a complex non-conventional case-study, drawn from industry, is considered; this regards the purification phase of the aniline production process implemented in *CUF*. The results obtained allowed the identification of a new heat-integrated separation structure, capable of drastically reducing the current operating costs and, simultaneously, enabling a more pure commercial product.

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Retrofit of crude distillation unit using process simulation and process integration

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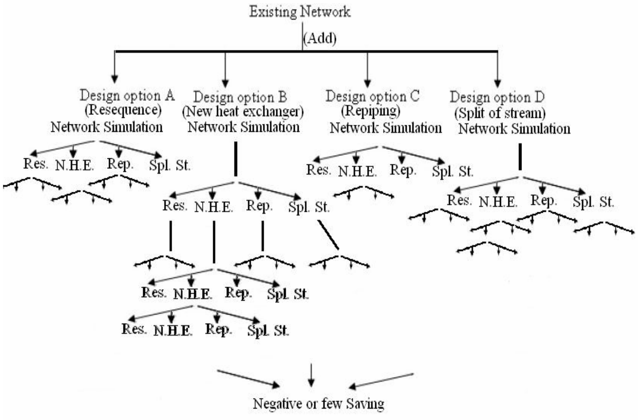
1. Summary

Crude distillation unit is the basic processing step in oil refinery and is a highly energy-intensive process and represents one of the most important areas for energy integration in a refinery. The HEN of the Distillation unit considered here consists of a crude preheat-exchanger network and flashing section, atmospheric distillation section, and vacuum distillation section. Because some of the heat exchangers in this unit have a relation to the S.R.G. unit we consider this unit, too. In the paper the approach is to produce different acceptable scenarios of retrofit using an integrated instrument: process simulator and process integration software. In this case Aspen Plus environment integrated with Aspen Pinch software are used to illustrate the pinch methodology. The incremental area efficiency methodology was used for the targeting stage of the design and the design was carried out using the network pinch method consisting of both a diagnosis and optimization stage. The stream data consists of 21 hot and 10 cold streams and cost and economic data required for the analysis were specified. The targeting stage using incremental area efficiency sets the minimum approach temperature at 33°C, thereby establishing the scope for potential energy savings. To achieve a practical project, the number of modifications is limited. The modifications include resequencing (changing the order of exchangers on a stream), addition of new heat exchanger units, repiping of existing exchanger and split of stream in best option we can save about 9.2464% of overall energy consumption in furnace.

Keyword: heat integration, crude oil, retrofit, heat exchanger network, Aspen Pinch

2. Extended Abstract

Since the early 1970s, energy conservation has been a major area of research in chemical engineering. Distillation unit is an energy-intensive process and has received significant attention for better energy integration in chemical plants. The systematic general approach involves three main steps: Simulation of unit using Aspen PLUS and Aspen B-Jac, analysis and targeting retrofit and finally heat exchanger network retrofit and harmonization with unit. First stage in simulation is specified the crude oil in assay and blending component. Second stage is defining the thermodynamic property model. A general correlation of the vapor–liquid equilibrium in hydrocarbon mixtures, the thermodynamic model Peng-Robinson with was used in the simulation. We import stream data, heat exchanger network and information and details of heat exchanger from Aspen Plus and Aspen B-jac in to Aspen Pinch. Stream data extracted for the current case study consists of 21 hot streams that require cooling and 10 cold streams to be heated. We study a lot of option of modification contain: Resequence, repiping, add of a new heat exchanger and split of stream, Fig (1) shows the strategic for heat recovery in add new exchanger. In each option we reconsider new networks with new Aspen B-jac file and simulate and research for heat recovery in aspen pinch environmental.



(For add new heat exchanger option we search for best add, and select a best options, put new exch. then we constitute four distinct network, in each network we search options of heat recovery (Resequence, repiping, add of a new heat exchanger and split of stream). This method to run on until heat recovery is negative or few. In each phase HEN is simulation in Aspen pinch and Aspen B-Jac. Finally changes of all options put in unit and then simulation and converges unit in Aspen plus and Aspen B-Jac then select best option.)

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Session S-6: The Future of European Chemical Engineering Education in a Globalized World

Abstract Number	Paper Title & Authors	Included
4163	The Chemical Industry in 2030 O Sparrow	Yes
4164	Frontiers in Chemical Engineering Education R C Armstrong	Yes
4165	The Chemical Engineer – A “glorified plumber” or the molecular engineer of the future? K Harg	Yes
4166	Chemical Engineering Education in Europe – An Industrial Perspective M Strohrmann	Yes
4167	Chemical Engineering in the Pharmaceutical Industry of Tomorrow A Zilian, B Schenkel	Yes
4168	Trends in Chemical Engineering Education in the far East D C Shallcross	Yes
4169	Trends in Chemical Engineering Education in Central Europe E Favre, C Roizard, L Falk, E Schaer	Yes
4170	Trends in Chemical Engineering Education in Eastern Europe based on Polish Experience J Baldyga	Yes
4171	Implementing Bologna in south European countries: Comparative analysis of some research findings AVeiga, A Amara, A Mendes	Yes
4172	UK Developments in Chemical Engineering Education P Sharratt	Yes
4173	Changing learning methods and curriculum of Chemical Engineering - CDIO and Chemical Product Engineering M E Vigild, S Kiil, J A Wesselingh	Yes

Session S-6

The Chemical Industry in 2030

Oliver Sparrow

The Challenge Network, London, United Kingdom

Abstract

The Challenge Network advises many large corporations and governments around the world about adapting their assets to the fast-changing future.

The lecture will give a tour of the horizon, covering those areas in which fast change is most likely to impinge on the chemicals industry. Indeed, it may well be that the concept of this industry sector as an integral whole is due for a change. Therefore it will be pointed to some of the natural fault lines along which this change may occur.

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Frontiers in Chemical Engineering Education

Robert C Armstrong

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Abstract

A dramatic shift in chemical engineering undergraduate education is envisioned, based on discipline-wide workshop discussions that have taken place over the last several years in the US. Faculty from more than 53 universities and industry representatives from 15 companies participated. Through this process broad consensus has been developed regarding basic principles for chemical engineering undergraduate education in the future; these principles address fundamental knowledge, skills and attributes, and methods of engagement with the students. From these principles a new set of organizing principles emerged for the discipline: molecular transformations, broadly interpreted to include chemical and biological systems and physical as well as chemical structural changes; multiscale analysis, from sub-molecular through super-macroscopic scales for physical, chemical, and biological systems; and a systems approach, addressed to all scales and supplying tools to deal with dynamics, complexity, uncertainty, and external factors. The curriculum integrates all organizing principles and basic supportive sciences throughout the educational sequence and moves from simple to complex. The curriculum is consistently infused with relevant and demonstrative laboratory experiences, and opportunities for teaming experiences and use of communication skills (written and oral) are included throughout. The curriculum is also designed so as to address different learning styles and to include a first-year chemical engineering experience. Finally an important theme is the widespread use of relevant and demonstrative examples, which provide open-ended problems and case studies and supply frequent integrative opportunities for students.

This radically different curriculum would produce more versatile chemical engineers, which are needed to meet the challenges and opportunities of creating products and processes, manipulating complex systems, and managing technical operations in industries increasingly reliant on molecular understanding and manipulation. Another benefit of the new curriculum is that it reconnects undergraduate education with ongoing research in chemical engineering in a way that has not been present for the past 40 years. This reconnection will serve us well as an engineering discipline in

attracting the best and brightest students and in reopening the path to continual renewal of the curriculum.

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The Chemical Engineer – A "glorified plumber" or the molecular engineer of the future?

Knut Harg

Hydro Oil & Energy, Hydrogen Technologies, Notodden, Norway

Abstract

The presentation will analyse the role of the chemical engineer in the industries of today and tomorrow. The following topics are addressed:

•How do we size and shape the chemical engineering education? Should demand forces dictate, through industry or through students' choices, or should national policies play a role?

•How can we supply relevant skills to serve both the needs of today's industry and to stimulate the formation of new industries?

•What is chemical engineering? What are the fundamental characteristics, and how long-lasting are they? How do we balance between lasting fundamentals and applied subjects?

•Do we primarily teach the students "how to acquire new knowledge", or do we expect them to acquire specific skills? Can a single subject change a young person's perception of the world?

•How will the life sciences (biology, genetics, biochemistry, molecular biology) influence or merge with chemical engineering curricula? What about the challenges in energy, climate, and the environment?

•How will globalisation influence universities, students, and industry?

•What do we want a technologist to know, except his technical subjects? Should non-technology subjects be mandatory? How do we prepare students for real life challenges in finance, health and safety, legal matters, management, cross-cultural communication, business ethics, etc.?

- Has teaching changed since Wilhelm von Humboldt? Should it? The role of research in teaching.

- The role of industry: Motivators, university partners, providers of relevant cases and examples, associate professors, innovators

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Chemical Engineering Education in Europe – An Industrial Perspective

Martin Strohrmann

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Abstract

Talking to German professors about chemical engineering education in the past five years one word drew all the attention: Bologna. In general, we support this process, and we fully support the recommendations given by EFCE in July 2005. I do not want to summarize what is written down in the respective papers. There are, however, developments in the current implementation steps, which should be reviewed critically:

> For European politicians Bologna appears to be a highly welcome opportunity to cut the cost of education, increasing the number of graduates while keeping or even reducing budgets. In our opinion, the strength of the European Universities is to provide an excellent education, reducing its quality means to jeopardize the innovative strength of the European Industry.
>
> A chemical engineer graduating in the first cycle degree (bachelor) should be qualified for an industrial job. Some universities transfer their traditional long-cycle programs with only few modifications to the new curricular demands giving the qualification of the first cycle graduate only little attention. The first cycle degree is considered only an emergency exit for those less qualified for higher education. To make it really clear: We have no job opportunities for these graduates.
>
> EFCE asks for scientific, innovation oriented skills in the second cycle degree. It shall combine deepening the knowledge on certain topics, train problem solving skills including analysis, evaluation and selection of alternative solutions and the synthesis of novel solutions. We consider this an excellent aim.
>
> Some courses offered by German universities of applied science however do not really include those skills profoundly. In other cases, some graduates had even been admitted to PhD work right after their first cycle degree. We were

in some cases disappointed when talking to them about topics outside the area covered directly by the PhD thesis. Students should select carefully the second cycle degree, checking whether EFCE recommendations have been implemented. Second cycle degree should be kept a qualification required for PhD work.

One of the most positive effects of the Bologna process is the higher mobility achieved by defining ECTU credits for all the educational topics. In general, we are in favor of mobility, of students having the proven ability to adapt to a new environment. This proof is especially valuable when not only lessons are taken when staying abroad a limited time but a thesis or a chemical engineering project is performed under conditions the student is not completely familiar with.

EFCE asks industry to play an important role in the education of chemical engineers. We fully agree that industrial experience serves to illustrate applications and limitations of theory, puts contents in a wider context, provides social skills and motivates for the remaining study. We are willing to provide the respective placements, especially for second-degree thesis's and for design and conduction of experiments. The industrial assignment should be at least 3 months, else we loose too much time for the initial training and other non-productive issues and of course we like to define the topics jointly with the professors.

Bologna is dramatically increasing the number of educational programs, making it more difficult for industry to judge which one suits best for a certain job family. Therefore, we strongly support audits, assessments and other review options for the educational process.

Chemical engineering will serve to solve Europe's problems in the century, which has already begun: energy, sustainability, mobility and innovation in a more and more competitive globalized world. Well-trained chemical engineers are the key to accept this challenge.

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Chemical Engineering in the Pharmaceutical Industry of Tomorrow

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Abstract

The need for the input of Chemical Engineers in the Pharmaceutical Industry is growing. Current and future assignments of Chemical Engineers in the Pharmaceutical Industry will be described. Typical tasks of Chemical Engineers in today’s development and manufacturing of Drug Substances and Drug Products (Galenical Forms) will be aligned with latest trends in Pharmaceutical Industry to improve and extend research, development and manufacturing.

Trends in Chemical Engineering Education in the far East

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Abstract

Booming economies in the Far East, most notably the People's Republic of China, are fuelling demand for graduate chemical engineers. Enrolments in chemical engineering programs are booming with China's 175 chemical engineering departments producing over 8000 graduates in 2005. This number is growing rapidly with at least one department having 2000 undergraduates enrolled in its programs this year. In countries such as Malaysia, Singapore and Thailand demand for entry into the undergraduate programs is also strong. Government-funded universities are growing, increasing the number of chemical engineering places available while in some countries private universities have recently been established to meet the needs of the local communities. Universiti Technologi Petronas is an example of a private university recently established in Malaysia primarily to educate engineers while the University of Nottingham of the UK has established a campus in Malaysia with private equity in recent years. Across the Far East local universities and private capital are entering into arrangements with Australian, European or North American interests to either establish new chemical engineering programs or to grow existing ones. The growth in the number and size of such programs has led to the growing demand for appropriate engineering educators.

This presentation will address these issues as they relate in particular to Australia, Malaysia, PRChina, Singapore and Thailand. Opportunities for possible collaborations between Western institutions and their Far East counterparts will be presented and discussed.

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Trends in Chemical Engineering Education in Central Europe

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Abstract

Chemical engineering, as already stated by Danckwerts decades ago, has to keep permanently in touch with the evolution of the underlying science, as well as with the changes in the Chemical Process Industries (CPI). These two domains, together with the portfolio of new educational means, have undergone significant changes recently, which call for a constant reexamination of the currently existing curricula [1-3].

This lecture intends to provide a brief state of the art analysis of the different degrees in chemical engineering in central Europe, as well as tentatively identify the evolution and needs in the near future.

In a first part, a survey of typical chemical engineering curricula in Germany, France, Netherlands Switzerland, Belgium will be described and compared to other countries.

In a second step, the possibilities of evolution of chemical engineering teaching are explored. Several key issues will be addressed:

i) the role and place of product engineering vs chemical engineering

ii) the teaching requirements of sustainable chemistry and processes, including green chemistry approaches [4]

iii) the possibilities and limitations to include biology and life science topics in a chemical engineering syllabus?

iv) the potentialities and concrete use of modern teaching techniques (such as e-learning).

While scientists tackle problems that can be solved, a chemical engineer has to face

problems in the CPI that must be solved. This oversimplified definition is likely to remain true in the future. Nevertheless, the type of problems of the chemical industries, the strong needs for innovation, the minimal "time to market" constraint within a globalized environment have obviously to be taken into account in actual and future curricula.

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Trends in Chemical Engineering Education in Eastern Europe based on Polish Experience

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Abstract

In 2005 I was asked by the Minister of National Education and Sport of the Republic of Poland to prepare a draft of new Education Standards for Chemical and Process Engineering. The new standards (or core Chemical Engineering curricula) are now ready; they are based to some extent on old standards and they include main ideas of EFCE Bologna Recommendations for Chemical Engineering Education in a Two Cycle Degree System, covering relevant learning outcomes based on general chemical engineering skills, transferable skills and the learning outcomes. The new standards are not just a compromise between old and new ideas; however, it can be shown that several older teaching ideas can be transformed to the new Chemical Engineering curricula. In the first part of presentation this transformation is presented, practical implications for education in several polish institutions of higher learning in Chemical Engineering are reported, and compared with experiences of other Eastern Europe countries.

Next problem that is discussed is related to continuous tuning of Chemical Engineering curricula in a response to changes in a job market and appearing new paradigms and new-area emergence that are often experienced by young people as the current fashions. This is most often done by introducing Chemical Engineering specialities (like Bioengineering, Biomedical Engineering, Environmental Protection etc.) in a second cycle degree study or equivalent. This problem is discussed in the context of several significant changes of the chemical engineering profession observed in Eastern Europe over the last 50 years.

Spreading of methods developed in Chemical Engineering to other disciplines as well as new opportunities for chemical engineers, which results in increasing number of graduates moving to non-traditional areas.

Finally an important social problem of emigration of Chemical Engineering graduates to old European Union countries is presented in relation to education and job opportunities.

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Implementing Bologna in south European countries: Comparative analysis of some research findings

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Abstract

In this paper the authors argue that the analysis of policy implementation within Bologna process should focus on the state of implanted, rather than on the state of readiness. Some research findings stress that in Italy the implementation of Bologna reforms is going too fast "[members of disciplinary fields] resent the declining (or changing) role of the intellectuals inside academia. Unfortunately, the rapid pace of reform has prevented any real debate on that complicated matter" [1]. In Portugal, for several years HEIs had been waiting for the necessary legislation framework to implement the Bologna reforms. The unexpected flood of proposals presented at very short notice can only be explained by the peculiarities of the Portuguese implementation process [2]. In Spain the law approved in 2001 generated considerable controversy. Voices claim that the new law does not make provisions for funding the system of higher education. Nonetheless there are a number of pilot projects undergoing within HEIs focusing on the adaptations of different fields of specialization (Mathematics, Biotechnology and Geography) to Bologna [3].

The Bologna process officially and formally started upon the signature of Bologna declaration and expresses the interest of a significant number of European states to build up the European Higher Education Area (EHEA) based on the principles of transparency, legibility and comparability of their higher education systems. The establishment of EHEA interlocks a number of policy areas that are impacting institutions at various levels of policy making and policy implementation.

From the European and national perspectives the analysis of policy implementation tends to focus on the state of readiness. At these levels institutions offer "the vision of a triumphant march towards the objectives set for 2010" [2]. There are a number of factors fostering this perspective: policy implementation is viewed as a linear process which is an outdated perspective and obscures a number of interlocking dimensions;

on the other hand, political time is not aligned with academic time preventing a reform in substance and, last but not the least, the competitive emulation practices emphasizing the role of performance indicators stresses the economic dimension [2,4]. From the local perspective the perceptions gathered at local level show that often HEIs use alternative interpretations of Bologna to suit their institutional strategies.

In this paper the complexity of the reforms will be analysed using as empirical data the material collected under the framework of two research projects - UNIMON project [5] and the survey involving all Portuguese higher education institutions that presented new degree programmes or adaptations to the new degree structure. The paper is based on comparative analysis aiming to know more how far Bologna is integrated into the academia. The paper may contribute to shed light on the state of implanted of Bologna in Greece, in Italy, in Portugal and in Spain challenging the assumption that such a fast implementation rate may not correspond to implementation in substance.

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UK Developments in Chemical Engineering Education

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Abstract

Chemical engineering education in the UK faces a period of substantial challenge driven by a wide range of national and international factors. The UK system is strongly driven by the market, with departments needing to become increasingly agile in their development as a result of direct links between course success and the income of universities and departments. Departments face a range of partly conflicting pressures, with the drivers including the following.

•A desire to attract non-EU students as a means of generating fee income outside the constraints of the UK funding framework. Many of these students aim to develop skills relevant to chemical engineering in bulk industries and relevant to the needs of developing nations.

•A need to meet the needs of home students in a rapidly moving employment market, where there has been a substantial shift away from traditional bulk process industries towards pharmaceuticals, personal care, water, pulp and paper, contracting.

•A recognition that many students do not enter the process industries at all, but rather consultancy, financial services etc.

•A shift in the skills base of entering undergraduate students, with generally weaker skills in relevant mathematics and science.

•A developing culture of cynicism in student approach to examination – partly driven by learned behaviours in secondary schools – with many students working through their courses on a diet of “cram-exam-forget”. This is combined with a lessening culture of personal responsibility for learning – increasingly students see their failure as one of the university and not themselves, and are more likely to appeal against decisions or even go to law.

•Pressure from professional bodies to deliver 4-year rather than 3-year undergraduate programmes.

•A desire driven by universities in response to the need for more cost-effective teaching to adopt e-learning techniques.

•A lessening enthusiasm among academics to devote time to teaching at the expense of research.

•The high cost of teaching chemical engineering compared with other subjects.

•Pressure on the curriculum from a wide range of sources to deliver personal skills, business and enterprise skills, knowledge of sustainable development etc.

This paper will discuss the approaches that are being adopted in the UK, and particular report on some of the innovations being implemented at the University of Manchester. These include a move to remove artificial barriers between topics and to increase skills in problem solving that require a broad range of technical skills to be applied, as well as the use of senior teaching fellows, peer-assisted learning, e-learning and “egg race” events.

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Changing learning methods and curriculum of Chemical Engineering - CDIO and Chemical Product Engineering.

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1. Summary

Chemical Product Engineering represents an evolving part of the Chemical Engineering Curriculum introduced by universities in response to the changing employment conditions for chemical engineers in industry. Simultaneously, it facilitates the adaptation of new methods of learning and teaching which are aligned with the CDIO approach of rethinking engineering education in order to train better engineers for the future.

Keywords: chemical product design and engineering, CDIO, curriculum change, learning engineering skills

2. Extended Abstract

This presentation will report on the experiences gained from teaching classes and preparing a text book on Chemical Product Engineering. [1] At DTU this subject was introduced into the curriculum as dedicated classes in 2000. Over the last decade Chemical Product Engineering has evolved as part of the Chemical Engineering Curriculum at several universities in Europe and America. [2] Chemical Product Engineering is solidly based on chemical technical and engineering knowledge. Furthermore, the subject naturally calls for a holistic approach to teaching and learning and introduces elements which target transferable and professional engineering skills. Such skills are especially important in Chemical Product Engineering when dealing with open-ended problems, creative problem solutions, operating in a team working environment and exercising project management.

In 2004 the World Chemical Engineering Council (WCEC) conducted a survey on how chemical engineering education meets the requirements of employment of young chemical engineers. [3] The survey shows a discrepancy on what skills are the more important during education versus employment. Application of basic science and appreciation of the potential of research were the most relevant skills during education. However, completely different skills like team work and communication, ability to gather and analyse information, and self-learning were considered the most important abilities for employment. This gab between engineering education and engineering employment is not unique to chemical engineering, and similar evidence is found in other engineering disciplines. The *CDIO initiative* springs from this situations and aims at closing the gab, without loosing the firm basis of technical scientific knowledge.

The CDIO approach of rethinking engineering education takes the authentic lifecycle of engineering problems as the framework for engineering education. [4] This lifecycle is described by Conceive-Design-Implement-Operate (CDIO). Especially, the CDIO approach focuses on simultaneous training of engineers on both disciplinary knowledge and various skills covering personal, interpersonal and system building capabilities.

In our course we emphasise team activities, formative feed back to the students as well as helping the individual to become more assertive and understanding of personal assets. All this is done within the technical framework set by the product or the problem area in question. These teaching elements included in Chemical Product Engineering represent a series of issues which are general to Chemical Engineering Education, and which must be discussed as the education is going to adapt to the changes of the surrounding world and a globalized society. This presentation will put Chemical Product Engineering into perspective with the *EFCE* recommendations on Chemical Engineering Education [5] and also relate curriculum discussions with the *CDIO Initiative* for producing the next generation of chemical engineers.

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Session S-7K: EP & S Keynote Lectures

Abstract Number	**Paper Title & Authors**	**Included**
1777	Sustainable Processes – The Challenge of the 21st Century for Chemical Engineering M Narodoslawsky	Yes
4090	Sustainability Integration In Chemical Process Engineering A Irabien, R Aldaco, I F Olmo, A Garea	Yes

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Sustainable Processes – The Challenge of the 21^{st} Century for Chemical Engineering

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1. Summary

The 21st century inherits stark challenges for human society: environmental degradation, global warming and shrinking fossil resources. All these problems are paired with a dramatic growth of the economy in China and India, home to 2.3 billion people. We need to make more from less and we need to do this while reducing our impact on nature by the order of magnitudes.

This challenge is particularly tough for chemical engineering. This sector is on the one hand responsible for providing most of the products of daily consumption, the base for modern agriculture as well as energy carriers for power generation, transport, heating and cooling. On the other hand chemical engineering has a considerable impact on the environment, via its resource consumption, its emissions and the impact of its products. Chemical engineering will have to explore new ways in order to stay ahead of these challenges. The most important changes for this sector in the 21st century will include:

The change of the raw material base

Today chemical industry is mainly dependent on fossil oil and gas as its main raw material base. Both resources will face their production peak during this century, forcing process industry to look for alternative resources. One obvious candidate are renewable, biogenic resources.

Such a change in the raw material base however entails a profound revolution in the structure of processes, the technologies employed and the economical framework of process industry. For one, these resources constitute a “limited infinity”: although they may be provided for infinite time, their productivity is limited. The chemical sector here enters competition not only with the energy sector (who also sees renewables as alternative resources) but with the food sector, too.

Another problem lies in the altered logistics of renewable resources: they are produced de-centrally and mostly discontinuously in contrast with the continuous point sources of fossil materials. This will lead to complete new structures of chemical processes, with the raw material logistics a solid part of the process.

Life cycle stewardship

Efficiency will be key to success. This will start with the choice of the right raw materials, where process industry will play out its high flexibility, allowing it to utilise raw materials not suited for food like straw and other agricultural residues. Utilising every part of its raw materials as it does now with fossil resources will become an imperative when using renewable resources. On top of this process industry will also become more responsible for re-integrating its products after use into the biosphere. A close and efficient co-operation with agriculture will ensure long-term fertility by closing material cycles from agriculture via process industry, society and back to agriculture.

New construction principles

For the first time since many decades process industry will have to generate new industrial structures for whole value chains. Besides economic optimisation the reduction of the ecological impact over the whole life cycle will become a necessity. This means for chemical engineering to apply new principles for the construction of its processes: process synthesis and ecological process evaluation will become prominent tools for the chemical engineer in the 21st century.

Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Sustainability Integration in Chemical Process Engineering

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1. Summary

The global nature of the Environment demands global environmental thinking but many decisions are taken at a local scale combining in different ways economic, social and environmental issues. Integration of Sustainability criteria in Chemical Process Engineering is an emerging task, which needs to be based on: (a) Sustainability Metrics, and (b) Previous Lessons from Case Studies in order to develop a suitable methodology to be applied for an operating unit, which can correspond to a functional unit in a process plant, a process plant (or a group) , the supply chain (or a part) or other process system . The Aluminium Fluoride Manufacture has been taken as a Case Study, in order to describe the identification of the operating unit and the selection of indicators and weight factors for the objective functions.

Keywords: Sustainability, Life Cycle Assessment, Environmental Management

2. Extended Abstract

The world economy globalizes as national economies integrate into the international economy through trade, foreign direct investment, short term capital flows; international movement of workers and people in general and flows of technology.

As economies open up, more people become involved in the processes of knowledge integration and the deepening of non-market connections, including flows of information, culture, ideology and technology.

The global nature of the environment demands global environmental management and designing more sustainable processes and products is one of the key challenges, for a sustainable development of the chemical process industry. This is not a trivial task as it requires translating the principles of sustainable development into processes and products. Taking into account the long-term constraints imposed by the finite carrying capacity of the Earth is the main challenge

At present, there is not any established methodology to guide sustainable chemical process engineering and almost no practical experience. The management of complex systems involving material and energy flows will be essential and system-based tools for environmental management based on chemical engineering principles are common.

In an attempt to contribute to this emerging area, new methodologies for integrating sustainability considerations into chemical process engineering are necessary. Two main guidelines have to be considered:

(1) Life Cycle Thinking, this methodology guides the chemical engineer through different stages to enable integration of technical, economic, environmental and social criteria. The objectives seem to be how to assess the level of sustainability and how to use the obtained information to make the company, chemical processes and products more sustainable.

(2) The sustainability metrics. Many frameworks of sustainability assessment that focus on the performance of companies, processes and/or products have been suggested by now. They propose an evaluation based on numerous sustainability, indicators, which are generally measured in very different units.

The keynote presents a sustainability analysis based on Life Cycle Thinking and the Metrics and Harmonization of the different sub-systems taking part in the chain supply.

Chemical Process Engineering has undertaken significant progress over the last twenty years in order to improve the efficiency of production and in the last ten years in order to introduce the environmental performance but, sustainability needs to examine and improve other aspects, which have not received much attention in the past: (a) global environmental responsibility, (b) a broader scope of economic return, considering wealth creation and, (c) social development.

It can be translated to the technical language in the way from one dimension optimization problems based only on the benefit for investors to "at least" a thee dimensions optimization problem based on an objective function which should be able to weight the three components of sustainable development.

In order to apply the Life Cycle Thinking the first important technical question to be clarified is the identification of the OPERATING UNIT. Three main scales are identified for the operating unit: (1) The operation unit scale, which corresponds to the equipment and facilities units where physico-chemical changes take place, (2) The Process Plant (or plants), which combine unit operations and reactors in order to achieve the transformation from raw materials to final products and, (3) The Supply Chain, which considers all the steps from the raw materials supply to the final destination of the products in the Environment.

The second important question to be answered is the selection and harmonization of the environmental, economic and social indicators to be used in the operating unit and the weight factors to be applied in the definition of the objective function to be optimized. Three different scenarios can be envisaged corresponding to the maximum and minimum values of the weight factors. A GREEN scenario, where the weight factor for the environmental indicators is 1, being 0 and 0 the weight factors for the economic and social aspects a RED scenario where the social aspects are of main concern and a BLACK scenario taking only economic aspects.

An analysis of sensitivity using different weight factors is recommended in order to achieve the best results.

A sustainability analysis of the operating units related to the chemical, aluminium fluoride will be developed as case study showing the application of the two main steps:

(1) Identification of the operating unit.

(2) Selection and application of indicators and weight factors in an objective function.

Results will be discussed to integrate sustainability in Chemical Process Engineering.

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Session S-7A: Environmental Protection & Sustainability - I

Abstract Number	Paper Title & Authors	Included
2102	Biodegradation Of Irradiated Toxic Aromatic Compounds B O Oboirien, E M N Chirwa	No
2245	Degradation Of Textile Dyes By Application Of Ultrasound H T Gümüşdere, A Güvenç, Ü Mehmetoğlu	Yes
3188	Modelling of Bulk and Surface Reactions during Electrochemical Oxidation of Organic Compounds at BDD Anodes M Mascia, A Vacca, S Palmas, A M Polcaro, F Ferrara	Yes
3327	Novel Catalytic Non-Thermal Plasma Reactor for the Destruction of Volatile Organic Compounds L K Minsker, C Subrahmanyam, A Renken	No

Session S-7A

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Degradation of textile dyes by application of ultrasound

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1. Summary

The aim of this study is the ultrasonic degradation of three textile dyes (Reactive Red 2, Reactive Blue 4, Basic Yellow 2) by the application of ultrasonic irradiation in pulse mode or in continuous mode at 20 kHz. Maximum degradation percents were found as 81 %, 71 % and 56 % for RR2, BY2 and RB4, respectively at the end of 6 hours for initial dye concentration of 10 mg/l when the ultrasound was given into the system in continuous mode with mixing. Although, the textile dyes could be degraded by ultrasound in this study, the hybrid methods may be applied for the completely degradation of textile dyes.

Keywords:Reactive Red 2, Basic Yellow 2, Reactive Blue 4, Ultrasound, Degradation

2. Extended Abstract

Enormous amounts of textile wastewater which is heavily charged with unconsumed dyes and other assistant chemicals are being produced in the textile industry processes. Dyes which include nearly 10.000 different types are produced over $7*10^5$ tons annually on average. Ten percent of these dyes have been discharged to environment by effluent of industrial wastewater treatment systems. It is not desired to discharge the effluents formed by this way, because these effluents destroy nature and threaten human health. It is well known that advanced oxidation processes are used to remove hazardous organic compounds and dyes from water and effluents of wastewater treatment plants. Among the advanced oxidation techniques, it can be said that sonolysis is one of rapidly developed techniques. Sonolysis is called to use of ultrasound in chemistry. Sonolysis has the potential for use in environmental remediation due to the formation of highly concentrated oxidizing species such as hydroxyl radicals ($HO^\bullet$), hydrogen radicals ($H^\bullet$), hydroperoxyl radicals($HO^\bullet_2$) and H_2O_2.

In this study, the degradations of Reactive Red 2 (RR2), Reactive Blue 4 (RB4) and Basic Yellow 2 (BY2) were investigated by the application of ultrasonic irradiation at 20 kHz. The initial concentrations of dye solutions (Co) were studied as 5, 10, 25, 50 and 100 mg/l. The system was operated in pulse mode (P/01-US; 0.1s on/9.9s off or P/5-US; 5s on/5s off) or in continuous mode with mixing (C/M-US) or without mixing (C/nonM-US) during 6 hours. Aqueous dye solutions sonicated of 1 ml were withdrawn at every hour, and the dye solutions before and after ultrasonic irradiation were analyzed by UV-VIS spectrophotometer at 538 nm, 596 nm and 430 nm for RR2, RB4 and BY2, respectively.

The effects of the reaction time, application type of ultrasound, initial concentration of dye solution and type of dye on the degradation were investigated. It was found that the degradations of each dyes increased rapidly with increasing reaction time for three application type (C/M-US, C/non M-US and P/5-US) except P/01-US. It was thought that ultrasonic energy was not enough for the degradation of dyes at (P/01-US). It was observed that the most effective application type of ultrasound was C/M-US as shown in Figure 1. The effect of mixing on the degradation of all dyes was not very clearly observed.

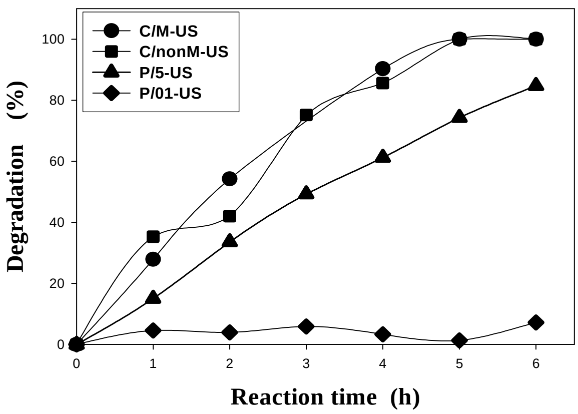

Figure1. The effect of reaction time and ultrasound application type on the degradation of BY2 (Co: 5 mg/l)

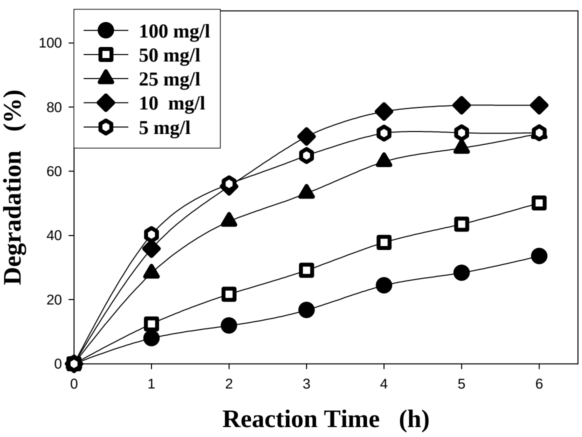

Figure2. The effect of reaction time and the initial dye concentration on the degradation of RR2 (C/M-US)

The degradation percent decreased with increasing the initial concentration of RR2 for C/M-US as shown in Figure 2. The same observations were valid for other two dyes. It was thought that, ultrasonic energy per mole of dye decreased with increasing initial concentration of dye, due to ultrasonic energy given to system was constant. This condition caused a decrease in the generation of hydroxyl radicals. So, dye degradation decreased. Maximum degradation of BY2 was found as 100 % for C/M-US for initial dye concentration of 5 mg/l at the end of 5 hours. Maximum degradation of RR2 was found as 81 % for C/M-US for initial dye concentration of 10 mg/l at the end of 5 hours. Maximum degradation of RB4 was found as 80 % for P/5-US for initial dye concentration of 5 mg/l at the end of 6 hours. RR4 more difficulty degraded than the others because of its molecular structure. To be limited of solubility in water of BY2 restricts its degradation. It was observed that the most easily degraded dye was RR2 among dyes tested. Consequently, the textile dyes could be degraded by ultrasound in this study. However, the hybrid methods such as ultrasound/H_2O_2, ultrasound/ozone, ultrasound/biological treatment may be applied for the completely degradation of textile dyes.

Acknowledgments

The authors gratefully acknowledge the founding of this work by Ankara University, Scientific Research Council (Turkey) (Project No: 2005-0745006HPD).

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Modelling of bulk and surface reactions during electrochemical oxidation of organic compounds at BDD anodes

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1. Summary

This paper presents the results of an experimental and numerical study on the kinetics of electrochemical oxidation of different organic substances at boron doped diamond (BDD) anodes. A mathematical model was implemented which accounts for the complex behaviour of aqueous solutions containing organic compounds during electrolysis at BDD. The model allows to quantify the effect of different variables related to the chemistry of both organic compounds and solution, in terms of kinetics of direct electrochemical oxidation and chemical reactions with electro-generated oxidants. The effect of reactor hydrodynamics on the mass transfer was also considered. The parameters of the model were the kinetic constants, mass transfer coefficients and geometric parameters of the system. The numerical solution of the model was validated through comparison with experimental data obtained from electrolyses of different phenols which exhibited different behaviour during the electrochemical oxidation process. The results showed that the proposed model interprets well the complex effect on removal efficiency of such operating parameters as current density, hydrodynamics of the reactor and chemistry of the solution.

Keywords: BDD Anodes, Electrochemical Oxidation, Mathematical Model, Numerical Prediction, Organic Compounds

2. Extended Abstract

Different electrochemical reactions may occur during electrochemical oxidation at the BDD surface, such as oxidation of the organic to radicals or more oxidised substances, OH radicals generation from water oxidation and oxidation of inorganic substances which may generate long-life oxidants. OH radicals can react with organic compounds to give more oxidised substances. OH radicals can also react with water or with each other to give oxygen. Moreover, long life oxidants may be generated by reaction of such inorganic species as Cl^- with OH radicals. Because of the high reactivity of OH radicals the volume in which these reactions can occur is a thin film adjacent to the electrode surface. However, oxidation may also occur in the bulk of the solution by means of the electrogenerated long-life oxidants which may diffuse and oxidise the organics to more oxidised intermediates or CO_2. The model utilised in this work describes the reactor by two diffusion layers and a mixed bulk[1]. The boundary conditions account for the electrochemical reactions at the electrodes. The reaction path of the investigated compounds is represented by the following[2]:

- Phenolic compound => cyclic intermediates => aliphatic intermediates => CO_2

whereas the reaction rates are described by second order kinetics.

The experimental data utilised to validate the model were obtained under different conditions by using an impinging jet flow cell inserted in a hydraulic circuit in a closed loop. Different values of recirculation flow rate, electrolyte composition and current density were adopted. In order to study the effect of electro-generated bulk oxidants, chlorides were added in some runs. The concentrations of the different reactants and intermediates during the runs were analysed by HPLC. The values of the parameters utilised in the model were obtained from the literature or from experimental data[3,4]. As an example, Figure 1 shows the comparison between experimental and model predicted data for electrochemical oxidation of m-cresol under different experimental conditions: as can be seen from the figure, the solid lines calculated by the model show good agreement with the experimental values.

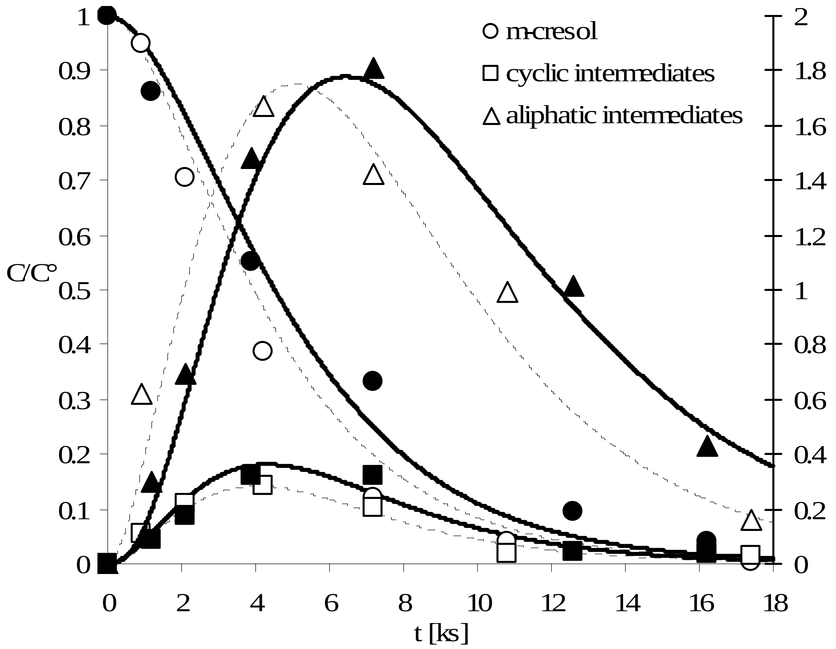

Figure 1: comparison between experimental (symbols) and model predicted data for the trend in time of m-cresol cyclic intermediates and aliphatic intermediates (secondary axis) during electrolyses of aqueous solutions of m-cresol with $NaNO_3$ (full symbols) or $NaNO_3$ + KCl (empty symbols) at Re = 7000 and i= 8 mA cm^{-2}

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Session S-7B: Environmental Protection & Sustainability – II

Abstract Number	Paper Title & Authors	Included
498	Sustainable Active Pharmaceutical Ingredient production through efficient resource intake: quantifying feedstocks, mass agents and utilities by one single metric J Dewulf, G V Vorst, W Aelterman, H V Langenhove	Yes
1174	Incorporating Sustainability Into The Superstructural Synthesis Of Municipal Solid Waste Management N I Bedenik, Z Kravanja	Yes
1920	Application of the water source diagram procedure (WSD) for freshwater minimization in a batch process A P S Immich, M Gusatti, J M M Mello, S G U Souza, F L P Pessoa	Yes
3763	Alternative Fuels in Cement Production – Contributing to a Sustainable Future M B Larsen	Yes

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Sustainable active pharmaceutical ingredient production through efficient resource intake: quantifying feedstock's mass agents and utilities by one single metric

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** presenting and corresponding author*

1. Summary

We present a method that enables to quantify all resource inputs (mass and energy) going into a chemical operation in the pharmaceutical industry. Feedstocks, mass agents and utilities are all quantified by means of the second law of thermodynamics, resulting in one single measure for all inputs that are required for a process. It is illustrated by a comparison of chromatographic separation and crystallization as two alternatives for one specific step in a pharmaceutical synthesis.

Keywords: pharmaceutical synthesis, green chemistry, resource efficiency, exergy

2. Extended Abstract

It is obvious from the E-factor as defined by Sheldon (1997) that the chemical industry and particularly the fine chemical and pharmaceutical industry are prominent sources of pollution: for 1 kg of pharmaceuticals the intake can be up to 25-100 kg. This means that waste production can be 100 times higher than the net production. It is obvious that the best approach to reduce environmental impact is through reduction of resource intake: it results in resource depletion reduction and decrease of emissions at the same time.

It is not surprising that indicators for mass resource efficiency (e.g. reaction mass intensity, kg raw materials/kg product, ...) are of common practice in fine chemistry to assess environmental sustainability (Lapkin, 2006). Energy resource requirements however are usually hardly considered. In the best case, 'red light' guidances are taken into account, e.g. setting minimum and maximum operating temperatures and pressures, rather than quantifying specific energy limits in terms of J/kg final product.

The scope of this contribution is to come forward with a quantitative environmental sustainability tool for fine chemicals and Active Pharmaceutical Ingredients (API) production that enables simultaneous mass (feedstock, mass agents) and energy resource (utilities) intake, in order to prevent that savings in mass resource intake are overrided by huge energy intakes, and vice versa.

The tool is based on the second law of thermodynamics, which today is a rapidly growing base for process evaluation (e.g. Dewulf et al., 2000; 2005; Haynes and Wepfer, 2002; Szargut, 2005; Dewulf and Van Langenhove, 2006). The tool is illustrated with a concrete process at the Janssen Pharmaceutica plant, Belgium, where two diastereomeric intermediates in the chemical synthesis of a new drug have to be separated. Taking both mass and energy intakes at the process level, the plant level and the overall industrial production chain, crystallisation and chromatography are evaluated, where crystallisation proves to be the most resource efficient process.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Incorporating sustainability into the super critical synthesis of municipal solid waste management

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1. Summary

The proposed work describes the development of a superstructural approach to the synthesis or reconstruction of those sustainable networks dealing with municipal solid waste (MSW) within rural and urban communities. This approach is based on long-term multiobjective mixed-integer nonlinear programming (MINLP) method(s). By considering economic and environmental criteria simultaneously, it gives rise to sustainable Pareto optimal solutions that are economically effective and environmentally benign at the same time.

Keywords: MSW management, MINLP optimization, synthesis of MSW network, sustainability, multiobjective optimization

2. Extended Abstract

The objective of overall MSW management is to propose optimal MSW management networks, where it is important to look at the broader picture including processes such as waste collection, transportation, treatment, recycling and the selling of secondary material and energy, and the final disposal. Until recently, only economic criterion had been considered (e.g. Iršič Bedenik and Kravanja, 2006), which gave rise to economically effective MSW network solutions. A typical network comprised elements for interregional waste collection, recycling, treatment and disposal, where a trade-off was established only between cost and revenue terms. In order to propose economically optimal, and yet sustainable, networks for MSW management based on long-term optimization, two modifications have now been put forward: a) sustainable alternatives have been identified and added to the superstructure and b) a suitable environmental criterion has been defined and incorporated in to the profit objective function.
Definition of the superstructure: The recycling of MSW to recover useful materials, and recycling energy from the waste by incineration is a well known sustainable way of dealing with MSW. Based on the mentioned idea, a sustainable superstructure is proposed. It comprises alternatives for minimal or zero waste emissions, minimal use of land, minimal transportation and operation costs, and maximal amounts of recycled material and energy.

Multiobjective optimization: Incorporation of sustainability into an optimization criterion can be accomplished either by the use of the weighted objective function or the ε-constraint method. In our case we have implemented the weighted method with the weighted economic and environmental relative indices in the objective function. A large-size MINLP model has been developed due to discrete decisions, which mainly concern the selection and allocation of waste collection and treatment centres, and due to concave cost terms in the objective function. A set of non-inferior Pareto optimal solutions with different optimal structures has been obtained, Fig. 1. As can be seen from Fig.1, the net present value has been significantly improved (five times), and the environmental burden has more than halved, compared to the base case.

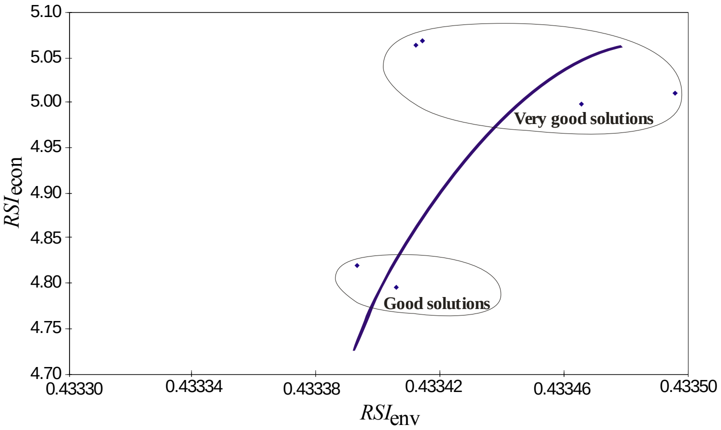

Figure 1: Pareto curve obtained by weighted objective function.

3. Conclusion

The obtained optimal networks simultaneously integrate and reflect different considerations for economic and environmental criteria. The solutions indicate that MSW management can be both profitable and sustainable at the same time. The Pareto curve obtained by the weighted objective function reflects dependence on the relative economic and environmental indices. Interactions between alternatives, thus exploited, can only be appropriately handled by a simultaneous approach to the synthesis of a MSW network.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Application of the water source diagram procedure (WSD) for freshwater minimization in a batch process

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1. Summary

An alternative to the scarcity of some natural resources such as water is the reuse and/or recycle of water streams sent to effluent treatment plan. Gomes et al (2005) developed a methodology to minimize the use of water and the generation of effluent for continuous process only. The authors presented an algorithm procedure named Water Source Diagram (WSD) defining the aim of the minimum water consumption for industrial processes by reuse and recycle of water streams, as well as the development of flowcharts which satisfy the established aims. The purpose of this study is to apply the WSD for a batch process. The obtained results were excellent.

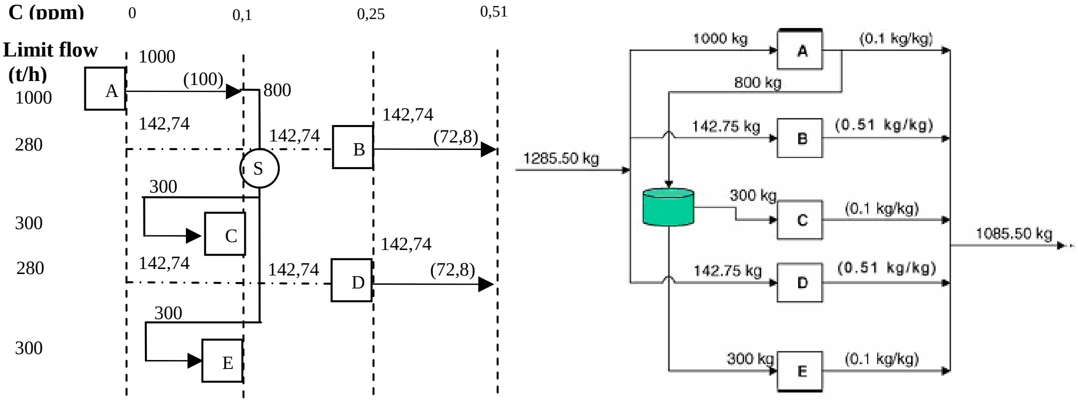
Keywords: WSD, batch process, reuse, storage tank

2. Extended Abstract

In exploring the recycle and reuse opportunities within a complete batch process, four scenarios are formulated. The first and third scenarios are based on a fixed outlet concentration from each water using operation without and with the existence of reusable water storage, respectively. The second and fourth scenarios are based on fixed water requirement for each water using operation without and with the reusable water storage, respectively. The purpose of the four scenarios is the minimization of freshwater.

The data for the studied case were taken from Table 2 presented in Majozi (2005). Prior to the exploration of water reuse/recycle opportunities, these operations used 2360 kg of freshwater.

The WSD technique is applied for all scenarios, but it will be showed here only for the third scenario, since this scenario showed the greatest reduction in freshwater consumption and effluent generation. For this scenario, following the constraints given by Majozi (2005), it is possible to build the WSD (Figure 1a) and, from this, to build the flowchart of the water reuse (Figure 1b).



(a) (b)

Figure 1: **(a)** Water source diagram for the third scenario **(b)** Flowchart for the reuse of water for the third scenario

It is evident from Figure 1(b) that the existence of central reusable water storage (S) allows the time constraint to be overridden, thereby providing an opportunity for reuse from operation A to operations C and E. Figure 1(b) shows that it is necessary 1285.50 Kg of freshwater and it is generated 1085.50 Kg of effluent. It corresponds to a reduction of 45.53% of freshwater required for this operation. This is due to the presence of a reusable water storage tank, which allows the storage of water used in previous operations when the time constraint of the end of some operation does not coincide with the beginning of others. For the scenarios 1, 2 and 4, with the application of the WSD it is required 1767.85 Kg, 2052.30 Kg and 1560 Kg of freshwater, and it is generated 1767.84 Kg, 2052.30 Kg and 1560 Kg of effluent, respectively.

The obtained results in this study using WSD were identical to the results obtained by Majozi (2005), through the computational method. Therefore, the simplicity of application of the WSD method makes it an important candidate to solve one of the greatest industrial problems referring to the scarcity of natural resources.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Alternative Fuels in Cement Production – Contributing to a Sustainable Future

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Abstract

Cement products are consumed worldwide in significant quantities as building materials. Cement production plants processes a well proportioned mixture raw materials consisting of clay minerals and chalk at temperatures up to about 2000°C, producing so-called cement clinker, which upon grinding with additives produces the final cement product to be sold.

During the last 150 years, the production processes used for Portland cement production have moved from shaft kiln units with production capacities of about 7 tonnes cement clinker per day to modern production plants with a production capacity of up to 12000 tonnes cement clinker per day. The development has mainly been driven by a desire to attain a lower specific energy consumption per mass of cement clinker produced. Initially, the shaft kilns were replaced by long rotary kilns fed with a wet slurry resulting in a specific heat consumption of about 1400-1500 kcal/kg clinker. A long rotary kiln fed with dry raw materials reduced the specific energy consumption to about 1075 kcal/kg clinker, as the evaporation of water from the slurry was avoided (Jensen, 2004). Further developments led to a separation of the processes involved in cement clinker production in order to improve energy efficiency. The modern kiln system of today consists of separate processes including raw material pre-heating, a pre-calcination unit for calcination of limestone, and a rotary kiln for the final cement clinker burning. The specific energy consumption of a modern dry process is about 700 kcal/kg clinker, where about 55% of this calorific demand stem from energy consuming chemical processes, e.g. calcination of limestone. The remaining energy consumption results from various heat losses.

Pyro processing of prepared raw materials involves preheating, calcination, clinker reactions as well as cooling. A flow sheet of a modern kiln system for cement production is shown in Figure 1. Raw materials are admitted to the preheater and heated counter current by direct contact with the hot flue gasses. The preheated raw material is then admitted to the calciner system where decomposition of $CaCO_3$ takes place. The energy needed for the endothermic calcination is supplied by combustion of the fuel added in preheated air. The calcined raw material is admitted to the rotary-

kiln, where the remaining clinker reactions as well as nodulisation take place. Fuel and preheated air are admitted to the rotary kiln in order to heat the reacting materials to a temperature where the clinker reactions take place. Finally, the clinker is cooled by air in the clinker cooler, producing a preheated combustion air that is used in the rotary kiln and in the calciner system. The flue gas from the rotary kiln may be passed directed through the calciner (1) or bypassed (2), i.e. In-line-calciner (ILC) or Separate-line-calciner (SLC) system respectively.

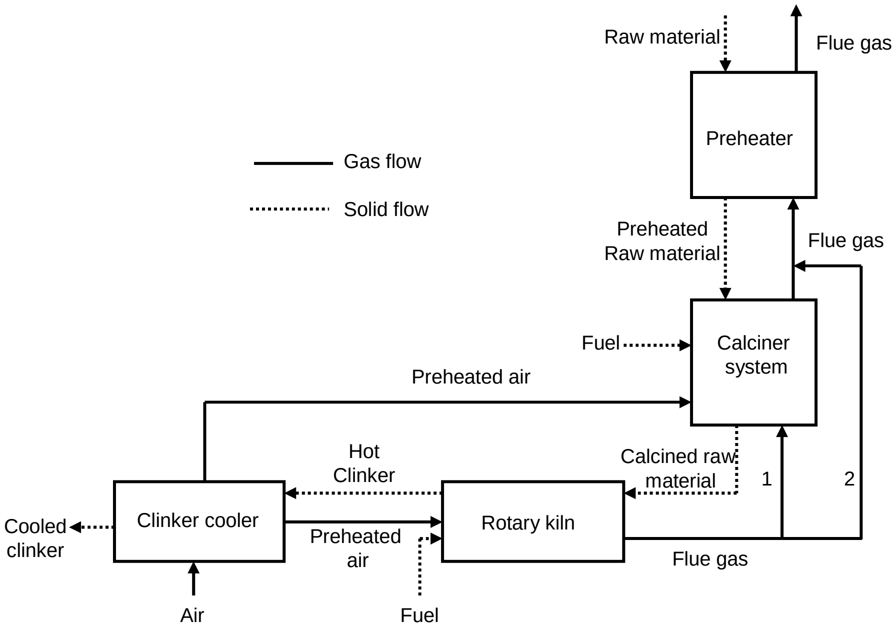

Figure 1: Flow diagram of modern kiln system for cement production.

The energy supply usual comes from fossil fuels of coal, oil and gas. Consequently, replacement of these fossil fuels with more environmental friendly alternative fuels contributes to a sustainable future. Alternative fuels comprise of waste and biomass. The main advantages using alternative fuels in cement production are: 1) Fossil fuels are saved, 2) Alternative fuels may be CO_2 neutral, 3) No solid residues are produced as the ash components are reused as cement clinker minerals, 4) High temperatures ensure good conditions for complete oxidation of organic compounds, and 5) Negative costs may be associated with alternative fuels, i.e. increasing revenues are to be expected for the cement producers.

This presentation briefly reviews modern cement production processes and the utilization of alternative fuels.

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Session S-7C: Environmental Protection & Sustainability – III

Abstract Number	Paper Title & Authors	Included
1511	A quantitative framework for Sustainability Assessment in the Process Industry A Tugnoli, V Cozzani, F Santarelli	Yes
2260	Systems approach for the estimation and management of sustainable development M Z Zgurovskiy, G A Statyukha	Yes
2373	Decision Support For Biotechnological Produced Peptides In A Design Stage By Sustainability Assessment A S Albrecht, B U Bos, C M Shibasaki	Yes
3487	Analysis of the contribution of information management for the implementation of pollution prevention measures into process industries A R Córdoba, P Sharratt, J A Sánchez	Yes
3664	Life Cycle Assessment Prognosis For Sustainability M Shibasaki, S Albrecht	Yes
4083	Pollutants Emissions In A Urban Area: Definition Of Emission Factors, Atmospheric Dispersion Modelling And Support Of Intervention Policies E Brizio, G Genon	No

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A quantitative framework for Sustainability Assessment in the Process Industry

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1. Summary

The shift toward a sustainable performance of process industry requires integrated analysis tools to drive process design. Present contribution introduces an assessment framework addressed to the comparison of process options in early design stages. An array of indicators for specific categories of impact is identified. Indicators are combined by a multi-criteria approach, yielding a hierarchy of aggregated indexes. The importance of the normalization stage is outlined in order to evaluate the process in the context of the site. Specific criteria for the determination of reference values are proposed. The role of weighting factors in connecting the design technical choices and the sustainability management policy of the specific site location is discussed. The outlined approach is demonstrated by the application to industrial case studies.

Keywords: sustainability assessment, process industry, multi-criteria analysis, normalization, inherent safety.

2. Extended Abstract

The adoption of a sustainable behaviour is nowadays a core issue for process industry, representing the effective answer to problems like societal acceptability, pressure on the environment, efficiency, safety, etc. In the process design, in particular at early stages, quantitative tools are required to drive decision-making and process improvement toward sustainability [1,2]. Despite of the considerable efforts devoted to the development of quantitative assessment tools, an approach to perform a balanced analysis of the multiple specific aspects of concern is still missing. Present work proposes an assessment framework specifically addressed to the comparison of process options in early design stages.

The first step in the comparison is the definition, for all the process options, of a common reference basis (e.g. production potentiality) and of consistent boundaries and/or battery limits. Moreover data on system input/output, inventories, operative conditions and economics need to be collected or estimated for each option.

The collected data yield the evaluation of an array of indicators addressing specific categories of impact related to the process of concern. The various indicators encompass the three main aspects of sustainability (environmental, economic and societal). Benchmark based indicators are chosen for representing environmental impacts, since they allow a direct correlation among flows and potential impacts [2,3]. The review of available metrics allowed selecting the indictors specifically suitable for the process analysis and proposing, whenever necessary (e.g. waste disposal), new simple ones on a common basis. In particular, in the field of societal issues, along with occupational impact, the level of inherent safety of the option is identified as a critical element to be assessed. An innovative index, based on the evaluation of hazard through the use of reference damage distances for expected accident scenarios, was thus introduced in the assessment framework.

The single impact indicators are combined through a multi-criteria approach aimed to the definition of a hierarchy of indexes with different levels of aggregation. Each aggregation step is based on the general formula:

$$AI_k = \sum\nolimits_i W_i \frac{I_{i,k}}{NF_i} \qquad (1)$$

where AI_k is the aggregate index for k-th option, $I_{i,k}$ is the index for the *i-th* impact considered for k, NF_i and W_i are respectively the normalization and weight factors.

The choice of normalization factors must reflect the context where the process has to be located. A spatial scale typical of each impact phenomena was identified. Reference values are calculated resorting to available databases for the specific impact areas. Weighting factors have the role to reflect the management policy in the chosen location of process activities. They are independent of the assessed process options and can be estimated by various ranking techniques (e.g. distance from objective, impact allowance, Analytic Hierarchy Process).

The proposed aggregation approach allows a connection between the technical choices at the design level and the sustainability management policy of the specific location of process activities. This bridges the gap that exists in common practice between the macro (national/regional) and micro (process/facility) scales of sustainability assessment, allowing transfer of goals from the former to the latter.

The outlined procedure was applied to several case studies of industrial interest, in which different process options were compared. The procedure allowed the assessment of the impact fingerprint of each process option and the ranking of options with respect to the overall impact on sustainability (e.g. Figure 1). Moreover the use of different levels of index aggregation, allow identifying the performance of single units within the process for as concerns specific impact aspects, providing suggestions for further design improvement.

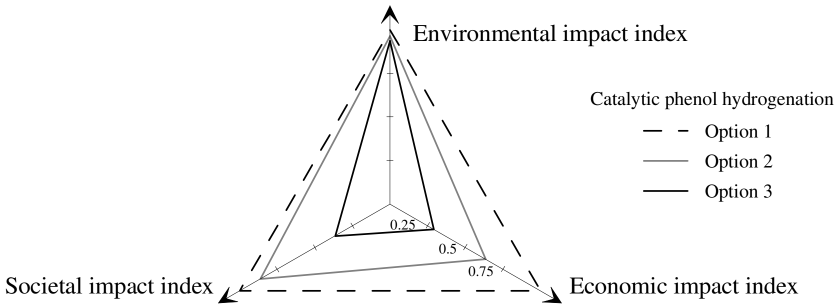

Figure 1: Example of impact fingerprint for the comparison of process options for cyclohexanone synthesis.

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Systems approach for the estimation and management of sustainable development

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1.Summary

Progress in the paradigm of sustainable development comprehension has passed into a phase of practical management of this process. However, the practice of sustainable development management has revealed a number of essential restrictions. The consideration of society processes in the form of cycles "use-restoration of resources" opens for us the prospect of model construction. This model is approximate, but ideologically correct for natural resources "circulation' in certain subsystem. The opportunity exists manage to build an index of sustainable development by means of which it is possible to manage of sustainable development process. In this paper, it is offered to construct for such model some coefficient η, in the form of ratio for sum of resources and target product streams to the sum of the streams restoring the nature stocks. The coefficient offered possesses of necessary integrity, principal aggregation and the certain independence from the level of system hierarchy. All this promotes its successful application for the purposes of management. There is a real opportunity of construction of methodological and analytical blocks for sustainable the progress, which will be called to estimate development of various subsystems of a society from positions of sustainability.
Keywords: the index of sustainable development, sustainable development management.

2. Extended Abstract

Progress in the paradigm of sustainable development comprehension has passed into a phase of practical management of this process. However, the practice of sustainable development management has revealed a number of essential restrictions. Along with social and organizational restrictions, the increasing weight gets the restriction connected with limited opportunities of the person to make concrete decisions in concrete circumstances. Presence of indicator set sharply reduces the efficiency of the optimum decision search. The aggregation of indicators often results to the loss of physical sense of the decision and here, the decomposition of an index up to concrete parameters is required.

Formalistic approaches in the realization of information aspects of sustainable development have blacked out the main idea of sustainable development process which can be transformed in such way: operating with sustainable development, it is necessary to support a level of a stocks of natural wealth accumulated by the nature for the future generations, using thus, the great opportunities of natural mechanisms – the work of ecosystem. This implies first of all, necessity for the stocks measurement of nature and the dynamics of stocks expenditure (the theory of the natural capital). Secondly, there is a requirement for quantitative estimation of the restoring potential of ecosystem, included into a cycle of restoration (updating) of natural resources.

The consideration of society processes in the form of cycles «use-restoration of resources» opens for us the prospect of model construction. This model is approximate, but ideologically correct for natural resources "circulation" in certain subsystem. Here, the opportunity exists manage to build an index of sustainable development by means of which it is possible to manage of sustainable development process. In this paper, it is offered to construct for such model some coefficient η, in the form of ratio for sum of resources and target product streams to the sum of the streams restoring the nature stocks. It is evident, that at the calculated estimation $\eta > 1$, the system will be unstable from the point of view of its potential preservation (consumption of natural resources is going more intensively, than their restoration); for $\eta = 1$, the system is on the border of sustainability; for $\eta < 1$, the system is sustainable one (restoration of resources of the nature goes with advancing rate). It is obvious, that all political decisions at levels of appropriate hierarchy should be those to achieve value $\eta \leq 1$, as both due to decreasing of resource expenditure and modernization of product technology, and to increasing of costs for the restoration and supplement of resources. The coefficient offered possesses of necessary integrity, principal aggregation and the certain independence from the level of system hierarchy. All this promotes its successful application for the purposes of management.

The measurement of natural parameters is presented the definite complexity. In spite of fact, that the part of this data exists physically (for example, stocks of natural resources are estimated even by the market prices), many natural parameters, nevertheless, are disseminated at various departments and hard accessible. And to such parameters of the natural capital as, for example, « to take aesthetic pleasure in nature » hardly somebody knows how it is quite beyond somebody means. Here, we have the great hopes with introduction in action of the World Center of Data in NTUU «KPI». There is a real opportunity of construction of methodological and analytical blocks for sustainable the progress, which will be called to estimate development of various subsystems of a society from positions of sustainability.

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Decision support for biotechnological produced peptides in design stage by using Sustainability Assessment

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1. Summary

Environmental friendliness of products is becoming more and more important in the societal discussion, accompanying with the costs of products and an increasing importance of social effects. These three topics, regarded over a product's life cycle, establish the basis of a products` "sustainability". The most important drivers can be determined for an ecological, economic and social optimised production by an early-stage decision support.

This work shows a development study with pre-analysis and consequential simulations on the basis of work conducted within the EU funded BASE project. It demonstrates the methodological approach of sustainability analysis especially for bio-based materials.

Keywords: life cycle analysis, sustainability, biotechnological production, green engineering

2. Extended Abstract

For all three columns of sustainability the most crucial decisions are made in an early design stage of a product (see Figure 1), there the most relevant changes can be determined for an ecologic, economic and social optimised production.

This leads to the idea of an early-stage decision support regarding the columns of sustainability. The purpose of the sustainability analysis is to support the decision making by providing "integrated decision support" in the R&D-stage of a product. It combines assessments covering environmental, economic, technical and social aspects. Therefore, a development study with pre-analysis and consequential simulations enables the pre-estimation of the sustainability of the technical processes.

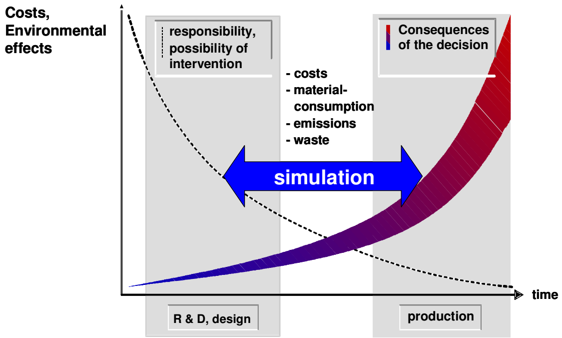

Figure 1: Simulation of costs and environmental effects during R & D is crucial

In the EU-funded project –"Bio-based Functional Materials from Engineered Self-Assembling Peptides (BASE)", an integrated consideration of all life cycle aspects of chosen peptides is made.

The BASE project aims at advancing the knowledge and technology of sustainable and functional materials. Specifically it targets innovative nano-coatings for plastics, metals and ceramic objects, exploiting the self-assembly capabilities of short (<25) amino-acid sequences (=peptides) in industrially relevant applications.

Self-assembly is a method of spontaneous organization of molecules into higher order structures and defined by set boundary conditions (e.g. pH, temperature hydrogen-bonding strength, ionic strength, polarity of the solvent and nature of substrate).

The innovativeness resides in the shortness of the peptides and associated structure forming capacity to create tailored bio-inspired functionality. Short peptides offer a more manageable science and open a window towards a cost effective availability through biotechnological routes.

Method: Within this project sustainability analysis is carried out during the development phase using the method of LCA, LCC and LCWE, which are described below.

Environment: Life Cycle Assessment (LCA) is a method to determine the environmental impacts of a product or system during its whole life cycle including the production and supply of all precursor substances, operating supplies, auxiliary materials, energies etc.. It is an addition of traditional research and development assessment, in which only cost and the function of the new technology are in the focus. All relevant impact categories are assessed, taking into consideration the goal of the study and emissions released from the product system under examination.

Economy: Life Cycle Costing (LCC) is a technique to establish the total cost of ownership or the total production cost of a product or service system.

A particular aspect in this analysis is that, unlike the situation in LCA, where insight into all the processes of the value chain is needed for an assessment of the environmental impacts, the economy offers the ‘rucksack-principle’ of prices, i.e. prices of products have the comfortable nature of summing up the whole value chain of the production. With a product bought for a certain price, one does not have to bother about the origin of this price, whether it is derived from the costs of a certain production step or from the profit of the producer, or even if the producer is making any profit at all, the costs within the boundaries of the other players can be viewed as a black box, without requiring any differentiation [1].

Society: Life Cycle Working Environment (LCWE) methodology [2] measures the work-related social effects of processes and products. It is based on the same product life cycle model as the LCA, ensuring consistency with the LCA- and LCC-part of the study. Similar to LCA, an insight into all processes of the system is required in order to assess the impacts.

Discussion: In this study, the concept of sustainability analysis is applied at the production of biotechnological produced peptides for several applications. The principle competing conventional applications serve as benchmarks.

The method of the early stage sustainability analysis for the mentioned biotechnological produced peptides will be discussed in this paper considering an example of one of the regarded possible applications in the project.

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Information management for the implementation of pollution prevention measures into process industries

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1. Summary

This paper focuses on the methodologies currently available for waste minimisation. The purpose is to analyse the features that render them applicable in specific cases and the gaps that have to be overcome when trying to use them for other situations. The methodologies under study will be evaluated in the light of knowledge management to understand the different information requirements that each of them entail. These considerations are summarised in a novel and more practical methodological framework to evaluate and select the proper models to organise and optimise the available data against the required information.

Keywords: Waste minimisation, information, knowledge, ontologies

2. Extended Abstract

Successful and widespread implementation of existing methodologies for waste minimisation has failed to provide significant benefits in industrial applications because there is not a comprehensive approach that integrates and guides the application of the proper tool depending on the case. Each of these methodologies has been developed for particular stages in the process life cycle and they require different information which may not be available and could result too costly to obtain. The presented approach aims to integrate these methodologies and provides criteria to select the appropriate framework for the case at hand. The methodology also provides tools to identify and manage key required information to analyse the process and derive waste minimisation strategies based on the application of the appropriate method.

In the first steps of the proposed approach, it is taken into account that effective gathering, representation and modelling of information from all the staff levels within the organisation is essential to ensure integration and success of the different waste minimisation actions.

Waste generation within a process has to be analysed from the different aspects that cause it. This involves not only the manufacturing process but also other stages of the product lifecycle such as raw material storage and preparation, product distribution and in general, the logistics of the overall supply chain. The modelling of the entire life cycle of the process represents an effective way for grouping the necessary information to describe the crucial parts of a process. This will provide an accurate way to identify the areas which need attention for the purpose of pollution prevention and the activities that have to be modified to implement it.

The methodology developed divides knowledge about a process into five main classes which contribute in different levels to the successful application of waster minimisation tools. Mapping and organising this knowledge provides an effective means of reducing losses due to gaps in the understanding of the process and of the signs that point towards waste generation. This contribution explores the use of an ontology-based approach for the structured organisation of information aiming to identify significant waste minimisation opportunities.

Once the available process knowledge has been organised within the ontology-based framework, the information categories are compared with the information needed for the adequate analysis that generates options for the optimal performance of the actual process being studied. The methodology will provide a more adequate evaluation of the completeness and accuracy of existing information and generate unambiguous waste minimisation options which adapt to specific situations for a given process.

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Life cycle assessment prognosis for sustainability

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1. Summary

This paper reports on a new approach aiming at the scale-up of technical processes in Life Cycle Assessment (LCA). For this purpose a systematical procedure is integrated in Life Cycle Assessment. The effect of scale-up is usually not considered in LCA studies, although the result does not necessarily correspondent to each other. Therefore a method is required, which enables a prognosis of a large scale plant, based on information of pilot plant.

Keywords: scale-up, life cycle assessment, method, laboratory, pilot plant

2. Extended Abstract

Life Cycle Assessment (LCA) is a widely used and standardized method on international base, which enables the analysis of environmental performance of products or technical systems. The result of LCA are usually presented as Global Warming Potential (GWP), Summer Smog Potential (POCP), Acidification Potential (AP) etc. depending on the aim of the study. The LCA analysis bases on “data”, such as energy consumption, material consumption, amount and type of emissions etc., which will present the actual state of the process and accordingly the products under consideration. Therefore, the LCA can be carried out for processes at different stage of development: laboratory experiments, pilot plant, mini plant, small scale process or large scale process.

The development of “processes” from the laboratory scale experiments up to the large scale plants leads to possible changes in the environmental performance of the processes. Every single technical development or change influences the inventory data – and finally the environmental performances of products, or materials produced by those processes. The effects on environmental burdens due to technical scale-up are commonly not or at least not systematically considered.

In comparing LCA studies, processes under development are often compared to processes, which are already implemented in large scale. That means, processes at different development stages are involved in the study. An adapt of the result of process under development is not or at least not systematically considered because of lack of a systematic method.

A method, which is on development at the LBP of University of Stuttgart, will enable the systematic procedure of such prognosis, especially for chemical engineering processes. This method considers the factors affecting significantly the LCA results of the considered process. For this purpose those relevant factors will be identified based on the principals of LCA. The experiences and LCA analysis carried out at LBP (former IKP), enables the introduction of general assumption for chemical processes. Relevant effects can be: scale-up of processes, further technical optimization of processes targeting more economical and environmental property.

A correlation between the environmental performance of processes and the mentioned relevant factors will be established. Along this correlation and either expert estimation or rough plan of the large scale plant enables the estimation of the environmental performance of a large scale plant – based on the according pilot plant (see figure 1). The publication of the developed method is planned for 2007.

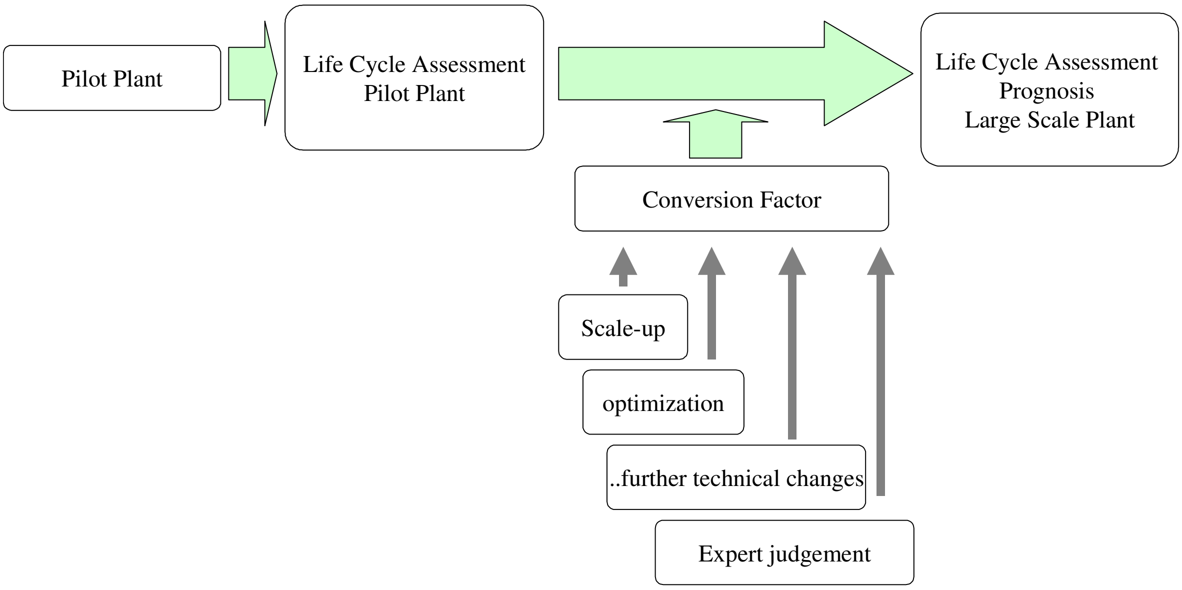

Figure 1: Principle method of LCA prognosis of a large scale plant based on pilot plant

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Abstract Number	Paper Title & Authors	Included
923	Influence Of Wastewater Treatment In The Life Cycle Assessment Of Aluminium Trifluoride A Dominguez, R Aldaco, A Irabien	Yes
574	Removal of Carbon Dioxide by Absorption in a Cross-flow Rotating Packed Bed C C Lin, B C Chen	Yes
577	Correlation of the equilibrium sorption of crude oil by expanded perlite using different adsorption isotherms at 298.15 k A Alihosseini, V Taghikhani, A A Safekordi, D Bastani	No
1688	Anaerobic Treatment Of Phenol In A Continous Fluidized-bed Biorreactor M S Gonzalo, M Martínez, P Letón	No
1783	Effects of Synthetic Temperature on the Microstructures and Basic Dyes Adsorption of Titanate Nanotubes K S Lin, C Y Pan, W R Chen, C P Lie, T P Perng	Yes
1963	Evaluation of the Chemical Absorption Technology for CO2 Capture of Industrial Gases Using Monoethanolamine (MEA) L Carvalho, A S Belloa, M L Andradea, W Diasa, Y Limaa, P R B Guimarãesa	Yes
2029	Numerical models to simulate pollution scenarios in Somes River E C Ani, P Ş Agachi	Yes
2155	Modelling of metal pollutant transport in natural humic environments P Sedláček, M Klučáková	Yes
2231	Proposing The Most Efficient And Environmental Safe Hydrocyclone To Depurate Ballast Water From Ship Hulls L F Martínez, A G Lavín, M M Mahamud, J L Bueno	Yes
2402	Arsenic removal from copper smelter wastewater by electrocoagulation in an airlift reactor H K Hansen, P Nuñez, C Jil	Yes
2465	Catalytic pyrolysis of high-density polyethylene on HZSM-5 and HY zeolite catalysts in a conical spouted bed reactor G Elordi, G Lopez, M Arabiourrutia, M Olazar, R Aguado, J Bilbao	Yes

2480	Catalytic hydroprocessing of polychlorinated derivatives of aromatic compounds K L Zanaveskin, L N Zanaveskin	Yes
2550	Different adsorption isotherms of carbon dioxide on raw and impregnated activated carbon M R Mehrnia, M M M Rahmati, M Safari, H D Amrei, A Ghanizadeh	No
3033	Oxygen transfer rate and acetone uptake rate in the airlift reactor using bacteria immobilized on solid particles creating the inverse fluidized bed B K Pietrenko, M Łazarczyk	Yes
3224	Novel metal oxide catalysts for low temperature selective catalytic reduction of NO with ammonia H Hamma, J Huang, A Riisager, S B Rasmussen, R Fehrmann	Yes
3639	An Experimental Comparison Of A Heat Exchanger In An Absorption Heat Transformer Operating In Falling Film And Pool Boiling S Silva, A Huicochea, J Siqueiros	Yes
4012	Parametric Optimization Of Cadmium And Chromium Adsorption On The Mediterranean Seagrass Posidonia Oceanica By Surface Response Analysis A Aydin, N Deveci	Yes

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Removal of carbon dioxide by absorption in a cross-flow rotating packed bed

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1. Summary

This study investigates the feasibility of applying a cross-flow rotating packed bed (RPB) to absorb carbon dioxide (CO_2) by NaOH solution from gaseous streams. The cross-flow RPB has an inner radius of 2.4 cm, an outer radius of 4.4 cm and an axial height of 12.0 cm. Wire mesh was used as packings. Rotor speeds ranged from 600 to 1800 rpm, providing 14~123 equivalent gravitational force. The removal efficiency of CO_2 was determined at various values of operating parameters, including the rotor speed, gas flow rate and liquid flow rate. Our experimental results demonstrated that the removal efficiency of CO_2 increased with the rotor speed, liquid flow rate, however, decreased with the gas flow rate. Furthermore, a cross-flow RPB provides a reduction in the usage of the NaOH solution for CO_2 absorption, suggesting that a cross-flow RPB has a great potential in the removal of CO_2 from the exhausted gases.

Keywords: rotating packed bed, cross flow, absorption, mass transfer, carbon dioxide

2. Extended Abstract

In 1981, Ramshaw and Mallinson (1981) first presented that the concept of intensifying mass transfer was to establish a dramatically more rapid regeneration of the interface between gas and liquid phases. To attain this concept, they took advantage of centrifugal force to contact gas and liquid in a high centrifugal field by rotating doughnut-shaped packing element. Thus, a rotating packed bed (RPB) was developed for enhancing distillation and absorption efficiency. This novel technology was referred to as "Higee" (an acronym for high gravity). Under RPB operation, thin films and tiny droplets generated owing to a rigorous centrifugal acceleration (2000~10000 m/s^2) could provide an enhancement in the gas-liquid mass transfer. Furthermore, the RPB could be operated higher gas and/or liquid flow rates owing to the low tendency of flooding relative to that in the conventional packed bed. Therefore, the gas-liquid mass transfer would frequently be enhanced by a factor of 10~100 and the dramatic reduction in the size of the equipment would be achieved, thereby reducing the capital and operating costs (Ramshaw, 1983).
Lin et al. (2003) investigated the absorption of CO_2 from gas steams containing 1~10 % CO_2 in a countercurrent-flow RPB using NaOH, monoethanolamine (MEA), 2-

amino-2-methyl-1-propanol (AMP), and a mixture of MEA and AMP as the absorbents. They found that a countercurrent-flow RPB applied to CO_2 absorption process could provide a great potential for replacing a conventional packed bed. Although the gas absorption performance of a cross-flow RPB has been examined (Guo et al., 1997; Lin et al., 2006), the experimental results were obtained under NH_3 absorption by water, SO_2 absorption by ammonium sulfite solution (Guo et al., 1997) and isopropyl alcohol (IPA) absorption by water (Lin et al., 2006).

The removal of CO_2 in a cross-flow RPB has not yet been reported. Owing to the lack of flooding limitation and the high absorption efficiency (Guo et al., 1997; Lin et al., 2006), a cross-flow RPB would be more useful in removing CO_2 from gaseous streams of a higher flow rate, whereas flooding may occur in a countercurrent-flow RPB. Therefore, the objective of this work is to elucidate the removal of CO_2 from gaseous streams by combining chemical absorption with a cross-flow RPB as shown in Figure 1. The aqueous NaOH solution is adopted as a model absorbent in this work. The results in this work could provide further insight into the feasibility of applying a cross-flow RPB to the removal of CO_2 from gaseous streams.This work has examined the absorption performance of a cross-flow RPB with the removal of CO_2 by NaOH solution from gaseous streams. As shown in Figure 1, the results were considered in relation with the removal efficiency, E values. As expected, increasing the rotor speed increased the E values; however, an optimum compromise between the consumption of energy (rotor speed) and the removal efficiency must be evaluated for industrial-scale applications. The E values appeared to increase with an increasing liquid flow rate but decrease with an increasing gas flow rate.

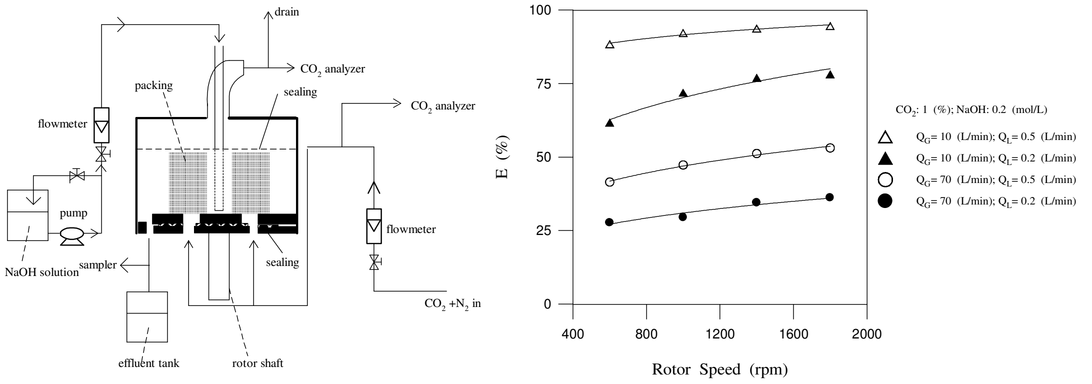

Figure 1: Experimental setup and results of a cross-flow RPB for CO_2 absorption process

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Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Environmental impact of wastewater treatment technologies in the Life Cycle Assessment of aluminium trifluoride

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1. Summary

Life Cycle Assessment (LCA) has emerged as a key tool in order to apply IPPC and IPP environmental policies in the European Union. In the current work, two technologies to the treatment of fluoride wastewater from aluminium trifluoride (AlF_3) production are assessed using the LCA approach: i) chemical precipitation for fluoride removal, which leads to a water rich sludge with poor dewatering characteristics and therefore, it must be stored in waste landfills, and ii) the recovery of fluoride by a crystallization process as synthetic fluorite to be reused in the HF manufacture (raw material in AlF_3 production). Different metrics were considered in the Life Cycle Impact Assessment stage: Ecoindicator-99, CML 2 Baseline 2000 and the environmental "IChemE Sustainable Development Progress Metrics". Data used in the Life Cycle Inventory (LCI) of wastewater treatment options have been taken from reliable sources. Despite environmental friendliness of crystallization option when compared to chemical precipitation, the environmental load of producing the functional unit (1 tonne of AlF_3) is markedly higher than the allocated load corresponding to the wastewater treatment system, so only a slightly reduction in global loads can be expected.

Keywords: sustainable production, life cycle assessment, aluminium trifluoride, chemical precipitation, crystallization

2. Extended Abstract

Progress towards Sustainability concept is a key feature of the policy making in the European Union (EU). As a consequence, an Integrated Prevention and Pollution Control (IPPC) Policy and an Integrated Product Policy (IPP) have emerged. Related to IPP, the Life Cycle Assessment (LCA) has been pointed out by the EU as the best framework to evaluate the potential impact related to products. This LCA approach is essential for an objective quantification, giving a vision of the relationship between human activities and environment, and identifying the high environmental impact stages. The latest developments show LCA as a powerful decision making tool in order to identify more sustainable options in process engineering (Azapagic, 1999).

Environmental impacts of two technologies for fluoride removal from industrial wastewater in the AlF_3 production have been considered: i) chemical precipitation for fluoride removal, leading to a water rich sludge, which has poor dewatering characteristics and therefore, it must be stored in waste landfills, and ii) the recovery of fluoride by a crystallization process as synthetic fluorite to be reused in the HF manufacture (raw material in AlF_3 production) (Aldaco, 2005, 2007). Life Cycle Assessment (LCA) has been used for this purpose.

The LCA software SimaPro 7.0 (PRé Consultants®) makes possible the comparison in terms of different methodologies like Ecoindicator-99 and CML 2 Baseline 2000. In this work, the integration of the environmental metrics published in "IChemE Sustainable Development Progress Metrics" allows the comparison of the results using these metrics, obtaining results expressed in common engineering process terms. The functional unit used for the comparison between different data sources is the production of 1 tonne of AlF_3. Data used in the Life Cycle Inventory (LCI) of wastewater options have been taken from reliable sources. The data used for the consumption of resources to complete the environmental impact life cycle assessment have been taken from the EcoInvent database v1.2.

Several data sources were considered to obtain the data for the LCI in order to avoid the influence of data source selection over final results. In previous works (Garea, 2006) crystallization process was presented as a friendlier alternative in relation to chemical precipitation from an environmental point of view in the aluminium trifluoride production. However, the wastewater treatment stage in the AlF_3 production has a minor environmental impact in the AlF_3 life cycle, and the environmental benefits derived from crystallization become close to negligible under assumptions considered. Raw materials consumption in the AlF_3 production was found to be the most environmental harmful step in the life cycle.

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European Congress of Chemical Engineering (ECCE-6)
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Effects of synthetic temperature on the microstructures and basic dyes adsorption of titanate nanotubes

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1. Summary

Titanate nanotubes (TNs) were prepared via a hydrothermal treatment of TiO_2 powders in a 10 M NaOH solution at 110–270 °C for 24 h. Effects of synthetic temperature (ST) on the morphology and pore structure of TNs were characterized with TEM, XRD, and nitrogen isotherms, respectively. The adsorption capacity of two basic dyes, Basic Green 5 (BG5) and Basic Violet 10 (BV10), was then measured to identify how the changes of the microstructure affected the basic dyes adsorption characteristics of TNs. It was found that when the synthetic temperature was above 160°C, the microstructure of titanate may transformed from nanotube into nanorod accompanying with the sharp decrease of titanate interlayer spacing, BET surface area, and pore volume. The effects of pore structure variation on the basic dyes adsorption of TNs were also discussed.

Keywords: titanate nanotube, synthetic temperature, nanorod, basic dyes, adsorption

2. Extended Abstract

The synthesis of nanotubes has become one of the most important research subjects in nanotechnology and various nanotubular materials have been produced during the last decades. Many groups have tried to analyze the characteristics of titanate, from which the synthetic mechanism was examined and the sheet folding mechanism was often assumed (Sun and Li, 2003). The effects of synthetic conditions on the microstructures of the TiO_2-derived nanotubes with the emphasis placed on the reaction time, calcination temperature, and HCl concentration were also investigated (Yu et al., 2006). However, it is hardly found in the literature to investigate systematically the effects of synthetic temperature on the microstructures of titanate although it also plays a key factor in the hydrothermal method.

A large amount of TNs with a diameter of 10-30 nm and a length of several hundreds nanometers are shown in Figure 1. The length and crystallinity of titanate compounds may increase with the increasing ST. For STs of 240 and 270 °C, the walls of titanate compounds become thicker and can be viewed as a nanorod structure. Further observation indicates that the prepared titanate compounds possess uniform inner and outer diameters along their length as well as multi-layered and open-ended. It is evident from Figure 2 that the XRD patterns for STs below and above 160 °C are distinct, indicating that ST may induce a significant change in the phase structure of titanates. The characteristic peak at around $2\theta = 10^{o}$ for all XRD patterns indicates that the samples are composed of a layered titanate. Moreover, because the reflection peak at $2\theta=10^{o}$ corresponds to the interlayer spacing of the samples, the peak shifting gradually to higher angles for temperatures larger than 160 °C means the decrease of the interlayer spacing. It is found in Figure 3 that for STs below 160 °C, the adsorption capacity increases with the increasing STs and reaches the maximum at 160 °C for both BG5 (211 mg/g) and BV10 (118 mg/g). For STs above 160 °C, the adsorption capacity decreases sharply and becomes very low as STs are larger than 170 °C. This result may be ascribed to the microstructure change from TNs into nanorod and the accompanying fast decrease in the pore volume of titanate samples. On the other hand, if we compare the adsorption capacity of BG5 and BV10, it can be seen that the adsorption capacity of BG5 is larger than that of BV10 in all examined STs due to the smaller size of BG5 and then the more efficient packing array of BG5 in the TNs. However, the high adsorption capacity of BG5 on the TNs indicates that TNs may be a good adsorbent for the removal of basic dyes from wastewater.

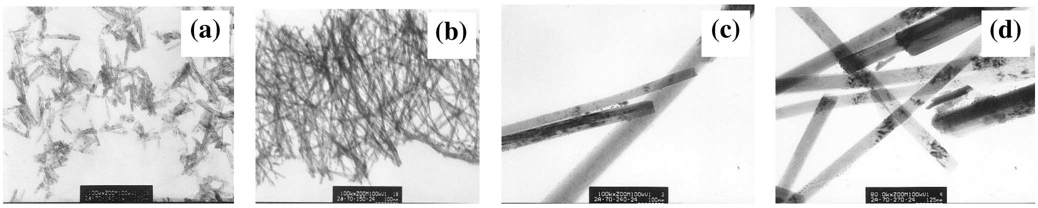

Figure 1: TEM micrographs of the titanate products obtained by hydrothermal processing at (a) 120, (b) 150, (c) 240, and (d) 270 °C for 24 h.

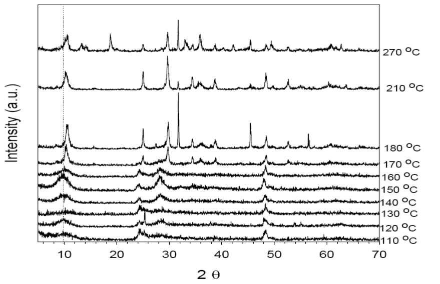

Figure 2: XRD patterns of the titanate products obtained by hydrothermal processing at 110－270 °C for 24 h.

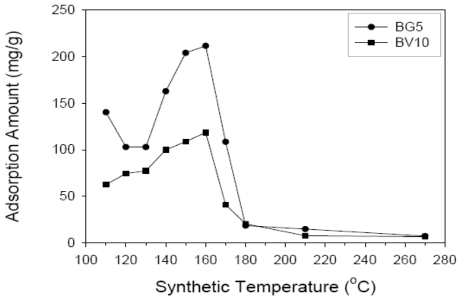

Figure 3: Adsorption capacity of BG5 and BV10 (2000 mg/L and 25 °C) on TNs obtained by hydrothermal processing at 110-270 °C for 24 h.

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European Congress of Chemical Engineering (ECCE-6)
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Evaluation of chemical absorption technology for CO_2 capture from industrial gases using monoethanolamine (MEA)

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1. Summary

The grave effects of anthropogenic pollution have been cause of great concern within the scientific community for a long time, and have lately gained much attention throughout society, particularly CO_2 emission, since this is a main player in global warming.

In order to minimise CO_2 emission, as well as its separation/capture from gaseous mixtures, not only contributes to reducing greenhouse effects and other climatic phenomena, but is also an opportunity for technological innovation. CO_2 absorption by amines has already been well studied, since it has proven to be an economically viable technique, with great industrial applicability. However, technological improvements are needed in order to improve operating conditions and CO_2 purity levels. Therefore, this research work has been concerned with studying the use of MEA in a pilot-plant, aiming at improving the technology of CO_2 absorption from industrial gaseous streams.

The results obtained from the experimental pilot-plant runs, approximately 98% pure CO_2, have shown to be satisfactory when compared to other previously reported data. Further studies on other alkanolamines, with lower energy requirements, as well as their blends, are being undertaken, as well as absorption by other organic solvents.

Keywords: absorption, amines, carbon dioxide.

2. Extended Abstract

A custom built pilot-plant has been used to evaluate CO_2 absorption by amines. This involves the continuous contact between a gas and a liquid through a cylindrical column filled with Raschig glass rings. After the proper pre-operating tests, gas leakage, MEA concentration and system homogeneity were determined through neutralimetry in both the absorption and stripping columns. The absorption test runs were undertaken for a gaseous mixture composed of 87.5% N_2, 11.5% CO_2 and 1% O_2, at 150 kPa and 35 ^{o}C. The amount of CO_2 absorbed by the amine was evaluated in the stripping column through parallel chromatographic and neutralimetric analyses.

The results obtained using MEA as absorbent are shown in Figure 1(a), where it can be seen that the maximum CO_2 concentration at the top of the stripping column was

98.053 %, after 120 min. A higher CO_2 recovery was accomplished after reduction of circulating flows in order to adjust the stripping column temperature profile. Figures 1(b) and 1(c) present the amounts of N_2 and O_2 discharged at the top of the stripping column. Discrepancies in the results can be observed after 20 min and 160 min, where there are steep decreases in MEA regeneration due to a non-ideal temperature profile. The N_2 and O_2 contents in this period of time are far from ideal, since CO_2 concentration is a little below 92%.

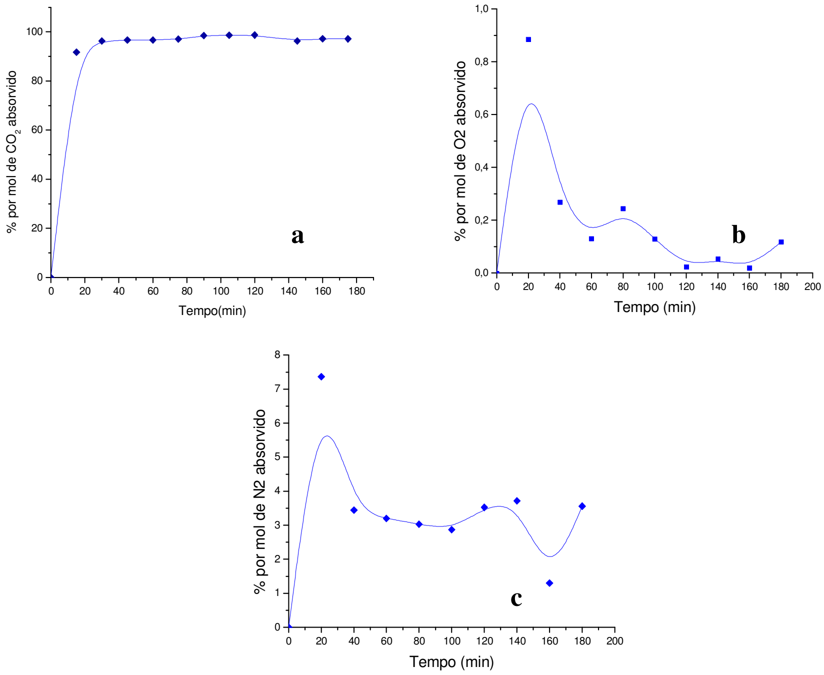

Fig.1. (a) CO_2 absorption in MEA; (b) O_2 absorption in MEA; (c) N_2 absorption in MEA.

The efficiency of CO_2 absorption in MEA has been proven, with a maximum CO_2 purity of 98.2 % at the top of the stripping column. This means that the absorption of CO_2 from gaseous streams could be applied in an industrial scale for obtaining high yields of CO_2 capture.

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Copenhagen, 16-20 September 2007

Modelling of metal pollutant transport in natural humic environments

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1. Summary

This contribution introduces newly developed method for metal ions diffusion study in humic gel. The main aim was to check the applicability of used experimentation (designed apparatus, mathematical model) in diffusion experiments. The experimental part focused mainly on determination of Cu^{2+} ions diffusion coefficient in humic gel and on the influences of copper(II) solution concentration and diffusion time on the total diffusion flux across the solution–gel interface. In none of all experiments any Cu^{2+} presence in side-water was determined, which confirms high capacity of humic gel for metal ions immobilization.

Keywords: humic, transport, diffusion, remediation

2. Extended Abstract

Humic acids are heterogeneous organic material, responsible for soil self detoxification. Because of their high sorption ability towards different common groups of pollutants (pesticides, PAHs, heavy metals etc.), they present itself highly promising in soil detoxification and remediation agents production. The use of gel form of humic acids as a model media for the study of metal transport is profitable, because it simulates well natural conditions, in which humic substances participate in immobilization of metal ions. Humic acids are usually found in the highly humid environments (water sediments, peat etc.) and thus in the swollen form. Copper was used as a model metal for experiments due to high affinity to humic acids and stability of formed complexes.

Our experiments focused on Cu^{2+} ions diffusion in humic gel. Simple mathematical apparatus, used for description of the diffusion with the participation of chemical reaction had been derived (final equations as well as preconditions are listed in [2]). In the first part, diffusion coefficient of ions in humic gel was derived from the slope of the total diffusion flux dependency on the square root of time duration for the case of diffusion from constant source (super-saturated $CuCl_2$ solution).

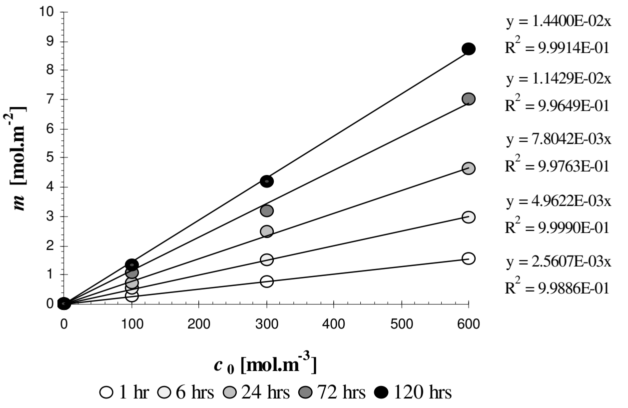

Figure 1: The total diffusion flux dependency on the initial ion concentration in solution (time-variable source)

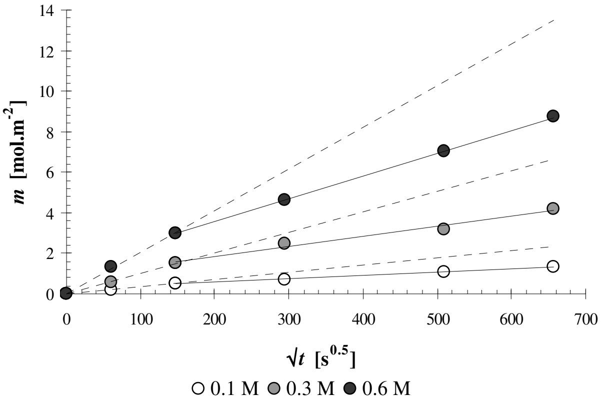

Figure 2: The total diffusion flux dependency on the square root of time (time-variable source)

The second part of diffusion experiment concerned diffusion from time-variable source of Cu^{2+} ions. All experiments took place in simple apparatus: humic gel was packed into plastic tube as 5 cm long cylinder and 2 ml of both copper ions solution and deionized water were filled into side containers. Total diffusion flux values was calculated as the sum of Cu^{2+} ions spectroscopically detected in gel slices and verified by measured decrease of the solution concentration. In Fig. 1, linear dependency of experimental diffusion flux values on the initial solution concentration for all measured time durations can be seen. The slope of this dependency increases with the time of diffusion experiment. In this case, the agreement between experiment and the theory is very good.

The time dependency of total diffusion flux is much more complicated. In the region of very short times, total flux value rises linearly with the square root of the time duration according theoretical relation. The slope of this line linearly increases with the initial Cu^{2+} concentration of the solution. Somewhere around 6 hours this theoretically linear function deflects to lower values (see Fig. 2). This indicates some changes in system occurring in later time which make the velocity of diffusion become slower than which corresponds the simple mathematical model.

The equilibrium on the solution/gel interface is described by ratio of the ion concentration in the gel and in the solution – ε. Its value is theoretically constant and can be calculated from diffusion flux values. Our experimental data show that while changing initial concentration of ions in the solution, ε really stays constant, but we have found some dependency of ε on the diffusion time which can be seen in Fig. 8. This fall of ε could be explained by formation of some stable chemical or structural complexes between gel and ions, not involved in reaction, assumed while deriving D_g. This binding affects the actual concentration of mobile ions in the gel and thus the velocity of the diffusion.

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Book of Abstracts
European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Proposing the most efficient and environmental safe hydrocyclone to depurate ballast water from ship hulls.

L. F. Martínez, A.G. Lavín, M. M. Mahamud, J. L. Bueno.

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1. Summary

Ballast water problem resides in introduction of invasive marine species into new environments by ships' ballast water. A combination of methodologies: mass balance (MB), granulometric analysis (GA) and Life Cycle Analysis (LCA) is applied here to optimize in terms of environmental sustainability a system composed by three hydrocyclones in series, integrating a ballast water treatment with the purpose of minimizing maritime pollution with a very low or positive direct environmental impact.

Keywords: Ballast Water Depuration, Hydrocyclone, LCA, SL separation

2. Extended Abstract

This work is focused on primary treatment to make suspended solids elimination feasible for ballast water treatment (Gollasch et al., 2007). It is highlighted how the combination of conventional analytical techniques (MB and GA) with (LCA) could provide a good method to estimate the most environmentally friendly hydrocyclone.
Three hydrocyclone sizes (5, 10 and 18 cm internal diameter), designed according to Rietema criterion (Catilho and Medronho, 2000), have been used to carry out the experiments described here and to contrast data.

A. Selection of Hydrocyclone size

First of all, efficiency is calculated by mass balance for the highest flow rate in each hydrocyclone. Secondly, an LCA analysis to carry out equipment selection is performed (Azapagic A., 1999). The same trend was found regardless of the impact parameter chosen: ecosystem quality, human health or resources sustainability (Björn et al., 2006). Here for different operating conditions, the ecosystem quality is chosen to study the influence of hydrocyclone size on environment. The combination of efficiency and LCA analysis results in the 10 cm diameter hydrocyclone as the most suitable one (see Figure 1).

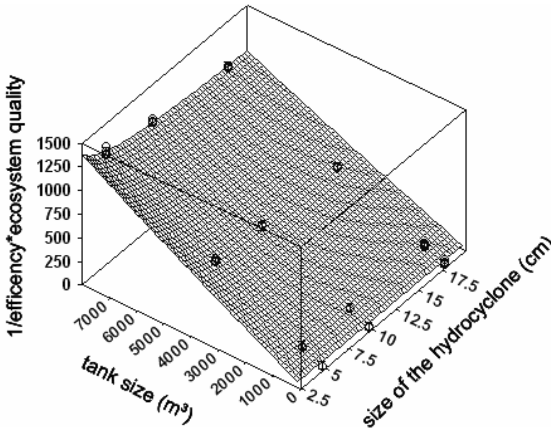

Figure 1. Combination of efficiency analysis and LCA methodology

B. Selection of vortex finder optimum introduction length.

Once establish the hydrocyclone size it is the moment of choosing the geometrical characteristics of this one to emphasize the depuration process. One of the most important geometrical characteristics is the vortex finder length ratio; this parameter severely affects separation efficiency (Martínez et al., 2007). The most efficient vortex finder length ratio results to be around 0.1 while the less efficient one it is found when the vortex finder length ratio arises to 0.2 (juncture between the conical and cylindrical regions), where heavy turbulences are generated due to the change of trajectory that this implies (see Figure 2). This result is contrasted with those obtained carrying out a granulometric analysis.

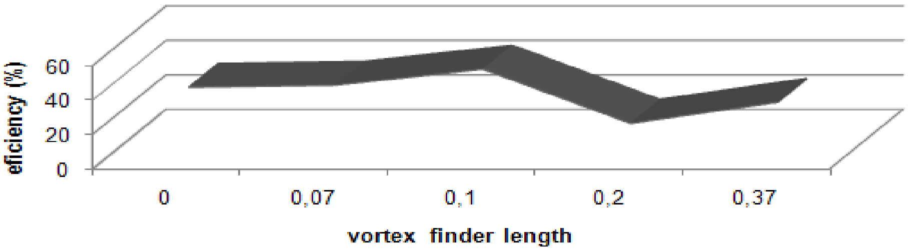

Figure 2. Efficiency vs. Vortex finder length for the selected hydrocyclone (10 cm diameter)

In summary, combining efficiency and LCA, 10 cm diameter hydrocyclone results as the most efficient. In order to full improve the efficiency of this hydrocyclone the ratio vortex finder/total length should be around 0.1.

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1. Summary

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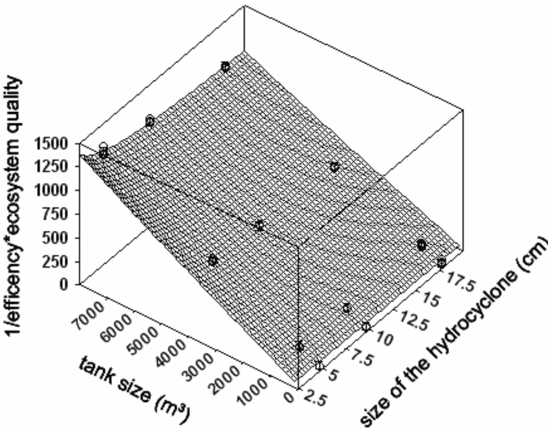

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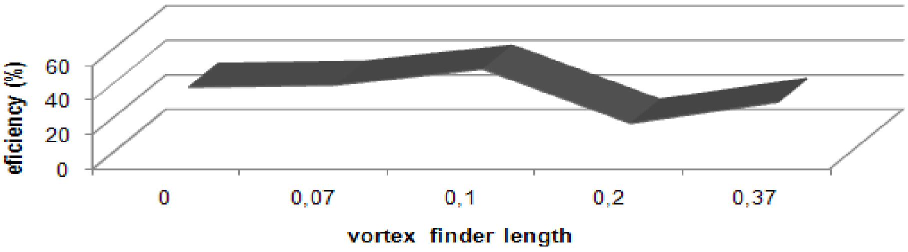

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In summary, combining efficiency and LCA, 10 cm diameter hydrocyclone results as the most efficient. In order to full improve the efficiency of this hydrocyclone the ratio vortex finder/total length should be around 0.1.

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European Congress of Chemical Engineering (ECCE-6)
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Arsenic removal from copper smelter wastewater by electrocoagulation in an airlift reactor.

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1. Summary

Electrocoagulation to precipitate the arsenic through the in-situ production of ferric hydroxide was tested in an airlift reactor. The initial concentration varied from 100 to 5000 ppm of arsenic. In general the arsenic removal was efficient – best results showed more than 98 % reduction in the arsenic concentration after 2 hours.

Key words: electric field, airlift reactor, iron electrodes, current density, oxidation

2. Extended Abstract

Copper smelters – and the sulphuric acid plants that are connected to them – generate large amount of wastewater containing heavy metals, where arsenic is the key contaminant. Heavy metals such as copper and lead can normally be removed by sulphide precipitation but arsenic needs other treatment.

Electrocoagulation to precipitate the arsenic through the in-situ production of ferric hydroxide was tested in an airlift reactor. The cell was developed by Hansen et al. (2007). This reactor was set up as two iron concentric cylinders. An airflow passing between the plates induced the mixing of the two phases - without the need of a stirrer -, generating turbulent conditions. Figure 1 shows the experimental cell.

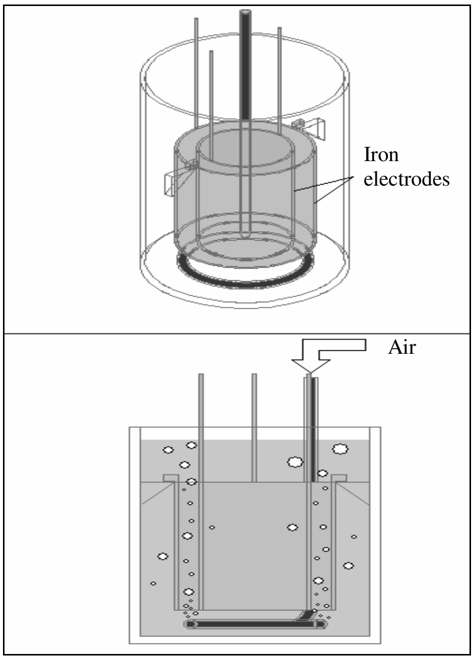

Figure 1. Experimental set-up.

A set of synthetic wastewaters was used to test the performance of the reactor. The initial concentration varied from 100 to 5000 ppm of arsenic. Direct current with current reversal each 120 seconds in order to avoid the passivation of the electrodes was applied. The gap between the electrodes was 10 mm for the reactor, and the current density was varied between 0.5 – 3 mA/dm^2 depending on experiment. The reactor was run in continuous and batch wise operation, and the elapsed time for each experiment was 120 to 180 minutes. The results from the batch experiments were used to predict the performance of the continuous experiments and vice versa as a validation procedure.

In general the arsenic removal was efficient – e.g. a batch reactor experiment run at 1.2 mA/dm^2 and initially 100 ppm arsenic showed that a more than 98 % reduction in the arsenic concentration after 3 hours was possible. Table 1 summarizes the experimental results

Experiment	Current density (A/dm^2)	Initial As concentration (ppm)	Time (min)	Arsenic removal (%)	Fe-to-As ratio (mol/mol)
1	0.8	100	120	55	8.9
2	1.2	100	120	> 98	6.7
3	1.2	1000	180	30	5.5
4	2.0	1000	180	70	4.8
5	1.2	5000	180	9	6.0
6	2.0	5000	180	15	4.3
7	3.0	5000	180	40	5.0

Table 1: Electrocoagulation experiments. Conditions and results.

The results show that arsenic can be removed efficiently from the solution. A 100 ppm solution can be treated in 2 hours the 1.2 A/dm^2. More concentrated solutions need more time and higher current densities to be remediated completely for arsenic.

Residence time distribution experiments were run on both types of reactors, and a model that takes in account a) the kinetics on the solid phase (electrochemical phenomena), b) the mass transfer process, c) the ferrous ion oxidation with the ferric hydroxide production, and d) residence time distribution models, was developed and the kinetic parameters were fitted.

A set of residence time distribution and kinetic experiments were run on pilot scale with an airlift reactor to determine a model for the hydrodynamic and the kinetic parameters. Based on these results a scale up procedure was developed to design an actual full-scale electrocoagulation reactor. The reactor is compared process wise and cost wise with the conventional industrial reactor that uses ferric sulphate addition the precipitate arsenic.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Catalytic pyrolysis of high density polyethylene on HZSM-5 and HY zeolite catalysts in a conical spouted bed reactor

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1. Summary

HDPE has been pyrolysed at 500 ºC using HZSM-5 and HY zeolites as catalysts. Batch runs have been carried out at atmospheric pressure in a conical spouted bed reactor. Product analysis has been carried out by means of a GC, connected on-line with a thermostated line. The degradation rate of the plastic is very similar in both cases. Products have been grouped into 6 lumps: light olefins, light alkanes, C_5-C_{10} non aromatic compounds, aromatics, heavy fraction and coke. HZSM-5 catalyst is appropriate to obtain light olefins, whereas HY catalyst is more suitable to obtain gasoline fraction products.

Keywords: plastic pyrolysis, catalytic pyrolysis, HDPE, conical spouted bed reactor, zeolites

2. Extended Abstract

The production and use of plastics are increasing considerably, about 4% per year, due to their contribution to all daily activities. At present, only a small percentage of plastic waste is recovered or recycled, less than 20% of the residual plastic. Pyrolysis is an alternative process for converting and upgrading plastic wastes.

In the pyrolysis of polyolefins, the use of catalysts in the reactor decreases the temperature required for pyrolysis and modifies the product distribution. Moreover, it improves the yield of volatile products and provides selectivity in the product distribution, especially for obtaining products of great commercial interest (gasoline and monomers) [1, 2].

In this study, one of the most used plastic, as is high density polyethylene (HDPE), has been pyrolysed at 500 ºC using HZSM-5 and HY zeolites as catalysts. A conical spouted bed reactor has been used in order to achieve flash pyrolysis data of polyolefins under conditions similar to industrial units [3].

Batch runs have been carried out to monitor the evolution of the different lumps. The catalyst bed consists of 100 g, and batches of 3 g of plastic are fed into the reactor for product monitoring. The nitrogen flowrate is 20% in excess of that required for minimum spouting velocity. Product analysis has been carried out using a gas chromatograph, being connected on-line to the reactor by means of a thermostated line. Furthermore, product identification has been carried out by means of a mass spectrometer.

Products have been grouped into 6 lumps. These are the lump of light olefins (C_2-C_4), light alkanes (<C_4), C_5-C_{10} non-aromatics, aromatics, heavy fraction and coke.

	Light olefins	Light alkanes	C_5-C_{10} non-aromatic	Aromatics	Heavy fraction	Coke
HY	18.0	6.5	44.6	24.1	3.9	3.0
HZSM-5	54.1	15.4	14.9	14.3	0.9	0.4

Table 1: Yields of the lumps for both catalysts, wt%.

On the one hand, the degradation rate of the plastic is very similar in both cases. Thus, degradation does not start until a period of a few seconds (3 or 4), due to the low thermal conductivity of plastics, the maximum product formation rate takes place at approximately 50 s in both cases and the polymer is totally degraded at 150 s.

On the other hand, as is observed in Table 1 and Figure 1, product distributions obtained for the two catalysts are very different. With the HY catalyst the main fraction consists of C_5-C_{10} non-aromatics, 44.6 wt%, whereas for the HZSM-5 is the lump of light olefins, 54.1 wt%. Light alkanes yield obtained using HZSM-5, 15.4 wt%, is slightly higher than with HY, 6.5 wt%. Furthermore, aromatics and heavy fraction yields are higher in the pyrolysis with HY catalyst.

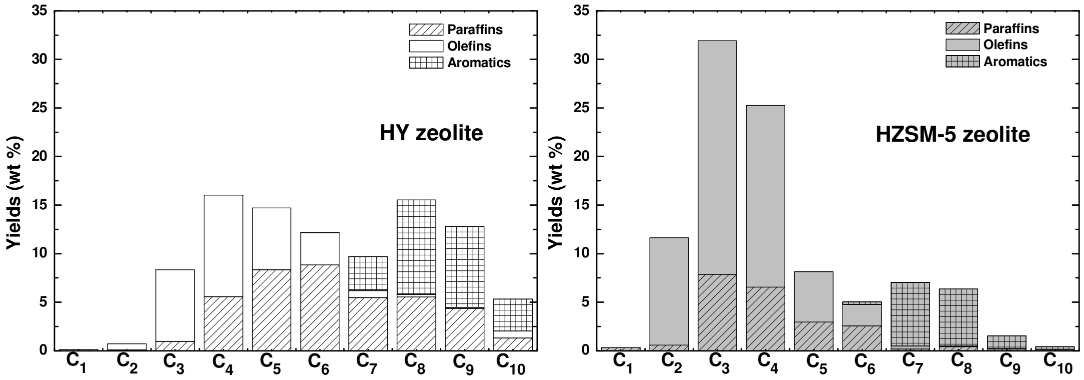

Figure 1: Yields of products for both catalysts ordered by carbon atom number, wt%.

In conclusion, HY catalyst is appropriate to obtain gasoline fraction products, whereas HZSM-5 catalyst is more suitable to obtain light olefins, which can be used as monomers.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Investigation of technology of processing of polychlorinated derivatives of aromatic compounds

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1. Summary

Polychlorinated derivatives of aromatic compounds as well as biphenyls, are highly toxic products. The combustion of these compounds results in formation of secondary pollutants. According to the Stockholm convention of transfrontier pollutants of air these compounds belong to stable organic pollutants. In this report we represent results of investigation of the conversion of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene. Experiments were carried out on Pd supported carbonic carrier in laboratory autoclave. The obtained experimental data showed that the growth of conversion can only be observed when concentration of Pd is less than 3%. Higher Pd content does not provide the increment of conversion of 1,2-dichlorobenzene and 1,3-dichlorobenzene. The rate of reaction slightly decreases when sodium hydroxide concentration is 13 %. Increasing of sodium hydroxide concentration above 13%, results in growth of the desalting effect. Because of that phenomenon fractional conversion decreases. Conversion of the reactants is directly proportional to the pressure applied and has classical temperature dependence. This investigation is an important stage of creation of the new non-polluting technology of polychlorinated derivatives of aromatic compounds processing.

Keywords: polychlorinated biphenyls, hydrodechlorination, waste processing, reduction, palladium catalyst.

2. Extended Abstract

Polychlorinated derivatives of aromatic compounds as well as biphenyls are highly toxic products. Polychlorinated biphenyls (PCBs), are a group of chlorinated organic compounds which have one to ten chlorine atoms attached to biphenyl. PCBs have extremely high thermal and chemical stability. The physical properties of PCBs make them highly useful in numerous commercial applications, including dielectric fluids in capacitors and transformers, heat transfer fluids, hydraulic fluids, lubricating and cutting oils. According to the Stockholm convention of transfrontier pollutants of air these compounds belong to stable organic pollutants. Another problem is to clean up the equipment from the leavings of polychlorinated wastes. Large amounts of PCB containing products such as transformer oils and capacitors are in service. These devices are subjects to or are currently awaiting disposals.

Nowadays the high temperature combustion process is used frequently. The problem of greatest concern is the generation of incomplete combustion products, which are formed in trace quantities. When PCBs are burned, dioxins and chlorinated dibenzofurans can be formed. Other materials contained in the stack effluents include HC1, CO, $C0_2$, NO_x. It might be very difficult and expensive to remove these materials from the stack gases. Catalytic hydrodechlorination can be used as an alternative disposal method for PCBs.

The reaction of reducing of polychlorinated derivatives of aromatic compounds has been investigated in the batch autoclave reactor. The autoclave has volume of 500 ml and it is equipped with a mixer, electric heater and bubbling system for hydrogen feeding.

1,2- dichlorobenzene and 1,2,4-trichlorobenzene were used as model compounds due to their presence as components in dielectric fluids. The reaction of hydrodechlorination proceeds in aqueous NaOH solution.

It is well known from the literature that the hydrodechlorination reaction is carried out on the Pd supported activated carbons. For our investigation we selected a special carbonic carrier – “sibunit”. It is characterized with higher durability then other known activated carbons.

Catalysts with various sizes of catalyst pellets and the same Pd content have been prepared. The experiment has been carried out at constant temperature, pressure and NaOH concentration. The results of the experiment can be summarized as follow. From the size of catalyst pellets 1 mm and bigger the reaction move into diffusion region and there are no difference in conversions. But the selectivity of formation of 1,2-dichlorobenzene rises as size of catalyst pellets increases while the selectivity of benzene decreases. The selectivity of the other substances remains constant. In other words, the rate of the reaction of hydrodechlorination of 1,2-dichlorobenzene decreases while it remains constant for 1,2,4-trichlorobenzene.

The hydrogenation of the aromatic ring did not occur and we did not observe the formation of cyclohexane in all experiments.

The catalyst fraction with pellets size 2-2,5 mm and various Pd content was prepared. The results of the experiment show that the conversion is independent from the content of Pd starting from 3% mass consentration. All further experiments were carried out on “sibunit” with pallets size 2-2,5 and 3% Pd mass concentration.

To investigate the temperature influence on the reaction of hydrodechlorination of 1,2-dichlorobenzene and 1,2,4-trichlorobenzene the experiments have been performed at pressure of 1 MPa and temperature range 60-140°C. For the reaction of 1,2,4-trichlorobenzene the steady-state conversion (43%) is achieved at the temperature above 80°C. The conversion of 1,2-dichlorobenzene ceases to grow at 140°C only and becomes constant (70 %). It is possible to explain this independence on temperature by shortage of hydrogen in the reaction medium.

Dependence of conversion on pressure has linear dependence. The concentration of hydrogen in the liquid reaction medium increases, as the pressure rises.

The influence of sodium hydroxide concentration on the reaction has been investigated. Experiments with various concentrations of NaOH and constant amount of water have been performed. The rate of reaction slightly decreases when the concentration of sodium hydroxide is 13 %. Increasing of concentration of sodium hydroxide above 13% results in increasing of the desalting effect. Because of that phenomenon fractional conversion decreases.

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European Congress of Chemical Engineering (ECCE-6)
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Oxygen transfer and dimethylketone degradation rate in the airlift reactor using immobilized bacteria

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1. Summary

Dimethylketone biodegradation is carried out using *Acinetobacter calcoaceticus* bacteria. The minimum fluidization velocity diminishes during the biodegration time. The lowest biodegradation time is observed if pH value exceeds a little the value 7 for gas velocities up to the double minimum fluidization velocity value. The biodegradation time increases with an increase of the initial dimethylketone concentration and decreases with an increase of the bed height. The oxygen transfer rates in the suspension airlift reactor and in the reactor with fluidized bed in the riser are lower than the oxygen transfer rate in the inverse fluidized bed reactor .

Keywords: waste water, ketone, biodegradation

2. Extended Abstract

A possibility of the biodegradation of antropogenic compounds depends on their chemical structure. Bacteria are used to improve degradation of such compounds. Because cells are sensitive to shear stresses the protection methods are recommended to stabilize the cell structure. One of the method is the bacteria immobilization. A fluidized bed with immobilized bacteria in an airlift reactor downcomer is convenient because there shear forces are much lower than these in the riser. Oxygen for the bacteria metabolism is delivered in the circulated liquid stream absorbing it in the riser. The aim of the work is to investigate the acetone biodegradation in the airlift reactor using the *Acinetobacter calcoaceticus* bacteria immobilized on particles creating the inverse fluidized bed in the downcomer. The next aim is to compare the oxygen tranfer rate in the inverse fluidized bed airlift reactor, suspension airlift reactor and the airlift reactor with the fluidized bed in the riser.

Experimental

Experiments are carried out in the external loop airlift reactor (volume 9 dm^3, d_{Ri}/d_{Ro} =0.051 /0.060 m; d_{Di}/d_{Do} = 0.082/0.090 m). Polystyren particles (d_S = 2 mm; ρ_S = 200 $kg \cdot m^{-3}$) are used as the carrier of the *Acinetobacter calcoaceticus* bacteria.

Microorganism cultivation and immobilization is provided as follows. The three stage adaptation of the bacteria *A. calcoaceticus* is carried out using fresh mineral salt solutions. The bacteria – dimethylketone adaptation time is 300 hours. The enriched suspension of the *A. calcoaceticus* bacteria cells is placed in the bubble pre-column and immobilization is provided in the conditions of the nutrient deficit during 72 hrs.The time-dependent concentration of the dimethylketone is determined using the gas chromatograph.The time-dependent oxygen concentration is determined by the dynamic method. Liquid circulation velocity is determined by the tracer method.

Results and discussion

The uptake rate of the dimethylketone depends on the biomass amount and the microorganism proliferation rate. The dimethylketone and biomass concentrations influence each other. It is included in the equation $-dc/dt = \mu(c) \cdot X/Y$ (c - dimethylketone concentration, X - biomass concentration, $\mu(c)$ - specific microorganisms growth rate, Y - biomass yield coefficient on substrate). In a practice the substrate consumption and the microorganism growth are investigated separately. Additionally the consumption rate of impurities during the aerobic wastewater treatment is measured most frequently without analysis of the microorganisms growth rate. Such calculations are made also in this work.

Time-dependent changes of the dimethylketone concentration in the reactor with immobilized bacteria *A. calcoaceticus* show that the lowest biodegradation time occurs if the pH value is slightly above 7. It is the important observation taking into account potential practical applications.

An increase of the initial dimethylketone concentration results in an increase of the biodegradation time. The highest dimethylketone degradation rate is observed if the gas flow velocity ranges betwen the minimum fluidization velocity u_{GMF} up to about the double u_{GMF}. However a distinct increase of the gas velocity above the minimum fluidization velocity results in a decrease of the degradation rate. The reason could be an increase of shear stresses.

It is found that the minimum fluidization velocity decreases during the biodegradation time. It is a result of the biomass growth on the carrier particles and the increase of the density of the carrier particle -biomass agglomerates.

An increase of the initial carrier particle bed height means an increase of the biomass amount in the bed and an increase of the contact time of the dimethylketone solution with the immobilized bacteria. Therefore the bed height increase results in a diminishing of the total biodegradation time. However an increase of the initial bed height above some value doesn’t influence the degradation time. Probably another restrictive factors appear. It could be a limited oxygen transfer rate.

Oxygen transfer coefficient values in the inverse fluidized bed reactor are higher than values obtained in the suspension airlift reactor as well as in the airlift reactor with the fluidized bed in the riser for the same solid concentration. Therefore experimental biodegradation time values in the inverse fluidized bed reactor are lower than these observed in the airlift reactor with immobilized bacteria on solid carrier particles creating the fluidized bed in the riser.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Novel metal oxide catalysts for low temperature selective catalytic reduction (SCR) of NO with NH_3

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1. Summary

Several solutions have been developed to comply with the environmental emission standards of nitrogen oxides (NO_X). Selective Catalytic Reduction (SCR) is one of the prevailing technologies in reducing NO_X from stationary sources. The main reaction occuring in this process is the reduction of NO_X with ammonia over a catalyst to elemental nitrogen and water vapor. Various metal oxide based catalysts have promising SCR activities at low temperatures. Manganese–cerium mixed oxide catalysts with different molar ratio were prepared and investigated concerning their activity behavior.

Keywords: Selective Catalytic Reduction, Nitrogen oxides, Manganese–cerium mixed oxides.

2. Extended Abstract

Intoduction

Common sources of nitrogen oxides (NO_X) are motor vehicles, electric utilities and other industrial, commercial and residential sources that burn fuels. NO_X itself and after reaction with different compounds cause respiratory deseases, damage the vegetation and deteriorates building and monuments. A variety of different catalysts have been reported to be effective in SCR of NO_X but only few of them are applied. The prominent catalyst used under industrial conditons is V_2O_5/TiO_2 promoted by WO_3 and/or MoO_3 at 350-400°C [1, 2]. However, the existence of compounds like K_2O, CaO and As_2O_3 in the flue gas reduces the performance and the durability of this catalyst [3]. Fe-Mn based bimetallic catalysts exhibit a superior SCR activity related to their high activities for the intermediate step, NO oxidation to NO_2, at lower temperatures [4]. Ce-Mn catalysts have also revealed a good potential for the SCR of NO, but the catalytic performance depends critically both on the cerium/manganese ratio as well as the calcination temperature [5]. The interest in alternative low temperature SCR catalysts could be extended to other mixed oxides. Thus, in this work we have prepared and characterized various new combinations of metal oxide-based catalysts, in an effort to find candidates which allow a good NH_3- SCR catalysts activity in combination with a high selectivity towards nitrogen and water.

Results and discussion

Our experiments have been inspired from works referred above. We first tried to reproduce, at the same conditions, the earlier results and compared it with an available commercial catalysts. In Figure 1, we display the rate constant k vs. temperature. The Mn-Ce bimetallic catalyst exhibits higher activities up to 250°C compared to commercial commercial catalyst. Further optimization of the catalyst is ongoing.

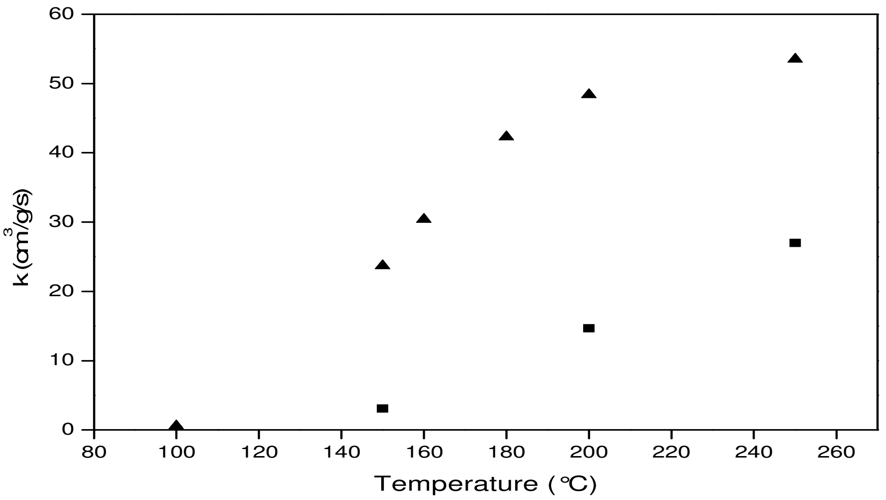

Figure 1. NO-SCR temperature dependency with ammonia on MnOx-CeO_2 (triangle) and commercial catalysts (square).

Acknowledgements

Support of the work by the Danish Research Council for Technology and Production, The Lundbeck Foundation and Elkraft Systems (PSO FU5201) are gratefully acknowledged.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

An experimental comparison of a heat exchanger in an absorption heat transformer operating in falling film and pool boiling

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1. Abstract

This work shows the experimental comparison of two operation modes for a heat exchanger into an absorption heat transformer. Absorption heat transformer has five main components: absorber, generator, condenser, evaporator and economizer. Heat exchanger was operated as generator mode. The versatile design of this equipment allowed prove it in both forms of operation as falling film on horizontal tubes and pool boiling. The experimental tests were carried out with lithium bromide – water solution and a heat source between 1400 and 2000 W. Plots of heat flow against water mass flow are shown for both modes. The absorbed heat into the connected generator in pool boiling mode was until 117% upper in comparison with the falling film mode.

Keywords: heat exchanger, pool boiling, falling film, heat transformer, generator

2. Introduction

An absorption heat transformer is the equipment able to elevate the temperature of a low temperature heat source [Herold et al, 1996]. It has five main components: absorber, generator, condenser, evaporator and economizer, figure 1 shows a schematic diagram of an absorption heat transformer. They use a working mixture, in this case water – lithium bromide was tested, with a constant concentration of 52% weight. In the present work, the heat exchanger was operated as generator. The function of the generator is to remove some water from the working mixture.

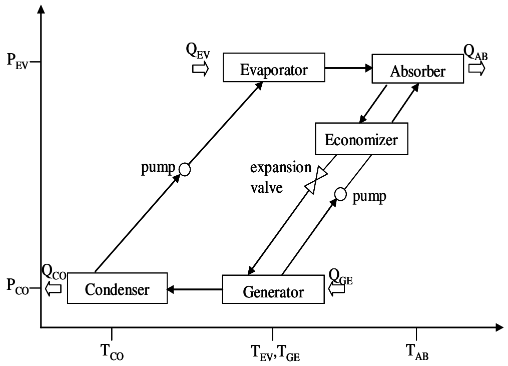

Figure 1. Schematic diagram of an absorption heat transformer

3. Experimental Set - up

The heat exchanger was constructed in stainless steel 316L, with a thermal power design of 3000 W. Its versatile design allows operating in two forms: falling film on horizontal tubes and pool boiling. The mean of heating in both modalities was water with an electrical input between 1400 and 2000 W. Initially the heat exchanger was operated in falling film on horizontal tubes. The inlet of solution was located in the superior part of the heat exchanger, however the heat flow obtained in this mode of operation was low; therefore, it was decided to change the configuration of the equipment and to operate it in pool boiling mode, it was change the inlet of solution to the inferior part of the heat exchanger, additionally, it was installed a recirculation of the solution leaving the generator, this solution is concentrated in lithium bromide and the combination with the solution inlet, coming from the absorber (which is concentrated in water), leads to an increase in the solution temperature, which benefits the heat transfer. Figure 2 shows the comparison between both modes of operation. Figure 3 shows the heat flow in both operation conditions against the heating water temperature.

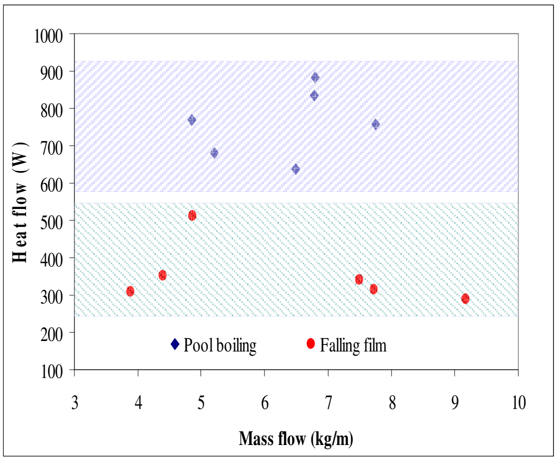

Figure 2. Comparison between falling film and pool boiling operation modes

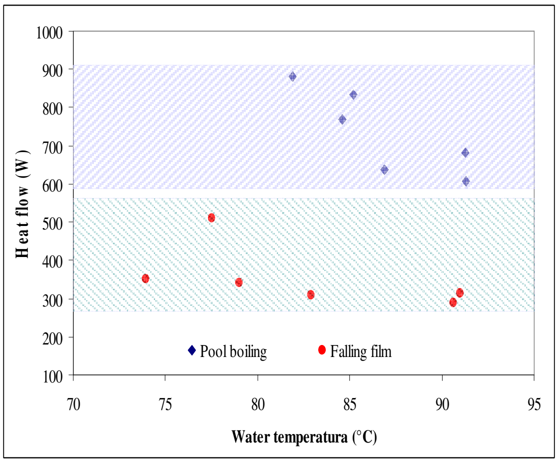

Figure 3. Heat flow against water temperature for both modes of operation

4. Conclusions

It was evaluated a heat exchanger operated as generator in an absorption heat transformer in two forms of operation: falling film on horizontal tubes and pool boiling with a recirculation solution. It was demonstrated that for the actual conditions in the equipment, were obtained better results from the pool boiling condition with a recirculation solution, the heat flow obtained by this condition was 117% greater. It was observed that, for both operation modes, it was convenient low temperatures in the heating water, under 90 °C.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Parametric optimization of Cd^{2+} and Cr^{6+} adsorption on the Mediterranean sea grass *posidonia oceanica* by surface response analysis

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1. Summary

The study aimed to ascertain the potential of Mediterranean sea grass *posidonia oceanica* to remove Cd^{2+} and Cr^{6+}. The effects of process parameters namely, pH, initial metal ion concentration, and adsorbent dosage on the extent of adsorption were investigated in ranges 2-12, 1-10 g/L and 2-50 mg/L, respectively. The experiments were designed concordant with surface response experimental design technique. The outcomes of the experimental work exhibited 92.48% Cr^{6+} removal from a solution of 42 mg/L concentration, while 91.88% Cd^{2+} removal was detected from a solution concentrated as high as 10 mg/L. Adsorption data was found to exhibit Freundlich isotherm character. After regeneration in 0.1M HCl, regenerated *posidonia oceanica* retained 67%, 82% of its Cd^{2+} and Cr^{6+} adsorption capacity even after five adsorption cycles. Models were constructed for prediction of the extent of removal within the defined interval. Confirmation of the model was accomplished by experiments run at determined optimum levels. Reliability of the models were found to be higher than 0.93.

Keywords: cadmium, chromium, adsorption, experimental design

2. Extended Abstract

2.1 Introduction

As consequence of industrial activities, heavy metal accumulation has leaded to severe damages in aquatic environment and detrimental physiological and health effects in humans [1]. Adsorption, as being one of the conventional physicochemical methods, has been widely employed for removal of these ions despite the high expense of conventional adsorbents. Hence, current research on heavy metal adsorption has been addressed to utilization of alternative cost effective adsorbents such as bark/tannin rich materials [2], lignin [3], pectin [4], chitin/chitosan, dead biomass [5], barks and husks of several materials [6]. The effectiveness of the process is dependant upon the properties of the material itself, and the process parameters. Thus, to attain highest degree of metal removal, the optimal set of process parameters should be determined. Optimization by classical methods involves the change of one variable at a time which is time consuming when a large number of variables are considered. An efficient alternative to classical methods is response surface method in which, the main objective is to optimize the response surface that is shaped under the influence of process parameters [7].

In current study, we have investigated the potential of a certain type of sea grass *posidonia oceanica* for cadmium and chromium adsorption. The data generated from this work has been used in derivation of a predictive model that would be practical in calculation of the extent of removal at each factor level within the studied range.

2.2 Experimental

The total number and sequence of experimental runs were determined using the MINITAB software. All experiments were conducted batchwise at room temperature in triplicates. The adsorbent material was washed excessively and dried overnight at 80°C. Average particle size of 0.8 mm was employed in the experiments. The concentration of Cr^{6+} was analysed by diphenyl carbazide method while atomic absorption spectromety was utilized in Cd^{2+} detection. The main effects and interactions of the factors were determined by the interpretation of surface plots and probability values calculated by ANOVA method. The significance level was chosen as 0.05. The constructed model was tested at optimum factor levels.

2.3 Results

Surface plots and variance analysis proved that pH had the greatest influence upon adsorption of cadmium and chromium. The main effects of initial concentration and adsorbent dosage followed the effect of pH. However, interrelationship between initial concentration and adsorbent dosage was found to be significantly high. In the case of chromium adsorption, 92.48% removal was attained from an initial chromium solution of 42 mg/L concentration at pH 2.0 using 8 g/L adsorbent material. 91.88% Cd^{2+} removal was detected at pH 4.5 with 6g/L adsorbent dosage from a solution of 10 mg/L initial concentration. The adsorption of both ions were found to conform to Freundlich isotherm with regression coefficients higher than 0.95. Desorption studies showed that the material was not durable at pH below 1.5. Although almost one third of *posidonia oceanica* was dissolved and lost during regeneration, the regenerated material could still be utilizable for especially chromium adsorption since it retained 82% of its original capacity after five successive cycles.

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Session S-8K1-K2: CPD&E Keynote Lectures

Abstract Number	Paper Title & Authors	Included
1981	Development of a new biosynthetic hyaluronic acid for enhanced skin moisturization and anti-aging K Schwach-Abdellaoui, F Guillaumie	Yes
4089	The mechanism of adhesion between tyre-cords and rubber, as governed by interfacial phenomena J W M Noordermeer, W B Wennekes, R N Datta	Yes

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Development of a new biosynthetic hyaluronic acid for enhanced skin moisturization and anti-aging

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1. Summary

Novozymes Biopolymer A/S has developed a unique method for the large-scale manufacture of hyaluronic acid (HA), a natural and high molecular weight anionic polysaccharide. Here, we briefly introduce the metabolic engineering of a *Bacillus subtilis* strain that is capable of secreting large amounts of medium molecular weight HA, and then show that the hyaluronic acid product from this recombinant system has several advantageous characteristics for cosmetic applications.

Keywords: Hyaluronic acid, biosynthetic, anti-aging, skin moisturization, skin elasticity

2. Extended Abstract

Hyaluronic acid (also referred to as HA or hyaluronan) is a linear, unbranched polysaccharide made of alternating *N*-acetyl-D-glucosamine and D-glucuronic acid monomers (**Figure 1**).[1] HA is ubiquitous in human and animal tissues, where it has significant structural, rheological, physiological, and biological functions. HA's distinctive viscoelastic properties, coupled with its lack of immunogenicity or toxicity, have led to a wide range of applications in the cosmetic and pharmaceutical industries including skin moisturizers, osteoarthritis treatment, ophthalmic surgery, adhesion prevention after abdominal surgery, and wound healing. At present, the annual worldwide market for HA is over $1 billion.

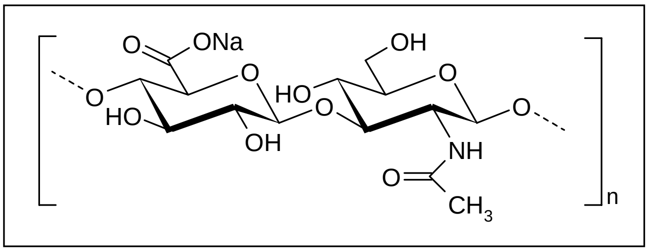

Figure 1: Chemical structure of the hyaluronic acid disaccharide repeating unit.

Hyaluronic acid is currently obtained commercially from rooster combs, and certain strains of *Streptococcus* that synthesize this biopolymer to form a non-immunogenic outer capsule.[2] However, these are less than ideal sources. Recovery of HA from rooster combs necessitates extensive purification to remove antigenic avian proteins, while capsule-producing *Streptococci* are fastidious organisms that can be fastidious to grow, are natively pathogenic, and have the potential to produce exotoxins. Moreover, both extracted HA and Streptococcal HA are purified using harsh organic solvents.

Using its core competencies, Novozymes Biopolymer A/S, a biotech-based company, has developed a new fermentation process relying on an alternative, non-pathogenic and safe host, namely *Bacillus subtilis*, for producing HA and to avoid the above complications. The low protein background produced by the *Bacillus subtilis* host as well as the lack of pathogenicity allow the use of a unique production process relying on defined recovery steps, during which no organic solvents are used and followed by spray-drying. This leads to the production of a medium molecular weight HA (750 kDa-1 MDa) with a polydispersity below 1.5 in the form of a very fine powder. The latter is composed of micro- and nanospheres and has enhanced dissolving properties (**Figure 2**).

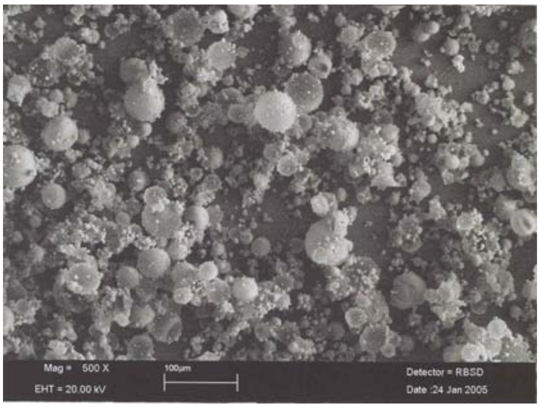

Figure 2: Scanning electron microscope (SEM) pictures of *Bacillus* derived HA.

Finally, clinical tests have shown that hyaluronic acid produced by fermentation of *Bacillus subtilis* exhibits advantageous moisturizing, anti-wrinkle and skin elasticity properties.

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The mechanism of adhesion between tyre-cords and rubber, as governed by interfacial phenomena

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1. Summary

A new mechanism of adhesion of Resorcinol/Formaldehyde/Rubber-Latex treated textile cord to vulcanized rubber is proposed. Enrichment by migration of rubber vulcanization ingredients to the RFL-rubber interface can be observed during vulcanization of the rubber compound. Dependent on the composition of the rubber-latex in the RFL, excessive migration of the curatives results in unwanted embrittlement of the interfacial layer between the RFL dip and the rubber compound due to over-cure. This results in poor adhesion. By proper adjustment of the rubber-latex composition this problem may be avoided, resulting in enhanced adhesion properties.

Keywords: rubber, textile cord, adhesion, RFL-dip, curatives

2. Extended Abstract

Tyres need reinforcement with textile and metal cords in order to withstand internal pressure and to stabilize the tread. The adhesion between virgin textile cords and rubber is always poor, because of significant differences between fibre and rubber in modulus, elongation, polarity as well as in chemical reactivity. In order to improve this adhesion, it is common to use adhesive systems, which act as bridges in the interface between elastomer and reinforcing cord. These are commonly based on Resorcinol/Formaldehyde/Rubber-Latex (RFL) dip systems. Although this system dates back as far as 1938 and is commonly used for rubber reinforcement till today, the mechanism by which the adhesion is obtained is still unclear.

The paper provides new fundamental insights into RFL to rubber bonding. Enrichment by migration of rubber vulcanization ingredients to the RFL-rubber interface can be observed by use of Scanning Electron Microscopy, coupled with an Energy Dispersive X-ray spectrometer. The same method is used to determine the degree of enrichment for several RFL formulations, based on rubber-latices with varying polar vinylpyridine-contents. The vinylpyridine-content in the RFL indeed turns out to be the governing factor for the enrichment. The vinylpyridine-content also turns out to influence the adhesion: for most rubber compounds adhesion decreases with increasing vinylpyridine content. For a Natural Rubber / Styrene Butadiene Rubber blend, an optimum vinylpyridine content of 10% is observed.

A new mechanism of RFL-rubber adhesion is proposed based on the experimental results. The mechanism is explained in terms of unwanted embrittlement of the interfacial layer between the RFL dip and the rubber compound for high vinylpyridine containing RFL formulations, due to over-cure by excessive migration of curatives to the interface.

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Session S-8B: Chemical Product Design & Engineering – I (CPD&E - 1)

Abstract Number	Paper Title & Authors	Included
901	Development Of Styrene-methyl Metacrylate Copolymer Microcapsules Containing Phase Change Materials M L Sánchez, J F Rodríguez, P Sánchez, A De Lucas, M Carmona	Yes
1477	Enzyme-based Antifouling Coatings S M Olsen, L T Pedersen, S Kiil, M H Laursen, K Dam-Johansen	Yes
3853	Formulation of an agrochemical product using neural network driven design G A Bell, R D Brockbank	Yes
4094	GRINDSTED Soft-N-Safe - a new efficient green plastisizer B Nielsen	Yes

Development Of Styrene-methyl Metacrylate Copolymer Microcapsules Containing Phase Change Materials

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1. Summary

Paraffin wax was microencapsulated by suspension polymerization with a polymer shell of methylmetacrylate (MMA)-styrene (St) copolymer. The influence of the copolymer/paraffin mass ratio and the MMA/St mass ratio on the encapsulation process and the physical properties of the microcapsules obtained were studied. It was observed that paraffin is difficultly encapsulated when the ratio polymer/paraffin was lower than 2.5, as a consequence of a shortage of copolymer that could not completely cover the amount of paraffin added. When a large proportion of monomer was employed the polymer trends to polymerize outside the bead in a segregated way. As the amount of MMA increases, the reaction time decreases and the mean particle size decreases.

2. Extended Abstract

Microencapsulation is often employed to encapsulate PCMs as core using plastic or cross-linking polymers as shell. Although the PCM is the responsible of the storage and absorption or release of thermal energy the encapsulation of them inside a mechanically and physical-chemically stable shell is the main technical and scientific problem.

Up to now some attempts to develop a cheap and technically simple process for the microencapsulation of paraffin have been done. The most common methods used are interfacial polymerization, emulsion polymerization, in situ polymerization, spray drying and coacervation (Hawlader et al., 2003). The development of simple, cheap and robust methods for the encapsulation of PCMs in suitable sized particles is very important for textile applications. The microencapsulation method developed in this work is simpler than other methods referenced in literature. In this work, we used a copolymerization process with styrene (St) and methyl metacrylate (MMA) to form the microcapsule shell.

Suspension like polymerization was carried out in a 2 L double-jacketed glass reactor at 100ºC. A mixture of St monomer, MMA monomer and benzoyl peroxide initiator was added into a continuous phase containing poly(vinylpirrolidone) and water. The influence of polymer/paraffin (from 0 to 4) mass ratio and MMA/St (from 2 to 5) mass ratio on the encapsulation process was studied.

DSC analyses of samples obtained at different paraffin/polymer values and a constant MMA/St of 4 demonstrated the effectiveness of the encapsulation process and agrees with around a 40% wt of paraffin inside the microcapsule.

Figure 1 shows that a paraffin/polymer of 2 and 2.5 exhibit unimodal PSD ranging in the interval between 20 to 2000 microns, whereas a bimodal PSD was obtained when a 3.5 and 4 polymer/paraffin mass ratio was studied. This heterogeneity of sizes is due to the agglomeration of the microparticles formed. In the second case, the smaller particles formed correspond to polymer bead without paraffin wax and the bigger particles obtained correspond to microcapsules containing paraffin wax. Finally, it was observed a homogeneous particle size distribution for polymer/paraffin ratio of 3.

Figure 2 shows the experimental conversion data obtained for the sample obtained at 3 polymer/paraffin mass ratio as an example due that all the samples exhibit the same trends. The kinetic of the process agree with that of a suspension free radical polymerization reaction. From a kinetic point of view, each bead may be regarded as a small isolated reactor and the observed copolymerization kinetic corresponds directly to that for bulk polymerization (Cordoví, 2000). Figure 2 also shows the increment of volume particle size during the copolymerization process. The final particle size is already established at very low conversion (≈40%). Polymerizing droplets maintain their identity during the experiment, and subsequent variance in stirring speed has no influence on particle size.

Concluding a paraffin/polymer mass ratio of 3 was selected to study the effect of MMA/St mass ratio. When a MMA/St mass ratio of 2 and 5 was used the microencapsulation was not successful. DSC analyses of samples obtained with a MMA/St of 3, 3,5 and 4 show a phase change enthalpy of 75.4, 87.5 and 104.8 J/g, respectively. Moreover, when the amount of MMA increases, the reaction time decreases. This fact is due to the high reactivity of methyl methacrylate. Finally, the particle size decreases when the mass ratio MMA/St increases.

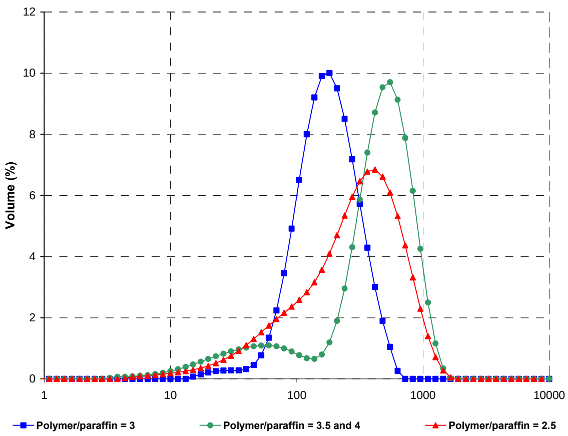

Figure 1: Particle size distribution for different polymer/paraffin mass ratios.

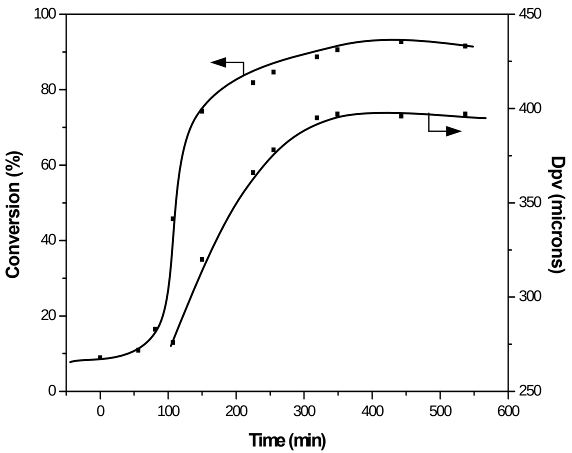

Figure 2: Evolution of conversion and volume average diameter of microcapsules during the polymerization.

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Enzyme-based Antifouling Coatings

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1. Summary

This presentation is concerned with marine antifouling coatings. The development of environmentally benign coatings based on enzymes as active antifouling ingredients is considered. It is the aim to provide an overview of the obstacles faced, when dealing with enzymatic antifouling, and considerations on how to face these obstacles will be presented.

Keywords: antifouling, antifouling coating, enzymes, hydrogen peroxide.

2. Extended Abstract

The accumulation of polymers and living species (i.e. fouling) on seawater-immersed constructions is connected with a variety of problems. On ship hulls, increased fuel consumption, due to higher drag resistance is the major problem, but promotion of corrosion, and the potential of introducing foreign species to new habitats are also of concern. Fouling has been fought for thousands of years, and the means, with which antifouling has been undertaken, have been plentiful and diverse (Yebra et al 2003). Recently environmental considerations forced paint manufacturers to discard the more toxic of the compounds utilized. The primary substitute, cuprous oxide has a long residence time in seawater, and is therefore prone to bioaccumulation. In the near future, antifouling coatings based on controlled release of short-lived antifouling agents are likely to be introduced.

Enzymes are in general easily degradable proteins; they can therefore, presumably, be added to antifouling paints without harmful environmental consequences. Generally enzymes can be applied as antifouling agents in two different ways. They can be used directly, meaning that the enzymes are used as a substitute to biocides; or they can be applied indirectly, describing the use of enzymes for biocide generation in-situ in the coating.

Hydrogen peroxide is reported to have inhibiting effect on fouling organisms (Ikuta et al. 1988). Its lifetime in seawater is however short, as it decompose to water and oxygen. The instability and high seawater solubility makes it virtually inapplicable in antifouling coatings as a common biocide. Application of hydrogen peroxide as antifouling agent can come about by production of the compound in-situ. Several enzymatic reactions produce hydrogen peroxide (Schneider and Allermann 2005). Some of these enzymes are found in the marine environment, where they are believed to contribute to antifouling properties of algae (Poulsen and Kragh 2002). Hexose oxidase (HOx) oxidises hexose sugars under release of hydrogen peroxide and a lactone. The reaction is presented in (1).

$$C_6H_{12}O_6 + O_2 \xrightarrow{HOx} C_6H_{10}O_6 + H_2O_2 \qquad (1)$$

The substrate as well as the enzyme must come from the coating, and as hexose sugars are water soluble, they are expected to leach from the coating rapidly, leaving the enzyme with no substrate. Therefore also the sugar must be produced in-situ. Amyloglucosidase (AMG) hydrolyses the water insoluble starch molecule to yield glucose. This reaction is shown in (2), where n indicates the number of glucose residues in the starch molecule.

$$\text{starch}_n + H_2O \xrightarrow{AMG} C_6H_{12}O_6 + \text{starch}_{n-1} \qquad (2)$$

The incorporation of enzymes into antifouling paints posses certain challenges. The enzymes must be stable in organic solvent, robust in solvent free coating, and have a controlled activity once activated. Making the enzyme compatible with paint is therefore one of the major challenges in developing an enzyme based antifouling paint. It can be done by a variety of known biotechnological methods (e.g. encapsulation, covalent immobilisation, etc.). Loss of enzyme activity during operation of the coating must be compensated by exposure of fresh coating layers (i.e. polishing) during operation. Polishing can be achieved by selection of coating constituents based on mathematical modelling (Kiil et al. 2002).

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Formulation of an agrochemical product using neural network driven design

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1. Summary

Agrochemical multi-phase formulations are complicated mixtures. Modelling is rarely used in the design of these products as there are a large number of variables and the behaviour is often non-linear. A mixture of oil, water and solid particles was formulated using a coarse grained approach to optimisation. Initial experiments were used to find the approximate optimised region which was then studied in greater detail with further experiments. Neural network modelling and Monte Carlo simulation was used to direct the experimental work. The models produced had very poor predictive power however they did lead to optimised solutions. A random approach to the same problem would have required a very much larger set of experiments. One benefit from this method of optimisation is that it can be automated however in this case the initial selection of ingredients was not suitable. This was detected by the modelled system however operator experience was then required to initiate the next step of the process.

Keywords: Agrochemical, neural network, formulation, design

2. Extended Abstract

Agrochemical suspo-emulsion formulations are very difficult to formulate. They are aqueous suspensions of particles which also have an emulsion of oil droplets. Interactions between the components mean that the behaviour is often non-linear. The prevention of crystal growth, heteroflocculation, creaming, ripening or settling is a balancing act between the properties of the dispersants and emulsifiers. A novel way to avoid some of these problems is to dissolve the oil in the water phase using a hydrotrope (Friberg). A simple formulation might therefore be an oil/hydrotrope blend, a particle/dispersant blend and water. A simplex mixture design for a five component formulation with non-linear behaviour might require 35 data points for the initial screen. This would normally be avoided as it is considered to be an inefficient use of time. The alternative however requires a skilled formulator to design the experiments and work out what to do at each subsequent iteration.

In this experimental work a much smaller initial set of experiments was carried out. A neural network model was developed and used to find the optimum in the design space. As the amount of data was clearly too small for a predictive model to be developed the idea was only to steer the formulator towards the right region. Subsequent iterations were applied to a smaller region which in theory was in a better part of the design space.

After four iterations it was not possible to find optimised solutions to the design problem by using the models. It was assumed the formulation was too simple and a simple screen was carried out and a further ingredient was added. The modelling procedure was then repeated. In this fashion it was eventually possible to locate two regions of the design space where optima existed.

It required a total of ten iterative steps to find these optima, and 61 experiments. There were two stages where the ingredient list had to be altered. If the amount of work is compared to that required to find the optima by simplex design methods then the method was very much more efficient, requiring about one quarter of the number of experiments. The neural network models had very poor predictive power which indicated that the system was only able to find the general area of optimisation. Other modelling methods were tested using the data produced from the experiments and these also failed to produce predictive models. Methods such as multiple linear regression, pls and recursive partitioning also failed to find the optimal regions using the complete dataset. This indicated the high degree of non-linearity present.

In this case the method did not require the operator to have any skill or knowledge in the area of formulation optimisation. The method may therefore be useful in an automated system, possibly in combination with robotics.

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New plasticiser for PVC

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1. Summary

Danisco has developed a new plasticiser for PVC, targeted at applications such as food packaging, medical devices and toys for young children. Several studies have questioned the use of conventional phthalates in these applications. A novel acetylated mono-glyceride derived from hydrogenated castor oil, GRINDSTED® SOFT-N-SAFE represents a good alternative as it belongs to a class of natural oils and fats which are globally approved as direct food additives. In view of its vegetable origin and the manufacturing process, it is believed to be a very reliable and safe alternative to phthalates.

Keywords: plasticizer, PVC

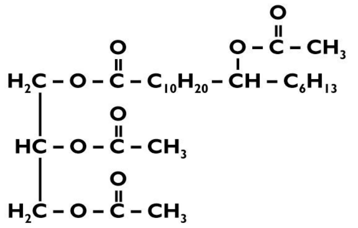
2. Extended Abstract

GRINDSTED® SOFT-N-SAFE has proven to be a fully functional replacement for products such as DEHP and DINP in numerous tests. In most cases, the new plasticiser can be substituted one to one with DEHP, functional properties and durability of the final product remaining unchanged.

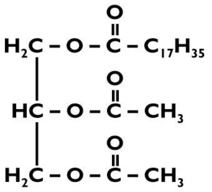
GRINDSTED® SOFT-N-SAFE chemistry

GRINDSTED® SOFT-N-SAFE is a novel fully acetylated monoglyceride based on fully hydrogenated castor oil. The product is manufactured by applying the same principles used for regular acetylated mono and mono-diglycerides – products that are approved and used worldwide as direct food additives.

The raw materials used to manufacture GRINDSTED® SOFT-N-SAFE are glycerine and hydrogenated castor oil. The two main



Fully acetylated glycerol monoester on 12-hydroxystearic acid is the main component, representing 85% of the product



Fully acetylated glycerol monostearate represents around 10% of the product composition

Figure 2. The main components of GRINDSTED® SOFT-N-SAFE.

components of GRINDSTED® SOFT-N-SAFE are drawn in Figure 2. They make up around 95% of the product's total composition. Remaining 5% being other forms of glycerol ester chemistry.

Test results

GRINDSTED® SOFT-N-SAFE has been evaluated in many PVC applications and has always come out as a very reliable and efficient plasticiser compared with, for example, DEHP, DINP and DOA. No alterations to processing and handling equipment are required or any major formulation changes when replacing conventional plasticisers with GRINDSTED® SOFT-N-SAFE.

The comparison with DEHP and DINP shown in table 1 serves to illustrate that the new plasticiser is a good and reliable alternative whenever the use of phthalate chemistry is brought in to question

PLASTICISER	CONCENTRATION, PHR	SHORE A, AFTER 15 SEC	TENSILE STRENGTH, MPA	100% MODULUS, MPA	ELONGATION, %
GRINDSTED® SOFT-N-SAFE	40	88.0	25.0	9.1	367
DEHP	40	90.0	22.2	8.5	320
DINP	40	91.5	24.1	9.3	344
GRINDSTED® SOFT-N-SAFE	60	78.0	18.4	3.9	434
DEHP	60	76.5	17.7	3.8	439
DINP	60	80.0	19.2	4.3	441

Table 1. Plasticiser test results - a comparison between GRINDSTED® SOFT-N-SAFE, DEHP and DINP.

The results in table 1 indicate that GRINDSTED® SOFT-N-SAFE is a fully functional and viable alternative to DEHP. The strength and flexibility of the plasticised PVC remain unchanged.

Safety

GRINDSTED® SOFT-N-SAFE responds to growing consumer and legislative pressure for safe and sustainable alternatives to phthalates. Food brand protection is no longer just about the safety and quality of the food. Today, the spotlight is also on food packaging and the risks createded by additive migration from food contact materials. Similar concerns relate to medical devices, children's toys and other applications where consumers, in one way or another, are directly exposed to the plasticisers in PVC.

Session S-8C: Chemical Product Design & Engineering - II (CPD&E - 2)

Abstract Number	Paper Title & Authors	Included
1761	Effect of the Microstructure of Paracetamol Granules on Tablet Properties U Bröckel, H Beilharz	No
1870	Polymer property modelling using grid technology for design of structured products K C Satyanarayana, J Abildskov, R Gani	Yes
2249	Simultaneous product and processes design using reverse design algorithm V Soni, J Abildskov, G Jonsson, R Gani	Yes
3285	Integrating Mixture Design within the Property Clustering Framework C C Solvason, F T Eljack, N Chemmangattuvalappil, M R Eden	Yes
3614	Transport Properties from Molecular Simulation with the SPEADMD Model J R Elliott, Z N Gerek, N H Gray	Yes
3690	A Chemical Engineering Approach to Catalyst Development K A Christensen	Yes

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Polymer property modelling using grid technology for design of structured products

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1. Summary

Development of group contribution plus models, for the prediction of polymer properties from the drawn chemical structure, which can be later used in computer aided molecular design (CAMD) for predicting the polymer structure from the given set of target properties is the goal of this work.

Keywords: polymers, property prediction, grid technology, structured products

2. Extended Abstract

To satisfy consumer and regulatory demands, chemical and pharmaceutical industries continuously must focus on developing and producing improved/modified products.

Previous trial-and-error methodologies to produce new products, with specific desired properties, are not feasible as these are capital intensive, time-consuming and difficult to automate. Computer-aided molecular design (CAMD) methods, can partially replace these in determining molecular structures matching specific sets of target properties. Extending CAMD techniques for identifying macromolecular (here polymers) structures having a set of target properties, requires new property models. Developing new property models for predicting polymer properties based on the analysis of polymer structure is the main objective of this paper.

The approach involves inductive learning: Experimental data are collected, a property model is derived from the data set and finally the properties are predicted using the developed model.

Polymer property modeling involves both linear and non-linear models. When modeling several properties, time taken for parameter estimation increases proportionately with the number of properties modeled. Grid technology greatly facilitates this work as different property models (based on either group contributions [1], connectivity indices [2] or other methods) can be generated in parallel. In this work, we present a suite of new polymer property models based on groups and atomic contributions. These models are more suitable for computer-aided polymer design algorithms than their predecessors. A comparison of the time required for generating the models in series and in parallel, using grid technology is also presented in this paper.

The models in this work are developed for volumetric properties, glass transition temperature, solubility parameter, optical properties and electrical properties. In order to validate these developed models for accuracy, a comparison between predicted properties using these models, experimental results and other literature models such as Van Krevelen's [3] models and Bicerano's [4] models is made.

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Simultaneous product and processes design using reverse design algorithm

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1. Summary

For a better design of the chemical processes for a given product specification it is advantageous to design the process and the product simultaneously. The simultaneous design would require the integration of the process model with the product/property models and their simultaneous solution. These models could be of different scales for example the process models are generally macro-scale and product property models could be meso- or micro-scale. This kind of integration could be computationally expensive. A reverse design algorithm has been used for the simultaneous design but the strategy is to split the solution steps in two stages such that the process and the product property models need not be solved in an integrated manner. This saves a lot of computational resources and also time and energy for trial and error approach.

Keywords: Integrated process product design, reverse design algorithm, vacuum membrane distillation

2. Extended Abstract

In order to meet the demands of specifically architectured fine chemicals it is advantageous to design the process and product simultaneously. A systematic model based approach, is developed which consists of a framework of multiscale process and product models. The idea is to design simultaneously process and product and generating design alternatives for a given set of performance criteria with proper justification and validation. This gives us more flexibility in terms of choosing the design variables that could either be the process parameters (like temperature, pressure etc.), product parameters (like molecular structure, selectivity, solubility etc.) or both in order to achieve the process demands. A design algorithm based on the reverse design methodology and a generic model that is able to handle wide variety of products and processes will be presented.

The solution strategy based on reverse design approach, for designing the process and product, splits the solution steps in two stages. In the first stage, the process model that includes the balance and constraint equations are solved keeping of property parameters of the system as unknown variables. In the second stage various property models (constitutive equations of the original process model) are solved in order to get the design variables, that matches the target properties calculated in stage I. These are the key properties of the system which affects the performance of the process. For example, reaction rate constant or dissociation constant for reactive systems, driving force for distillation or liquid-liquid extraction etc., thermodynamic or kinetic properties for solution diffusion kind of separation, selectivity of solvents for solvent based separation etc. These key properties in turn depend on parameters like process conditions (temperature, pressure, flowrates etc.), parameters related to the equipment, chemical structure of solvent or entrainers (for azeotropic distillation), microscopic structure of polymers and/or support layer for membrane based separation processes etc. Instead of choosing these parameters for any process and evaluating property parameters using constitutive equations during the solution of process model and then checking if the desired performance criteria is achieved or not, it is computationally convenient to split the solution steps in two stages as mentioned before. In this way, the hierarchal approach converges from the inlet and outlet specifications of a process to the product and process properties which leads to the design of the product to match the performance criteria of process, hence designing both of them simultaneously in one framework.

This methodology as compared to the conventional forward approach is computationally inexpensive as it does not require the property models to be embedded in the process model and solved simultaneously. It also gives the opportunity of combining models that are multidisciplinary and multiscaled. In the second stage of the algorithm, as many property models can be used in order to generate the design alternatives for both product and process. It is not an iterative process like the forward approach where different designs are tested in a trial and error method in order to match the performance criteria.

The methodology along with its application to design membrane based separation processes will be shown for processes like Vacuum membrane distillation (VMD), pervaporation and membrane based gas separation. The physics of the system depends very much on the separation process and the kind of polymer used as membrane in the process. For example, for both pervaporation (liquid separation) and gas separation the polymer generally used is dense polymer and hence the transport mechanism is solution-diffusion mechanism, which makes permeability the key property in the separation process. While on the other hand for VMD, usually porous membranes are used making porosity, tortousity etc. as properties that enhance or retard the separation process. Property models to calculate some of these properties will also be shown. Results for permeability calculations done using molecular modeling for different structures of polymers (polyethylene and polyisobutylene in particular) will be highlighted.

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Property custering tchniques for mxture dsign

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1. Summary

Mixture Design is a Design of Experiments (DOE) tool used to determine the optimum combination of chemical constituents that deliver a desired response (or property) using a minimum number of experimental runs. The approach often suffers from combinatorial explosion when dealing with multi-component mixtures found in pharmaceutical excipient design. The recently developed property clustering technique can alleviate this problem. Here the properties are transformed to conserved entities described by property operators, which have linear mixing rules even if the operators themselves are nonlinear. To solve the mixture design, components are mixed according to property operator models in a reverse problem format until the mixture falls within the target feasibility region. Candidate solutions can be screened using additional criteria per the experimenter's preference. The accuracy of this technique depends heavily on the ability of the property operator models to adequately describe the property within the design space. In this work, linear Scheffe and Cox models are implemented as property operators in the clustering framework.

Keywords: Property clusters, mixture design, principal component regression

2. Extended Abstract

Design of Experiments (DOE) utilizes statistical methods to plan and execute informative experiments (Box et al., 1978). A model is postulated to represent the response surface. Experimental design points are placed in areas where observations can be collected to which the model can be fitted. In the final step, the adequacy of the model is tested. The procedure may require much iteration until the fitted equation is considered sufficient (Cornell, 2002), thus optimal choice of model and location of design points is imperative. The best set of points is chosen subject to the following constraints: (1) Size and shape of the experimental region, (2) number of desired experimental runs, and (3) model type used for constructing the response map (Kettaneh-Wold, 1991). Polynomial models are usually selected to represent the response surface since they can be expanded by Taylor series to the desired accuracy (Cornell, 2002). First or second degree polynomials are usually chosen as they require fewer observations and higher models are seldom required. Two types of models (the Scheffe canonical model and the Cox model) are traditionally chosen:

$$\hat{y} = \sum_{i=1}^{u} \hat{\beta}_i^* x_i + \sum_{i<j}^{u} \sum_{j>i}^{u} \hat{\beta}_{ij}^* x_i x_j \quad , \qquad \hat{y} = \hat{y}(s) + \sum_{i=1}^{u} \hat{\beta}_i x_i + \sum_{i\le j}^{u} \sum_{j\ge i}^{u} \hat{\beta}_{ij} x_i x_j$$

The Scheffe model accurately predicts the mixture property and is suitable for direct use in property clustering (Eden et al., 2003). However, the constituents of this model are highly co-linear which means interpretation of the regressors is limited. Most mixture designs are screening designs, thus it is necessary to properly interpret the chemical constituent regressors by removing the co-linearity. Cox (1971) recommends that the model is rewritten in terms of a standard property and regressors that represent the constituent contributions to the mixture property. It has been shown that Scheffe and Cox derived property operators produce identical property response plots. In this work, it is shown that the property clustering framework can be augmented to handle Cox property operators and produce identical candidate solutions as the Scheffe based models. To utilize the Cox property operator, the true property cluster is broken into a standard property cluster and a pseudo property cluster. The pseudo property cluster can be parlayed into a similar type of mixing rule as the true property cluster to facilitate candidate simulation:

$$C_k = F^s C_k^s + F^z C_k^z \quad , \qquad C_{kM}^z = \sum_{i}^{u} \delta^z C_{ki}^z$$

Using the Cox techniques, the cluster points of pure species represent the pure component impact on the mixture property void of most co-linearities. Cluster points close to the feasibility region have little impact on the mixture, while points far from the feasibility region are key components having large impact. The property operators are comprised of regressors, thus some clusters may be negative, implying the point has negative impact on the mixture property.

Visualizing the experimental design space using the property clustering method enables easier understanding of the results. In addition, the accuracy of the design is visually apparent and the impact of the chemical constituents is intuitively understood. The method avoids combinatorial explosion associated with traditional mixture design. Furthermore, early indications suggest the method may be a good supplemental tool for use with principal component regression techniques.

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Transport properties from molecular simulation with the SPEADMD model

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1. Summary

Molecular dynamics simulation holds the prospect of predict both thermodynamic and transport properties through a single characterization of molecular interactions and liberal application of Newton's Laws of motion. The SPEADMD model (Step Potential Equilibria And Discontinuous Molecular Dynamics) has been developed based primarily on thermodynamic properties until now. This presentation illustrates how an analogous approach can form the basis for semi-empirical correlations of transport properties that can be applied at present. The key qualitative behavior is found to be dominated by the repulsive interactions, which are rigorously simulated in detail. Quantitative agreement with experimental data is obtained by correlating the effects of attractive forces in a semi-empirical manner. Results are presented for diffusivity and thermal conductivity.

Keywords: Physical properties, molecular dynamics simulation, thermodynamic perturbation theory, diffusivity, and thermal conductivity.

2. Extended Abstract

When new molecules are synthesized, their target properties may be well known but their engineering properties may be completely unknown. For example, a small molecule drug candidate may be known to have high biological activity, but measuring its vapor pressure, bulk density, viscosity, and thermal conductivity would require gram quantities. Even the melting temperatures measured by millions of freshman chemistry students require purified quantities near 0.01g. Developing those quantities with that purity can be overwhelming for the large number of trial products that may be encountered in the early stages of development.

The Step Potential Equilibria And Discontinuous Molecular Dynamics (SPEADMD) model provides a basis for molecular modeling of thermodynamic and transport properties. It is based on Discontinuous Molecular Dynamics (DMD) and second order Thermodynamic Perturbation Theory (TPT). DMD simulation is applied to the repulsive part of the potential, complete with molecular details like interpenetration of the interaction sites, 110° bond angles, branching, and rings.[1,2] The thermodynamic effects of disperse attractions and hydrogen bonding are treated by TPT. This approach accelerates the molecular simulations in general and the parameterization of the transferable potentials in particular. Transferable potentials have been developed and tested for over 200 components comprising 22 families.[3,4]

Unfortunately, there is no theory comparable to TPT when treating transport properties.[5] Most theories of transport properties rely on empirical variations of correlations for spherical reference fluids. Furthermore, existing correlations are typically specific to a given range of conditions: gas, dense gas, or liquid, for example. To overcome this situation, we must leverage the dynamics from the reference fluid simulations while accurately correlating and predicting experimental data. We show how to achieve this combination of rigorous fundamentals and empirical accuracy and compare to the accuracy of existing engineering correlations for diffusivity, thermal conductivity, and viscosity.

The diffusivity analysis shows that previous correlations based on the hard sphere model are fundamentally flawed. When applying the conservation of volume principle, as is typical, the scaling in the low density limit deviates strongly from the Rouse scaling typically observed for unentangled polymer liquids. Our simulations show clearly that the Rouse scaling is the proper result in the low density limit for n-alkane chains. We derive a generalized correlation for any n-alkane based only on the molecular weight. For non-alkanes, we show how adapting an equivalent alkane perspective provides reasonable predictions and accurate correlations with fewer parameters than previously reported.

The thermal conductivity shows that an asymptote is approached at high molecular weights when isotherms are correlated with respect to mass density. Once again, this deviates strongly from the currently popular hard sphere perspective.

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A chemical engineering approach to catalyst development

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1. Summary

The desire to reduce production costs and energy consumption in industry has been a major driving force for the development of new catalysts and catalytic processes, and in the past decades an increased focus on environmental protection has called for new catalysts for removal of SO_2, NO_x and organic compounds from off-gases in the chemical industry, from power plants, refineries and from auto-exhaust. The development of catalytic products includes both practical and theoretical knowledge and experience with a palette of disciplines known to the chemical engineer, e.g. inorganic chemistry, physical and chemical characterisation techniques, nano-scale materials, unit operations, chemical reaction engineering, catalyst kinetics, and transport phenomena. As a case study of chemical product design in the catalyst industry, the strategy and the methods used for catalyst development and design at Haldor Topsøe to develop and design a new commercial low-temperature sulphuric acid catalyst called VK69 are presented. The individual tasks and methods used for the development are described and a selection of results are presented and discussed.

Keywords: catalysis, product development, sulphuric acid

2. Extended Abstract

The starting point for development of a new commercial catalyst is typically new market opportunities or requirements to performance identified in a competitive market, cf. fig. 1. However, ideas fostered from observations in the laboratory or elsewhere in an organisation may also be recognised as a source of new product opportunities. In the first stages of the catalyst development, formulations with different carriers, shapes, compositions and calcinations are tested with respect to catalytic activity, mechanical strength and pressure drop. In the later stages of the development, full-scale production is demonstrated, the catalyst stability and durability are validated and detailed performance data are acquired. An innovative attitude is important especially in the first stages of development, where different catalyst formulations are proposed and selected, but in all steps of the testing much can be learned from the experimental observations. The decisions to move forward through the stages of the development process are based on evaluations of the profitability of the catalyst product based on the measured performance, estimated production cost and market analyses. However, the profitability should be taken into account throughout the development process in order to avoid e.g. exotic production routes or expensive raw materials that will fail to pass the evaluations anyway.

The main driver for development of VK69 sulphuric acid catalyst (cf. fig. 2) was the desire to reduce SO_2 emissions from sulphuric acid plants without costly tail gas cleaning or an additional interbed absorption step, which would require high investment cost and reduce the energy efficiency of the process. Because of the unfavourable position of the equilibrium at high temperature, this task addressed a serious limitation of the vanadium-potassium-based sulphuric acid catalyst, being a drastic decrease of activity below 400-430°C. The development was based on Cs as an excellent low-temperature promoter, carrier optimization and clever pellet design.

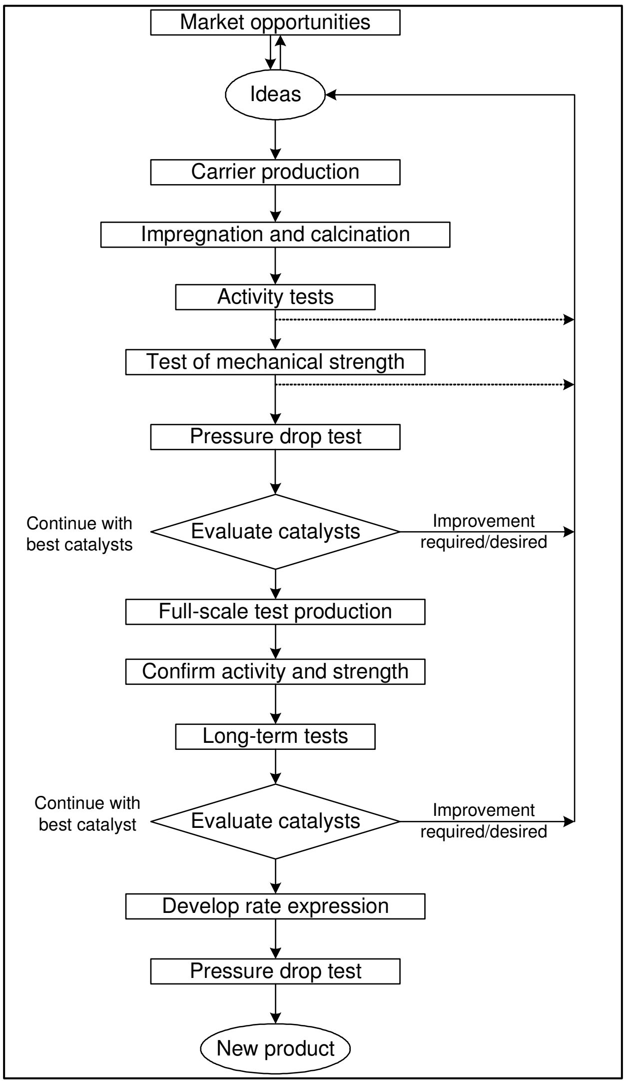

Figure 1. Strategy for design of a new catalyst.

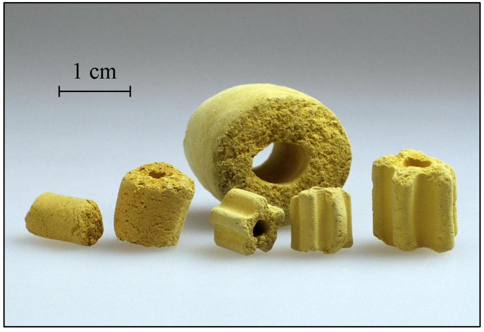

Figure 2. The five variants of size and shape of sulphuric acid catalysts from Haldor Topsøe.

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Session S-8E: Chemical Product Design & Engineering - III (CPD&E - 3)

Abstract Number	**Paper Title & Authors**	**Included**
1242	Green Starch Conversion Technology: Studies on Starch Acetylation in Supercritical CO2 A H Muljana, B H J Heeres, C L P B M Janssen	
2318	Wood adhesive emulsions from thermsetting polyketones Y Zhang, F Picchioni, A A Broekhuis	
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Green starch conversions: studies on starch acetylation in supercritical CO_2

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1. Summary

We here present our experimental results on the acetylation of starch with acetic anhydride in supercritical CO_2 in a batch reactor. The effects of several variables such as pressure (60 – 98 bar), temperature (40 – 90^{o}C), rotational speed (200 – 1500 1/min), amount of reactant (2 – 5 equiv/AGU), amount of catalyst (0.1 -1 equiv/AGU), water content (1 % - 15.2 %-w/w), and particle sizes (40 – 100 um) on the degree of substitution (DS) as well as selectivity of the reaction were explored. Acetylated potato starch with degrees of substitution (DS) ranging between 0.01 and 0.43 could be obtained with acetic anhydride selectivity for the main reaction ranging from 0.02 until 0.16.

Keywords: acetylation, potato starch, starch acetate, supercritical CO_2

2. Extended Abstract

Supercritical CO_2 has shown to be an excellent solvent and processing aid for polymer processing. In addition, it is also an attractive medium for chemical reactions as it is considered to be ‘green’, it is non-flammable, relatively non toxic and inert. Another advantage is the ease of separation from the (reacting) system by simple reduction of the pressure (Savage *et al.*,1995; Eckert *et al.*,1996; Beckman.,2004). With these advantages, supercritical CO_2 could be an excellent alternative for common solvents like water for chemical and physical modifications of starch.
Recently, Harris *et al*, have shown that starch modification reactions can be done in supercritical CO_2 (Harris *et al.*, 1999). However, further studies are required to broaden the scope of reactions and to gain insights in the processes taking place on a molecular and starch particle level.
Starch acetates are commercially produced and have a broad range of applications. The products are commonly made by reacting starch with an acetate source like acetic anhydride in water. Selectivity is a key issue and considerable amounts of acetic acid are produced by the simultaneous reaction of the anhydride with water, limiting the effectiveness of the anhydride.
The reaction scheme with the desired starch acetylation reaction (Eq 1.1 and Eq 1.2) and the hydrolysis of acetic anhydride as the undesired side reaction (Eq 1.3) are given by:

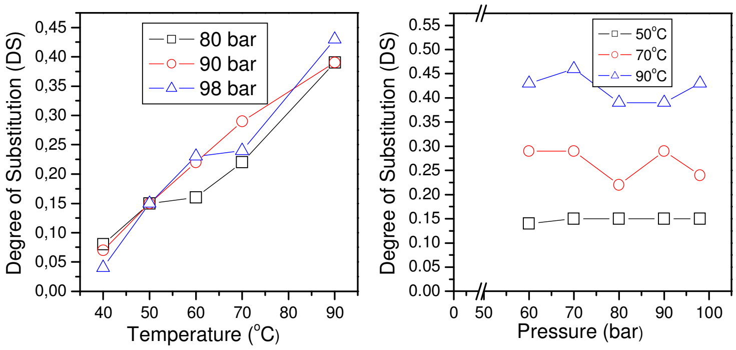
$$ROH + CH_3COONa \Leftrightarrow RONa^+ + CH_3COOH \quad (1.1)$$

$$RONa^+ + CH_3COOCOCH_3 \rightarrow ROCOCH_3 + CH_3COONa \quad (1.2)$$

$$CH_3COOCOCH_3 + H_2O \rightarrow 2CH_3COOH \quad (1.3)$$

In Eq 1.1 and 1.2, ROH represents a starch molecule, with R the starch backbone and OH an hydroxyl group.

We here report our studies on the acetylation of starch with acetic anhydride using sodium acetate as catalyst in supercritical CO_2. The DS and anhydride selectivity depend strongly on the reaction temperature, see Figure 1. At 90°C, starch acetate with a DS of 0.43 could be obtained. The effect of pressure within the pressure window (80 – 98 bar) is rather limited, see also Figure 1 for details. The highest selectivity (16%) for the main reaction was obtained at a pressure of 98 bar and a temperature of 90°C.



(a) (b)

Figure 1. The DS of acetylated starches at elevated temperatures (a) and at elevated pressures (b).

The DS reduced from 0.16 to 0.12 at higher acetic anhydride to starch ratio (from 2 to 5 equiv/AGU, T = 50°C, P = 80 bar). A similar trend was observed at higher catalyst to starch ratio's. Here, an increase in the catalyst to starch ratio from 0.1 to 0.4 equiv/AGU led to a reduction in the DS from 0.15 to 0.11. The water content of the starch granules also plays an important role. The DS values were reduced considerably from 0.15 to 0.02 and the selectivity dropped from 10% to 2% when the water content was reduced from 15%-w to 9%-w.

Further, systematic studies using Design of Experiments (DOE) are in progress to optimize the reaction with respect to reaction rates and selectivity.

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Wood adhesive emulsions from thermsetting polyketones

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1. Summary

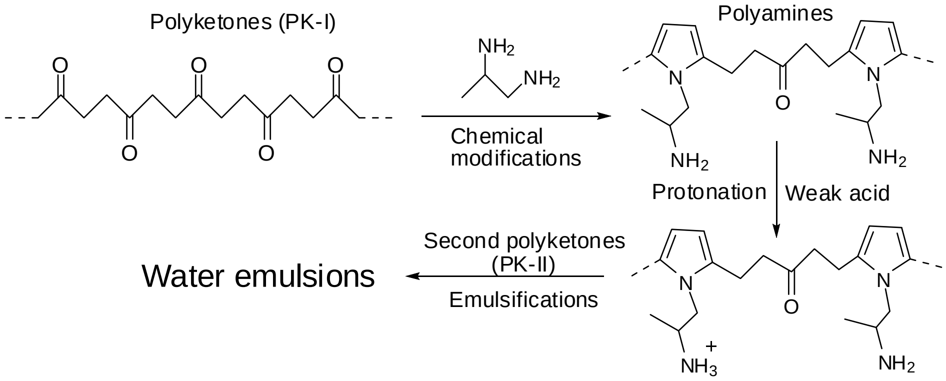
Aqueous polymer emulsions were prepared by chemical modifications of thermosetting alternating polyketones in a one-pot reaction. Polymeric amines derived from the polyketones can act as polymeric surfactants for the self-emulsification of polyketones. Emulsions with an average particle size smaller than 500 nm and a viscosity less than 1 Pa.s could be achieved and remained stable for at least one year. The prepared emulsions were qualified as wood adhesives for wood composite industry, according to the European Standard for wood adhesive testing.

Keywords: polyketones, wood adhesives, polymeric surfactants, water emulsions

2. Extended Abstract

Water based polymeric emulsions have found wide applications in recent years, especially in the wood adhesive industry due to the environmental restrictions on solvent based systems. Polymeric emulsions in water are generally produced by using surfactants or direct emulsion polymerization (Chern, 2006). Here we developed a simple route to prepare waterborne polyketone emulsions (Scheme 1), using the polyamines derived by polyketone modification, as polymeric surfactants (Broekhuis and Freriks, 1999). Alternating polyketones were produced by copolymerization of carbon monoxide and olefins (mixtures of ethene and propene) in the presence of homogeneous palladium catalyst systems (Drent and Keijsper, 1993). The polymeric surfactants were synthesized by the Paal-Knorr reaction of the starting polyketones (PK-I) with a diamine having a sterically hindered primary amino group. During the reaction, around 70 % of the carbonyl groups can be converted into pyrrole units in the backbone bearing in γ-position a primary amino group. Interesting aqueous solution behavior is observed for the polyamines after protonation with weak acid. Spherical polymer micelles with average size of 50 nm are formed at a minimum 40% protonation level (Figure 1a) ending up with an average particle size of even less than 10 nm at 100 % protonation level. The surfactant solutions can be stable even after one month storage at room temperature. During the emulsification step, a second quantity of polyketones (PK-II) is added into the protonated polyamine solutions to achieve a final fixed 50 wt% solids resin composition. The stability and structure of the resulting emulsions have been studied by the dynamic light scattering, rheological measurements and Cryo-SEM upto one year storage time at room temperature (20°C).

The properties of the resulting emulsions are dependent on the emulsification process, the protonation level and the relative content of the polymeric surfactants (polyamines). The prepared emulsions exhibit extremely long shelf life at room temperature for at least one year. Particle sizes (less than 500 nm) of the emulsions (Figure 1b) remain basically unchanged in time thus demonstrating high kinetic stability of the prepared emulsions. The viscosity of the system decreases greatly in the first week which may due to a rearrangement of the polymers within each particle, a kind of “arms” (free polymer chains) retraction on the surface of the polymer particle and then levels off to a stable value between 0.5-0.7 Pa.s within the storage time upto 15 months. According to the European Standard (EN-314) for wood glue testing, the quality of the emulsions as glue for wood was evaluated by measuring the shear strengths on the applied maple substrates. Average shear strengths 2.7 MPa could be achieved, which far exceeded the requirement (1 MPa) of the EN-314.



Scheme 1: Preparation of aqueous polymeric emulsions based on thermosetting polyketones.

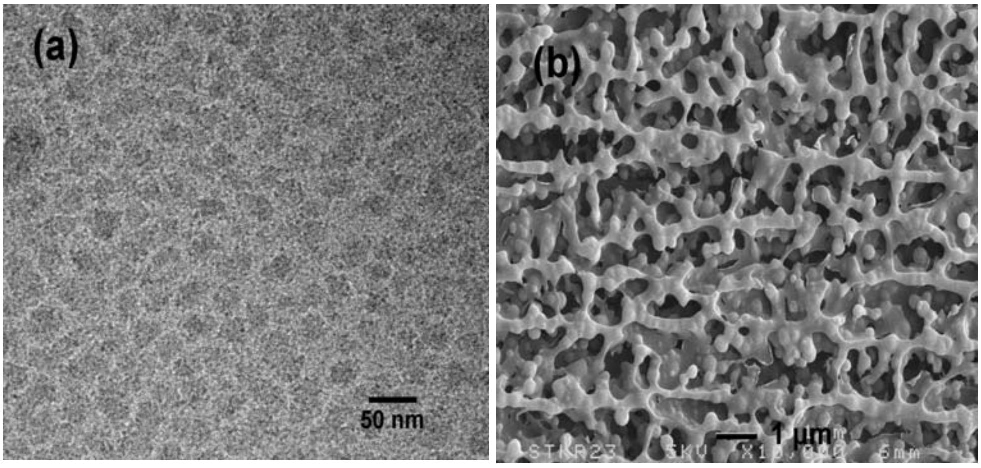


Figure 1: (a) Cryo-TEM image of the polyamines in water; (b) Cryo-SEM image of the polyketone emulsions.

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Gyroid membranes made from nanoporous block

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1. Summary

Block copolymers are very interesting materials from both scientifical and applicational points of view because of their amazing self-assembly properties. It is possible to control the morphology of the self-organized structures in the nano-scale level by choosing the proper ratio (volume fraction) of the blocks. Here a diblock copolymer showing the gyroid structure is crosslinked and etched to obtain nanoporous material. Membranes are prepared from this material and investigated for separation of polyethylene glycol molecules dissolved in methanol/water mixture.

Keywords: block copolymers, nanoporosity, ultrafiltration

2. Extended Abstract

Block copolymers have an amazing possibility to self-organize into specific structures on the nanoscale. Chemical incompatibility between the copolymer blocks is the main driving force for the self-organization. [1] We can choose the copolymer morphology by controlling the total molecular weight and the composition of the block copolymer during the polymerization. We obtain a nanoporous material by removing the minority block from the matrix of the majority block. There are many applications for such a nanoporous material with well defined pore size. [2] Ultrafiltration membrane is one of them.

Here we present a nanoporous material with gyroid morphology [3] from 1,2-polybutadiene-polydimethylsiloxane (PB-PDMS) crosslinked by dicumyl peroxide (DCP). The PDMS block was etched by tetrabutylamonium fluoride (TBAF) after the crosslinking of the PB block. Figure 1a shows the schematic phase diagram for diblock copolymer. We can change the morphology by changing the volume fraction f_A of one block. Increasing the f_A causes change in morphology from body centered cubic (BCC) spheres to hexagonally packed cylinders (HEX), and then to gyroid (GYR) and lamellar. Further increasing f_A will cause inversed GYR, HEX and BCC morphologies.

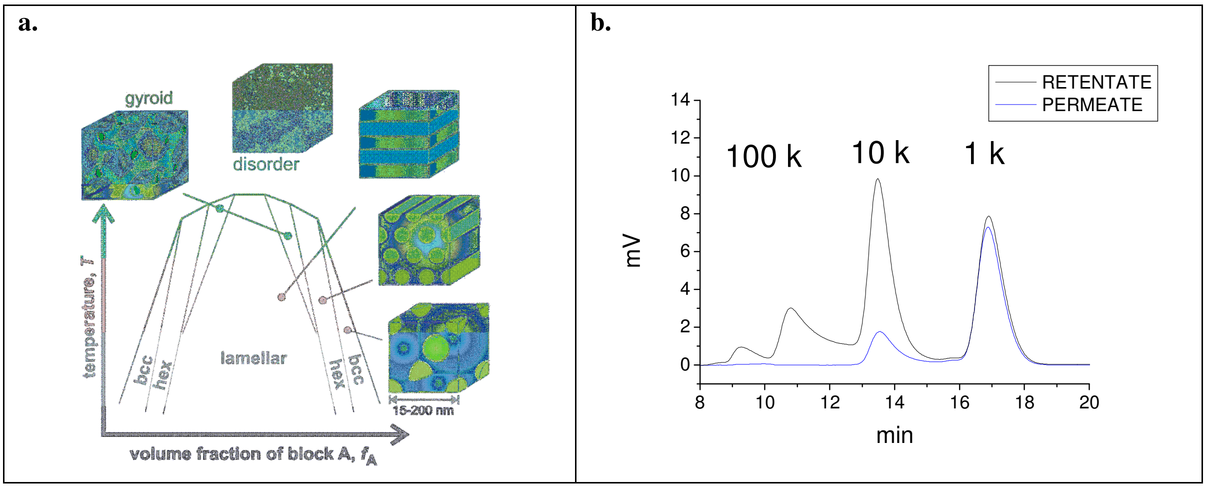

Figure 1 a. Schematic phase diagram for diblock copolymer b. Comparison of size exclusion chromatography (SEC) data obtained from the retentate and permeate of the PEG solution in methanol/water mixture.

There are potentially two morphologies of diblock copolymer which can deliver channels and be used for membrane application: hexagonally packed cylinders (HEX) and gyroid (GYR). The gyroid morphology, unlike the HEX, is a bicontinuous cubic structure. It does not need to be aligned in any specific direction to assure channels percolation between the two membrane surfaces.

The nanoporous membrane material was characterized by small angle x-ray scattering (SAXS), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption technique.

The membrane permeability was firstly checked for nitrogen gas. Secondly the separation property of the membrane was tested. A solution of three polyethylene glycols (PEG of 100, 10 and 1 kg/mol) was filtered by the membrane. The time needed to collect a given permeate volume was used to calculate fluxes. Figure 1b shows first tentative results of the permeates and retentates as characterized by size exclusion chromatography (SEC).

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Effect of Water Activity on Lipase Enantioselectivity

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1. Summary

Lipase (Novozym 435) catalyzed enantioselective esterification of 1-phenyl-1-propanol with capric acid was carried out in trimethylpentane solvent under controlled water activity (a_w) conditions. The water activity of the reaction medium was controlled by using salt hydrate pairs and saturated salt solutions. When salt hydrate pairs were used, conversion and reaction rate increased with increasing a_w from 0.06 to 0.33 and decreased above this a_w value. Similarly, enantiomeric ratio (ee) increased from 2 % to 93 %. With the saturated salt hydrate solutions, although the highest reaction rate was observed at high a_w, ee was at low a_w.

Keywords: Water activity, lipase, enantioselectivity, 1-phenyl-1-prophanol, kinetic resolution

2. Extended Abstract

The advantages of using organic solvents or low water activity media to operate enzymatic reactions have been pointed out. It is well known that water content in the reaction media is an important parameter when using enzymes in organic media. It can influence the rate and equilibrium yield as well as the stability of enzymes. It is therefore important to measure and control water content in these systems. The effect of water in organic solvents is best described by a_w. In lipase catalyzed esterification reactions in organic solvents, water plays a crucial role. A minimal amount of water is necessary for the enzyme to ensure its optimal conformation and to become optically active but an excess of water decreases the enzyme catalytic activity. In order to control a_w several methods can be used. To maintain constant a_w during a reaction, a_w of headspace above the reaction medium is adjusted by circulation of headspace gas through a drying column. Another a_w control method is to perform the reaction in a vessel with a saturated salt solution in contact with the reaction mixture via the gas phase, so that the saturated salt solution continuously absorbs and releases water vapor to keep the a_w constant. Another way for the continuous control of a_w is the use of a salt hydrate pair. A salt hydrate pair controls the water level in the reaction mixture by taking up or releasing water as required keeping a constant a_w condition during the reaction (Han and Rhee, 1998). In this study, a_w is controlled by adding salt hydrate pairs and saturated salt solutions. The salt hydrates are Na_2HPO_4(7/12) (a_w:0.90), Na_2SO_4(10/0) (a_w:0.76) Na_2HPO_4 (2/7) (a_w:0.69), $C_2H_3NaO_2$(3/0)(0.33), $MgCl_2$(6/0)(a_w:0.06). The equal amounts of each salt form (0.1 g) were added directly into reaction medium to keep the water activity constant during the reaction.

The saturated salt solutions, namely; $K_2Cr_2O_7$ (a_w:0.98), $(MgNO_3).6H_2O$ (a_w:0.54), CH_3COOK (a_w:0.23), LiBr (a_w:0.11), are used to investigate the role of initial water activity. In the experiments with saturated salt solutions, lipase and solvent were incubated in desiccators containing saturated salt solutions for a week. The optimal a_w for esterification reaction is 0.33 in the presence of salt hydrate pairs (Fig 1). The water level affects the equilibrium of reversible esterification reaction because water is formed during the reaction. Therefore, the reaction rate decreases with increasing a_w. Also, high ee (93 %) was obtained with 0.33 $a_{w,}$ under this a_w value, ee decreases as monolayer of water is necessary to retain the activity of enzyme (Fig 2). While a_w of the reaction medium is controlled by using saturated salt solutions initial reaction rate is high and ee is lower than those by direct adding various salt pairs to the reaction system. It might be the relevance of acid-base ion-exchange effects of salt hydrates on enzyme in nonaqueous solvents.

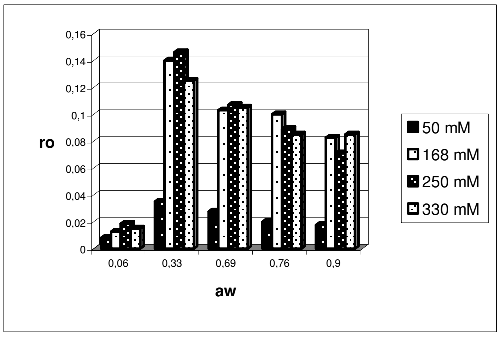

Figure1. Effect of a_w controlled with salt hydrate pair on initial rate in various substrate concentration.

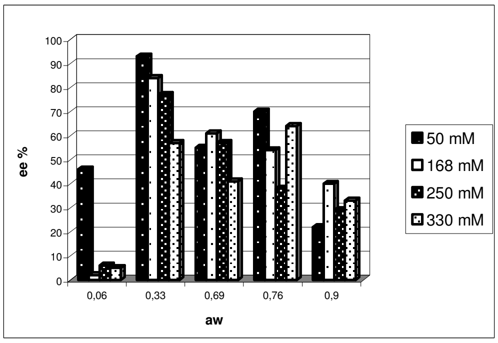

Figure2. Effect of a_w controlled with salt hydrate pair on ee in various substrate concentration.

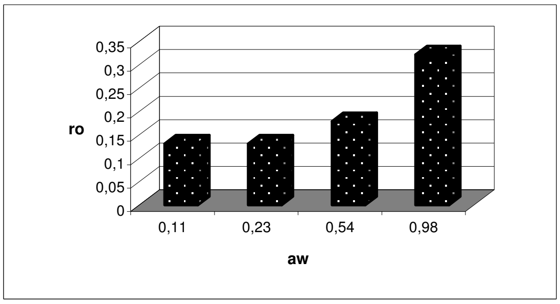

Figure3. Effect of a_w controlled with saturated salt solution on initial rate.

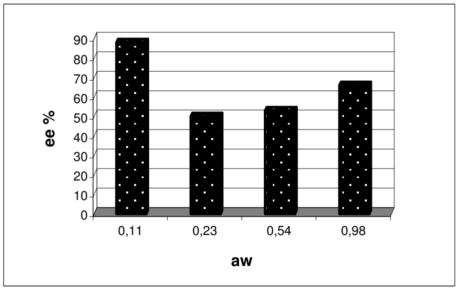

Figure3. Effect of a_w controlled with saturated salt solution on ee.

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Acknowledgements

The authors gratefully acknowledge the financial supports given to this work by Ankara University, Institute of Biotechnology (Project no:2001K120140-162).

Session S-8F: Chemical Product Design & Engineering - IV (CPD&E - 4)

Abstract Number	Paper Title & Authors	Included
604	Biocompatible Polymeric Materials Intended for Drug Delivery and Therapeutic Applications S Hvilsted, D A Pedersen, A D Thomsen, I Javakhishvili, M Bednarek	Yes
1123	Particle production for controlled drug release S Nalawade, F Picchione, L P B M Janssen	Yes
2168	Carbon cartridges and their use as a purification step in pharmaceutical API processes N Iverlund, A Parsons, F Muller	Yes
2281	Biocompatible Metallic Materials For Osteosynthesis Made By Icem – Sa, Romania A M C Anca, B S Ştefan	Yes
2304	Anticipation of scale up issues in pharmaceutical development F L Muller, J M Latimer	Yes

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Biocompatible polymeric materials intended for drug delivery and therapeutic applications

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1. Summary

Strategies for design and preparation of biocompatible polymers by use of novel, versatile synthetic methods are presented. The application of Atom Transfer Radical Polymerization (ATRP), ring-opening polymerization (ROP) and “click chemistry” alone or in combination to produce amphiphilic block copolymers are elucidated. The merits of the different synthetic methods and imperative strategic choices in order to reach the focused goals will be elaborated.

Keywords: controlled polymerization, block copolymers, poly((meth)acrylates), polycaprolactone, poly(ethylene glycol)

2. Extended Abstract

With the advent of the controlled free radical polymerization techniques and the novel highly efficient coupling technique (“click chemistry”[1]) a number of new design principles for biomedical polymeric materials emerge. We’ve recently initiated a comprehensive research programme aiming at elucidating *strategies* for combination of biocompatible polymers in unique but amphiphilic manners. The targeted, documented biocompatible polymers like polycaprolactone (PCL), poly(2-methoxyethyl acrylate)[2] (PMEA) with the highest known blood compatibility, poly(methyl methacrylate) (PMMA), and the two water soluble polymers, polyethylene glycol (PEG), and poly(acrylic acid) (PAA) with good mycoadhesive properties, are all prepared by living/controlled polymerization techniques.[3,4]

These techniques, atom transfer radical polymerization (ATRP) and ring opening polymerization (ROP), ensure at the same time both good molecular weight control and well defined, manageable structural end groups that sets the scene for combination of the different polymer blocks. With this tool box at hand the choice becomes to decide between all polymerization strategies or build in chemical functionalities allowing coupling of polymer blocks by "click chemistry". An all polymerization strategy would imply preparing polymers by living/controlled techniques in such a manner that one block after polymerization can be converted to a macroinitiator enabling the second block to polymerize. The coupling strategy invariably inserts a linking unit, 1,4-triazole, resulting from the catalyzed, irreversible 1,3-dipolar cycloaddition reaction between an alkyne and an azide. Thus, this strategy necessitates the proper end functionalization of the polymeric building blocks. Fortunately the 1,4-triazole unit is FDA approved already existing in formulated drugs.

Examples of combinations of PMEA with PMMA or PEG will be elaborated. Similarly combinations of PCL with PAA (prepared from a protected precursor polymer) or PEG will be provided.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Particle production for controlled drug release

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1. Summary

Controlled release of medicine requires the application of micro particles. These particles should be in the range of 10 to 500 μm for oral administration, 1 to 5 μm for inhalation and subcuteanous applications and less than 1 μm when injected into the circulatory system. Moreover the particles should have a narrow size distribution and have a low organic solvent residual content. For the production of these particles the application of supercritical carbon dioxide has several advantages above the classical processes like milling, freeze drying and precipitation in organic solvents. Three different methods are possible for micro particle formation with supercritical solvents: precipitation by compressed anti-solvent (PCA), rapid expansion of supercritical solutions (RESS) and precipitation from gas saturated solutions (PGSS). Using this last method, we studied the behaviour of polyethylene-glycol which was first saturated with supercritical carbon dioxide and then sprayed over a nozzle (figure 1). The main effects of supercritical carbon dioxide on the process was twofold: due to a considerable viscosity reduction (eight to ten fold) the spraying effect is far more effective than without CO_2 and, because after pressure release the supercritical carbon dioxide becomes gaseous, the polymer particles explode into smaller particles. By changing temperature, pressure and molecular weight the size and morphology of the particles can be controlled.

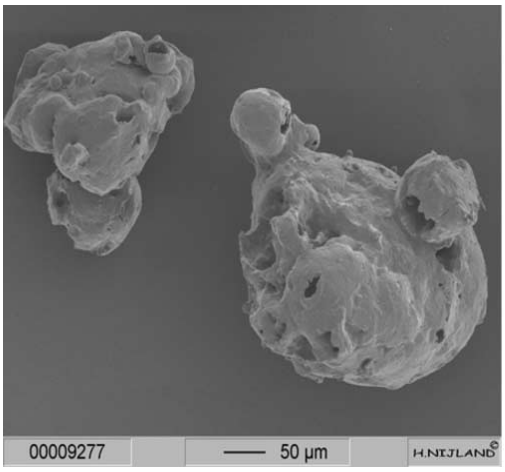

Fig 1: PEG particles produced by supercritical carbondioxide assisted spraying.

Keywords: product technology, supercritical carbon dioxide, micron particles, controlled release.

2. Extended Abstract

The batch production of particles from PEG of different molecular weights is possible using supercritical CO_2 as a processing solvent. An autoclave with the PEG was first put under vacuum after which the CO_2 was added and brought under supercritical conditions. The CO_2 was dissolved into the PEG under gentle to and fro motion of the autoclave. Finally the nozzle was opened and the CO_2-saturated PEG was sprayed in a container. Relatively bigger particles were obtained for PEG 10000 (Mw) compared to PEG 6000(Mw). The higher the molecular weight the higher is the viscosity of the polymer and hence, the more difficult is the expansion of the high molecular weight polymer melt despite the same CO_2 solubility. The decrease in temperature and the nozzle diameter resulted into smaller particles. This effect is explained by high CO_2 solubility at low temperatures and high de-pressurization rate (thermodynamic instability) in a smaller nozzle. The effect of pressure on the particle size and particle size distribution has been found absent in all PEG. Not only the size but also the shape and the density of the PEG particles can be controlled in the process studied. Depending on the processing conditions, both hollow and dense particles can be produced that can easily be related to high and low CO_2 solubility, respectively. Nearly spherical particles were produced from PEG 6000 and 10000 as the temperature was increased above the melting temperature. Solidification theory is a good tool to explain the role of temperature and the CO_2 solubility in determining the shape and morphology of the particles. The size distribution of the particles obtained in this way appeared to be far narrower than obtained by classical grinding. The product properties like solubility of drug and/or polymeric matrix material in the supercritical solvent determine which method (PCA, RESS or PGSS) can best be chosen.

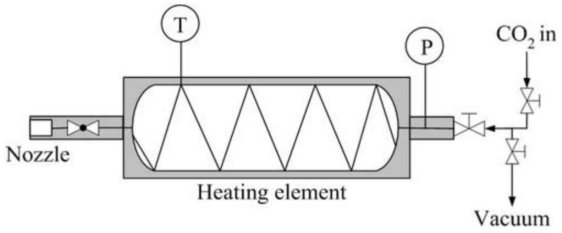

Fig. 2: Set-up for supercritical carbon-dioxide assisted spraying of PEG

Finally, a PGSS process as used here provides possibilities of processing various other pharmaceutical and polymeric compounds that are difficult to process by conventional methods.

3 Acknowledgments

This research is supported by the Technology Foundation STW, applied science division of NWO and the technology programme of the Ministry of Economic Affairs.

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Copenhagen, 16-20 September 2007

Carbon cartridges and their use as a purification step in pharmaceutical API processes

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1. Summary

The presentation will cover the following:

- Advantages of using carbon cartridges over lose carbon in a process
- Description of carbon cartridges and theoretical discussion of their operation
- Two case studies showing how carbon cartridges have been used in pharmaceutical processes (i) percentage level impurity reduction (ii) removal of low level coloured impurities
- Scale up of carbon cartridge processes

Keywords: carbon treatment; carbon cartridges; impurity removal; colour removal; scale-up

2. Extended Abstract

In the pharmaceutical industry powdered carbon is frequently used to remove impurities, both those present in unacceptable percentage amounts and those present in almost undetectable amounts, but still affecting the colour of the API. The handling of powdered carbon is problematic due to its dusty nature and cleaning of carbon from the equipment can be difficult. As a result, carbon cartridges have been developed. The carbon is immobilized in a cellulose matrix and made into filter discs (see Figure 1), which are contained in a jacketed filter housing. After a flush to remove "extractables" (material leached from the cellulose matrix), the process fluid flows through the filter discs and the impurities are adsorbed onto the carbon. The cartridges are disposed of after use. This effectively removes the charging of dusty, powdered carbon,

Figure 1: Example of CUNO ZetaCarbon discs for three different scale filters (~80 ml, ~ 32 l, ~ 300 l)

the stirring operation, the filtration of carbon particles and the cleaning of carbon particles from the process. Carbon cartridges are also more effective than powdered carbon since the process fluid is transferred through immobilized carbon, which essentially acts like a carbon bed with gradual build-up of impurities as the process fluid passes through. This means that as the process fluid passes through the bed it gradually becomes cleaner and the bed it comes into contact with will also contain fewer impurities, allowing a higher removal of impurities than powdered carbon.

Carbon cartridges from suppliers CUNO and PALL have been tested for use in two pharmaceutical API processes. In process 1, the goal was to reduce impurity A from ~3% to below 2%. In process 2 the goal was to reduce a low-level, unidentified, red coloured impurity B to such levels that the API was judged as white to off-white.

For process 1, a suitable carbon type had been selected. The process was run using two CUNO lab scale filters (~80ml and ~8L Process Volume) and impurity A and product concentrations were measured at the CUNO outlet at intervals during the transfer. We were able to see a breakthrough curve and a mass balance was completed for the CUNO transfer step to quantify impurity A adsorption. Using these results, the process was scaled up to a ~300L manufacture. We proved, experimentally, that the flush was successful and “extractables” did not end up as product impurities. We found that we were able to scale up the process based on constant Process Volume / CUNO Area (effective disc surface area) and that lowering the product concentration whilst maintaining a constant impurity A concentration led to increased impurity A adsorption.

For process 2, only one type of powdered carbon had been tested and because of that, discs with different carbon types from both CUNO and PALL were tested. The colour reduction varied between different discs, but the best disc from each supplier had equal colour reduction.

Large-scale filter housings have been purchased for both processes and will be used during manufacturing campaigns. For process 1, the filter housing is a CUNO (one or two 16”, 14 disc cartridges, 3.2 or 6.4 m^2 CUNO Area) and the large-scale process volume is ~0.3 m^3. For process 2, a four-module 16” jacketed PALL filter housing was chosen (see Figure 2) and the large-scale process volume will be 4 m^3. The results from these campaigns will be included in the full paper.

Figure 2: Large scale PALL filter housing

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Biocompatible metallic materials for osteosynthesis made by ICEM – SA, ROMANIA

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1. Summary

The orthopaedic implant is a mechanical device which replaces or supports parts of the human skeleton structure, being exposed to a variety of biological and mechanical stress. The implant must perform requirements without causing any adverse effects on the human body. The paper presents the applied research developed by ICEM – SA for the manufacturing and validation of bars (3 – 5 mm) and wires (< 1,0 – 2,5 mm) from austenitic stainless steel for the production of accessories for osteosynthesis medical kits and of temporary orthopaedic implants.

Keywords: orthopaedic implant, austenitic steel, biocompatibility

2. Extended Abstract

Biomedical materials are a section of materials science what deals with the design, synthesis and use of materials for surgical implants in the human body in order to re-establish the function and/or the structure of damaged human structures. The large range of applications of metallic materials may be due to the multiple combinations of chemical, physical and mechanical properties making them compatible with the biological environment.

2.1. Technological route:

The elaboration in ICEM SA of austenitic stainless steel for osteosynthesis requires:

- a severe control of raw materials;
- elaboration and casting in vacuum induction furnace;
- electric slag remelting;
- cold drawing in bars with diameter Ø 12 - 45 mm for grade 8MoNiCr170M;
- cold drawing in bars with diameter Ø 3 - 5 mm for grade 3MoNiCr170M, with intermediary austenitisation treatments severely controlled;
- cold drawing in wire with diameter Ø 0,5 – 2,5 mm for grade 3MoNiCr170M;
- final checking in accordance to the company standard of ICEM SA.

The creep strength of austenitic stainless steels is generally low. The method to increase the creep strength – nitrogen alloying – leading to material hardening.
It was elaborated a new generation of austenitic stainless steel, nitrogen alloyed.

2.2. THE qualitative results:

- fine granulation (> 4.0);
- low content of non-metallic and precipitate inclusions (for example complex chromium and molybdenum carbides);
- absence of delta ferrite;
- absence of alloying elements segregation;
- surface quality of semi-finished products with influence on the mechanical characteristics and on the corrosion resistance;
- high tensile strength (> 800 N/mm^2).

Products achieved in ICEM SA was clinically verified and tested and homologated:

Grade 3MoNiCr170M- products for orthopaedic implant:
- bars Ø 3 mm and Ø 5 mm;
- wire Ø 2.5 mm, Ø 2.0 mm, Ø 1.5 mm, Ø 1.0 mm and below Ø 1.0 mm.

Grade 8MoNiCr170M- products for accessories medical emergency cases used in surgery of orthopaedic implant:
- bars Ø 12 mm and Ø 45 mm;

In accordance with the Directive 94/27/EEC of the New Approaches, the research in ICEM SA will be continued to respect the next requirements:
- Restriction of nickel metallic product use on and inside the human body;
- Design, research and manufacturing of products made of austenitic stainless steels without nickel, nitrogen alloyed.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Anticipation of scale up issues in pharmaceutical development

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1. Summary

This paper presents a methodology to evaluate the robustness of pharmaceutical batch processes on scaling up. The Scale Up Risk Evaluation (SURE) is applied on new processes that are mid way through their development. During a SURE study one first collates current process understanding and then extrapolates this understanding to evaluate scenarios at plant scale. The output of the SURE study is a ranked list of scenarios that development teams use to prioritise further development.

Keywords: Batch Process, Process Development, Scale up, Risk Assessment, Robustness & Reliability.

2. Extended Abstract

The pharmaceutical industry is currently expanding the role of process engineers from their traditional roles in chemical manufacturing and capital projects. Significant process engineering populations can now be found in process development, which has typically been the domain of the process chemist. Some drivers for this trend are the regulatory push for increased process understanding, and the frequency at which scale up issues occur in processes moving to commercial scale (Sherlock & Brewis 2006). This paper is focused on identifying scale up issues in batch processes early in development.

Hulshof (2000) demonstrates that scale up problems lead mainly to loss of yield, productivity or quality. An additional issue in the pharmaceutical industry is the high cost of any delay in the drug reaching the market. Hulshof identified the main cause of scale up problems to be related to mass transfer and mixing, followed by longer processing times and heat transfer.

The basis of a batch process is the process recipe. A typically recipe is often 30 to 50 operations to convert raw materials and intermediates in to the next intermediate or final product. The paper reviews the nature of the operations, and concludes that most batch processes have a multiphase aspect. One can infer that the chance of encountering a scale up issue in batch process development is thus high.

In this paper we present a Scale Up Risk Evaluation (SURE) tool that is developed to anticipate scale up issues early on in the development of a new compound. The principal of SURE is based on that of a hazard and operability study (HazOp) for each operation in a process recipe various scale up/down scenarios are identified. A scenario represents an unplanned change in conditions from those specified in the recipe. The potential impact of a scenario on the process is qualitatively assessed and identified as a "threat" or an "opportunity". The scale up scenario is then scored on:

(i) The likelihood process conditions change with scale
(ii) The likelihood the operation affects the product quality or process operability.

A number of examples from SURE studies will illustrate the use of the tool.

The output of a SURE study is risk matrix, and a prioritised list of the threats and opportunities that provide development drivers for the development team. We conclude with an analysis of the data generated by SURE studies in AstraZeneca that demonstrates how risk changes as processes move through the stages of development.

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Session S-8G: Chemical Product Design & Engineering - V (CPD&E - 5)

Abstract Number	**Paper Title & Authors**	**Included**
532	Scale-up of the top-spray fluidised bed coating process in terms of thermodynamics and spray conditions P D Hede, P Bach, A D Jensen	Yes
1180	High-pressure spray microcapsules for the control of biofouling zebra mussels R Costa, R Schatz, E Schlücker, D Aldridge, G D Moggridge	Yes
1846	Concept Design of a chewing gum that does not foul the streets N Nikolic, S V Pelt, H Webers, G J Harmsen	Yes
2677	Chemical modifications on Curaua Fibres (*Ananas erectifolius*) A A L F S d´Almeida, B V M A Calado, C J R M d´Almeida, D D W Barreto	No
2824	Fluidized bed spray granulation – From process understanding to modelling of nucleation and dust integration G Grünewald, A Dinkova, M Kind	Yes

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Scale-up of the top-spray fluidised bed coating process in terms of thermodynamics and spray conditions

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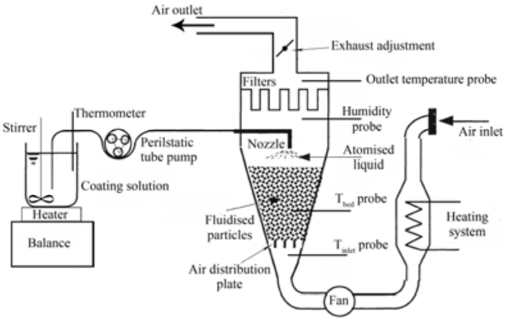
1. Summary

Scale-up of top-spray fluid bed coating processes was studied in terms of two parameters named the relative droplet size and the drying force. Successful scale-up in terms of agglomeration tendency and match of particle size fractions was observed for conditions where the drying force and the relative droplet size were kept constant across scale.



Keywords: Fluid bed, coating, granulation, scale-up

2. Extended Abstract

In the production of solid enzyme products, coating of the enzyme formulation onto inactive filler cores in fluid beds is a common choice. The desired product is thereby a product consisting of unagglomerated individual carrier particles coated homogeneously with a layer of enzyme. If formulation or process conditions are incorrectly chosen either excessive agglomeration or excessive loss of feed due to premature spray drying will happen. In both cases a poor product quality is achieved and in any case control of agglomeration is essential during scale-up. Often product and process properties are optimised in small- and medium-scale fluid beds and then transferred to large production-scale. The scale-up of a fluid bed granulation process requires decisions to be made at many levels. Scaling decisions must be closely related to a large number of parameters including: fixed parameters, parameters related to the starting material and the type of fluid bed, input parameters, operating conditions including spraying and mixing conditions as well as processing time etc.

With such a variety of interlinked parameters and properties combined with a general lack of fundamental understanding of the granulation process, it is obvious that the scaling of a fluid bed granulation process is a difficult task.

A number of different scaling laws and principles have been suggested on either the unit-operation (macro) scale or on the particle-level (micro-) scale. Recent investigations by Rambali et al (2003) on fluid bed granulation processes indicate successful scale-up of agglomeration processes from small-scale fluid bed to medium-scale fluid bed in terms of the relative droplet size being the spray rate in g/min divided by the squared air flow through the nozzle in g/min. Further studies indicate that the relative humidity as well as the temperature inside the fluid bed vessel during coating are vital properties with respect to agglomeration. Both properties may be combined into a single drying force parameter suggested to be kept constant during scale-up.

This paper presents fluid bed coating scale-up results in terms of the drying force parameter and a relative droplet parameter defining the agglomeration tendency as the response parameter. Two types of placebo enzyme granule cores were chosen being non-porous glass ballotini cores (250 - 350 μm) and porous sodium sulphate cores (250 - 350 μm). Both types of core materials are coated with aqueous solutions of Na_2SO_4 using Dextrin as binder. Coating experiments have been performed for various drying force and relative droplet size values in three top-spray fluid bed scales being a small-scale (GEA Aeromatic-Fielder Strea-1), medium-scale (Niro MP-1) and large-scale (GEA MP-2/3) each time quantitatively determining the tendency of agglomeration in terms of particle size distributions. Results indicate that the particle size distribution may be reproduced across scale with good precision fixing values of the drying force as well as the relative droplet size across scale, but that none of the two parameters alone may be used for successful scaling. Morphology and microscope studies indicate that the coating layer is homogenous and have similar structures when applying combined constant drying force and relative droplet size. These scale-up results combining thermodynamics with spray conditions may be seen as an important first step towards the development of modern scaling principles combining particle-level properties with fluid bed process conditions.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

High-pressure spray microcapsules for the control of biofouling zebra mussels

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1. Summary

This work addresses the development of a new control strategy for controlling the biofouling zebra mussel, a major aquatic pest. Such a strategy is based on the encapsulation of biocides, exploiting the great filtration capabilities of the species. PGSS (Particles from Gas-Saturated Solutions) is a high pressure atomization process for fine powders with a narrow particle size distribution and defined morphology. It is a promising method for the encapsulation of chemicals leading to an increased retardant power. In this work, a new formulation of toxin-loaded microcapsules for zebra mussel control was designed, and the potentialities of PGSS in processing such a formulation were evaluated.

Keywords: encapsulation, particles from gas-saturated solutions, supercritical spray process, zebra mussel control, biofouling

2. Extended Abstract

The zebra mussel, *Dreissena polymorpha*, is an invasive species whose biofouling activity has major impacts on fresh water-dependent industries.

A new control strategy for this pest based on the encapsulation of biocides has been recently proposed (Aldridge *et al.*, 2006). This approach, which exploits the great filtration capabilities of the species, may provide significant economic and environmental benefits over traditional physical and chemical control methods. Previous studies highlighted the potentialities of this strategy, showing that the entrapment of potassium chloride within a matrix of vegetable oil and vegetable wax enhances the toxicity of the salt. However, an economically viable formulation for the toxin-loaded microcapsules has not yet been found. Guaranteeing that the microcapsules have adequate size distribution and retardant power are the major challenges in developing such a method.

PGSS (Particles from Gas-Saturated Solutions) is an established high-pressure process using supercritical carbon dioxide and dissolving it in a melt of the later particle material. By atomization of this saturated melt, a fine powder with a narrow particle size distribution and a defined morphology is produced. A promising method for the encapsulation of chemical agents is adding non-melting particles to the melted material, which solidifies during the spray process covering the active material. Using this method, the noted deficiencies in the entrapment of biocides for zebra mussel control may be reduced, and the retardant power of the particles may therefore be increased.

In this work, a new formulation of toxin-loaded microcapsules for zebra mussel control was designed, and the potentialities of PGSS in processing such a formulation were evaluated.
Varied spray parameters have been compared to show their effects on particle formation. Microcapsules produced by the PGSS process were then characterised in terms of their microstructure, size distribution and release characteristics and tested for their toxicity through laboratory renewal bioassays.

Preliminary results show that the formulation designed may constitute a competitive strategy for zebra mussel control. Furthermore, there are considerable opportunities to diversify the technology developed both in the control of other invasive species and in aquaculture applications (e.g. delivery of nutrients and antibiotics).

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Concept design of chewing gum that does not foul streets

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1. Summary

A group of students under the presenter's supervision undertook a 3 months long project to design a chewing gum that does not foul streets and is also for appearance, taste, health and price reasons attractive to consumers.
The final product designed consists of the following elements:
a) The gum consisting of polyvinyl alcohol/polyvinyl acetate block co-polymer that slowly hydrolyses in the mouth after 15 minutes, into water solubles. The resulting monomers can be swallowed. If the chewing is still dropped onto the pavement it can be quickly removed by warm water of 37 C. If it is left untouched it will hydrolyse in a matter of days to weeks, depending on rainfall. The resulting water-soluble monomers will biodegrade in the sewage system. b) Taste ingredients Xylitol and sorbitol that due to the endothermic hydration reaction with water, a cool feel. c) Taste ingredient inside microglobuls with slow release.
d) Colouring ingredient and e) Antioxidants. The final product is as a classic package of 12 tablets that can be sold profitably for the price of 50 Eurocents to retailers.
The product designers followed a method developed by Korevaar and contained the following major phases: problem definition phase, materials phase, integrated product concept phase and detailed design phase. The latter includes target specifications, marketing analysis, technical feasibility, Safety, health, environment, and economic feasibility. For each phase the Korevaar method provides guidelines.

Keywords: non-fouling, chewing gum, product, design, concept

2. Extended Abstract

About 50 % of all spend chewing gum ends up on public pavements. Present chewing gum, based on polypropylene, a very stable material, stays there for 25 years, unless it is removed by cleaning. Cleaning of this sticky insoluble material is a costly affair and therefore it is desirable to find a different gum, which does not foul streets.
A group of students under my supervision undertook a 3 months long project to design a chewing gum that does not foul streets and is also for appearance, taste, health and price reasons attractive to consumers.
The final product designed consists of the following elements:

a) The gum. This is a polyvinyl alcohol/polyvinyl acetate block co-polymer with specified degree of polymerisation and no syndiotacticity, with glycerine as plasticizer to obtain the rubbery state and calcium carbonate filler for hardness. The polymer of choice is such that it slowly hydrolyses in the mouth after 15 minutes, into water solubles, causing no turbidity. The resulting monomers can be swallowed. If the chewing is still dropped onto the pavement it can be quickly removed by warm water of 37 C. If it is left untouched it will hydrolyse in a matter of days to weeks, depending on rainfall. The resulting water-soluble monomers will biodegrade in the sewage system.
b) Taste ingredients at the outside. Xylitol and sorbitol are placed at the outside of the gum as a powder to give instant taste and due to the endothermic hydration reaction with water, a cool feel.
c) Taste ingredient inside the gum. Microglobuls made by emulsifier Lecithin contain a mixture of flavours: xylitol (syrup), sorbitol (syrup) and L-menthol. Xanthan gum is added for a slow release of the taste components.
c) Colouring ingredient. Titanium- di-oxide is added for a white appearance
d) Antioxidants: Butylated hydroxyanisole and butylated hydroxytoluene are added to obtain a shelf life of 12 months.
The production of the product has also been designed and evaluated. It appears that the whole production can be done with conventional chewing gum equipment. An overall assessment of Safety, Health, Life Cycle Environmental, Economics and Market acceptance has been made. The assessment showed that the new product scores positive on all aspects, except for health. It appeared that FDA approval for the polyvinyl alcohol for this use is not available yet, so has to be pursued. Polyvinyl alcohols are already used in medical applications so a positive outcome is expected. The final packaged product is as a classic package of 12 tablets that can be sold profitably for the price of 50 Eurocents to retailers.
The product design followed the method developed Korevaar (2004). It contains the following major phases: problem definition phase, materials phase, integrated product concept phase and detailed design phase. The latter includes target specifications, marketing analysis, technical feasibility, safety, health, environment, and economic feasibility. For each phase the Korevaar method provides a few guidelines.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Fluidized bed spray granulation – from process understanding to modeling of nucleation and dust integration

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1. Summary

Fluidized bed spray granulation is an advanced technology to produce coarse-grained particles from suspensions, solutions or melts, ready for sale without any need for post-treatment. The process combines spray drying with granulation and classification, therefore allowing adjusting the product particle size distribution according to customer demands. Well-known applications include pharmaceutical products as well as mass products like detergents or fertilizer. Because of the process intensification combining several normally consecutive unit operations in one apparatus, it is imaginable, that design and specification of process parameters is mainly decided on the basis of intuition or experience, if available. There are models available in literature, helping when designing the process but neglecting kinetics like nucleation and dust integration so far unknown. Both are important for a continuously running process deciding on whether it is possible to achieve steady state or not. In this work these mechanisms have been examined experimentally with the help of tracer methods and analysis of continuous experiments (cf. *Grünewald et al. (2006)*. The kinetics has been modeled by combining strongly simplified fluid dynamics with mass and heat transfer. The kinetics along with a population balance approach allows the dynamic modeling of the process including transient effects.

Keywords: fluidized bed spray granulation, nucleation, growth rate, tracer, dust integration

2. Extended Abstract

Being able to run computer experiments prior to expensive laboratory validation when debugging running processes or establishing new products, it is necessary to be aware of the kinetics of the individual mechanisms occurring. Considering granulation, four mechanisms are important, namely spray drop deposition on particles, dust formation, dust integration into wet particles and nucleation. *Zank et al. (2001)* examined drop deposition and modelled the kinetics. In this work dust integration and nucleation were investigated experimentally. In order to deduce the kinetics of dust integration, semi-batch experiments were carried out where tracer-marked dust was supplied at the beginning. Thus, by analyzing the particles with respect to tracer content after the experiment, the amount of dust incorporated into growing particles could be calculated (fig. 1, left). The deduced model for the kinetics is able to reflect the influence of different dust concentrations in the spray on the particle growth rate (fig. 1, right). The kinetics of nucleation was investigated by steady-state experiments obtaining the nucleation rate directly as the difference of the number streams of particles entering and leaving the apparatus.

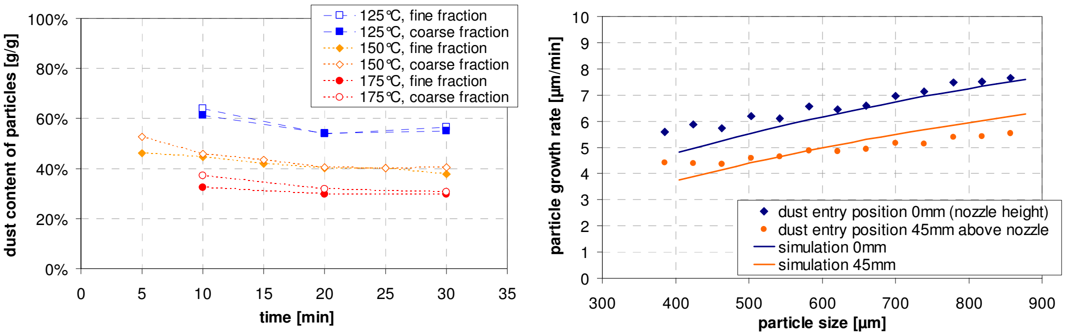

Figure 1: Contribution of dust integration to total particle growth rate for fine and coarse particles at different temperatures (left), individual particle growth rate depending on dust concentration in the spray (right)

In order to verify the simplified fluid dynamics used for the kinetics, CFD calculations with PIV/LDA validations were done (fig. 2, left). Linking the kinetics with the population balance approach, a full process model was developed to describe transient effects up to steady-state production (fig. 2, right).

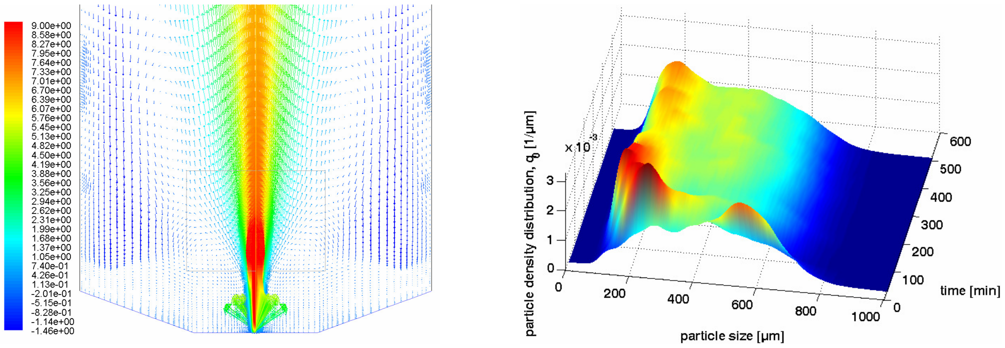

Figure 2: Particle vector field (CFD calculations, gray rectangle shows measurement area for PIV and LDA, left); oscillations of the particle distribution over time up to steady-state due to the internal nucleation rate (right)

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Copenhagen, 16-20 September 2007

Improving wood color by vacuum-drying

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1. Summary

The forest industry operates in a dynamic, global market where change and competition are the rule rather than the exception. The colour of wood is one of the most attractive features in modern woodworking industry. The formation of colored substances from phenolic compounds oxidized with air and the formation of dark materials from hydrolysis have been considered the causes of discolouration during drying (Schniewind, 1989). In order to reduce hydrolysis and oxidation reactions, vacuum drying process can be used, which offers reduced drying times and higher end-product quality in comparison with conventional drying.

In this work, antioxidant capacities were evaluated in dust of oak-wood after vacuum drying by using ABTS+• cation method. Vacuum drying kinetics with conductive heating, FTIR spectras are obtained, and discoloration mechanisms are disputed in the scope extractives degradation. Our results suggest that in vacuum conditions, peaks at 1505, 1595 and 1741cm-1 increased when degradation of antioxidant capacity decreased, these results are explained by degradation of phenolic compounds and probably hemicelluloses degradation (carbohydrates), since by one hand C=O compounds results from oxidation of phenolic substances, and by other hand lignin spectrum peak at 1505 and 1595cm-1 is more intense when carbohydrate degradation exist. We found that temperature gradients have an important influence in C=O formation.

Keywords: Vacuum-Drying, Color, Oxidation, Oakwood, FTIR analysis.

2. Extended Abstract

Clearly, hardwood has become increasingly important during the past decade in meeting the markets demand for solid wood and wood fibre-based products. While scanning, colour technologies and computer simulation are in place in a number of operations to help with much of this, areas still needing attention are efficiency in throughput and manufacturing flexibility (Hansen et al. 2001). The desire to create different or new appearances in furniture style led to the use of different manufacturing methods and materials. Examples of methods and materials include the invention of veneering and inlay, frame and panel construction, bending techniques, and the use of plywood and composite materials. The appearance is often of primary importance when choosing furniture woods for items where the wood surface is readily visible (Thompson et al. 2004). Hardwoods operations mainly focus on reducing product degrade, while softwood operations are more interested in achieving high productions levels (Alexiadis et al. 2006).

Vacuum-Drying (VD) technology reduces the boiling temperature point of water and oxygen concentration, moreover enables an important overpressure inside the material which is advantageous for drying and especially for species that do not support a high temperature level, where discoloration can arise. Also vacuum drying offers the possibilities of preventing atmospheric emissions, since during wood drying a complex mixture of chemical compounds is released.

In this work the $ABTS^{+\bullet}$ scavenging test was used to determine the antioxidant activity of wood flour, Fourier Transform Infra Red (FTIR) spectroscopy has been found effective to analyse the chemical structure of wood. FTIR spectra of the ground wood samples (100 µm-sieved) as shows Figure 1. In vacuum drying the conductive heat source is maintained at different temperatures (46, 61, 70 and 80°C) and pressure in the chamber is controlled at different intervals (60-100, 150-250, and 250-300 mbar).

Vacuum Drying shows a considerable shorter drying times (Figure 2). Our findings suggest that antioxidant extractives are thermally degraded and formed C=O entities, since antioxidant potency of wood decreases as carbonyl stretching peak intensity increases. Effect of pressure could indicate that oxygen disponibility is important to control wood discolouration. Important application of wood colour could be oriented to assessing Wood Color for high quality markets, wood coatings, glued formulation, biological decay resistance and weathering.

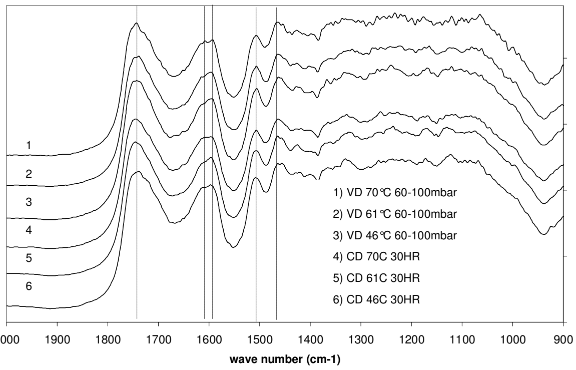

Figure 2. Fourier Transform Infrared Spectras.

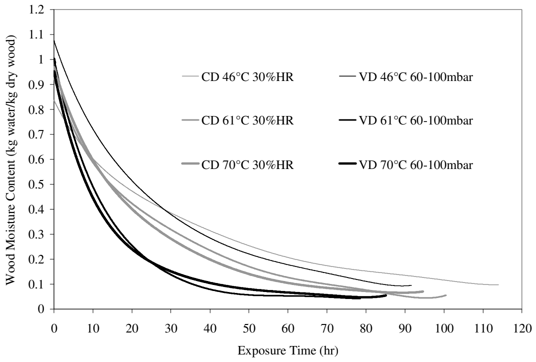

Figure 1. Drying Kinetics.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

The use of an experimental design method to evaluate the influence of process parameters in the graft polymerization of acrylic acid onto cassava starch

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1. Summary

Grafting of acrylic acid onto starch offers the prospect of replacing many current applications of polyacrylic acid by more biodegradable products based on renewable raw materials. Even though a large number of research reports has appeared in literature, there is not a comprehensive understanding of the grafting reaction yet. This is a first condition to consider any scaling up to commercial production in the future. One of the reasons is that there is a large number of variables and interactions between them. Therefore it is difficult to arrange this into a systematic and integrated analysis. The use of experimental design would support such an analysis by reducing the number of experiments.

Keywords: acrylic acid, cassava starch, experimental design, Fe^{2+}/H_2O_2, grafting

2. Extended Abstract

This research focused on the grafting polymerization of the acrylic acid onto cassava starch using FAS (ferro ammonium sulphate)/H_2O_2 initiator. Sodium hydroxide was used as the gelatinization aid. The use of an Experimental Design method is not very common in this field but has been found useful in evaluating which of these variables have the largest influence on the grafting results, with a limited number of experiments. Also, within the selected ranges, optimal values could be elucidated for these variables. Design Expert software version 6.0.6 was used as a tool in solving this experimental design. In line with the objective of the experiment, the suitable Design of Experiment (DOE) was the 2-level fractional factorial from 8 factors consisted of 32 graft experiment runs. These were carried out in a laboratory scale stirred batch reactor.

From a comprehensive literature study the most important variables were selected. These variables are: the degree of starch gelatinization, the starch concentration, the starch to acrylic acid ratio, the concentration of Fe^{2+}, the Fe^{2+} to H_2O_2 ratio, the grafting temperature, the grafting time, and the speed of stirring. The following parameters are used to measure the efficiency of the grafting polymerization: % add on, % grafting efficiency (%GE), % graft ratio and % monomer conversion.

Name	Units	Low	High
A: Degree of gelatinization	-	-	+NaOH
B: [Starch]	%w	4.90	9.86
C: St : AA	mol AGU/mol	0.5	2
D: [Fe^{2+}]	mol/kg	0.0032	0.011
E: [Fe^{2+}: H_2O_2]	mol/mol	0.11	1.1
F: Temp.	^{0}C	40	80
G: Time	min.	30	180
H: Stirring Speed	rpm	200	400

Table 1: Factors selected for the experiments

The analysis of the reaction products was done using a.o. HPLC and NMR techniques. Statistical analysis with the DOE program results in probability plots. Then from analysis of the variance (ANOVA) it was screened which of the reaction variables have most influence. These are reaction temperature and the starch to monomer ratio. These are shown in the figure below:

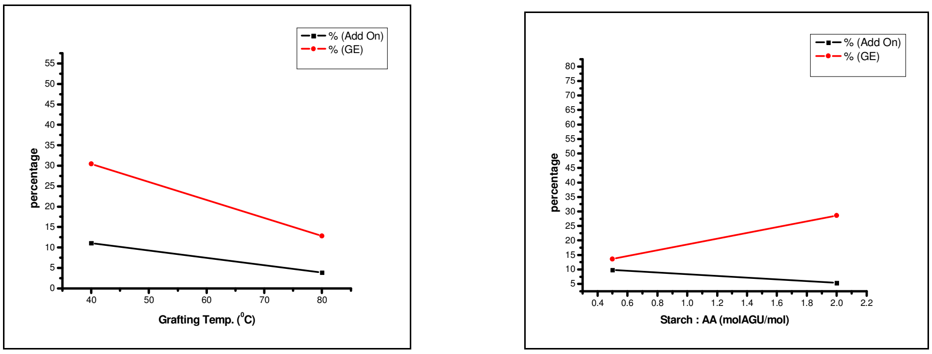

Fig.1. The effect of two selected reaction variables.

For the temperature, the lower value of 40^{0}C was found optimal. The influence of the starch to monomer ratio is more complex. A high monomer-to-starch ratio favoured add-on but decreased graft selectivity, i.e. much homopolymer was then formed. This result of our study is in line with literature information. The actual optimum for add-on and/or graft selectivity will depend on the specific application of the grafted starch.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Mechanochemical activation of mixtures for low-melting glasses production

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1. Summary

During the mechanochemical activation various structural changes of material and at the same time changes of its properties as well as reactivity increase are taking place. Whereas numerous chemical reactions are happening during the glass production, investigating of the influence of previous mechanochemical treatment on those reactions and on the glass production at once is very attractive. Because of the great interest for low-melting glasses, PbO-B_2O_3-SiO_2 system was chosen for this research. The referent glass mixture and mechanochemically activated glass mixtures were subjected to differential thermal analysis (DTA). Differential thermal analysis showed the existence of qualitative changes in thermal properties of prepared glass mixtures depending on the time period.

Keywords: mechanochemical activation, low-melting glass, DTA

2. Extended Abstract

Raw materials used in the experiments were minium (Pb_3O_4), boric acid (H_3BO_3) and quartz sand (SiO_2). Five glass mixtures with the following chemical composition: 40 mol% of PbO, 34 mol% of B_2O_3 and 26 mol% of SiO_2 were prepared. The referent glass mixture was not mechanochemically activated. Other four glass mixtures were activated in high-energy vibro mill with rings. Four time periods of activation were selected: 7min, 14min, 28min and 49min. Glass mixtures were subjected to DTA. Differential thermal curves of those mixtures are presented in the Figure 1.
The effects of mechanochemical activation on mixtures behaviours during heating were analysed through total accumulated energy of activated mixtures in relation to referent mixture (Figure 2). The content of energy accumulated in mixture was obtained by calculation of differential thermal curve area. Differential thermal curve area i.e. accumulated energy of referent mixture was defined as unit and accumulated energies of other mixtures were compared with it (legend in Figure 2).

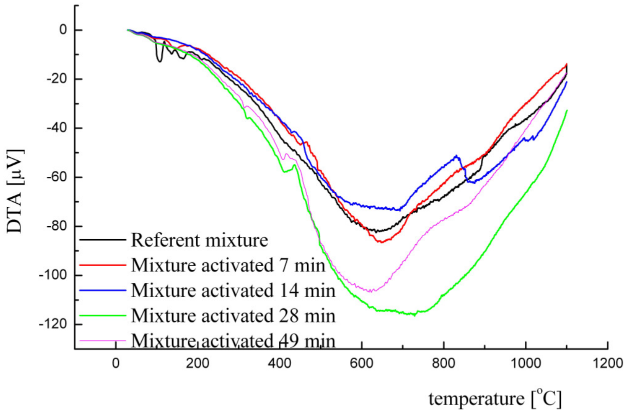
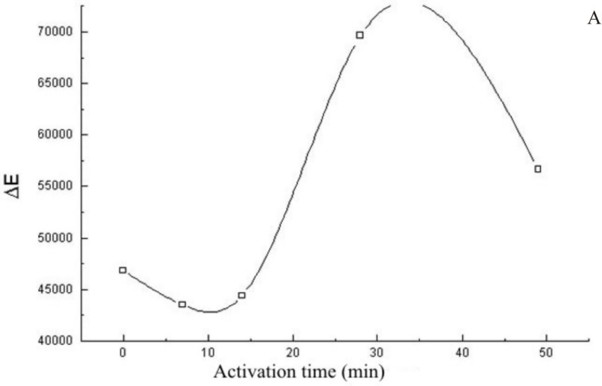


Figure 1: Differential thermal curves of referent and activated mixtures



Activation time (min)	Energy
0	1
7	0.93
14	0.95
28	1.49
49	1.21

Figure 2: Thermal transformation energy change depending on activation time

According to this analysis, comparing to the referent mixture, it is obvious that mixtures activated for 7 and 14 min accumulate cca 8% and 5% less energy respectively, mixtures activated for 14 and 28 min, cca 50% and 20% more energy, respectively. It can be considered that mixtures activated for 7 and 14 min act like the referent mixture (differential thermal curves comparable!) and thereby activation of 14 min doesn’t induce remarkable changes in the system. During the activation from 14 to 28 min the most significant changes are happening. Activation after 28 min, doesn’t produce any noticeable quality, so the mixture modifies and returns to the initial state. It can be concluded that mechanochemical activation provides better utilization of thermal energy necessary for glass forming, whereby a small amount of this energy is spent on melt formation. So the main effect of activation is reducing of energy necessary for melt formation, i.e. for viscosity change of the system.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Absorption of menthol from yogurt drink into PET bottle: Determination of diffusion coefficient of menthol

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1. Summary

The interaction of menthol with polyethylene terephthalate bottles during storage time at three different temperatures was investigated. Menthol is a mint flavor agent commonly added into Iranian yogurt because of its pleasure taste in combination with yogurt drink. In order to study the effects of environmental conditions on flavor stability, the yogurt drink samples were stored at 4°C, 25°C and 45°C for three month. After different time periods, absorbed flavor was extracted from PET bottles and quantified using gas chromatography. Subsequently by possessing the concentration of absorbed menthol, the coefficient of diffusion (D) of menthol into PET bottles was determined. It was concluded that the amount of menthol absorbed into PET bottle are increased based on storage time and temperature increase. Diffusion coefficient of menthol did not change with respect to time, but increased at higher storage temperatures and followed Arrhenius relation.

Keywords: menthol, absorption, yogurt drink, polyethylene terephthalate, diffusion coefficient

1. Introduction

The absorption of flavor compounds by polymeric materials refers to the loss of flavors and aroma components from food into plastics. Menthol is an aroma compound and because of its pleasing flavor adds into Iranian yogurt drinks. It is of major importance to study the migration level of aromas into a specific plastic polymer like PET because the absorption of favorite flavors has a bad effect on the quality of yogurt drink during time and the final product couldn't be as palatable as the first one. To understand the mechanism of flavors absorption into packaging material and predict the shelf-life of food products, determination of diffusion coefficient is valuable.

2. Experimental

2.1. Materials

Menthol purchased from Fluka company with the purity of >%95 (GC).

2.2. Sample preparation

To study the mechanism of menthol absorption into PET bottles about 100 ppm menthol was added to the yogurt drink samples.

2.3. Menthol Determination

Extraction of menthol from PET bottles performed using Dispersive liquid-liquid microextraction (DLLME) method and the quantification of menthol in the extract solution performed using gas chromatography coupled with Flame Ionization detector [1].

2.4. Measurement of diffusion coefficient

The diffusion process of menthol from the yogurt drink to the packaging material obeys Fick's second law of diffusion. To simplify the model, the edge effect between the yogurt drink and PET bottle was ignored, and the diffusion process was considered to be one-dimensional only. Finally the measurement of diffusion coefficient performed using a mathematical model [2].

3. Results and Discussion

Table 1 shows the amount of menthol absorbed from yogurt drink into PET bottles at different time and temperature conditions. In general, the absorption level of menthol ranged from 13.52 to 700.50 ng per gram of PET bottles.

Table 1. Absorption of menthol from yogurt drink into PET bottles at different temperatures as a function of time.

Time (day)	Amount of absorption (ng/g)		
	4°C	25°C	45°C
0	0	0	0
0.67	n.a.	27.65	n.a.
0.75	n.a.	28.60	n.a.
1	13.52	37.05	207.15
2	21.15	52.65	264.50
5	29.15	68.60	343.50
9	32.95	82.10	447.10
14	35.70	110.00	517.20
21	37.95	136.20	568.90
50	38.20	173.23	664.75
90	38.21	186.66	700.50

n.a. = Not analyzed

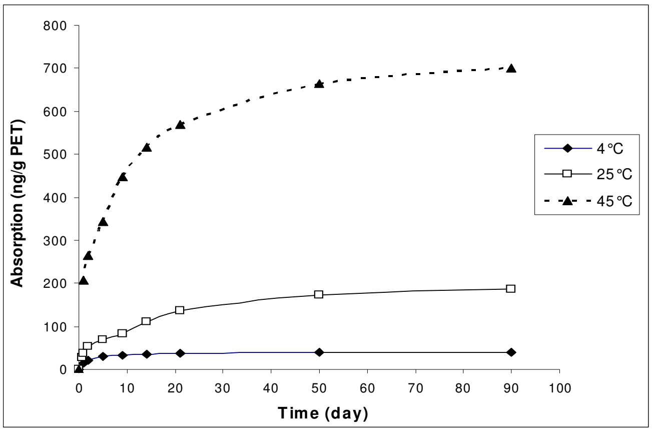

Fig. 1. Absorption of menthol from yogurt drink into PET

Absorption of flavor compounds into packaging materials may result in products with an imbalance of flavor and aroma. Tawfik, M. et al. (1997) showed that absorption of D-limonene into PET bottles increased consistently when storage temperature of model solutions elevated from 4°C to 25°C and 37°C [3]. At the present study the results showed that the absorption of Menthol is a function of storage temperature.

On the other hand increasing storage time resulted in higher absorption of menthol into PET bottles (Figure 1). Determination of diffusion coefficient of menthol into PET bottles showed that there is not any significant difference between the diffusion coefficients of menthol into the PET bottle at a constant temperature. As shown in Figure 2, the diffusion coefficient of menthol into PET bottles is significantly affected when the storage time increased. At the equilibrium point, the diffusion coefficient of menthol into PET bottles stored at 45°C is about five times more than the samples stored at 25°C and 12 times more than the samples stored at 4°C. It is concluded that the diffusion process of menthol is absolutely temperature dependent and follows Arrhenius relation. Showed that

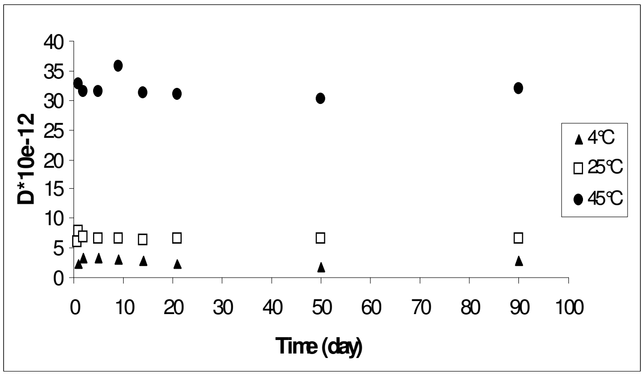

Fig. 2. Diffusion coefficient of menthol as affected by time and temperature

4. Conclusions

The absorption level of menthol is clearly dependent on the storage time and temperature. Thus to maintain the acceptable taste of products like yogurt drink which are packed in plastics packaging, it is necessary to establish proper time and temperature conditions. Diffusion coefficient of menthol (D) did not change during the time. Comparison of D of PET bottles stored at different storage temperature showed that the diffusion process was temperature dependent and followed the Arrhenius relation and diffusion coefficients increased with increase of storage temperatures.

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Effect of environmental conditions on the migration of DEHA, DEHP and ethylene glycol from PET bottles into yogurt drink

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1. Summary

The migration of Di(2-ethylhexyl) adipate (DEHA), Di(2-ethylhexyl) Phthalate (DEHP) and Ethylene Glycol from PET bottles into the Iranian yogurt drink was investigated. Effect of storage time, temperature and the contact solution on the migration of these contaminants was evaluated. The acetic acid samples were stored at 4°C, 25°C and 45°C for four months and analyzed periodically by gas chromatography. Differential Scanning Calorimetry (DSC) was used to investigate if contact with the food stimulant could affect the PET material. It was concluded that the storage time and temperature had a considerable effect on the migration of DEHP, DEHA and Ethylene glycol. Determination of Glass Transition (Tg) and crystallinity percent of PET bottles using DSC method showed that the variations in the concentration of migrating substances did not concern to the change of PET material in contact with acetic acid.
Keywords: migration, DEHA, DEHP, Ethylene glycol, Polyethylene terephthalate.

2. Introduction

DEHA and DEHP are used as plasticizers in some plastic products like PVC and PET, and ethylene glycol is one of the main components of polyethylene terephthalate. Since these compounds are soluble in most organic solvents like organic acids so it seemed that they are quite susceptible to migrate into yogurt drink. The traditional Iranian Yoghurt drink has the pH about 3.5-4, so according to European Commission regulations we used 3% acetic acid solution as stimulant (EEC 1985) [1]. In this study the migration of model contaminants into yogurt drink quantified by GC and the effect of stimulant on PET material investigated by DSC.

3. Experimental

3.1. Materials

DEHP and DEHA purchased from Riedel-deHean Company and Ethylene glycol from Fluka Co.

3.2. Migration from PET bottles into stimulant

Acetic acid 3% was used as the food stimulant. The extraction of migrants from acetic acid performed using dichlorometane solution.

2 µl of concentrated extract was injected into a gas chromatograph equipped with a flame ionization detector. The instrument used was Chrompack cp9000 and the column used was a cp-sil 8 column (30m × 0.52mm i.d.). The flow rates of helium, hydrogen, and air were 4, 30, and 300 ml/min, respectively. The temperatures of the injection port and detector were kept at 250 and 280°C. Oven program, 50°C for 3min, rising at 15°C/min to 260°C, then held isothermal until the final chromatogram obtained.

3.3. DSC Analysis

The samples analysed with differential scanning calorimetry (DSC-2010 model, USA). Each sample was heated from 25 to 280ºC with a heating rate of 10 $^{\circ}\mathrm{C\,min}^{-1}$. Te measured heats of fusion were compared with published values [2] in order to estimate the degree of crystallinity.

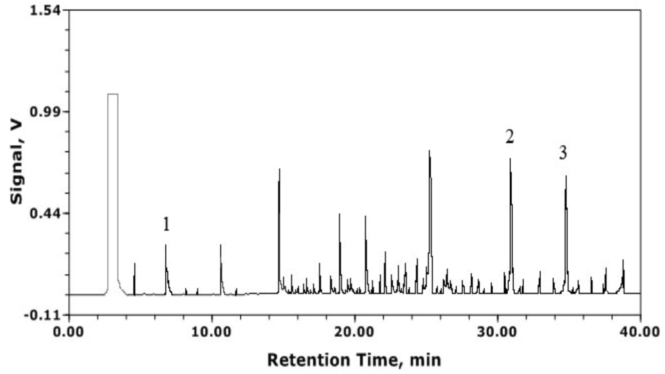

Fig. 1. Chromatogram of extraction solution of PET bottle wall. 1) Ethylene Glycol, 2) DEHP and 3) DEHA

4. Results and Discusion

Initial concentrations of Ethylene Glycol, DEHP and DEHA in PET bottle wall were 21, 670 and 510 ppm, respectively. The chromatogram of extraction solution has shown in Figure 1.

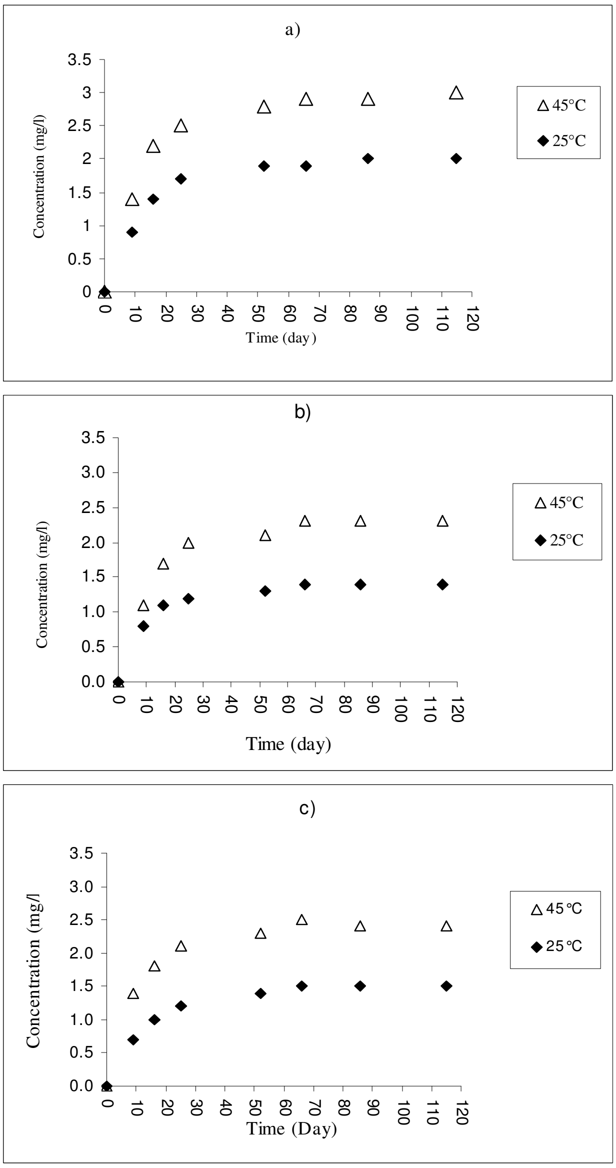

Fig. 2. Migration of EG(a), DEHA (b) and DEHP (c) from PET bottles into stimulant during 100 days storage at 25 and 45°C.

The results showed that no detectable migration occurred for the samples stored at refrigerator condition (4°C). Under experimental conditions with increasing time and temperature migration of selected compounds into food stimulant has increased (figure 2). The maximum limit of migration was seen after 65 days at 45ºC, with the concentrations of 2.9, 2.3 and 2.4 mgl^{-1}, respectively for EG, DEHP and DEHA. The solubility of migrants in acetic acid was an inevitable factor affecting on the migration.

From DSC results, which have shown in table 1, concluded that the degree of crystallinity and Tg for the PET samples containing 3% acetic acid and stored at constant temperatures (25 or 45ºC) did not changed significantly so higher amount of migration into acetic acid at higher temperature does not related to structure changes of PET bottles in contact with solution. Higher glass transition of the PET bottles stored at 45°C, attributed to the enthalpy relaxation process of amorphous regions of semicrystalline PET [3].

Table 1: ΔH melt and crystallinity percent of the samples stored at 25 and 45ºC

Storage time (Day)	Tg (ºC)		ΔH melt (J/g)		Crystallinity %	
	25ºC	45ºC	25ºC	45ºC	25ºC	45ºC
0	73.26	73.26	38.27	38.27	28.18	28.18
9	70.82	79.51	38.98	43.45	28.70	32.00
14	70.60	84.46	42.86	41.5	31.56	30.56
26	73.67	83.03	38.92	37.57	30.13	27.67
34	71.83	83.51	42.82	40.93	31.53	30.14
76	72.44	83.72	41.86	40.82	30.82	30.06
120	72.27	85.92	41.95	40.88	30.89	30.10

5. Conclusions

Storage time and temperature had considerable effects on the migration. Higher amounts of migration at 45ºC could be explained by an increase in the diffusion coefficient of migrants. The concentrations of migrating substances did not exceed of their specific migration limit (EEC regulations). DSC analysis showed that the interaction between polymer material and acetic acid did not affect the structure of PET and higher amount of migration at higher temperature considered to higher solubility of contaminants and higher diffusion rate.

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European Congress of Chemical Engineering (ECCE-6)
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Mass transfer of the bioactive substance in the solid-liquid extraction

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Abstract

The bioactive substance mass transfer from the medical herbs in the solid-liquid system was investigated. The experiments were carried out with *Oenothere biennis L.* and *Betula pendula Roth* L. in laboratory and pilot-plant conditions at the atmospheric pressure. The bioactive substance from *Oenothere biennis L.* on γ- linoleic acid was standardized, and from the *Betula pendula Roth L.* on hyperazide was standardized. The specific mass transfer rate and mass transfer coefficients were determined.

Keywords: Medical herb, Bioactive substance, extraction, mass transfer, free and inner diffusion

Introduction

Mass transfer coefficients determination in the solid-liquid extraction of nettle *Urtica dioica L.* and hawthorn *Crataegus oxycanta L.* were investigated in a paper [1]. In this paper biomass transfer in the extraction of *Oenothere biennis L. and Betula pendula Roth* L.. was investigated.

Mass transfer phenomena in herb extraction

$$K=\frac{1}{(1/k)+(l/D_{in})+(\delta/D_l)} \qquad (1)$$

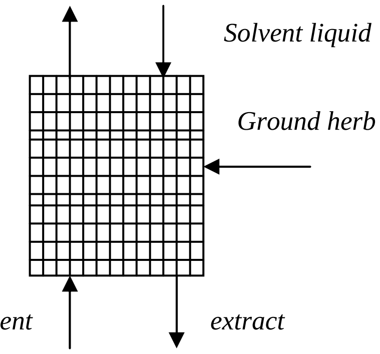

Fig.1 Streams flow in a herb packed bed

Mass transfer of the bioactive substance between the solid and liquid phase occurs in a drug packed bed shown in Fig.1. In the liquid extraction period, called fast extraction, the cell content of ground herb is rinsed out. In the slow extraction period diffusion of the bioactive substance occurs. The overall mass transfer coefficient is defined by eq.(1) which involving convection (k), inner diffusion D_{in} and bounded layer (D_l)diffusion.

Experiments

Experimental investigations were performed laboratory and pilot- plant scale Soxhlet columns. The solid liquid extraction experiments were carried out by ethanol-water solution for *Betula pendula Roth* L. and petroleum ether for *Oenothere biennis L.* at atmospheric pressure.

Results

The obtained experimental results of the extracted substances are given in Table 1. Quality of bioactive substances were determined by spectrometric methods. The mass transfer coefficient for *Oenothere biennis L.* was obtained $K=2.089\ 10^{-9} m/s$, and for *Betula pendula Roth* L., K = $5.5\ 10^{-9} m/s$.

Table 1. Results of extraction in laboratory conditions

Charge	Mass,g, for *Betula pendula Roth* L.	%hyperazide	Fatty oil density,g/cm^3 at the 20˚C	% γ-linoleic acid	% linolic acid
1	200	4.34	0.9248	6,21	71,68
2	100	5.49	0.9089	6,23	71,13
3	100	6.84	0.9212	6,35	71,12
4	100	6.06	0.9071	6,32	71,72

Conclusion

The obtained results show that the yields of bioactive substance for both examined herbs are higher in the laboratory than in the pilot- plant Soxhlet columns. The results of the obtained biomass transfer coefficients show that the inner diffusion coefficients are the lowest.

Reference

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Valorisation of lignocellulosic waste materials: Tannins as a source of new products

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1. Summary

Tannins extracted from lignocellulosic industrial wastes, eucalyptus bark and chestnut shell, under different conditions (type and concentration of alkaline chemicals in aqueous solution and temperature), were analysed in order to establish their properties for different potential applications including: their use as phenol substitutes in the formulation of adhesives for wood derivatives and as chrome substitutes in leather tanning, and as a source of alternative antioxidants. Extraction yield was significantly greater for chestnut shell than for eucalyptus bark and the corresponding extracts showed much better properties for the uses proposed. For both materials the highest extraction yield was obtained using 10% NaOH and the lowest using water, however, water extracts showed the best properties. Extraction at 90ºC with a 2.5% Na_2SO_3 aqueous solution has been selected as the optimum as extraction yield increased significantly with respect to the extraction with water and the characteristics of the extracts remained almost constant.

Keywords: eucalyptus bark, chestnut shell, biomass conversion, tannins, adhesives

2. Extended Abstract

The increase in environmental awareness and in petroleum cost has raised the interest in the exploitation of renewable resources, such as lignocellulosic materials, for the development of new products and processes with a lower environmental impact. Moreover, the valorisation of wastes from industrial productions constitutes a new challenge of economically sustainable and environmentally friendly processes.

Eucalyptus globulus wood, one of the main forest species in Galicia (NW of Spain), is mainly used to produce cellulose pulp and wood panels. In both cases, bark is separated as a waste and used as fuel. On the other hand, chestnut (*Castanea sativa)* consumption in the food industry involves about 10000 t/year to produce derivatives such as marron-glacé, chestnut purée, etc. In the peeling stage chestnut shell is separated and also used as fuel.

In this work, tannins extracted from both industrial lignocellulosic wastes under different conditions, were analysed in order to establish their properties for different potential applications including: their use as phenol substitutes in the formulation of adhesives for wood derivatives and as chrome substitutes in leather tanning, and as a source of alternative antioxidants.

Chemical composition of both lignocellulosic materials was determined. Chestnut shell contains more extracts and lignin but less carbohydrates and ash than eucalyptus bark. The influence of extraction conditions (type and concentration of alkaline chemicals in aqueous solution and temperature) on extraction yield and Stiasny number, tannin content (hide-power test), total phenols content, FRAP (Ferric reducing/antioxidant power) antioxidant capacity and molecular weight distribution of the extracts was analysed. FTIR spectra of crude materials and the extracts obtained were compared.

Extraction yield was significantly greater for chestnut shell than for eucalyptus bark. For both materials the highest extraction yield was obtained using 10% NaOH and the lowest using water (49.4 and 8.7% for chestnut shell and 18.9 and 6.8% for eucalyptus bark). However, water extracts showed the best properties. The Stiasny number, the total phenols content**,** the tannin content and the antioxidant capacity decreased when the alkalinity of the solution was increased. With respect to the influence of temperature, an increase from 70 to 90ºC implied, for all the alkaline compounds used, not only an increase in the extraction yield but also an improvement in the extract properties. For both materials linear relationships with high correlation coefficients were found among Stiasny number, tannin content, total phenols content and antioxidant capacity of the corresponding extracts.

Molecular weight distribution was in most cases bimodal for chestnut shell extracts whereas eucalyptus bark extracts showed multimodal distributions. Molecular weights of chestnut shell extracts were significantly higher than those of eucalyptus bark extracts. Both number and weight average molecular weights of the extracts diminished when increasing the severity of the alkaline extraction for chestnut extracts but increased for eucalyptus extracts.

For both materials, extraction at 90ºC with a 2.5% Na_2SO_3 aqueous solution has been selected as extraction yield increased significantly with respect to the extraction with water and the characteristics of the extracts remained almost constant. On the other hand, it can be concluded than chestnut shell tannin extracts, due to their significantly higher polyphenols contents, offer much better properties than eucalyptus bark extracts for all the applications proposed.

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New developments in solid-state modification of polypropylene

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1. Summary

In this work we present a new method for the modification of isotactic polypropylene to yield the same polymer having long-chain branches. In particular, the use of organic peroxides (free radical initiators) as well as co-agents (multifunctional monomers) in the solid-state (i.e. below the melting point of the polymer) is investigated. As compared to the currently used technologies (irradiation and extrusion), modification in the solid-state displays two clear advantages: minor influence of degradation reactions and a relatively low working temperature. To the best of our knowledge this is the first report regarding the use of solid-state modification to yield long-chain branched polypropylene.

Keywords: polypropylene, long-chain branches, solid-state modification, rheology

2. Extended Abstract

The modification of isotactic polypropylene (iPP) in the solid state has been widely investigated in the past 10 years in order to modify the chemical structure of the PP backbone, while at the same time the degradation reaction via β-elimination should be avoided[1-3]. In particular an industrial process (Hivalloy), in which iPP is grafted with several vinyl monomers by means of a radical mechanism, has been developed by Basell. The final product is characterized by a very fine morphology in which the in-situ polymerized component is dispersed in the form of small droplets (inclusions of the order of 100 nm) in a PP matrix. On the other hand, long-chain branched iPP (LCB-iPP) constitutes a very important basic material for many applications and processes (among others blow molding and extrusion coating). Current technologies for production of LCB-iPP include the use of irradiation and melt modification techniques. Aim of this work is to investigate the possibility to combine the advantages of solid-state modification with the production of LCB-iPP.

In this work we present first the scientific basics of solid state modification of polypropylene via radical mechanism. In particular attention is paid to the use of radical reactions in the solid state and to the grafting reactions onto iPP. We then discuss the latest developments of iPP modification in the solid phase. In particular focus will be directed to the formation of long chain branches (LCB) via solid-state modification. From a product technology point of view, the presence of LCB is an essential prerequisite for applications of iPP in the production of foams or films. Indeed LCB-iPP, contrary to normal iPP, shows pronounced strain-hardening behavior in extension, i.e. a significant increase of viscosity with the strain. A radical initiator (peroxide) and several (multifunctional) co-agents have been used in this work to obtain the desired macromolecular structure. The rheological behavior together with the determination of the molecular weight by gel permeation chromatography (GPC) clearly indicate the formation of LCB-iPP. To the best of our knowledge this constitutes the first example of a solid-state process (not including the use of irradiation techniques) to obtain a LCB-iPP. This new process will be briefly compared to the established ones in order to underline its advantages and disadvantages as compared to the current technology. Due to the very large choice of possible co-agents, very simple criteria for the choice of the co-agent will be further discussed.

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Modelling of active ingredient release from an emulsion and its dependence upon formulation

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1. Summary

The rate at which an ingredient is released from a product formulation is a relevant issue in different applications, namely pharmaceutical, agrochemical, food and personal care products. The design of such products to attain a desired release profile of the active ingredient (AI) may be supported by physico-chemical models having two components: (i) a mass transfer model describing AI transport in the product and into the surrounding environment; (ii) constitutive models relating physico-chemical properties (e.g. AI equilibrium and transport parameters) with product composition. This paper presents such a model for the case of AI release from an emulsion formulation, with AI equilibrium and transport parameters being estimated as a function of emulsion composition. The model is applied to a pharmaceutical ointment and used to study the effect of formulation over the drug release process.

Keywords: Active ingredient release, Partition/diffusion models, Emulsions.

2. Extended Abstract

Since the pioneering work of Higuchi[1], who proposed the first mechanistic model of drug release from a solid matrix, a great number of related and further detailed models have been developed[2, 3], but in general they do not incorporate constitutive relationships. Recently, Muro-Suñé *et al.*[4] overcame this limitation for the case of pesticide release from polymeric microcapsules, combining the basic mass transfer model with constitutive predictions for pesticide solubility and diffusivity in the polymeric matrix. In this paper, we pursue the same goal for the case of active ingredient (AI) release from an emulsion formulation, with the effect of emulsion composition being incorporated in the modelled phenomena.

The system under analysis is an emulsion layer applied over a flat surface that absorbs the AI. The emulsion consists of an internal phase homogeneously dispersed as droplets in an external continuous phase, with the droplets being surrounded by a stabilizing layer of surfactant. The AI release is described as the result of two main phenomena: interfacial transfer (from each droplet to the continuous phase) and diffusion in the continuous phase, with interfacial transfer comprising permeation through the surfactant layer followed by dissolution in the continuous phase.

The resulting mathematical model is a system of two partial differential equations with the constitutive parameters being P_s (surfactant layer permeability), K_{cd} (partition coefficient between continuous and dispersed phases) and D_c (diffusion coefficient in the continuous phase), and with geometrical parameters L (emulsion layer thickness), ϕ (dispersed phase volume fraction) and L_d (droplet mean diameter).

The generic release model is applied to a pharmaceutical ointment for cutaneous use, which consists of an emulsion of a solution S (drug + solvent) dispersed in a highly viscous lipid phase L, comprising four excipients (surfactant included). For this particular application, the constitutive parameters are estimated as follows: (i) K_{cd} is calculated based on regular solution theory with activity coefficients estimated making only use of pure components solubility parameters; (ii) D_c is predicted based on free-volume theory as applied to the mixture of excipients comprising the continuous phase and with parameters estimated from pure excipients data (density and viscosity); (iii) P_s is estimated from a very simplified free interfacial area model requiring information on the surfactant surface density.

The overall model (release model altogether with constitutive models) is then used to study the effect of emulsion formulation over the drug release process, for two different situations: release to a perfect sink (a theoretical scenario that may also resemble the conditions of release tests obtained with a permeable membrane) and transfer into skin. In the latter case, the mass transfer model is expanded to include the several skin layers, with the drug partition coefficient between the continuous phase and the outermost skin layer (K_{2c}) being estimated as a function of emulsion composition.

The results obtained so far indicate that the formulation has an important impact over the dynamics of AI release, affecting all the four constitutive parameters (K_{cd}, K_{2c}, D_c and P_s). The effect of the formulation is weakened when the emulsion is applied on skin, given that drug diffusivity through skin is very low and considered independent of emulsion composition, but still persists, namely due to the more hydrophilic excipient that influences the partition coefficient, K_{2c}. In this respect, a more controlled drug release is predicted for more hydrophilic formulations (lower K_{2c}).

As a conclusion, we believe that the developed models can be extremely useful to support the design of emulsion products that must release a certain AI. The general framework supporting such models (mass transfer + prediction of equilibrium and transport parameters) can also be applied to other product structures, under the general scope of a multiphasic system with multiple dispersed and continuous phases.

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Copenhagen, 16-20 September 2007

The Corrosion Process of Brass and its Inhibition in Acidic Solutions

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Abstract

The corrosion behaviour of brass was studied in acid sulphate solution at pH-value 2 with additional chloride ions and five organic inhibitors namely: thiourea (TU), benzotriazole (BTA), ethylene diamine tetraacetic acid (EDTA), hydrazine sulphate (HS) and 2-butin-1,4 diole (DS-3) using potentiodynamic polarization techniques. Increase of a concentration of the Cl^- ions, exept for value of $5 \cdot 10^{-2}$moldm^{-3}, resulted in a significant increase of value for corrosion current densities. Polarization measurements showed that the organic compounds investigated are mixed type inhibitors, inhibiting the corrosion of brass by blocking the active sites of the metal surface.

Many authors [1-10] from this field have tested different methods and concluded that zinc dissolves mostly in the initial period of dezincation. Individual attack appears in a shortly-defined time period and penetrates through several monolayers at the surface of brass. Further separation of zinc within the same process is unlikely, since the process requires extra energy in order for atoms of zinc to difund through the solid phase and reach brass surface. As the result, copper also starts to turn into solution after some time, together with zinc, with comparably less speed, including the change of potential. Redeposition of copper immediately follows the dissolution of remaining zinc in the solution. In the light of this investigation and interpretation, the phenomenon of dezincation is initiated by selective dissolution of zinc and intensified by simultaneous dissolution of copper and zinc, followed by redeposition of copper. Simultaneous dissolution and redeposition of copper are mutually independent processes, but both processes cause the change of experimental conditions.

Brass is widely used in various industrial operations and the study of corrosion of brass and inhibition is subject of practical significance. BTA, thiourea, hydrazine-sulphate, DS-3 and EDTA, have been used as effective acid corrosion inhibitors [9-16].

Nagiub [13], Jinturkar [15] and Sayed [17], studying the effect of **BTA** on alpha-brass exposed to a nitrate solution concluded that the presence of BTA inhibited the dissolution of brass due to the formation of a copper oxide layer on the brass surface.

According to some research on protective effect of BTA inhibitor [18,19], it was established that copper oxide (Cu_2O) was the basis for forming Cu(I)-BTA film. The presence of oxide Cu_2O facilitates the initial chemisorption of BTA inhibitor. According to other authors [20,21,22], film Cu(I)-BTA is formed on an ‘empty surface’ of copper or brass. While analysing the film formed on brass surface, the same authors found that the formed film on brass surface was in the form of Cu(I)BTA complex, which was oxidised to Cu(II)BTA. Two inhibiting mechanisms of BTA inhibitor can be found in literature [23-28]: adsorption of BTA inhibitor on copper surface and forming of polymer film that includes complex ions Cu(I) and $(Cu^+BTA^-)_n$.

As good inhibitor of non-ferrous metals and copper corrosion in acids (HCl, H_2SO_4, HNO_3) thiourea is used with inhibition degree from 65% to 98%, depending on inhibitor concentration [16,29]. Investigation interest was focused on establishing the influence of the above mentioned corrosion inhibitors on corrosion behaviour of cold-deformed brass samples in acid solution of sodium sulphate with addition of Cu^{2+} and chloride ions.

Inhibitor **EDTA** (Ethylene Diamine Tetra-Acetate) has one of its uses in chemical cleaning of generators from copper residue in nuclear plants [30-32]. Considering that critical potential for dissolving copper in ammoniac solutions is in the area of -0.3÷0.2V, the role of EDTA inhibitor is to maintain the potential within the indicated area, so that copper residue would be removed from the generator of a nuclear plant, with the use of ammonia and hydrogen peroxide.

Inhibitors **hydrazine-sulphate** and **DS-3** are the inhibitors of steel corrosion in solutions of sulphuric and hydrochloric acid, and the inhibitor of copper and copper alloys in nitric acid and alkaline solutions [16].

The results of studies show that only thiourea, in concentration of 10^{-2}%, inhibit the corrosion of brass in chloride solutions. Inhibitor benzotriazole in concentration of 10^{-1}% inhibit the corrosion of brass with inhibition efficiency more then 94%. The film improved significantly the protecting ability of brass surface to corrosion in chloride solutions. When the films were modified with benzotriazole the quality and corrosion protection of films improved rapidly.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Innovative technology of atmospheric fluidized bed freeze drying for production of pharmaceutical powders with predefined structure

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1. Summary

Spouted bed freeze drying is innovation technology, which gives a number of advantages in comparison with traditional vacuum freeze drying. The mathematical model of spouted bed freeze drying is proposed. The mathematical model consists of two parts, which describe kinetics and hydrodynamics of atmospheric freeze drying. The results of mathematical model solution are presented.

Keywords: innovation, freeze drying, active hydrodynamics, nano- and micropowders, modeling

2. Extended Abstract

A new method of drying process to produce dispersed pharmaceutical powders with nano- and microstructure was suggested: atmospheric fluidized bed freeze drying. The suggested method is innovative it and has the number of advantages: due to active hydrodynamics the intensive heat and mass exchange, and, respectively, the high rate of moisture removal; short-time process; no need to use vacuum; low energy consumption; possibility to organize the continuous regime; effective on-line control of the material temperature and moisture content, preservation of biological activity; possibility to produce particles with regular shape and defined size with porous nano- and microstructure. These advantages provide fast and total final product dehydration, allows to use as an inhalation preparation.

During working the complex of experimental and analytical researches has been realized, that allowed us to define the influence of this drying method on particle shape and structure and quality of product. Basing on the theory of mechanics of heterogeneous media and nonequilibrium thermodynamics, the mathematical model has been developed, which allowed to calculate parameters of atmospheric fluidized-bed freeze drying for fine-dispersed powders.

The drying parameters on dryer height were defined for different types of materials and the stable work conditions were evaluated. The Fig. 1 shows the diagram of gas and cellulose particles velocities. The particle diameter is 1000 µm; the velocity of inlet dryer air is 2 m/s.

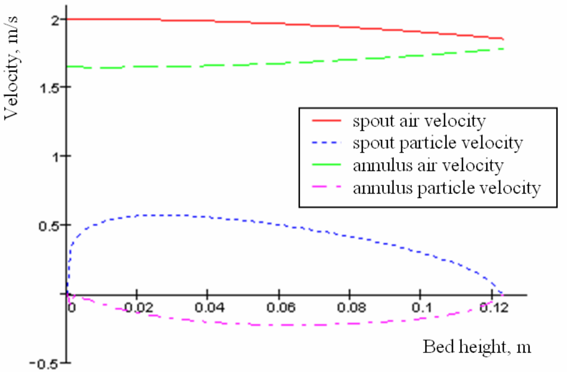
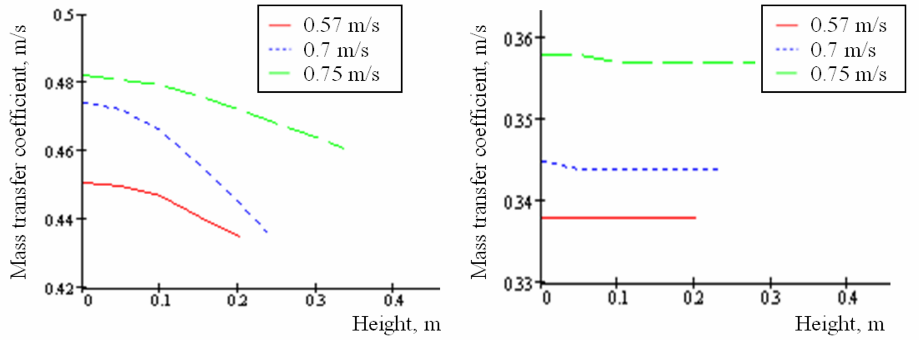


Figure 1. Distribution of gas and particle (cellulose, d_p=1000 µm) velocities at apparatus in spout and annulus zones

The Fig. 2 shows the diagrams of mass transfer coefficients calculated at different velocities of inlet air for mannitol particle (d_p=150 µm; ρ_p=959 kg/m3) versus bed height for spout and annulus zones.



a) **b)**

Figure 2. Diagrams of mass transfer coefficients versus bed height for spout (a) and annulus (b) zones

As a lot of moisture is intensively removed during the process, the particles mass strongly decreased that resulted in their release out of the bed, their adhesion on filters and, as a result, ineffective drying process. Thus, the problem of drying agent rate control for stable hydrodynamics during whole process was solved.

The recommendations for new design of drying chamber and technological scheme have been done and economically proved.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Accelerated testing; faster development of protective coatings.

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1. Summary

Ever since the development of high-performance, long-lasting coatings began, it has been a major goal to be able to test coatings in the laboratory under accelerated conditions and translate the measurements into meaningful information on real time coating lifetimes. Electrochemical methods may provide important knowledge but has not yet been standardized and rely on accelerated weathering methods. Consequently the development of accurate and fast accelerated weathering methods is a perquisite for the faster development of protective coatings.

Keywords: protective coatings, accelerated testing, corrosion, coating degradation

2. Extended Abstract

Protective coatings will according to their area of application be exposed to the combined action of sea spray, rain, snow, freezing, sun rays, salt and pollutants. Modern high performance coating systems are so durable that they upon exposure to natural weathering may show little signs of deterioration. If an anticorrosive coating is intact during service life it may, for the best present products, maintain a high performance for maybe 15-20 years. VOC legislation has resulted in increased focus on environmental friendly coatings systems, thus coating manufacturers can no longer rely on the extensive track record of their time served product ranges to convince customers of their suitability for usage. This has resulted in more emphasis being placed on accelerated laboratory testing to evaluate coating performance. Many of these accelerated exposure tests will not, within their exposure time show the negative effects visually on intact coated surfaces. Therefore behaviour of the coatings around artificially made damages are given significant considerations, and many prequalification tests are based amongst others on underfilm corrosion and blistering as well as detachment from scores, NORSOK M-501, ISO 20340, etc. The accelerated weathering methods seek to intensify the effects from the environment so that the coating breakdown occurs more rapidly. However, despite the nature of these accelerated weathering methods underfilm corrosion on the best performing systems is typically a few mm or even less after 25 weeks of exposure. Consequently the value of underfilm corrosion is close to the magnitude of the experimental uncertainty. The need of faster development of high performance protective coating systems therefore calls for even stronger exposure tests, which correlates with natural exposure tests. The key to develop such a tool is fundamental understanding of corrosion and the chemistry behind the mechanisms responsible for coating breakdown.

Electrochemical methods relaying on impedance measurements have become a widespread tool for characterization of protective coating (Bierwagen et al., 2003). However electrochemical methods must also rely on direct exposure of the coating to accelerated weathering methods in order to obtain a signal, therefore fast and accurate accelerated tests are needed. The dependency of the delamination rate on the hydrated size of the cations in the electrolyte solution (Deflorian and Rossi, 2006) suggests that the effects of an electrolyte solution may be intensified by modification of the electrolyte, which is applied in saltspray chambers. Similarly the importance of thermal chock and modification of the electrolyte solution has been investigated. Skerry and co-workers (1991) provided evidence that true emulation of the effects of exterior exposure on corrosion protective coatings systems requires inclusion of UV effects. Thus exposure to UV-radiation is included in most accelerated test of the durability of protective coatings. The purpose of this paper is to describe the development of an accelerated cyclic weathering method. Results from cyclic corrosion tests (NORSOK M501, Rev.5) on Zinc epoxy primed systems will be used as reference to the new tool.

In spite of accelerated test standards, it is still not possible to perform tests of new anticorrosive products in a reliable fashion, mainly because several important degradation reactions take place simultaneously and they may be accelerated to various extends when one stress factor (e.g. temperature) is altered compared to "real life". Furthermore, a sequence of weather conditions over a given period of time never repeats itself meaning that a coating will be exposed to alternating dry and wet, and dark and sunny cycles during service life. A mathematical model of the fundamental coating failure mechanisms as encouraged by a large number of articles on coating research and development (Wicks et al., 1999; Pilcher, 2001) may be the solution for the coating industry if the mechanisms can be quantified.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Correlation between contents of the friction and lubrication compounds and structures of the friction materials

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1. Summary

The researches in the field of friction materials were oriented to the realization of some materials that must have the high friction coefficient stable at different temperatures, reduced wear, respectively high lastingness, high conductivity ,etc. In order to obtained these results it is very important to have a homogeneous structure of friction materials .That is why for the achieving of homogeneous structures are very important the following factors : * nature of matrix; *nature of friction and lubrication compounds ; * the sintering parameters of friction materials. The paper presents some results obtained after laboratory experiments for to produce some friction materials for the agriculture equipments.

Keywords: structure, friction coefficient, lubrication elements, friction elements, sintering parameters.

2. Extended Abstract

In order to obtained good results it is very important to have a homogeneous structure of friction materials. The homogenization of the mixture powder is the operation which ensure homogeneous distribution of metallic and non-metallic particles in to finished parts. It was used a Fe-based at matrix alloyed with friction elements(copper, nickel,tin,SiO_2)and lubrication elements(graphite,lead,$BaSO_4$,MoS_2) in variable rate.

2.1 Experiments .

The elementary powder were characterization from viewpoint of physical characteristics. For homogenization was used a planetary mill with ball. After homogenization ,the mixture obtained ,was characterization from viewpoint of chemical composition and values of the apparent density. It was achieved the compressibility curve of the mixture .Then ,the mixture of powders was submitted cold pressing operation. For pressing it was used a hydraulic press .The most important technological process to obtain friction materials is sintering under pressure operation. The sintering was made in a sintering furnace under pressure , at to different temperatures , 960 ^{0}C,duration 1 h and respectively 1060 ^{0} C ,for ½ h .To specific pressure for sintering was for both temperatures 25kgf/cm^2. The protective environment was dry hydrogen.

2.2 Results .

The samples of friction materials which was obtained were characterized from viewpoint values of friction coefficient , intensity of wear , density and hardness, table 1 .We can see that the sample which contents nickel present the better friction coefficient ,the lower intensity of wear and high values of density and hardness .
In figure 1 are presents fracture aspect of samples of friction materials from we can see that the all samples presents a ductile fracture .

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Sample Nr./ elements	Friction coefficient (average)	Intensity of wear [cm^3/daN] (average)	Density [g/cm^3]	Hardness [kgf/mm^2]
1/Fe,Cu,$BaSO_4$,SiO_2,C	0,30	0,19x10^{-6}	5,09	37,1
2/Fe,Cu,Sn,C,$BaSO_4$,MoS_2	0,34	0,17x10^{-6}	5,47	42,4
3/Fe, Ni,C,SiO_2,Pb,MoS_2	0,37	0,13x10^{-6}	6,69	56,6

Table 1: Properties of friction materials .

a) b) c)

Figure 1 – Fracture aspects of samples of friction materials : a)-sample 1; b)-sample 2; c)-sample 3

X 600

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

About the structure and properties of heavy alloys for special use

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1. Summary

Elaboration of complex multifunctional materials with nanometric structure and controlled characteristics for special applications, implies the use of advanced techniques of powder metallurgy such as mechanical alloying, allowing the structural modeling and designing of material properties. The aims of paper consist in the development of complex multifunction materials with nanometric structure for special use (civil and/or military) for industrial applications. The paper presents briefly some aspect regarding the present stage in production of homogenous mixtures of W-Ni-Cu powders system for manufacturing the materials made of heavy alloys type.

Keywords: multifunctional materials, nanometric structure, heavy alloys.

2. Extended Abstract

2.1. Introduction
Hard alloys based on tungsten have an unique configuration of remarkable properties consisting of: high density, superior mechanical resistance, high ductility, good corrosion resistance, high capacity of radiation absorption, good processing properties, remarkable toughness. Mechanical alloying is a versatile method for producing advanced materials by solid state powder processing and has already received numerous industrial applications. At a qualitative level, the phenomena occurring during mechanical alloying have been understood and consist, essentially in a continuous process of deformation, fracturing, local heating, solid state welding and re-fracturing of powder particles under the effect of the transferred energy from the milling balls.

2.1. Experimental conditions
As raw materials is has been used pure W, Ni, and Cu powders with the following weight ratio: W:Ni:Cu = 95:3.5:1.5. A mixture of tungsten, nickel and copper powders were ground in an attrition, without protective atmosphere or lubricant.

For milling it has been used an attrition with the following parameters: milling speed :100 rot/min; milling time:195 hours; ball/powder weight ratio:3:1;filling grade:25 %;

Material	Flowing rate [$^{s}/_{50g}$]	Apparent density [g/cm^3]	Particle size FSSS[μm] 4
W	not flowing	3.40 ± 0.01	1.62 ± 0.01
Ni	not flowing	2.46 ± 0,01	4.86 ± 0.01
Cu	not flowing	1.34 ± 0,01	5.81 ± 0.01

Table 1: Raw powders characteristics for the starting materials

The mechanically alloyed powder was taken out of the container periodically to follow the progress of alloying every 20 hours. After 30 hours milling we have observed the sticking of the powder to steel balls and tank of attrition. After a longer time the powder started to agglomerate. The effect of mechanical alloying on the powder mixture characteristics are presented in table 2.

Powder type	Flowing rate [$^{s}/_{50g}$]	Apparent density [g/cm^3]	Particle size FSSS[μm] 4
WNiCu	not flowing	4.88 ± 0.01	0.20 ± 0.01

Table 2: The characteristics of processed powders

The data in Table 2 show that increasing the milling time has resulted in an increased apparent density and a decreased particle size. Increasing of the apparent density could be explained by particle shape changes during milling. Further investigation was carried on the sintered product. In table 3 are indicated the physical and mechanical characteristics of the sintered markers obtained from mechanically alloyed powder mixtures.

Material type	Density [g/cm^3]	Brinell Hardness HB	Stretch resistance [N/mm^2]
Sintered markers 1250^{0}C	16.99	220	790

Table 3: Physical and mechanical characteristics of sintered markers

The SEM micrographs in Figure 1 emphasize the uniform repartition of the two phases present in the material: the Ni-Cu metallic binder phase and the tungsten (W) phase from the mechanically alloyed $W_{95}Ni_{3.5}Cu_{1.5}$ powder mixture.

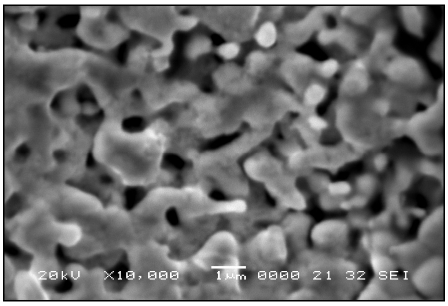

Figure 1: Microstructure of the mechanically alloyed $W_{95}Ni_{3.5}Cu_{1.5}$

Murakami etchant X10000;

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Synthesis of super fine aragonite-type calcium carbonate by reciprocation in ultrasonic field

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1. Summary

Aragonite, the high pressure polymorph of calcium carbonate, was synthesized by liquid-liquid reaction, at low temperature, in ultrasonic field in the presence of organic additives. In the presence of alcohols, rod-like crystals with nanometer size diameters were formed. The material is quite pure and the particle size distribution is uniform.

Keywords: calcium carbonate, aragonite, ultrasonic field, additives, alcohols

2. Extended Abstract

Introduction.The synthesis of calcium carbonate with submicron dimensions and specific morphology by a simple route, at low temperatures, is interesting due to the possible applications of this material in new fields like biotechnology. Properties like purity, morphology, dimensions and particle size distribution, porosity, aggregation degree must be carefully controlled.

The aim of this work was to develop an aragonite type calcium carbonate with uniform particle size distribution and submicron dimensions by precipitation in liquid-liquid reaction using as starting reagents 0.1M solutions of calcium nitrate and potassium or sodium carbonate.

There are three stable polymorphs of calcium carbonate: rhombohedral calcite, needle or rod like aragonite and spherical vaterite.

The synthesis of calcium carbonate by precipitation in liquid-liquid reaction depends on many parameters as supersaturation, pH, temperature, reaction time, agitation speed, feeding order of the reacting solutions, the nature and the presence/absence of the additives [1]. Usually a mixture of the three polymorphs is formed.

Experimental. The synthesis was carried out in a batch reactor placed in an ultrasonic field of 45 kHz. The optimum acoustic amplitude was established at 50% of the full amplitude of the ultrasonic device.

The influence of several additives as Tween 20, AOT as growth inhibitors and alcohols as precipitation agents was investigated.

Other parameters, like pH, temperature, reaction time and feeding order were also varied.

All solid samples were examined by FT-IR spectroscopy, optical and electron microscopy and grain size distribution.

Results and discussion. In ultrasonic field aragonite developed in the absence of any additive at pH > 9. At pH=7 calcite was formed. The particles mean diameter was in the range of several microns. The particle size distribution shows the presence of two particles populations, one with submicron dimensions and one in the micron range. The material was impurified with vaterite and calcite.

In the presence of Tween 20 or AOT as growth inhibitors the formation of aragonite is also dependent of pH which must be adjusted at 9-10. The material is a mixture of calcium carbonate polymorphs but aragonite is predominant. The mean particle size is still in the range of microns as recorded by laser granulometer but many nanometer size particles of aragonite are present among large crystals of calcite as determined by electron diffraction microscopy and transmission electron microscopy.

Replacing the surfactants with an alcohol as precipitation agent, in ultrasonic field, aragonite develops at 50°C and pH = 7. We studied the influence of methanol, ethanol and 2-propanol. We varied the feeding order of the reactants and we started with Na_2CO_3 or K_2CO_3. In all cases, independent of the nature of the alcohol, rod like crystals of aragonite are formed (figure 1c). Laser granulometer measurements shows that the particles mean size is 1.0 -1.3 µm (figure 1b) but TEM microscopy images shows that the rods diameter is smaller than 100 nm (figure 1c), their lengths getting to 2-3µm. The material is quite pure as results from the FT-IR spectra (figure 1a).

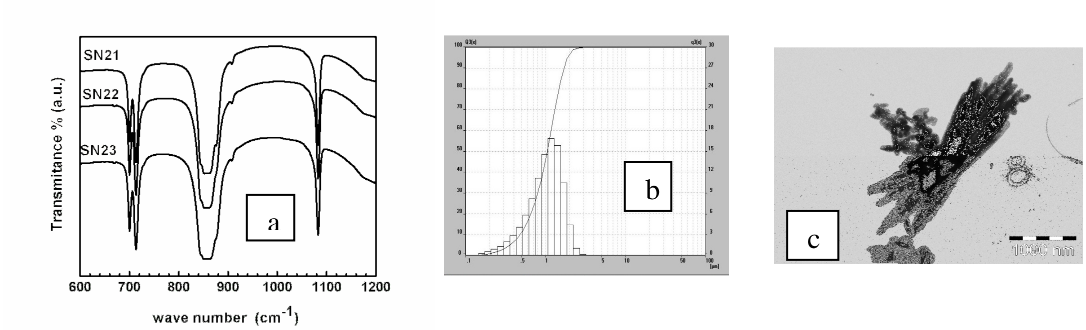

Figure1a. FT-IR spectra for aragonite precipitated in ethanol (SN 21), 2- propanol (SN 22) and methanol (SN23). Figure 1b. Particle size distribution characteristic for aragonite precipitated in alcohols. Figure 1c. TEM image of a bundle of aragonite rod like crystals.

Conclusions. This research established a simple method to synthesize super-fine, rod like aragonite by liquid-liquid reaction at low temperature. Ultrasonic field is the main factor determining the precipitate morphology. Alcohols prove to be more efficient than other additives in decreasing the particles sizes.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Case-based reasoning system for development of tablet formulations

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1. Summary

A case-based reasoning system (CBR) is a problem-solving technique which imitates a human reasoning and tries to make a decision based on earlier experiences. In this study, a CBR system for tablet formulations has been developed which contains data of tablet formulations of a number of active ingredients.

Keywords: Tablet formulation, Case-based reasoning system

2. Extended Abstract

Tablets are by far the most popular medicinal preparations since they serve benefits of good compliance for the patients and good stability for the manufacturers. The design of tablet formulations involves identifying not only an active ingredient providing curing effect, but other necessary excipients, i.e., fillers, binders, lubricants, disintegrants, which improve the quality of the tablets. Therefore, the characteristics of the tablets are a set of the properties of the active ingredient and excipients and information about interactions among each components. Occasionally, tablet formulation deals with conflicted situations where high strength is required together with rapid disintegration. The design of a new tablet involves identifying not only appropriate excipeints but also their quantities in order to balance the properties of the drug for robust manufacturing and for control of dose absorbed by the patients.

A case-based reasoning system (CBR) is a problem-solving technique which imitates a human reasoning and tries to make a decision based on earlier experiences. It solves a new problem by reusing past situations and applying them to the current case. CBR is beneficial when the problems are rather complicate in which the exact model can not be derived [Vetrov A.V. et al., 2004]. In this study, a CBR system for tablet formulations has been developed which contains data of tablet formulations of a number of active ingredients. The CBR system is composed of:

the

1) database of tablet formulations, which includes fields of tablet composition, amount of active ingredient and excipients, tablet properties (diameter, hardness, disintegration time, drug dissolution),
2) knowledge base for adaptation containing formulation repository; chemical and physical properties of each drug and excipient,

3) similarity measurement tool which has a set of rules and functions for measuring similarity; criteria for desired tablet formulations (diameter, hardness, disintegration time, drug dissolution),
4) data analysis unit with rules for adaptation and specific properties following Pharmacopeia's criteria.

The system is able to formulate a tablet exemplars by identification of the problem type and and modification the properties of tables according to rules. The case attributes that identify the problem type are used as indices in retrieval. Then the exemplars retrieved on the indices are further filtered by applying similarity measurements to determine their closeness to the problem. Usually, the similarity measure is the distance between cases. Every case can be characterized by a set of its features which can be detected as a point in the N-dimensional or multi-dimensional space. Each feature has a weight of importance. The correlation among features is analyzed and the set of features, which most affect on the result, are given. Finally, the most frequently occurring excipient in the retrieved exemplars is selected for the desired formulation.

In this study CBR is applied for formulating tablet formulations of the common drugs, such as drotaverine, glibenclmide and paracetamol.

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European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Highly productive droplet formation by vertical elongation of focused laminar flow in microchannel

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1. Summary

We developed a microfabricated device to form droplet by vertical elongation of focused laminar flow. The prepared droplet diameter increased with increase in the fraction of dispersed phase flow rate in total flow rate, and was independent of the total flow rate. We have successfully applied the droplet formation by vertical elongation to the parallel droplet formation from the array of dispersed phase flows, which enables high productivity for industrial applications.

Keywords: droplet formation, microchannel, flow-focusing, vertical elongation, high productivity

2. Extended Abstract

Droplet formation process with microfabricated devices has been applied to production of fine chemical materials, for example, microcapsules and polymerized particles. Preparation techniques of monodisperse droplets with two- or three-dimensional microchannel structures such as T-junction (Thorsen, 2001), flow-focusing (Anna, 2003), or step (Chan, 2005) have been reported. However, the productivities of the previously reported methods are not enough for industrial applications. In this study, we developed a microfabricated device to form droplets by vertical elongation of focused laminar flow. The method is applicable to the parallel droplet formation from the array of dispersed phase flows.

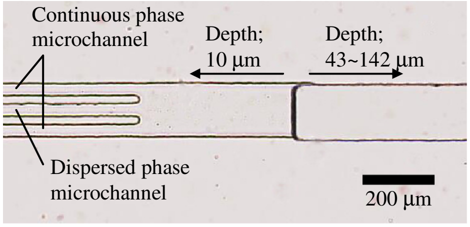

Fig. 1. Geometry of microchannel for droplet formation by vertical elongation.

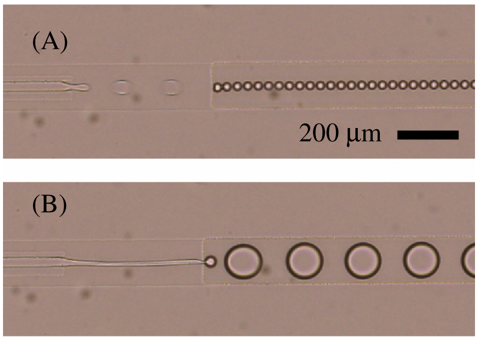

Fig. 2. Optical microscope image of droplet formation. Fraction of dispersed phase flow rate was 0.15 (A) and 0.33 (B). Continuous phase flow rate was 100 μL/hr. Downstream depth was 67 μm.

The polydimethylsiloxane microchannel was fabricated by the softlithography technique. Fig. 1 shows the geometry of the fabricated microchannel. Milli-Q water was used as dispersed phase, and n-hexanol with 5% tetraglycerin-codensed ricinoleic acid ester as continuous phase, respectively. The laminar flow of dispersed phase and continuous phase was formed, and transformed to droplets at the point that the microchannel depth changes. The resulting water-in-oil droplets were shown in Fig. 2. The droplet diameter increased with the fraction of dispersed phase flow rate in total flow rate and was not affected by the microchannel depth at downstream (Fig. 3). When the fraction of dispersed phase flow rate was smaller than 0.167, droplets were formed before the vertical elongated structure as shown in Fig. 2A. The total flow rate had no effect on the droplet diameter (Fig. 4), which indicating the possibility of higher droplets productivity. Fig. 5 shows droplet formation by parallelized microchannel. The array of dispersed phase flows were transformed in to same sized droplets by vertical elongation, which enables high droplet productivity for industrial applications.

Acknowledgement

A part of this work was conducted in AIST Nano-. Processing Facility (NPF).

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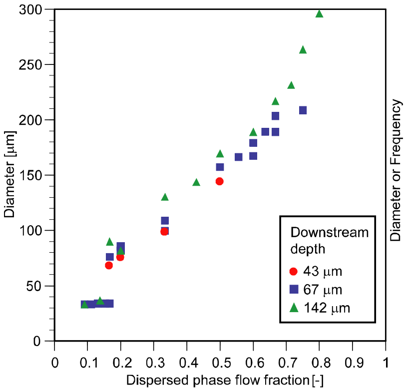

Fig. 3. Effect of fraction of dispersed phase flow rate and microchannel depth at downstream on the formed droplet diameter. Continuous phase flow rate was 100 μL/hr.

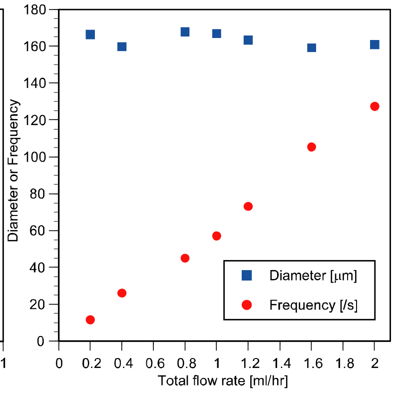

Fig. 4. Droplet diameter and droplet formation frequency at different total flow rate. Fraction of dispersed phase flow rate was 0.5. Downstream depth was 67 μm.

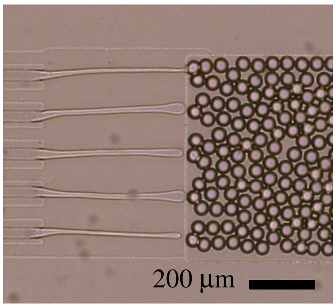

Fig. 5. Optical microscope image of droplet formation from the array of dispersed phase flows. Fraction of disperse phase flow rate was 0.33. Continuous phase flow rate was 200 μL/hr. Downstream depth was 67 μm.

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Evaluation of tomato paste as a potential raw material for lycopene extraction

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1. Summary

Commercial tomato pastes with a dry matter content between 20 and 35% w/w were investigated as a source of natural lycopene. The total lycopene content of the starting material ranged from 40 to 50 mg per 100 g of tomato paste. Lycopene extraction from untreated samples gave only about 2 mg of the pigment per 100 g of wet material. In contrast, significantly higher yields were attained when the materials were pretreated by cell wall degrading enzymes. Under the best conditions (T = 25 °C; enzyme to tomato paste ratio = 0.04 g/g; total processing time = 8 h) percent recoveries were of the order of 70%.

Keywords: lycopene, tomato paste, solvent extraction, cell wall degrading enzymes

2. Extended Abstract

Increasing clinical evidence suggests that lycopene, the major carotenoid pigment found in ripe tomato fruits and one of the most powerful natural antioxidants, can provide protection against cardiovascular disease and some epithelial cancers. This has lead to an increasing demand for dietary supplements and functional food products containing lycopene. Natural lycopene is currently obtained from whole tomato fruits that are specifically grown for this purpose but, due to the fast growing market for this compound, new raw materials are actively being investigated.

In this paper we present the results of a study aimed at assessing the suitability of tomato paste as a potential raw material for lycopene extraction.

Experiments were carried out on different commercial products purchased from the local market. They included concentrated, double concentrated and triple concentrated tomato pastes. Each of them was characterized for moisture and total lycopene content. Moisture content was determined by oven drying at 105 °C to constant weight. The amount of lycopene in each tomato paste was evaluated by a slight modification of a standard procedure using a 50:25:25 hexane/ethanol/acetone mixture as the extracting solvent. The dry matter content was around 20, 25 and 35% w/w for concentrated, double concentrated and triple concentrated tomato pastes, respectively. The lycopene content was between 40 and 50 mg per 100 g of wet tomato paste, depending on the sample considered.

Extraction experiments were performed at 25 °C in thermostated and magnetically stirred flasks. In a typical experiment, about 4 g of tomato paste were contacted with 35 ml of hexane for 3 h. After this time, a sample of the liquid was withdrawn, filtered and analysed for lycopene content. Total lycopene concentration in the extract was determined spectrophotometrically at 503 nm.

Under the conditions employed, recoveries were of only 2 mg of lycopene per 100 g of tomato paste. Moreover, minor improvements were obtained by raising the temperature and/or the extraction time. This was ascribed to the difficulty for the solvent molecules to penetrate the plant tissue and the cell structures where the pigment is localized. To overcome such barriers the tomato paste was pretreated by an aqueous solution containing cell wall degrading enzymes. In particular, commercial enzyme preparations with pectinolytic, cellulolytic and hemicellulolytic activities were used (Citrozym CEO and Citrozym ULTRA by Novozymes; Peclyve LI and Peclyve EP by Lyven). In these runs the temperature was maintained at 25 °C and the influence of pretreatment duration and type of enzyme preparation was investigated. Control experiments were also performed by pretreating the samples with pure water. Representative results from experiments on concentrated tomato paste using hexane as the solvent are presented in Figure 1. Similar results were observed for the other tomato pastes. Extraction conditions were as follows: T = 25 °C; enzyme to tomato paste ratio = 0.04 g/g; pretreatment time = 5 h; extraction time = 3 h. As can be seen, the enzymatic treatment leads to a significant enhancement of extraction. Recovery yields increased, with respect to untreated samples, by a factor ranging from more than 10 (Citrozym ULTRA) to about 20 (Peclyve EP and LI). Interestingly, pretreatment with water alone has some beneficial effect on extraction, which may be due to its ability to swell the plant tissue, thus facilitating solvent penetration into the tomato matrix.

Although the enzymatic process described in this work is not yet optimized, we note that it allows recoveries that are already of the order of 70%. In addition, due to the low temperature and short processing time involved, lycopene can reasonably be expected to be unaffected by the extraction procedure. These considerations, along with the high lycopene content of this material, lend further support to the use of tomato paste as a raw material for producing natural lycopene.

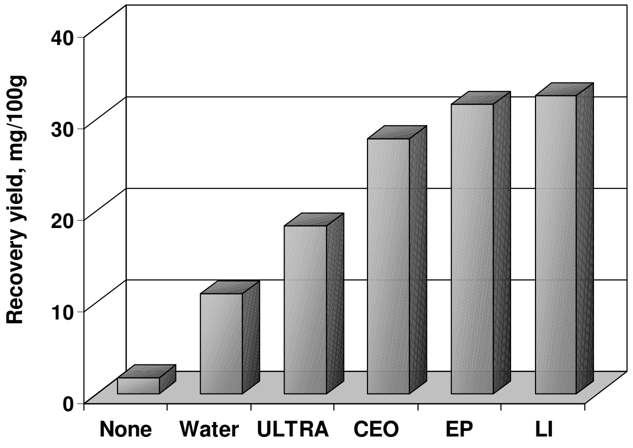

Figure 1: Lycopene recovery from untreated, water-treated and enzyme-pretreated (ULTRA, CEO, EP, LI) concentrated tomato paste.

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Development of reactive prepolymers with terminal NCO groups as rheology modifiers of lithium lubricating greases.

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1. Summary

The main objective of this work is to develop new diisocyanate-terminated prepolymers which can be potentially used as additive of greases by studying the influence of some structural parameters such as molecular weight and functionality on the rheological response of the final product. The addition of reactive isocyanate-terminated prepolymers increased significantly the values of the linear viscoelastcity functions of greases.

Keywords: polymer, rheology, lubricating greases, isocyanate

2. Extended Abstract

Lubricating greases are highly structured suspensions consisting of a thickener dispersed in mineral or synthetic oils. Particularly, lithium 12-hydroxystearate soap is the most widely used thickening agent. Greases also contain some performance additives. Among these additives, the use of polymeric materials is a common practice in the lubrication industry to modify the rheological properties of greases by reinforcing the role of the thickening agent [1,2]. The use of reactive diisocyanate-terminated polymers can be satisfactorily used as rheology modifiers of lubricating greases [3] by promoting the reaction between terminal isocyanate groups and the hydroxyl groups located in the hydrocarbon chain of the 12-hydroxystearate lithium soap. It was demonstrated that the poly (1,4-butanediol) tolylene 2,4-diisocyanate (PBTDI) with a relatively low molecular weight shows a similar effectiveness to that achieved with non-reactive polymers of much higher molecular weights.

Reactive polymers used as additives in grease formulations were manufactured by inducing the reaction between polypropylenglycol and polymeric 4,4'-diphenyl methane diisocyanate (MDI). Polymeric MDI is the residual bottom fraction coming from the distillation of pure MDI, being its average functionality 2.7. Resulting polymers and main structural parameters are listed in Table 1.

Prepolymer	Functionality	Mw
1	3.4	1100
2	3.4	1700
3	3.4	2700
4	3.4	4700
5	5.1	4050
Polymeric MDI	2.7	350

Table 1: Structural parameters of the polymers used

Polymers are added to grease formulation during the final cooling ramp applied in the manufacturing process [4]. The polymeric materials used and/or resulting lubricating greases were characterized by FTIR spectroscopy, differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and atomic force microscopy (AFM). The effectiveness of such additives was tested on final greases by performing small-amplitude oscillatory shear (SAOS) and viscous flow measurements as well as standardized mechanical stability tests.

Results show that the addition of reactive isocyanate-terminated prepolymers increased significantly the values of the linear viscoelastcity functions of greases (Figure 1a). In general, the higher the polymer molecular weight, the higher this increment in SAOS functions is. However, lower effectiveness were found for greases containing the polymer with the highest molecular weight (M_w=4700) as additive. It must be noticed that the ratio NCO groups/Mw decreases with Mw for the same additive concentration (% w/w). Consequently, the effectiveness of such polymers depends on the balance between this ratio and the length of polypropylenglycol chain. In addition to this, the rheology modification of greases containing polymers with similar Mw is slightly more marked when the functionality increases (Figure 1b).

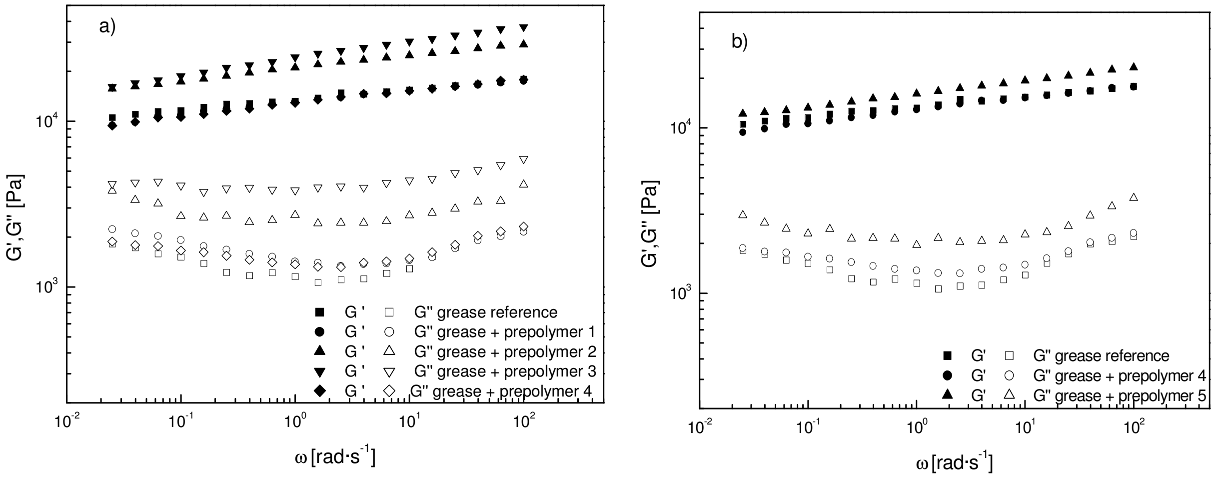

Figure 1: Frequency dependence of the storage and loss moduli for lubricating greases containing different polymeric additives, at 25ºC.

Moreover, results are highly affected by the ageing time of greases. The values of the rheological functions evolve for several months, which indicate that the kinetics of the reaction promoted is very slow. As expected, the rheological parameters are more influenced in the case of adding low-molecular-weight polymers, since the number of free NCO groups is higher. Thus, for instance, prepolymer 1 does not produce any modification during the first days after the manufacture but significantly modifies grease rheology after 2-3 months.

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European Congress of Chemical Engineering (ECCE-6)
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Environmental assessment of foundry sand based brick in different steps of its life-cycle using leaching tests

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1. Summary

The aim of this work has been the study of the leaching behaviour of mixtures clay/foundry sand in different steps of its life-cycle. The used assessment criteria have been the diffusion leaching test proposed in Dutch Building Materials Decree at the service-life step (utilization scenario) as monolithic material and the equilibrium leaching test proposed in the EU Directive on the landfill of waste at the end-life step as granular material (disposal scenario).

Keywords: foundry sand, brick, leaching tests, sustainable process, recycling

2. Extended Abstract

Foundry sand generated from casting of ferrous pieces in the process of manufacturing of cores and moulds are composed mainly of silica. Its high content of silica incentives reuse options. Since the release into the environment is controlled by transport through the water phase, leaching tests are suitable to assess the environmental impact of this type of products. Clay from a masonry and foundry sand from an automotive factory were mixed, V0: 100% clay and V1: 90% clay and 10% foundry sand, and extruded to obtain green products. These products were given in industrial firing cycle until a temperature of 1050ºC.

End-life Step (Disposal scenario): EN 12457 Equilibrium Leach Test is proposed by CEN as Compliance Test for leaching of granular waste materials. This test is based on the utilisation of different liquid to solid ratios (L/S=2 and 10) over 24 hours. Pollutants proposed by Landfill of Waste Directive has been analysed to compare their concentrations in leachates with proposed limits. Most of the elements specified are in sample V1 below the threshold for inert waste category landfill, except for As, Cr, Pb. Only these elements could pose a problem in the end-life step of mixture clay/foundry sand studied. Although, in sample V0 these metals and sulphates are upper the proposed limits. Therefore, it could be a problem in ceramic bodies with clay only.

Table 1. Experimental and regulated limit concentrations of selected elements in the leachates from the EN 12457 leaching test and NEN 7345 Diffusion Leach Test.

Element	EN 12457 Equilibrium Test with granular material						NEN 7345 Diffusion Leach Test with monolithic material		
	L/S=2			L/S=10					
	Conc sample V0	Conc sample VI	Limit EU Directive 2003/33	Conc sample V0	Conc sample VI	Limit EU Directive 2003/33	ε_{64} sample V0	ε_{64} sample V1	Limit Dutch Decree
	mg/l						mg/m^2 per 100 years		
As	0,043	**0,056**	0,05	**0,057**	**0,066**	0,05	0,0922	0,0289	435
Ba	< d.l.*	< d.l.	3,50	< d.l.	< d.l.	2,0	< d.l.	< d.l.	6300
Cd	< d.l.	< d.l.	0,02	< d.l.	< d.l.	0,004	< d.l.	< d.l.	12
Cr	**0,662**	**0,445**	0,10	**0,707**	**0,650**	0,05	< d.l.	< d.l.	1500
Cu	< d.l.	< d.l.	0,45	< d.l.	< d.l.	0,2	< d.l.	< d.l.	540
Mo	< d.l.	< d.l.	0,15	< d.l.	< d.l.	0,05	< d.l.	< d.l.	150
Ni	< d.l.	< d.l.	0,10	< d.l.	< d.l.	0,04	< d.l.	< d.l.	525
Pb	< d.l.	**0,300**	0,10	**0,112**	**0,335**	0,05	< d.l.	< d.l.	1275
Sb	< d.l.	< d.l.	0,01	< d.l.	< d.l.	0,006	< d.l.	< d.l.	39
Se	< d.l.	< d.l.	0,03	< d.l.	0,001	0,01	< d.l.	< d.l.	15
Zn	< d.l.	< d.l.	1,00	< d.l.	< d.l.	0,4	< d.l.	< d.l.	2100
Cl-	1,534	1,420	275	1,654	1,618	80	10480	6677	30000 (per year)
F-	0,600	0,800	2,00	0,768	0,955	1,0	523,0	424,7	56000
SO4=	115,5	98,2	280	**102,5**	99	100	21977	23520	45000 (per year)

*: <d.l.: below the detection limit

Service-life Step (Utilization scenario): NEN 7345 Diffusion Leach Test over 64 days is proposed by Dutch Building Material Decree to determine the leaching of inorganic components from monolithic materials in a closed tank. According with this Decree the inmision values (ε_{64}) of arsenic and fluoride over 100 years, and chloride and sulphate over 1 year do not exceed the regulatory limit (Table 1). Therefore, the clay/foundry sand mixture investigated in this work does not present environmental limitations in their service-life step.

3. Acknowledgements

This research as supported by the Spanish Education and Science Ministry (Projects CTM 2005-07282-C03/03 and CTM 2006-07960)

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