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PhD-projects in miniposter form

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Preface 2009

It is with proper pride that I now present you the 17th edition of this book of reference issued annually. It again provides an overview of all research projects currently being carried out at the Dutch universities in the broad field of Process Technology: from catalysis to separations, from transport phenomena to process systems engineering, and from micro-fluidics to product technology.

Earlier this year, the Position Paper Process Technology (see http://ospt.tnw.utwente.nl) was issued to raise awareness as to the growing gap between the needs of process industries and the much more science driven research at the universities. There are some positive signals that this message and the urgent plea for a higher level of financial commitment from government and industry with the field of process technology have been heard and understood. Only then will the academic process technology community be capable of educating sufficient numbers of young chemical engineers and of carrying out relevant research projects. Quite rightly, society expects that chemical engineers are devoted and most equipped to contributing to the solution of societal issues such as global warming and a sufficient energy supply chain by designing new processes and plants which are substantially more sustainable than the current ones.

In the meantime, important steps were made with respect to both the Dutch Separation Technologies Institute (DSTI) and the novel Action Plan Process Intensification (APPI). These developments seem to bring new excitement to the field of process technology as practised, studied and taught at the Dutch (technical) universities of Twente, Delft, Eindhoven, Groningen and Wageningen.

Amidst these challenging issues and developments, the Annual Poster Book of the Netherlands Research School in Process Technology (OSPT) keeps supplying a want in providing guidance as to 'who is doing what and where in the academic community of chemical engineers'. The OSPT comprises some 40 full-time and part-time professors active in the proliferation of sub-disciplines of Process Technology.

This Poster Book may assist the readers in finding her or his way in the colourful gamut of Dutch Process Technology research. This book not only presents projects and PhD students affiliated to the OSPT but also to adjoining research schools such as VLAG, NIOK and the J.M Burgers Centre for Fluid Mechanics. The projects carried out under the umbrellas of DSTI and GSPT can be found with the hosting university group.

Furthermore, this Poster Book, like its predecessors, acknowledges through its format the essential efforts and most valuable contributions of all our PhD students. This year, we again provide an alphabetical list of PhD students as well as a list of key words, which both will enable you to more easily find your way in this treasure of information.

We are ready to accommodate recommendations and suggestions for improvements as to the format of this Poster Book from our readers and users.

Professor Harry E.A. Van den Akker,
Scientific Director OSPT
September 2009

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Activities of the Dept. of Multi-Scale Physics

The Department of Multi-Scale Physics (MSP) studies phenomena and processes at the molecular scale and how these are related to the material and energy flows in the large-scale plants common in industry for producing energy, products and materials. We face enormous challenges when we try and analyse industrial processes by describing them in terms of the underlying molecular and mesoscopic events (flows, transport limitations, chemical reactions).
The great potential of a wide variety of computer simulations (Computational Fluid Dynamics, Lattice-Boltzmann simulations, Monte-Carlo techniques) makes it possible to simulate all aspects of industrial processes in great detail and pretty truthfully. Such a better understanding should lead to a better control of various processes producing better products in a cleaner and more efficient way. In this way, MSP contributes to more sustainable industrial processes and a better world.

The research focuses on four areas:

Multi-Phase Flows (Prof. Mudde)

The portfolio of multi-phase flows in MSP has a number of main activities. Firstly, there is the work on multi-phase aspects in flow lines for *e.g.* the simultaneous transport of oil and gas. We have the disposal of unique experimental test rigs for horizontal, vertical and inclined air-water two and three-phase flow. The experimental work supports modelling studies of the real world of oil and gas. Furthermore, we study particle laden, environmental flows, like clouds and sediment transport.
A second class of research projects relates to the dispersed multi-phase flow in chemical reactors such as bubble columns, sparged bubble loop reactors, aerated stirred vessels, and slurry bubble columns. We further study the details of the turbulent flows of riser reactors in the low solids loading regime. Finally, we are developing an X-ray tomographic system for the study of fluidized beds.

Thermal & Materials Processes (Prof. Kleijn)

The mission is to acquire better understanding of the fundamental physics of flow, heat transfer and reaction in thermal processes, and their influence on process efficiency and product quality. The focus is on measurement and modeling of phenomena taking place at small micro scales and on their interaction with larger scales. At the smallest scales we use experimental techniques such as micro-Particle Image Velocimetry and non-continuum simulation methods such as Direct Simulation Monte Carlo. At the larger scales we focus on the better understanding and modeling of turbulence in complex flow configurations.
Our research is currently centered around three themes: (1) hydrodynamic of micro-chemical processes and reactors, (2) low gas pressure processes for thin film technology, and (3) the application of magnetohydrodynamic phenomena to optimize processes such as steel casting and aluminum manufacturing, but also for targeted drug delivery in the blood.

Reactive Flows & Explosions (Prof. Roekaerts)

In the field of combustion and explosions, significant progress seems only possible via the development of better fundamental insight to be gained through both modelling and experimentation. Fundamental issues relate to the physics of turbulent reacting flows, turbulence-chemistry-radiation interaction and non-linear dynamics. Often, phenomena at different scales, from the molecular to the macroscopic scale, are coupled and a chain of models is needed.

Specific areas of research comprise clean and efficient combustion, mixing sensitive chemical reactors, pollutant formation and dispersion, hazard prevention and mitigation (fire spreading, explosions).

Computational Reactor Engineering (Prof. Van den Akker)

The idea is to revisit processes and chemical reactors by means of very advanced computational simulation techniques. Chemical reactions are explicitly part of the simulations. Lattice-Boltzmann methods are exploited throughout as these have proven to be very instrumental in acquiring very realistic simulations of the complicated interactions of flow and transport phenomena and detailed chemistry. The purpose is to explore and improve current or novel process options, reactor lay-outs and operating conditions. This activity is an expansion over our current CFD work as to a variety of operations in stirred vessels.

Another focus is on reactor safety in *e.g.* oxidation processes. Again, efforts are distributed over both modeling and experiments in unique test facilities.

Experimental Investigation of Cross Flow in a Tube Bundle Geometry

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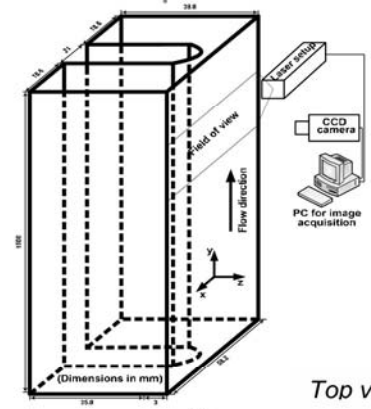
OSPT theme	: Computational & Experimental	**Research school**	: JMBC
Supported by	: HEC, NUFFIC, TUDelft	**Period**	: Jan. 2006 – Jan. 2010

Introduction

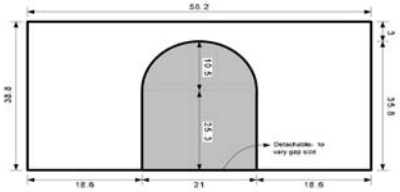
Motivation for the project is inter sub-channel transport of scalars and voids in a light water reactor fuel bundles and their effect on the system safety and stability.

Present study focuses at the experimental study, using Particle Image Velocimetry (PIV), of single phase cross flow in a compound rectangular channels connected by near wall curved gap.

Experimental Setup



Top view



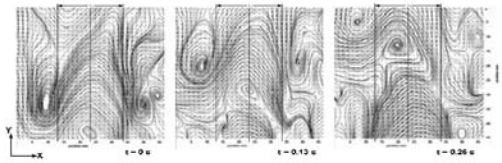
Operating Conditions

- Reynolds number
  864 to 20768
- Working fluid
  Water
- Ambient pressure and temperature conditions

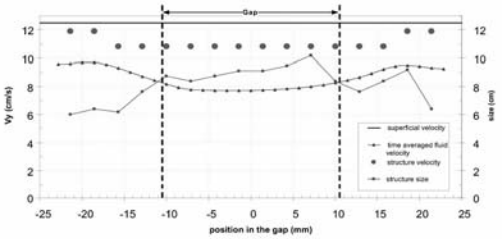
PIV Parameters

- Laser
  He-Ar, 25 W (CW)
- Seeding
  11 micron hollow glass spheres
- Laser sheet
  Rotating mirror

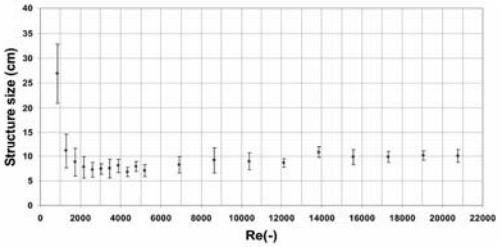
Results



Vector field (instantaneous minus average) – stream lines in the background (Re-3025)



Time averaged velocity profiles and structure characteristics (Re-3025)



Structure size as a function of Re. numbers

Preliminary Conclusions

- Large structures found at middle of gap
- Structure size become independent of Re numbers at higher values

Future Works

- Tracer injection to study cross flow
- Numerical work
- Cross flow in different geometries

Modelling of MILD combustion

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OSPT theme : **Energy conversion proc.**
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Period : Nov 2008 – Nov 2009

Introduction

Mild (Moderate or Intense Low Oxygen Dilution) combustion is a technique to improve the thermal efficiency of the combustor with lower pollutant emission.
In this mode of combustion fuel is mixed with product gases which has (low oxygen concentration and higher temperature (higher than the self-ignition temperature)). This can be achieved by recirculating the product gases inside the combustor efficiently.

In order use this concept in industry we need to gain further insight on the stability of flames and other issue. For this purpose a laboratory flame is under experimental and numerical investigation in our group which emulates the condition found in industrial combustor (burning in MILD combustion mode). In the following modeling methods and results will be discussed.

Method

Due to the symmetry of the burner 2d axisymmetric numerical grid was constructed using Gambit. The computational domain starts 3mm of jet exit and extended to 150 mm axially. Radially the grid extends to 52 mm. The inlet velocity and temperature boundary condition was specified (from measurements described in OSPT poster of Ernst Oldenhof) both in coflow and in the jet. The outlet was specified as outflow boundary condition.

For reacting cases the pure fuel was specified as the boundary condition for fuel inlet. However, for coflow which is mainly the product gases we assumed that flame generated in secondary burner is in equilibrium. Non adiabatic flame table was generated using FLAME code. The measured profile temperature at the coflow inlet was used to get interpolate the mass fractions of various species at constant mixture fraction of 0.0441.
Standard k-epsilon turbulence model and Eddy Dissipation Concept (EDC) combustion model was used.
In the following section results are described.

Results

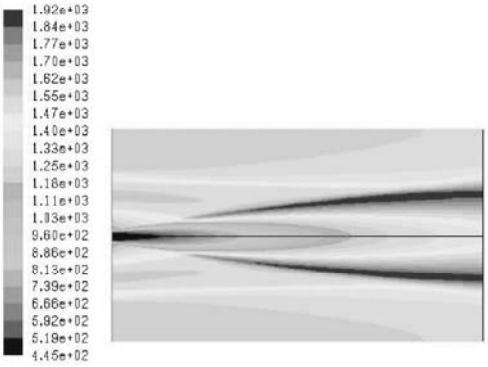

Fig.1 : Favre averaged temperature

Shown in Fig.1 is the preliminary results (temperature) obtained using EDC model. EDC model over predicts the temperature by 300 K at x=120 mm. This could be explained by underestimation of micro mixing time scale by EDC model. In future other combustion models e.g., flamelet models and pdf transport models will be investigated.

Acknowledgement

I would like to acknowledge financial support by STW.

Soft-sensing techniques for the control of the inflow distribution into the well

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OSPT theme	: Multi-Phase Flows	**Research school**	: JMBC
Supported by	: Shell, TNO	**Period**	: Oct., 2006-Oct., 2010

Introduction

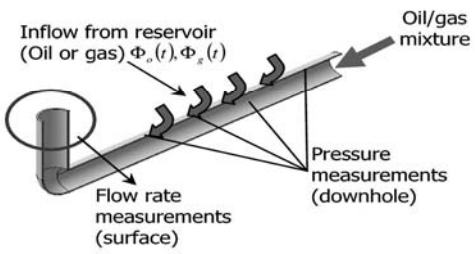
Multiphase flow meters are essential tools for providing optimal operation and control of oil wells as these meters deliver continuous and real-time information about production performance. However, existing multiphase meters are either expensive, or inaccurate, or accurate only within a limited operating range due to the harsh downhole conditions.

An alternative that can be used to overcome these disadvantages is to use multiphase soft-sensors, i.e. to estimate holdups and flow rates from relatively cheap and reliable measurements and a dynamic multiphase flow model. The aim of our work is to demonstrate some possibilities and limitations of such multiphase soft-sensors.

Soft-sensor

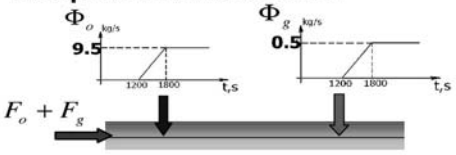
1) Soft-sensor is based on ensemble Kalman filter with 100 model realizations.

2) Uses the dynamic model of multiphase pipe flow, which is solved numerically by means of the control volume method with a collocated grid arrangement.



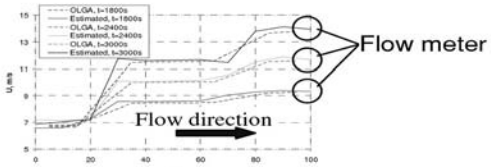
Values to be estimated:
- All flow rate values
- All holdup measurements.

Setup for inflow estimation

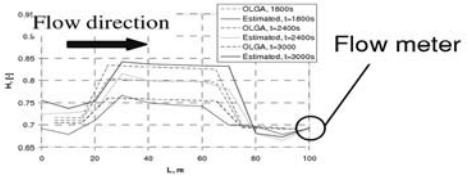


- Dispersed bubbly flow
- Unknown model error

Soft-Sensing under model error



Estimated and true gas flow rate along the pipe



Estimated and true liquid holdup along the pipe

Conclusions

- Inflow estimator is based on a simple but reliable wellbore model.
- EnKF can be used for a real-time inflow estimation for multiphase flow in wellbore.
- Required measurements: pressure (downhole), flow rate and composition (surface).

Acknowledgements

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Thermodynamic and Gas-dynamic Aspects of a BLEVE

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OSPT theme	: Multiphase Reactors	**Research school**	: BC
Supported by	: TU Delft, Delft Cluster	**Period**	: Dec. 2006 – Dec. 2010

Introduction

For a proper risk analysis of traffic accidents in road tunnels accurate estimates of the chances and effects of these accidents is required. This project aims at contributing to a better understanding of the accident known as BLEVE, or Boiling Liquid Expanding Vapor Explosion. The thermodynamic and fluid dynamic aspects, in particular of the rapid vaporization after a sudden depressurization will be investigated by a combination of modeling and experiments. The insights gained will be used in predictive models for maximum overpressure in case of a BLEVE-involved accident and will contribute to the safety evaluation of existing road tunnels and design of future ones.

Background

A BLEVE occurs when a vessel containing PLG (Pressure-Liquefied-Gas) above its normal boiling point fails catastrophically. In a very short time frame, a great portion of liquid experiences a rapid depressurization to the atmospheric pressure and starts to vaporize simultaneously. The rapid flashing and expansion of the liquid will drive the air to move. In most cases, this driving force can be so strong that a shock wave (pressure discontinuity) will be generated in the air and experienced by the tunnel wall.

Plan

A fluid dynamic model to compute the maximal overpressure experienced by the tunnel wall will be determined. In order to do so, accurate models will be developed for the rate of vaporization in the superheated state, and the resulting volume generation and pressure wave generation.

Results

A numerical model for the simulation of a BLEVE has been developed. It combines a two-phase model for the evaporating liquid (EVUT model) with the single phase Euler equation for the gaseous surroundings. A 1D version of the model was implemented in Fortran using MOC (Method of Characteristics) as solution method. Preliminary results were obtained for the explosion of propane and a sensitivity analysis of predictions on some parameters was made (e.g. depressurization rate, vaporization time scale). The most important observation so far is that under the same initial conditions, the maximum pressure predicted by TNO's model (expansion limited vaporization) is several times the pressure predicted by our model, and is confirmed to be conservative. However, our model definitely needs further improvement, in particular in evaluating the properties of the two phase mixture and the source terms for heat and mass transfer between the phases. On the other hand a detailed literature review on the available experimental work needed for model validation has been done. In the coming year specific model improvements will be implemented and model predictions will be validated by comparison with experiments from literature. Also, an alternative solution method (finite volume method) will be used for solving the model equations.

Acknowledgment

The financial support by TU Delft and Delft Cluster is gratefully acknowledged.

Reference

[1] Ferch, R.L. Method of characteristics solutions for non-equilibrium transient flow-boiling (1979) *International Journal of Multiphase Flow, 5* (4), pp. 265-279.

Slurry flows in polymer reactors

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OSPT theme	: Multi Phase flow	**Research school**	: OSPT
Supported by	: NWO/CW	**Period**	: Feb 2008 – Feb 2012

Introduction:
Suspension polymerization is highly efficient for large-scale production of polymers of high average molecular weight. By variation of the polymerization condition it is possible to produce a range of polymers with different properties. Also suspension polymerization offers considerable advantages over the single phase techniques in so far that heat removal control is no longer a problem.

Objective:
The objective of this research is to learn more about dissolution and coagulation of polymer particles(Latex) in an agitated vessel, by investigating the particles motion and the species transport processes around the particles as function of local rate of energy dissipation and the local shear rate.

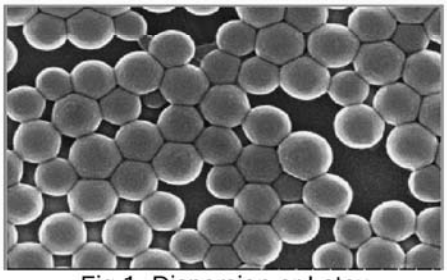

Fig.1- Dispersion or Latex

Approach:
Efforts to model suspension processes in chemical reactors need to combine fluid mechanics with coagulation processes description. The main difficulty is to consider together macromixing and micromixing phenomena, with complex reactions kinetics, and particle size distribution in the flow.

With the development computational fluid dynamics (CFD) codes, it is now possible to calculate satisfactorily the flow structure and mixing in reactors. By using a lattice Boltzmann algorithm with a large eddy model to handle turbulence, pseudo-single-phase turbulent fluid flow is simulated; this yields a local and instantaneous description for the shear rates and fluid velocities in the domain.

Also computational fluid dynamics (CFD) must be coupled with the population balance equations (PBE) to describe the evolution of the particulate phase.

The effects of micromixing will be included in coupled CFD-PBE computations to model turbulent aggregation and breakage, in which a variety of methods were used to approximate the probability density function (PDF),which is a statistical description of the fluctuating scalars at a subgrid scale.

Current study:
A coupled CFD-Population balance equations code is being developed.

Future work:
The numerical results must be validated against experimental results.

References:

[1] Van Vliet E.,PH.D. thesis, Delft University of Technology, 2003

Acknowledgment

This project is sponsored by the Dutch research foundation NWO/CW.

TUDelft

Protective Clothing

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OSPT theme	: Energy Conversion Proc.	**Research school**	: OSPT
Supported by	: TNO	**Period**	: Nov. 2008 – Nov. 2012

Introduction : adequate protective garments are one of the essential and vital features in nowadays soldier equipment. Despite different mission scenarios and objectives, chemical toxic gases are one of the most serious and dangerous threats in terms of life safety risk. A good protective garment must guarantee a high level of isolation from the surrounding environment and an acceptable level of comfort for who is wearing it.

Objective: the main goal of this research is to gain a reliable base model by accomplishing CFD simulations. Such a model must give immediate guidelines about protective clothing behavior in order to ease either the design of brand new garments or the currently in use product developments.

Results: protection against toxic gases can be achieved by sandwiching a carbon sphere layer in between garment woven layers as shown in figure 1. Changing the diameter of the carbon spheres (cylinders in a 2D approach) can give remarkable improvements in terms of protection according to figure 2.

Future work: processing more 2D simulations by varying parameters such as the number of carbon cylinders, the inlet flow velocity and the mass diffusivity, in order to gain as many information as possible before tackling a more complicated 3D problem.

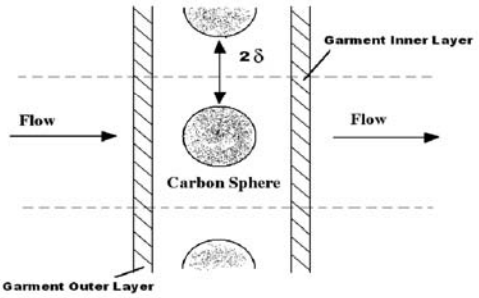

Figure 1: protective garment model sketch.

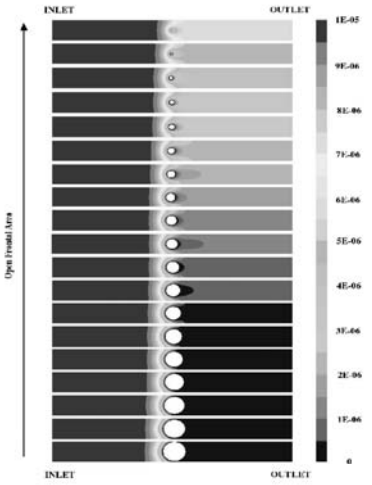

Figure 2: Changing in carbon cylinder diameter for a 2D approach. Contours refer to CO (carbon monoxide) mass fraction.

Structured packings in the Fischer-Tropsch Synthesis reactors (Micro scale approach)

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OSPT theme	: GSPT	**Research school**	: OSPT
Supported by	: STW	**Period**	: April 2008 – April 2012

Motivation

The structured packings have shown to have great potential for improving the performance of multi-tubular reactors in the Fischer-Tropsch Synthesis (FTS). This comes from the fact that they can improve flow distribution as well as heat and mass transfer inside the reactor. However, further investigation for finding an optimized design for the packing and reactor is essential.

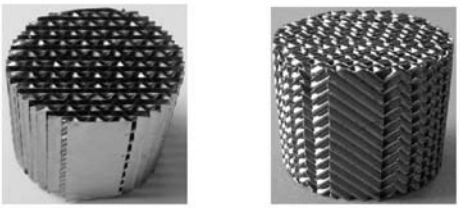

Fig.1- two different types of structured packings (left: CCFS right: OCFS)

Approach

In order to achieve an optimized structured design for the reaction environment a detailed computational and experimental knowledge in different scales involved is needed. In fact, different phenomena in structured multi-tubular reactors take place at different scales which are closely inter-related. The current work is defined as a multi-disciplinary team work between the Multi-scale Physics department, the groups Product & Process Engineering and Catalysis Engineering of DelftChemTech, and Delft Ingenious Design, all at Delft University of Technology. The project is divided in different scales from micro-scale till macro-scale.

The micro-scale deals with phenomena that take place at single channel of structured packing till single packing element. In this part of the project computational fluid dynamics (CFD) modelling combined with experiments will help to have better insight about the interplay between hydrodynamics, mass transfer and heat transfer. This leads to an improved design of the structured catalytic bed.

Current state

In the micro-scale project we have started with doing numerical simulations by using Lattice Boltzmann method. The first step of our approach was to build a standalone 2D code which is flexible for different multiphase flow configurations. Different physical aspects involved are gradually implemented into the model. We tested the model developed for some standard benchmark problems in single and two-phase flow systems like Poiseuille flow, capillary rise, and drop formation in periodic box and so on. Thus far, the model is applicable for 2D single phase and two phase flow simulations.

Conclusion

The Lattice-Boltzmann method was used and has shown to have promising potential for investigation of hydrodynamics in structured packings in different scales.

Future work

The numerical and experimental work will be further developed.

Acknowledgement

Financial support of STW is gratefully acknowledged.

Multi-scale modeling of reacting gas flows in micro-fluidic systems

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OSPT Theme: Energy Conversion Proc.
Supported by: MicroNed

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Period: November 2006 – November 2010

Introduction

The goal of the project is to develop a hybrid, computational model for simulation of continuum, transitional and rarefied reacting gas flows in micro fluidic systems, combining the particle based Direct Simulation Monte Carlo technique with continuum Finite Volume techniques. Coupling between continuum and particle based solver domains is based on the Schwarz method.

The project is part of the Fundamentals and Modelling Cluster of the MicroNed consortium, and aims at applications in micro-propulsion and micro-gas-reactor systems, as being developed in the Micro-Satellite and Smart Channels clusters of MicroNed.

In the first phase of the project, we develop models to be used in design and optimization of microthrusters as being developed in the Aerospace Department of TU Delft, the Department of Transducer Science and Technology of UTwente, and the Defence and Security Division of TNO. The first micro-satellite carrying such microthrusters will be launched in the next months.

Challenges

The main challenge of the project is in the consistent and efficient bi-directional coupling of two different modelling approaches:

- DSMC, a particle based simulation method for rarefied and transitional flows,
- CFD for continuum flows.

State of art

A preliminary CFD analysis was performed to study the performance of different micro-nozzle designs and to determine the validity of continuum CFD for such small systems. As a next step, we will integrate a hybrid DSMC/CFD approach as developed earlier in our department into TNO's X-Stream code, and apply this code for the study of transitional and rarefaction effects in micronozzels.

Analysis and results

A nozzle converts the energy stored in a pressurized gas into kinetic energy through an expansion; its efficiency is strongly geometry dependent. Due to the small dimensions, the flow was shown to experience strong rarefaction effects in a large part of the divergent. Such effects were studied applying the CFD solution as inlet boundary condition for DSMC in the region where rarefied regime is expected to occur.

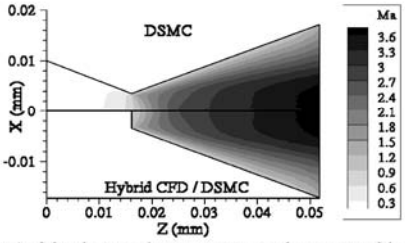

Figure 1: Mach number contours for a 25μN micro-nozzle with fully DSMC (top) and hybrid CFD/DSMC (bottom) solvers.

The thermal accommodation coefficient for gas-surface collisions was found to have a strong influence on the overall nozzle performance (Fig.2). This suggests that the use of specific coatings or the choice of different gases and wall materials can improve the performance of such devices.

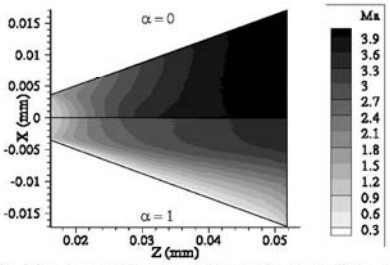

Figure 2: Mach number contours in the divergent of a 25μN micro-nozzle with fully specular (top) and fully diffusive (bottom) wall.

Hydrodynamics of Weld Pool and its Influence on Weld Structure

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OSPT theme	: Energy Conversion Proc.	**Research school**	: BC
Supported by	: M2I, Corus	**Period**	: Sept 2006 – Sept 2010

Introduction

In fusion welding, fluid flow influences energy transport from the weld pool to the surrounding material, affecting weld pool geometry and structure. Insight into weld pool hydrodynamics is essential in order to deliver efficiently high-quality weld.

Objective

This research is aimed at gaining insights into the influence of weld pool hydrodynamics on the formation and structure of fusion weld pools by numerical simulation.

Method

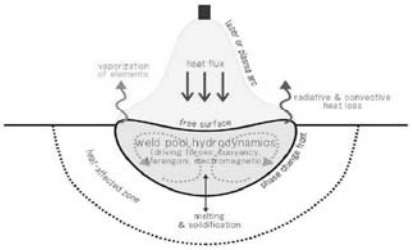

Fig 1. Relevant aspects in weld pool hydrodynamics

Simulations are performed using the open-source CFD toolbox OpenFOAM, in which the following aspect in figure 1 are implemented: laser heating, melting, buoyant convection, and surface-tension driven (Marangoni) convection. The code is being tested on a case of laser spot welding of steel with a flat surface assumption. The temperature gradient of surface tension depends on the surface temperature and the sulphur concentration. It influences the direction of the weld pool flow, heat transfer to the heat-affected zone, and the weld pool shape.

Results

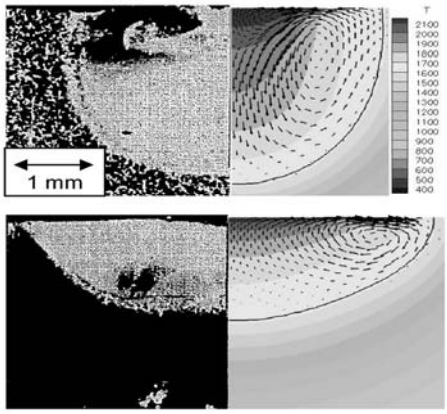

Fig 2. Weld pool shape for sulphur concentration of 150 ppm (top) and 20 ppm (bottom), 5200 W. Left: Experiment by Pitscheneder et al (1996), Right: OpenFOAM simulation

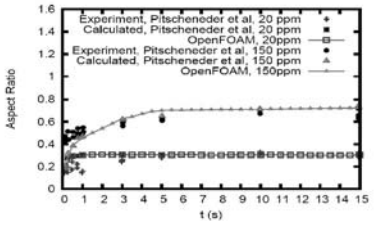

Fig 3. Comparison of aspect ratio

Future work

The next stage will be focused on extending the model to include effects of free surface, turbulence, and species transport.

Acknowledgement

This project is a collaboration between Materials Innovation Institute, Corus, and Dept. Multi Scale Physics TU Delft.

Multi-scale modeling of molecular phenomena in plasma-assisted thin film deposition

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Introduction

The goal of this project is to develop a comprehensive multi-scale simulation model for thin film deposition processes based on the application of an expanding thermal plasma. These processes are of great interest for example in micro-electronics, coating technology, manufacture of LCD (Liquid Crystal Display) screens etc.

In the group of Prof. Richard Van de Sanden at TUE the Expanding Thermal Arc Plasma (EPT) source has been developed.

A thermal plasma is generated at a relatively high pressure of 0.1-0.5 bar. The plasma jet rapidly expands into a vacuum chamber at 10-100 Pa. The particles mean free path length increases and the gas flow regime changes from the continuum, via the transitional to the rarefied.

Challenges

The main challenge of the project is in the consistent and efficient bi-directional coupling of the two different modelling approaches that will be applied: CFD solver where Knudsen number is low (Kn<0.05), and DSMC where it is high (Kn>0.05).

State of art

A compressible Navier-Stokes solver and a DSMC code have been written, validated and coupled using a Schwarz method. The code has been used to simulate the flow dynamics in the deposition chamber. The answers to two important questions about supersonic expansion in a low pressure environment have been found: (i) the importance of rarefaction effects on the flow field and (ii) the demonstration of an invasion of the supersonic part of the flow by background particles coming from outside it.

Acknwledgement

This research project is financially supported by DCSE (Delft Centre for Computational Science and Engineering)

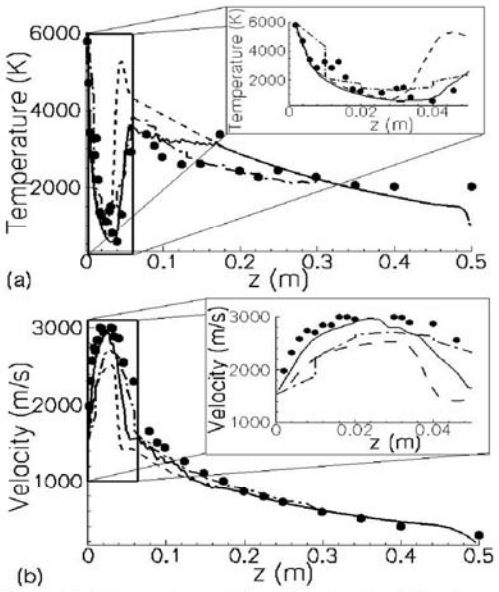

Figure 1: Temperature (a) and velocity (b) along the deposition chamber axis: comparison among CFD (· ·), DSMC (· —), hybrid method (—), and experimental data (●) at 20 Pa chamber pressure.

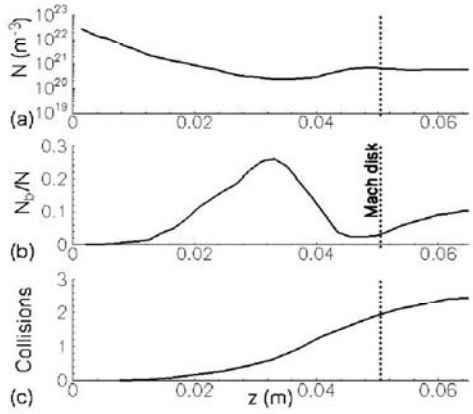

Figure 2: Number density N (m^{-3}) (a), invading background particles concentration N_b/N (b), and the number of collisions with invading background particles along the deposition chamber axis at 20 Pa chamber pressure.

Development of an NMR Multiphase Flowmeter

KROHNE
economieecologietechnologie

TU Delft

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OSPT Theme	: Multiphase Flows	**URL**	: www.msp.tudelft.nl
Supported by	: EET, Krohne	**Research School**	: BC
		Period	: May 2005 - May 2009

Motivation Multiphase Flowmeters

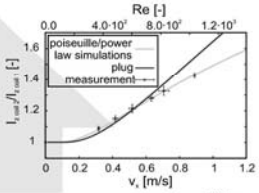
Measure the individual mass flow rates of the different phases fast and accurate.

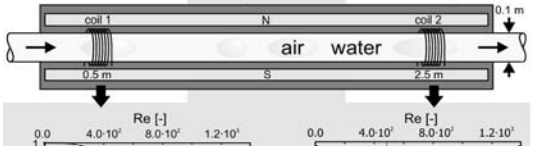
conventional multiphase systems	NMR flowmeter
• mixture is separated • measure each phase with ordinary flowmeters	• in-line measurement • no imaging: fast with minor delay
disadvantages	**advantages**
- complex - expensive - only snap shot measurements	+ non invasive + non intrusive + does not need optical access

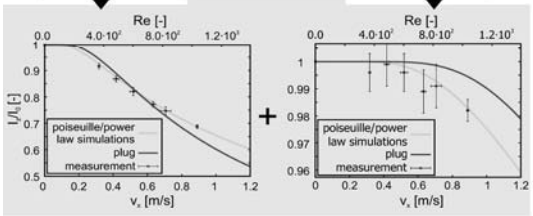
Principle NMR Flowmeter

The NMR signal of which the strength depends on the residence time of the fluid in a polarizing magnetic field is detected in two RF coils at different streamwise positions.

The average velocity is determined from the ratio of the NMR signals in both coils, which has a unique value for each velocity.





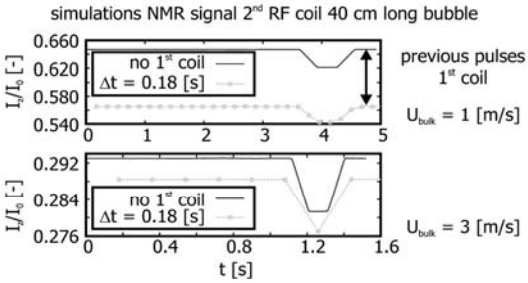


With the average velocity the average hold-up can be determined from the NMR signal measured in one of the detection coils.

Single-Phase Flow Results

A plug flow assumption was made in the past for this type of NMR techniques that do not provide information on the spatial velocity distribution. The exponential growth of I_z causes, however, systematic errors for non-uniform flow profiles. By comparing the laminar and turbulent flow results against numerical simulations is found that the accuracy of the plug flow approach for turbulent flow is sufficient, but that systematic errors are introduced in the evaluation of the laminar flow. Knowledge of the correct spin-lattice relaxation time T_1 is very important for the accuracy of the flowmeter.

Large Flow Structure (Bubble) Results



The average liquid velocity and hold-up are calculated from the ensemble-averaged NMR signal of a sequence of NMR experiments that are carried out at equidistant time intervals. The maximum flow velocity limits the measurement frequency, while the pulse frequency imposes a restriction on the detectable bubble length.

Acknowledgements

This project is supported with a grant of the Dutch Programme EET (Economy, Ecology, Technology) a joint initiative of the Ministries of Economic Affairs, Education, Culture and Sciences and of Housing, Spatial Planning and the Environment. The programme is run by the EET Programme Office, Senter Novem.

Mass transfer in Static Mixers

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Introduction

Gas-liquid flows in static mixers form an important industrial application of gas-liquid contacting. The advantages of the mixers are, in combination with mixing, creating dispersed multiphase flows and enhance mass transfer. Due to the mixing and shear in the mixer, a high interfacial area can be achieved. The static mixers can at present only be operated at rather low volume fractions of gas, i.e. usually around 5 %(v/v). The target of the present proposal is to expend reliable operation to gas volume fractions of 15%(v/v), thereby tripling the capacity. The emphasis is on turbulent flows.

In that project we aim to understand the complex interplay between the hydrodynamics, i.e. shear, turbulence, coalescence and break-up, and mixing, buoyancy, mass transfer and residence time.

Challenges

We propose to study the hydrodynamics and mass transfer of a (dispersed) gas-liquid flow in a static mixer:

- the nature of the research is experimental , numerical simulations can in our opinion only be done with sufficient accuracy in the single phase case

- We will investigate the influence of shear and turbulence on the bubble phase, study the bubble size distribution (both spatial and in terms of bubble diameters) and its connection to shear and turbulence.

- We will further measure and investigate the mass transfer (directly measuring the overall transfer, $k_l a$, and trying to measure separately the interfacial area a).

A second, equally important objective is to find and formulate design rules. These rules are vital for further development of the industrial applications. Our second objective is therefore, to find rules for the pressure drop, the gas fraction as a function of the flow rates and $k_l a$. Furthermore, these rules should be formulated in terms of the relevant dimensionless numbers, like the Reynolds number, the Froude number and the Weber number.

Fig.1. Helical Static Mixer

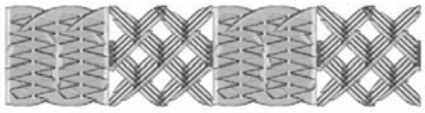

Fig.2. SMX Static Mixer

Fig.3. SMR S.M.

Fig.4. ISG

Acknowledgment

This research project is financially supported by STW / Primix

TU Delft
Delft University of Technology

Computational Fluid Dynamics of Fermenters

DSM

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: DSM	**Period**	: June 2005 – June 2009

Introduction

In the design and operation of fermenters, following limitations are encountered:
- Yield losses when scaling-up pilot scale results
- Limitations in air supply, carbon dioxide or heat removal, or liquid mixing
- Vital concentrations (e.g. dissolved oxygen, precursor molecules, ammonia, phosphate, etc.) cannot be controlled within the desired ranges

Aim: Using CFD to gain a better insight in the local hydrodynamics and mass transfer for further improvement of the performance of fermenters.

Current status

- Single- and two-phase simulations performed on a large-scale 22 m^3 fermenter
- Multiple Reference Frame (MRF) technique implemented for the modeling of moving parts
- Euler-Euler (two-fluid) approach used for multiphase modeling with k-ε for turbulence

Computational set-up

- Mesh: Gambit; solver: Fluent
- Tank diameter T = 2.09 m; liquid level H = 6.55 m; impeller diameter D = T/3
- 260x52x24 structured cells
- Zero-thickness walls, de-gassing boundary condition at free surface
- Ring sparger via momentum & mass source terms
- Working fluid: water – air
- Operating conditions:

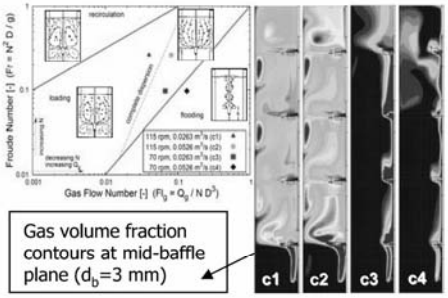
Stirring rate: 70, 115, 133 rpm
Aeration rate: 26.3 l/s, 52.6 l/s

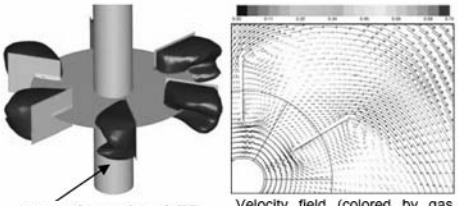
Single-phase results

+ As impeller-impeller spacing ΔC>2, parallel independent flow fields similar to single-impeller systems obtained (in agreement with literature)
+ Characteristic non-dimensional parameters (normalized by impeller #) are as expected:
  → Power Number N_P= 5.7
  → Flow Number N_Q= 0.78
  (Nienow, 1998: N_P= 5.5, N_Q= 0.78)*
+ MRF promising

Two-phase results

Simulation cases shown on flow regime map (Nienow et al. 1978) for bottom impeller:





- Holdups overestimated (fixed bubble size !)
  → Population balance modeling in progress
+ Transition from loading to flooding captured

Acknowledgements

This project is financially supported by DSM.

Hydrodynamic study of segmented multi-phase flow in a micro chemical reactor

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Research groups: Multi-Scale Physics, Delft ChemTech
OSPT theme: Green Process Alternatives
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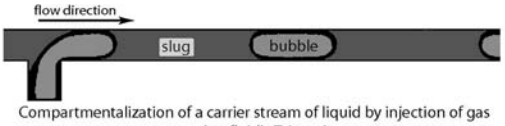
Period: Feb. 2005 - Feb. 2009

Introduction

Bubble and droplet-based laboratories-on-chips are beneficial in various biological and chemical applications.[1]



Compartmentalization of a carrier stream of liquid by injection of gas at a microfluidic T-junction.
The liquid slugs are well-mixed miniature chemical reactors in themselves.

Segmented flow in microchannels[2] offer an attractive route to enhance micromixing and mass transfer and to reduce axial dispersion.

Research objectives

Hydrodynamic study of segmented flow:

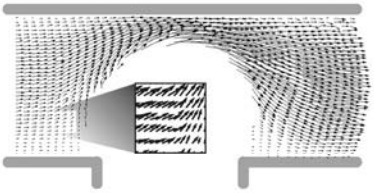
- 1. formation of bubbles and droplets [3]
- 2. distribution of bubbles and droplets
- 3. fluctuations in pressure and velocity induced by creation and destruction of bubbles[4]
- 4. exploit these fluctuations to enhance mass transfer

1. Formation of bubbles and droplets

We described the formation of bubbles from *high-resolution*, *time-resolved local* values of fluid velocity using μ-PIV and high speed camera images.[3]

Micrographs at four different instances in one cycle of bubble formation.

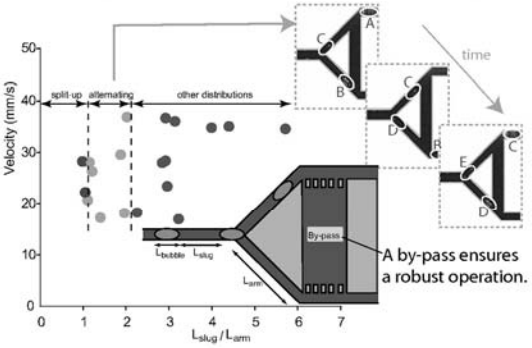
We demonstrated that 3-D aspects of the flow play an important role in the formation of bubbles and droplets and their final volumes.



Transient μ-PIV measurement in the carrier phase quantifies the leakage of carrier phase past the emerging bubble and allows one to predict the volumes of bubbles and droplets.

2. Distribution of bubbles and droplets

We generated alternating streams of bubbles by distributing a train of bubbles over two arms of a Y-junction.

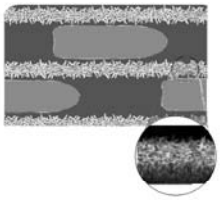


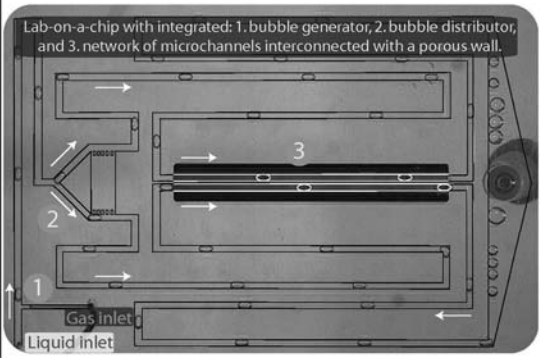
3. Fluctations in pressure and velocity

The motion of bubbles and droplets is distorted by pressure fluctuations caused by the creation and destruction of interfaces at the inlet and outlet.
We developed a simple scaling rule, which successfully predicts the order of magnitude of these fluctuations.[4]

4. Enhance mass transfer

We study radial flow induced in a network of microchannels interconnected with porous walls due to fluctuations in hydrodynamic resistance in the channels.





*Acknowledgement: We acknowledge Delft Centre for Sustainable Industrial Processes (DCSIP) for financial support

References

1. H. Song *et al.* (2006), Ang. Chem.-Int..Ed. (45), 7336
2. M. T. Kreutzer *et al.* (2005), Chem. Eng. Sci (60), 5895
3. V. van Steijn, M. T. Kreutzer, C. R. Kleijn (2007), Chem. Eng. Sci., 7505
4. V. van Steijn, M. T. Kreutzer, C. R. Kleijn (2008), Chem. Eng. J., S159
5. Bakker *et al.* (2007) Ind. Eng. Chem. Res. (46), 8574

Turbulent Reactive Flows in Chemical Reactors

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Period : Oct. 2007– Oct. 2011

Introduction

The emphasis of this research project is on development of time-efficient and accurate computational techniques for simulation of competing chemical reactions happening in a fed-batch reactor with the goal to provide tools for design of industrial chemical reactors that can substitute the common scale-up rules in practice in industry. The work is divided into two parts: fluid dynamics and chemical reactions.

Previous Research in This Field

This research is an extension of a previous work, carried out in the MSP department, which was done on a tubular reactor to the case of a stirred vessel. The open question that will be dealt with in this project would be the effect of temperature increase that will happen when higher concentrations of reactants are used. It is anticipated that this will have influence on density and viscosity, which has to be considered in the fluid dynamics part as well.

Fluid Dynamics

Large eddy simulation (LES) in conjunction with lattice Boltzmann method is used to mimic the fluid dynamics of the turbulent flow encountered in the simulations. We are now at the stage of preparing hydrodynamic simulations using LES LBM in a stirred vessel.

Chemical Reactions

Chemical reactions taking place in our simulations are going to be competing reactions between two agents already existing in the reactor and an agent added through a feed pipe.

The approach used in simulating the chemical reaction is based on filtered density functions (FDF) proposed by Colucci et al. (1998). The numerical method for solving the transport equations for the FDF is Monte - Carlo method (MC). The effect of micro-mixing is going to be investigated by varying Damköhler number.

Lattice Boltzmann Method

LBM is extensively used in our simulations for the fluid dynamics part. The reason is that LBM is fast, easy to implement and to parallelize. The LBM used here is an implementation of the method devised by Eggels and Somers (1995). LBM is a yet evolving CFD method and there can be some contributions to the development of the LBM relevant to our line of research, especially speeding up the solver and including thermal effects.

Monte Carlo Method

There are several ways to solve the transport equations for the filtered density functions of the composition vector of different species using available CFD methods such as finite differences. But MC methods prove to be less time consuming and CPU demanding compared to finite differences when larger number of species are considered and therefore it is the choice in our simulations.
Finally, speed up of our solver using effective tabulation techniques will be part of the tasks in this project.

Acknowledgments

This research project is supported by NWO/CW.

Long liquid slugs in stratified gas/liquid flow in horizontal and slightly inclined tubes

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OSPT theme	: Fluid Mechanics	**Research school**	: BC
Supported by	: STW	**Period**	: Oct. 2005 – Oct. 2009

Introduction

The slug flow pattern, forming in horizontal pipes, can be described as plugs of aerated liquid separated by elongated bubbles moving along the top of the pipe. Short hydrodynamic slugs are observed at relatively high flow rates. At lower flow rates slugs might grow to become extremely long causing serious operational upsets due to the strongly fluctuating supply of gas and liquid. Our objective is to predict the transition from short hydrodynamic slugs to long liquid slugs.

Methods

Growth model for dynamic slugs [1]:

The developed model predicts the average slug length as a function of time, given the flow conditions and pipe diameter for horizontal gas-liquid flow. The model considers the flow rates entering at the front and leaving at the back of a slug. The back velocity is considered as a bubble velocity, and the front velocity is calculated from the volumetric difference in the slug. The dynamic behavior of the liquid at the back of a slug depends directly to the behavior of the wave there. Once a slug is formed it propagates at a velocity order of magnitude higher than the velocity of the wave at the back. This results in a "pseudo-elastic" expansion of the wave. This behavior is presented using geometric considerations where the volume of the gas at the trough is assumed to be constant (the dotted area in Fig. 1). The model is used to predict the transition from hydrodynamic to long slugs.

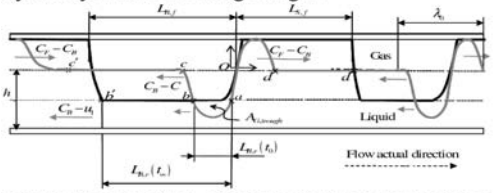

Fig. 1: Presentation of initial and final geometry of an average slug flow in a frame of reference moving with the back of the slug.

Results

The model enables us to plot lines with different final slug lengths as a function of superficial gas and liquid velocities. Of these lines, the $40D$ curve can be used to define the transition between long and stable hydrodynamic liquid slugs as shown in Fig. 2. Comparisons between theoretical predictions of the current model for the $40D$ curve and experiments for the long slug region by [2] show a satisfactory agreement. Moreover, the model is able to predict the average slug length for different fluids, pipe sizes, pressure and small inclinations.

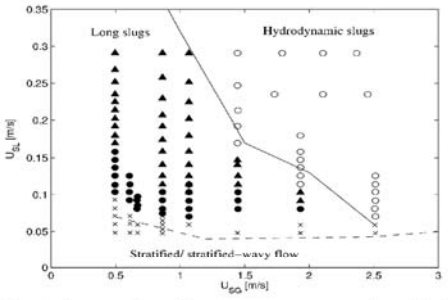

Fig. 2: Long slugs flow map – comparison between current model [1] and measurements [2].

Acknowledgement

This research project is supported by STW.

References

[1] Kadri, U., Mudde, R., Oliemans, R., 2008. A growth model for dynamic slugs in gas/liquid horizontal pipes. In proc.: BHR Conf., Banff, Canada.

[2] Zoeteweij, M. L., 2007. Long liquid slugs in horizontal tubes. Development study and characterisation with the electrical conductance techniques. Ph.D. thesis, Delft University of Technology, Department of Multi-Scale Physics.

Gaseous Dispersion in a Road Tunnel with Obstacles

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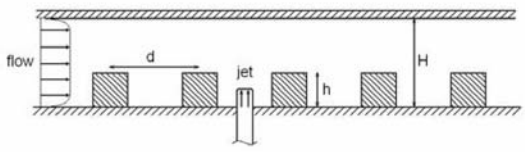
OSPT theme	: Energy conversion proc.	Research School: BC	
Supported by	: TNO	Period	: 03/2008 – 03/2009

Introduction

The goal of this experimental project is to better understand the formation of flammable mixtures after the accidental release of a "heavy gas" in a road tunnel with obstacles.

Experimental set-up

An array of cubes is mounted on the floor of a water tunnel in order to simulate obstacles in a road tunnel. The accidental release of a gaseous material is simulated by a jet of saline solution (density $\rho+\Delta\rho$), in a short time τ, issuing from a nozzle in the channel floor.



flow configuration

Parameters

height of the channel, H=0.16m
height of the cube, h=0.064m
density of water, $\rho=1.0\times10^3 kg/m^3$
velocity of the flow, U=0.15m/s

Dimensionless numbers

Reynolds number, $Re=Uh/\upsilon=9.6\times10^3$
Richardson number, $Ri=(g\Delta\rho h)/(\rho U^2)=1.4$

In order to achieve an identical Richardson number Ri between the realistic case and the experiment, the density of the saline solution is determined by the ratio $\Delta\rho/\rho\approx0.05$.

Future Work

To study the dispersion in the channel with obstacles, measurements of the instantaneous concentration and the turbulent velocity fields will be performed according the different parameters: injected fluid velocity, size of the nozzle, the duration τ, the density of the jet fluid, distance between the obstacles, size and arrangement of the obstacles.

Measurement techniques

Non intrusive measurement techniques are required to prevent disturbing the flow during the measurement. The mean flow field and turbulent fluctuations will be determined by using Particle Image Velocimetry (PIV). Planar Laser Induced Fluorescence (PLIF) will be used to determine instantaneous and time-averaged concentration fields. In using these two techniques simultaneously, it will be possible to study the relation between the fluctuations in the instantaneous concentration and in the turbulent flow.

Acknowledgement

This research project is financially supported by TNO.

Large Eddy Simulation of Turbulent Non-premixed Combustion

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Introduction

We report on the development of a compressible flow solver for Large Eddy Simulation of turbulent non-premixed combustion. For this goal we use a staggered compact high-order scheme, developed by Boersma [1]. The new developed code is applied to the Sandia jet flame D [2].

Computational method

A high-order (10^{th}) compact finite difference scheme for the compressible Navier-Stokes equations, developed by Boersma is used. Since this scheme is accurate, stable and low dissipative, it can be used for the proper validation of SGS models. The stability of the scheme is a result of the staggered arrangement of the variables.

Boundary conditions

Consider a transport equation for $\phi(x,t)$, $F(\phi)$. Then, in the vicinity of the in- and outlet boundary we add a small layer in which the convection velocity becomes locally supersonic [Fig. 1]. This results in a stable and low-reflective boundary condition. At the lateral boundaries we force the variables to reach their ambient values, $\phi \rightarrow \phi_\infty$.

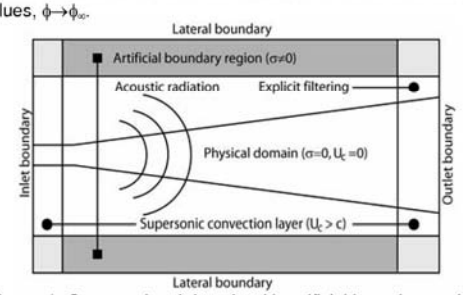

Figure 1: Computational domain with artificial boundary region.

Results

We present results of Sandia Flame D, which has a Reynolds number of 22.400. The Favre averaged transport equations for mass, momentum, total energy and mixture fraction were solved on a 3D Cartesian mesh with 2 million gridpoints. The LES was carried out with the Vreman model in which the model constant was set to 0.12. For the chemistry we use the steady flamelet model. The variance of mixture fraction was estimated with a simple gradient model. 2D plots of the instantaneous resolved axial velocity and resolved mixture fraction are shown in Fig. 2. The resolved axial velocity and mixture fraction at the jet centreline are shown in Fig. 3 and 4. In general there is a good agreement between the simulation results and the experiment.

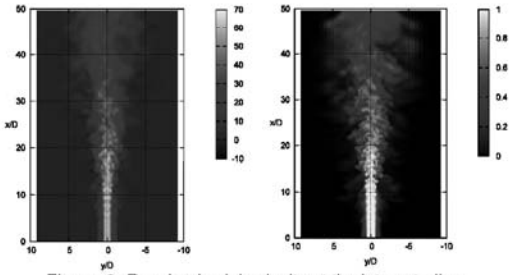

Figure 2: Resolved axial velocity at the jet centerline.

The main differences are believed to be caused by the use of the laminar inflow conditions, resulting in different mixing behaviour at the break-up region of the jet.

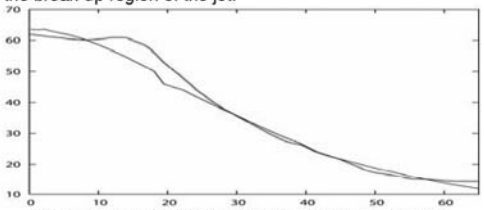

Figure 3: Resolved axial velocity at the jet centerline.

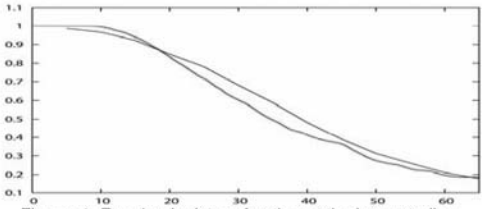

Figure 4: Resolved mixture fraction at the jet centerline.

References

[1] Boersma, B.J., 2005, J. Comp. Phys., 208, 675-690
[2] http://www.ca.sandia.gov/TNF/DataArch/FlameD.html

Acknowledgements

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Activities of the Biotechnology Group

Scientific Mission

The department of Biotechnology of the Delft University of Technology (TUD) performs application oriented, fundamental research and academic education in the field of biotechnology with a special emphasis on the development of concepts for clean, compact and efficient bioprocesses on the basis of fundamental insights in molecular biological phenomena and advanced experimental and theoretical tools and methods.

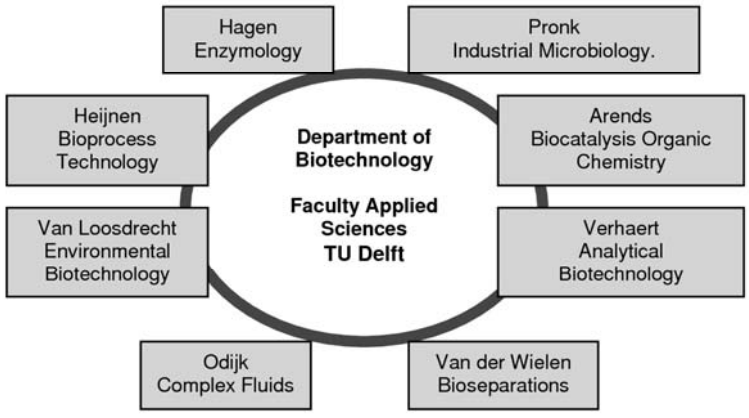

Figure 1. Expertises and professors in the Department of Biotechnology of the TU Delft.

The Department of Biotechnology is an integrated organisation of the sections of the Delft University of Technology with a strong link to Life Science and Technology. The names of the current professors as well as their field of main interest are shown in Figure 1. The Department is located in the Kluyver Laboratory for Biotechnology and houses scientists from basic as well as engineering sciences. To further complete the expertise, the Department of Biotechnology teams up with the Leiden and Wageningen researchers in Life Sciences within the framework of the Graduate School for Biotechnology (BSDL).

Because of the orientation on process concepts and applications, the Department of Biotechnology also participates actively in the Graduate School on Process Technology (OSPT) via the process engineering chairs: Prof.dr.ir. Sef Heijnen (Bioprocess Technology), prof.dr.ir. Mark van Loosdrecht (Environmental Biotechnology) and prof.dr.ir. Luuk van der Wielen (Bioseparation Technology). Research projects are often also multi-disciplinary and can comprise the efforts in various research groups within and outside BT. Some examples in the current research program are those on Counter-Current Chromatography (group Van der Wielen with group Krishna). Semi-Synthetic Antibiotics (Heijnen/Van der Wielen with group Gardeniers), Protein Precipitation (Van der Wielen and group Witkamp) and Micelle-Aided SMB Chromatography (Van der Wielen and group Keurentjes).

The Department of Biotechnology participates in the Kluyver Centre for Genomics of Industrial Fermentation. It employs microbial genomics to improve micro-organisms for use in industrial fermentation processes. Fermentation is used in the production, of renewable feedstock's, of food products and ingredients, beverages, pharmaceutical compounds, nutraceuticals, and fine and bulk chemicals.

Related to the aims of the OSPT is the participation of the groups of Heijnen, Van der Wielen and Van Loosdrecht in a large academic and industrial NWO/ACTS research program B-BASIC (Bio Based Sustainable Industrial Chemistry). B-BASIC is a nation-wide, academic-industrial research initiative to develop new production routes using renewable feedstocks and bio-based catalysts such as micro-organisms and enzymes.

Specific interests of group Heijnen

The still increasing speed of development of new molecular biological tools and rate of unravelling complete genomes make it increasingly attractive to consider micro-organisms as the factories for the production of all sorts of chemicals, natural products and energy of the future. ("Cell Factory" concept). These tools and information enables us to practically reprogram metabolism. However, the present lack of quantitative understanding of the cell factory leads to intuition-based choices of reprogramming targets. There is a strong need to change from intuition-based to rational based design of Cell factories. Therefore the group focuses on the quantitative understanding of the structure and kinetic behaviour of complex metabolic networks, especially the interaction between primary metabolism and product pathways to achieve rational design of all factories. Also developing tools for this aim, is within our interest such as metabolic network analysis, in vivo kinetics using fast pulse and other perturbation experiments, metabolome measurements using tandem Mass Spectroscopy as well as genome-wide profiling of mRNA expression using Biochips and Proteome Chips.

Specific interests of group Van Loosdrecht

The intensive removal of contaminants from municipal and industrial wastewaters is often occurring in bio film reactors. The many experimental and computational aspects of the dynamics of bio film formation is one of the focuses of group Van Loosdrecht. Also the efficient removal and recovery of particularly N, S and P containing components in various novel reactor concepts such as sequenced batch and airlift reactors has attracted academic as well as industrial interest. One of the key approaches is the conversion of cheap waste components into valuable products such as bio plastics. In this case, metabolic engineering is strongly interlinked with reactor design and process optimization.

Specific interests of group Van der Wielen

The Bio separations Group has in particular expertise in the field of (a) chromatographic separations at small and large scale including SMB, CAT and CPC, (b) in making and separating biological particles such as precipitates and crystals, and (c) in multifunctional bioreactors. Special attention is given to the fundamental physico-chemical aspects of bio separation processes in the sense of multi-component phase equilibria and transport processes, on the vase of thermodynamics. Reaction-diffusion kinetics of free and immobilised enzymes, particularly in relation to the multiphase systems as often occurring in multi-functional reactors, is another field of expertise of the group.

Infrastructure

The Department has a substantial hardware infrastructure for fermentation (over 200 laboratory and pilot scale fermentors), bio catalysis (various multipurpose and multifunctional bioreactors including membrane, chromatographic and crystallizer reactors), bio analysis (MS, gas and elemental analysis, GC-MS, LC-MS, Q-TOF, HPLC, CE, GC, image analysis) as well as downstream processing (various small and pilot scale chromatography equipment including SMB, CAT and CPC, HP extractors, crystallizers).

TU Delft
Technische Universiteit Delft

Software development for integrative modeling of transcriptome, proteome and metabolome

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OSPT theme	: Green Process Alternatives	**Research school**	: BSDL
Supported by	: Kluyver Centre for Genomics of Industrial Fermentation	**Period**	: June 2004 – May 2009

Introduction

Conventional modeling of metabolic reaction networks is based on the use of in vitro kinetics and suffers from the following problems:

- The model can not be solved analytically, only numerically
- The in vitro obtained kinetics (parameter values and in some cases the kinetic function) often do not apply to in vivo conditions.
- The number of parameters is very large which leads to major identifiability problems.

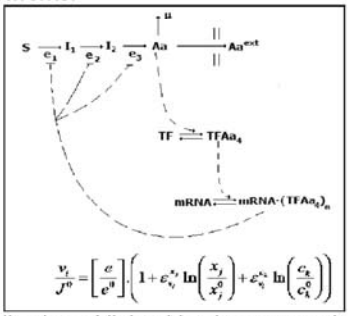
These problems are likely to increase enormously if integrated models, which will include genetic regulation (transcriptome, proteome, metabolome, fluxome), are to be developed.

In this project efficient integrative modeling strategies will be developed based on methods of model reduction and integrated use of a novel modelling approach termed 'linear-logarithmic (linlog) kinetics'. Both aspects were successfully applied to metabolic reaction networks in our group (see references). Here these concepts are to be applied to fully integrated models (from transcripts to flux).

In the linlog kinetic approach a non-linear approximate kinetic function of complex enzyme kinetics is used where the rate of reaction is modelled as a linear sum of logarithmic concentration functions. This approach has the advantage of considerable approximative accuracy and it provides analytical solutions of large perturbations on metabolic reaction networks. The linlog model parameters are the same as used in metabolic control analysis (MCA) i.e. elasticities.

In this project, the methods will be tested using existing models of reaction networks and will be extended to describe selected regulatory networks. After demonstration of their value these methods are to be implemented in a virtual cell model. The following activities are envisaged:

- Model reduction using linlog kinetics.
- Application of linlog kinetics in metabolic reaction networks.



- Application of linlog kinetics to genetic regulation and synthesis and degradation of mRNA and proteins.

This project is financially supported by the Kluyver Centre for Genomics of Industrial Fermentation and resides within the research programme "Novel Genomics Tools for Fermentation".

References

Visser D. and Heijnen J.J (2003). Dynamic simulation and metabolic re-design of a branched pathway using linlog kinetics, Metabolic Engineering, 5, 3, 164-176

Heijnen J.J., van Gulik W.M., Shimizu H. and Stephanopoulos G., (2004), Metabolic flux control analysis of branch points: an improved approach to obtain flux control coefficients from large perturbation data, Metabolic Engineering, 6, 4, 391-400

Wu, L., Wang, W., van Winden, W.A. , van Gulik, W.M., Heijnen, J.J. (2004) A new framework for the estimation of control parameters in metabolic pathways using lin-log kinetics, Eur. J. Biochem. 271, 3348–3359.

Metabolic Engineering of *Saccharomyces cerevisiae* for the production of C-4 Compounds from Renewable Substrates

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OSPT theme	: Green Process Alternatives	**Research school**	: BSDL
Supported by	: B-Basic, NWO-ACTS, Ministry of Economic Affairs	**Period**	: Dec. 2006 – Dec. 2010

Description

Fermentative production (production by large scale cultures of micro-organisms, like bacteria, fungi or yeasts) of commodity chemicals from renewable substrates (e.g. sugars and CO_2) is a promising alternative for the established petrochemical production processes which use fossil carbon sources as substrate. This approach, however, requires the availability of 'platform' micro-organisms that are capable of producing a wide variety of these (commodity) chemicals.
This PhD research project will focus on the study and optimization of the production of one such compound, whereby the yeast Saccharomyces cerevisiae will be applied as the 'platform' organism. A broad range of "–omics" approaches is available at the Department of Biotechnology and subsequent mathematical modeling and thermodynamic analysis will be applied to reshape the metabolic network in a rational way for optimal productivity and yield of the targeted product.

References

1. Mashego MR, van Gulik WM, Heijnen JJ (2007). Metabolome dynamic responses of Saccharomyces cerevisiae to simultaneous rapid perturbations in external electron acceptor and electron donor. FEMS Yeast Res. 7(1):48-66.
2. Nikerel IE, van Winden WA, van Gulik WM, Heijnen JJ. (2006). A method for estimation of elasticities in metabolic networks using steady state and dynamic metabolomics data and linlog kinetics. BMC Bioinformatics, 7:540 (doi:10.1186/1471-2105-7-540)
3. Wu L, van Dam J, Schipper D, Kresnowati MT, Proell AM, Ras C, van Winden WA, van Gulik WM, Heijnen JJ (2006). Short-term metabolome dynamics and carbon, electron, and ATP balances in chemostat-grown Saccharomyces cerevisiae CEN.PK 113-7D following a glucose pulse. Appl Environ Microbiol. 72(5):3566-3577.

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Technische Universiteit Delft

A Cell Factory for the Biosynthesis of Complex Peptides

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OSPT theme	: Green Process Alternatives	**Research school**	: BSDL
Supported by	: IBOS, NWO-ACTS	**Period**	: Aug. 2008 – Aug. 2010

Description

Various complex natural and semi-synthetic peptides are used as antibiotics, immunosuppressive and cytostatic agents. These peptides which include penicillins, vancomycin etc. are typically synthesised by non-ribosomal peptide synthetases (NRPSs) and are of growing importance for pharma and food industry. Here, we plan to develop a cell factory, for sustainable biosynthesis of desired complex peptides (NRPs).

Metabolic network analysis will be done on an NRPS and its product for quantification of the impact on central carbon metabolism due to redirection of fluxes for product formation.

Further, chemostat studies will be carried out to determine the in vivo kinetic properties (elasticities) of the NRPS. Finally, a fermentation process for an industrially important NRP will be designed and different options for the downstream processing will be considered.

This project is part of collaboration between the Technical University of Delft, the University of Groningen and DSM.

References

Kresnowati, M. T. A. P., van Winden, W. A. and Heijnen, J. J. (2005). Determination of elasticities, concentration and flux control coefficients from transient metabolite data using linlog kinetics. Metabolic Engineering **7**(2): 142-153.

van Gulik, W. M., de Laat, W. T. A. M., Vinke, J. L. and Heijnen, J. J. (2000). Application of metabolic flux analysis for the identification of metabolic bottlenecks in the biosynthesis of penicillin-G. Biotechnology and Bioengineering **68**(6): 602-618.

van Gulik, W. M., Antoniewicz, M. R., deLaat, W. T. A. M., Vinke, J. L. and Heijnen, J. J. (2001). Energetics of growth and penicillin production in a high-producing strain of Penicillium chrysogenum. Biotechnology & Bioengineering **72**(2): 185-193.

Verhaert, P., Uttenweiler-Joseph, S., de Vries, M., Loboda, A., Ens, W. and Standing, K. G. (2001). Matrix-assisted laser desorption/ionization quadrupole Time-of-Flight Mass Spectrometry: An elegant tool for peptidomics. Proteomics **1**(1): 118-131.

Wu, L., van Dam, J., Schipper, D., Kresnowati, M. T. A. P., Proell, A. M., Ras, C., van Winden, W. A., van Gulik, W. M. and Heijnen, J. J. (2006). Short-term metabolome dynamics and carbon, electron, and ATP Balances in chemostat-grown Saccharomyces cerevisiae CEN.PK 113-7D following a glucose pulse. Appl. Environ. Microbiol. **72**(5): 3566-3577.

Nitrogen recovery from concentrated ammonium waste streams – a combined biological and chemical process

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Description

The techniques for recovery and reuse of nitrogen from a high nitrogen loaded stream become more interesting and competitive nowadays [1]. The interest originates from the fact that high energy input is required to apply atmospheric nitrogen for ammonia production (N-fixation) via the Haber-Bosch process. With the increasing energy prices, nitrogen recovery from a highly concentrated ammonium source becomes an economically feasible process. A typical waste stream with a high N-content is rejection water from the dewatering of an anaerobic digester for treatment of e.g. manure. In this work, we propose a two step process for nitrogen recovery consisting of biological ammonium oxidation (nitritation) and subsequent chemical nitrite oxidation.

In the first step of the treatment approximately 50% of the ammonium is biologically oxidized to nitrite in a SHARON-like process [2]. The second step consists of a chemical conversion of nitrite to nitrate leading to an ammonium nitrate solution. The produced ammonium nitrate can be concentrated by utilising part of the thermal energy generated from the combustion of biogas. The concentrated product can be used as agricultural N-fertiliser. The sludge produced in the biological process can be returned to the anaerobic digester. In this way, the nitrogen cycle is closed and a sustainable process is established.

The objective of the project is to characterize the mechanisms and kinetics of both the biological and chemical oxidation processes proposed for N-recovery from concentrated ammonium streams (typically 6 g-N/l). Both experimental and modelling approaches will be used in this work.

The inhibition effect of nitrous acid and free ammonia at high concentrations to the biological nitritation will be examined. The evidence of chemical nitrite oxidation has been previously reported in literature [3],[4]. In this research, these findings were confirmed with experiments in a chemical reactor (see an example in the figure below). A mechanistic mathematical model has been developed and validated with the experimental data. Further investigations will be performed for optimisations of the process such as the use of alternative sources of oxygen (e.g. oxygen enriched air or hydrogen peroxide).

References

1. Maurer, M., P. Schwegler, and T.A. Larsen, *Nutrients in urine: energetic aspects of removal and recovery.* Water Science and Technology, 2003. **48**(1, From Nutrient Removal to Recovery): p. 37-46.
2. Hellinga, C., A.A.J.C. Schellen, J.W. Mulder, M.C.M. Van Loosdrecht, and J.J. Heijnen, *The Sharon process: an innovative method for nitrogen removal from ammonium-rich waste water.* Water Science and Technology, 1998. **37**(9, Upgrading of Water and Wastewater Systems): p. 135-142.
3. Chalk, P.M. and C.J. Smith, *Chemodenitrification.* Developments in Plant and Soil Sciences, 1983. **9**(Gaseous Loss Nitrogen Plant-Soil Syst.): p. 65-89.
4. Udert, K.M., T.A. Larsen, and W. Gujer, *Chemical Nitrite Oxidation in Acid Solutions as a Consequence of Microbial Ammonium Oxidation.* Environmental Science and Technology, 2005. **39**(11): p. 4066-4075.

Influence of nitrogen oxides on the metabolism of ammonia oxidizing bacteria

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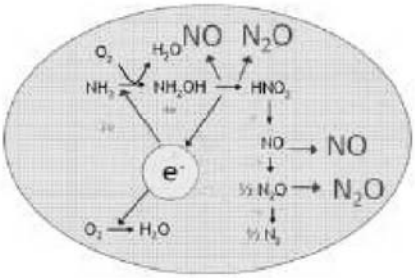
Supported by	: STW	**Period**	: Jan. 2005 – Dec. 2008

Description



Metabolic pathway of Ammonia Oxidizing Bacteria

Nitrogen removal from wastewater is usually performed by cooperation of three different groups of micro organisms: the autotrophic ammonia oxidizing bacteria, the nitrite oxidizing bacteria and heterotrophic denitrifying bacteria. During biological nitrogen removal nitric oxide (NO) and nitrous oxide (N_2O) emissions can be measured. The exact reason for the emission is unclear: it is generally believed to be mostly attributed to denitrification, but it can also be coupled to oxidation of ammonia.

Previous research has indicated that NO and NO_2 play an important role in the metabolism of ammonia oxidizing bacteria (Schmidt *et al*, 2001). Possibly they function as a signalling compound, which turns on the denitrification pathway in these bacteria. Addition of NO_2 and NO might result in denitrification by the autotrophic ammonia oxidizers. This would imply a significant improvement in nitrogen removal, compared to conventional wastewater treatment.

Nitrifying Sequencing Batch Reactor

The objective of the project is to increase our quantitative understanding on how NO_x influences the metabolism of ammonia oxidizers. This will be investigated by operating lab-scale nitrifying reactors, in which the NO_x production and consumption, microbial composition and nitrifying activities will be monitored. The knowledge gained by experiments will be used to build a metabolic model of ammonia oxidizing bacteria, including processes involving N_2O, NO and NO_2.

References

Kampschreur, M.J., N.C.G. Tan, C. Picioreanu, M.S.M. Jetten, I. Schmidt, and M.C.M. van Loosdrecht, 2006, Role of nitrogen oxides in the metabolism of ammonia-oxidizing bacteria, *Biochemical Society Transactions* 34, 179-181.

Schmidt, I., D. Zart and E. Bock. 2001. Gaseous NO_2 as a regulator for ammonia oxidation of Nitrosomonas eutropha, *Antonie Van Leeuwenhoek* 79, 311-318.

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Microbial Assessment of Aerobic Granular Sludge

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Supported by	: TU Delft	**Period**	: July 2008 – July 2012

Project description:

The new aerobic granular sludge (AGS) technology is a powerful innovation to reduce the large area requirement and energy consumption of conventional wastewater treatment plants (wwtp), as well as to achieve lower investment and operational costs. Since nutrient removal is a biological driven process, one needs to gain more knowledge about the structure and function of the microbial communities within the granules in order to be able to operate a stable system at higher efficiencies. Therefore, it is necessary to understand the relation between population dynamics and process performance better. Hence, it is of interest to explore the distribution of the microbial population within the granule and to measure their diversity and activity by the use of fingerprinting methods such as PCR-DGGE, qPCR, and FISH, as well as with microsensor measurements.

Since effluent standards are getting more stringent it is of importance to increase understanding about the biological N, P, and COD removal as well as improving conversion efficiencies. Thus, competition between the two populations of phosphate accumulating organisms (PAO) and glycogen accumulating organisms (GAOs) will be studied. The PAOs are responsible for the biological P-removal however, GAOs are able to form granules too and as both use the same substrate, it is a challenge to find conditions in which PAOs flourish over GAOs [1]. From activated sludge processes several conditions important in the competition of these organisms are already described, however local conditions inside the granules can differ from usual activated sludge conditions. Therefore, it is of interest to test for different conditions such as temperature, pH, and oxygen within the granules to investigate which environment is favored by the PAOs or the GAOs present within the granule. In this context cycle measurements of metabolic products, as well as spectroscopic measurements are tools to test for this relation.

A further research aim is to explore the different routs of N removal in order to enhance the efficiency of AGS. Moreover, filamentous bacteria are thought to be of significance to the structure of granules and thus to process stability. On the other hand filamentous growth can lead to biomass washout due to decreased settleability.

Consequently, their appearance, growth, and function are going to be investigated with microscopic and molecular techniques. An additional question is how the solid retention time of the bacteria and protozoa within the microbial population of an aerobic granular sludge based Nereda® pilot plant and conventional sludge of the excess, influent, and mixed liquor is. Therefore, a comparison between the washout from biofilm flocs and granular sludge is going to be made by the means of activity measurements such as qPCR and RNA-DGGE and FISH.

References:

1. de Kreuk, M.K. and M.C.M. van Loosdrecht, *Selection of slow growing organisms as a means for improving aerobic granular sludge stability*. Water Sci. Technol. FIELD Full Journal Title:Water Science and Technology, 2004. **49**(11-12, Biofilm Systems V): p. 9-17.

Ecology of mixed cultures producing PHA

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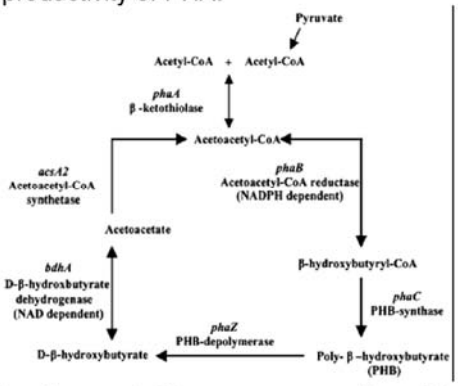
Description

Polyhydroxyalkanoates (PHAs) are a class of polyesters synthesised and accumulated as storage polymers for energy and substrate by many different groups of bacteria [1]. The potential industrial application of PHAs is the replacement of petrochemical plastics, because they are biodegradable and can be produced from renewable resources. The development of commercial production of PHAs focuses on pure cultures processes. High cost on substrates and operation limit pure culture PHAs production on a large scale. Compared to pure culture processes, the merit of mixed culture processes are lower costs but until now a shortcoming is the low productivity of PHA.



In the past 20 years, more than 50 PHA synthase genes and other genes related to PHA biosynthesis have been identified. Figure 1 shows the key enzyme reactions of synthesis (e.g. *phaA, phaB, phaC*) and degradation (e.g. *phaZ*) of PHA in *Azospirillum brasilense* [2]. Apart from the enzymes shown in Figure 1, other proteins, such as the granule-associated proteins (e.g. *phaP*) and regulators (e.g.*phaR*) are involved in PHAs synthesis [3]. Different bacteria adopt various strategies to synthesize PHAs.

Goal of this project is to obtain insight into the ecology of PHA-producing bacteria with the aim to improve the production of PHA. Different genomic tools will be used to study the diversity and expression of genes encoding key enzymes involved in PHA production.

References

[1] T.V.N. Ramachander, S.K. Rawal. PHB synthase from *Streptomyces aureofaciens* NRRL 2209. FEMS Microbiology Letters 242 (2005) 13–18

[2] Daniel Kadouri, Edouard Jurkevitch, and Yaacov Okon. Ecological and Agricultural Significance of Bacterial Polyhydroxyalkanoates. Critical Reviews in Microbiology, 31:55–67, 2005

[3] Anne Pohlmann, Wolfgang Florian Fricke *et al.* Genome sequence of the bioplastic-producing "Knallgas" bacterium *Ralstonia eutropha* H16. Nature biotechnology: 2006

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Sludge reduction with oligocheate worms

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Project description:

The conventional treatment system of domestic waste water produces about 20 kg dry weight of secondary sludge per people equivalent per year. Sludge is an ecological hazardous material so in most developed countries, the sludge is dewatered and incinerated. However this process is highly energy intensive.

Various alternative methods have been proposed to reduce the amount of sludge. However, the problem is that sludge is very hard to digest. For example: anaerobic digestion usually reduces the amount of sludge only by 20%. [1]

A promising method that is being developed is sludge reduction with oligocheate worms. These worms are specialized in consuming sludge [2] and can be cultured in special reactor systems. These reactor systems can reduce around 70% of the sludge. [3] The hypothesis is that the intestines of the worms contain extremely active bacteria and or enzymes.

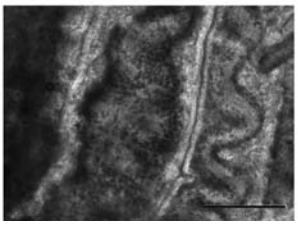

Figure: microscope picture of worm intestine

The goal of the project is to validate and optimize the effectiveness and stability of the system. A model is being developed to study the growth and behaviour of the oligocheates

A worm reactor with a volume 125 m^3 has been designed, build and is operated at the waste water treatment plant in Wolvega. This system currently processes about 200 tons of sludge per year. Also several 5m^3 pilot plants are being operated at different locations in the Netherlands for the purpose of research and validation of the process.

Figure: 5 m3 pilot reactor at Amsterdam Westpoort.

References:

[1] S. Tait, J.Tamis, D.J. Batstone (2009)
[2] Hellen J. H. Elissen Æ Edwin T. H. M. Peeters (2008)
[3] SR Technologie (unpublished data)

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Integration of fermentation and recovery of carboxylic acids

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Description

Carboxylic acids (CAs) in industry are very important compounds due to their application in industrial polymerization processes. This industrial field requires monomeric or oligomeric building blocks of >99.5% purity, often even 99.9%. Nowadays CAs are produced mainly from petroleum-based feedstocks, but as petroleum resources are becoming scarce, renewable feedstock alternatives processes like fermentation, are required to supply the future demand of these acids (Figure 1). Using traditional fermentation processes for obtaining high purities of CAs could lead to excessive downstream processing requirements and high gypsum production (due to the use of neutralizing agents in the fermentation[1]).

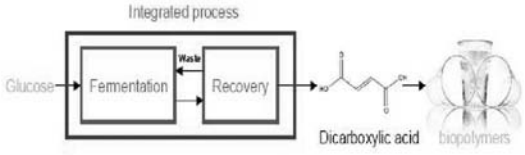

Figure 1: General process scheme for carboxylic acid production using integrated recovery

In this study modern fermentation processes are integrated with product removal techniques[2] in order to maximize the CAs production and to minimize waste production due to base addition in the fermentation step. The research will include modelling of the complete integrated process and proof of principle experiments (fermentation and removal techniques). The physical properties of the carboxylic acid should allow its selectivity recovery. Different compounds are evaluated with the proposed concept.

References

[1] Zhou Y, Du J, Tsao G T (2002) Comparison of Fumaric acid production by *Rhizopus oryzae* using different neutralizing agents, Bioproc. Biosyst. Eng. 179 – 181.

[2] Stark D, von Stockar U (2003) In situ product removal (ISPR) in whole cell biotechnology during the last 20 years. Adv Biochem Eng Biotechnol 80:149-175

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Countercurrent in-situ adsorptive and extractive product recovery

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Desciption

Society today mostly uses technology using fossil resources to provide its energy and resource requirements. Most industrial bulk products originate from hydrocarbon sources such as coal and oil. This industrial structure can not be continued indefinitely. Biological based production of industrial bulk chemicals using renewable carbohydrate (biomass) resources can provide a route towards a sustainable industry.

Biological bulk chemical production methods require advances in numerous fields, e.g. cell improvements or bioreactor design, in order to be successful. Most high cell density biological systems experience limitations as inhibitory or toxicity effect by product, feedstock or residual products. Also product degradation can negatively influence productivity. Countinuous product removal can increase the productivity and economic validity of such fermentations.

This PhD study aims to enhance bioconversions using in-situ product removal techniques. The downstream processing is closely linked to the fermentation process due to product inhibition and process integration plays a crucial role. To this end systematic design principles for the development of in-situ countercurrent product removal techniques will be generated based on the thermodynamic and physical properties of the systems. Special emphasis will be given to in-situ product removal by means of adsorption. Solid adsorbents in fluidized systems usually suffer from attrition and adsorbent loss. Simulated moving bed systems provide the use of stationary solid adsorbent phase while providing countercurrent operation possibility. Design and development of design principles for simulated moving bed systems will also be performed.

References

Van der Wielen, L.A.M., Luyben, K.C.A.M. Intergrated product formation and recovery in fermentation. Curr. Opin. Biotechnol. 3 (1992), 130-138

Straathof, A.J.J. Auxiliary phase guidelines for microbial biotransformations of toxic substrate into toxic product. Biotechnol. Prog. 1- (2003), 57-62

Integrated Recovery of C4 Building Blocks from Fermentation Broth

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Description

In recent years, the search for more sustainable and environmentally friendly technologies enhanced with the increasing sensitivity of modern society on the impact of development on the environment. Current chemical technologies with petroleum as their major raw material are no longer able to meet the demands of sustainable development. The increasing chemicals and energy production and the exhausting petroleum resources are urging the communities to search for replacement of currently available technology with alternatives.

The major objective of the current project is to produce C4 building blocks from renewable carbon sources in order to replace petrochemical C4 building blocks. Such building blocks can be succinic acid, gamma-butyrolactone or fumaric acid, which are utilized in a wide range of products, from polyesters to solvents.

Industrial polymerizations usually require monomeric or oligomeric building blocks of >99.5% purity. Traditional fermentation processes to obtain such purities could lead to excessive downstream processing requirements. To prevent this, modern fermentation technologies can be used and the by-product formation can be minimized to maximize the product titers. Besides, in the downstream processing, the physical properties of the target product should allow for an efficient final distillation or crystallization step.

The main obstacle in bioprocesses is the high production costs of the biochemical products. For bioproducts to be more competitive to chemical products, the bioprocesses should be designed in the optimum level.

Optimization of processes requires deep understanding of each unit in the process. In this project, the objective is the design and optimization of processes for the integrative production of C_4 building blocks. During the course of the project each unit operations will be considered in detail to gain more insight and to obtain the necessary parameters for the process optimization. Those parameters can be related to partitioning of solutes between two phases/ extraction (liquid liquid equilibrium), solubilities/crystallization (solid liquid equilibrium) or solid-solid interaction/adsorption depending on the type of unit operation.

The project is carried out in collaboration with academic partners from the TU Delft and the Wageningen University and Research Centre and industrial partner.

References

Efe C, Straathof AJJ, van de Wielen LAM, (2008), Feasibility of biochemical production of 4-hydroxybutyrate and its lactone as a substitute to petrochemical production, Biotechnology and Bioengineering, *In press,*

Buque-Taboada EM, Straathof AJJ, Heijnen JJ, van der Wielen LAM, (2004), In situ product removal using a crystallization loop in asymmetric reduction of 4-oxoisophorone by Saccharomyces cerevisiae. Biotechnology and Bioengineering 86: 795-800

Zeikus JG, Jain MK, Elankovan P, (1999), Biotechnology of succinic acid production and markets for derived industrial products. Applied Microbiology and Biotechnology 51: 545-552

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Protein refolding by chromatography

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Supported by	: NWO in the framework of the CASIMIR program	**Period**	: Sept. 2004 – June 2009

DESCRIPTION

Nowadays, several commercially important proteins are being produced by recombinant DNA technology using *Escherichia coli* as the host cell. The over expression of these eukaryotic proteins is commonly accompanied by the formation of inactive and insoluble protein aggregates, also known as inclusion bodies (IBs). To recover the active protein the inclusion bodies are isolated and washed, then solubilized using the proper buffer system and finally the protein in solution is refolded [1]. While the efficiency of the first steps can be relatively high, the refolding yield is limited to a large extend due to the formation of incorrectly folded species and aggregates. To avoid a considerable yield reduction, refolding is generally performed at low protein concentrations. This slows down the rate of aggregation, which has been shown to increase with a power function (≥2) of the initial protein concentration. It has also been suggested that optimum refolding yields can be expected if the starting protein concentration is within the range of 10 to 50 mg/ml. However applying this at large scale production means higher processing volumes, larger equipment, which will inevitably lead to higher processing costs.

The main objective of the project is to investigate the possibility of setting up a refolding system that allows higher yields, minimizes the product losses, operates at higher protein concentrations and is environmentally friendly.

REFERENCES

[1] De Bernadez Clark, E. 2001. Protein refolding for industrial processes. *Current Opinion in Biotechnology*. 12: p 202-207.

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Modeling-based rational protein purification process design

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OSPT theme	: Seperation Processes	**Research school**	: BSDL
Supported by	: NWO-ACTS, B-Basic	**Period**	: Sept. 2006 – Sept. 2009

Description

Rapid advances in molecular biology and drug development result in numerous new biopharmaceutical drugs of high clinical demand. Process development for the production and purification of these drugs is often based on a scale-up of any working laboratory bench-scale methods, even without considering alternative procedures. A typical process development program aims to increase process productivity, particularly by increasing product expression and purification yields, while addressing economics, operability, scalability, robustness, comparability and regulatory risks. The time required for such a thorough process development is often a great practical barrier since there is always extreme pressure to get new drugs into the clinic as soon as possible. Most successful biopharmaceutical companies are therefore moving down to an optimized process development program. A strategic development in the right technology can shorten process development timelines while delivering more highly optimized processes. The most obvious way to address this issue is to develop a platform of tools, techniques and approaches that are broadly applicable to bioparmaceuticals process development. The ambition of this project is to develop such an integrated approach to high-speed bioprocess design, especially bioseparation processes.[1]

The key to successful and efficient protein purification is the selection of the most appropriate purification techniques and their combination in a logical way to obtain the desired purification in the minimum number of steps. A safe and economical process must be found quickly somewhere in an extremely large design space. In this project, a modeling-based rational protein purification process synthesis and design methodology will be developed. At the heart of this methodology is the use of process modeling and optimization tools for rapidly but systematically screening several feasible process options to select and design the best one. In this way, product quality, economics, operability, scalability, robustness and controllability issues are simultaneously addressed without the need for numerous additional experiments. The necessary model input data are acquired by means of a high throughput experimental platform for the fractionation and characterization of crude protein mixtures. The use of the developed methodology will be demonstrated with relevant industrial case studies.

Reference

1. Nfor BK, Ahamed T, Dedem Gv, Wielen LAMvd, Sandt EJAXvd, Eppink M and Ottens M, Design strategies for integrated protein purification processes: Challenges, progress and outlook. *J. Chem. Technol. Biotechnol.* **83:** 124-132 (2008).

TU Delft
Technische Universiteit Delft

High-throughput experimentation for protein crystallization process design

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OSPT theme	: Separation Processes	**Research school**	: BSDL
Supported by	: DC-LST-SIP	**Period**	: March 2007 – March 2011

Description

Novel bio-pharmaceuticals such as monoclonal antibodies (Mab's) and other proteins are increasingly purified and formulated by means of crystallization. Industrial crystallization of proteins is still in its infancy and essentially empirical. The many possible process conditions require substantial experimenting and the result of all labour and costs is too often poor. In addition, other protein-based structures can also be formed, provided that the local degree of supersaturation and the rate-ofchange in supersaturation are carefully controlled. This has led to an entirely new scientific field, with great potential in food, biocatalysis, consumer products and, most importantly, novel pharmaceutical applications. These developments urge for the combined development of High-speed experimental methodologies for the acquisition of relevant thermodynamic and kinetic data for forming proteinbased structures, and to extend concurrently the required theoretical framework that is till essentially based on conventional crystallization/precipitation theory.

Recently it has been postulated that solution conditions for crystallizing proteins correspond to a slightly negative osmotic virial coefficient (B22). This is a key measure for the interaction between components and can be used for prediction and description of the phase behaviour of proteins. A novel method to measure B22 is by Self-interaction chromatography which uses conventional liquid chromatography equipments for quantitative determination of protein self interactions (B22) amenable to high-throughput screening [1]. The aim of this work is to develop a miniaturized, parallel experimental procedure based on the measurement of protein-protein interactions through Self-Interaction Chromatography (SIC) coupled to high-throughput crystallization (nucleation/growth) experiments (HTE). The link between SIC results and HTE screening results will be utilized in developing general design rules for protein crystallization processes. Larger scale crystallization experiments will test the validity of the recommended design rules and will identify scale-up issues.

A major fraction of the next generation biopharmaceuticals will be Mab's and the work will also be focussed on these components, as well as on model proteins and industrially relevant technical enzymes.

Reference

[1] Ahamed T.; Ottens M.; Dedem Gijs W.K van.; Wielen L.A.M van der. Design of self-interacting
chromatography as an analytical tool for predicting protein phase behavior. Journal of Chromatography A, **(2005),** 1089, 111-124.

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Activities of the Product and Process Engineering Group

The PPE group's ambition is to advance the fundamental understanding of fluid mechanics, chemical dynamics and transport phenomena that play a pivotal role in chemical transformations. We want to creatively design new reactors, devices and labs-on-chips that allow us to make materials, such as nanostructured particles, that we could not make before, to integrate chemistry with other functions onto a device, and to improve the rate and accuracy of process monitoring and chemical discovery and analysis. The relation between structure in the fluid mechanics and performance plays an important role in our research.

Enclosure 1

Screening of Supramolecular Catalysts with Droplet-Based Microfluidics

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OSPT theme	:	**Research school**	:
Supported by	: European Union (IEF)	**Period**	: July 2008 – June 2010

Introduction

In this project we are developing new technologies to prepare and screen large catalyst libraries based on supramolecular self-assembled ligands using droplet-based microfluidics. The ultimate goal of this project is to reduce the current bottleneck in reaction screening methodologies and enable the screening of thousands of potential catalysts within hours with microgram quantities of reagents.

Presently, the discovery and design of efficient homogeneous catalysts still relies on time intensive trial-and-error methodology. To overcome these limitations, a new paradigm shift for the discovery of effective ligands relies on the supramolecular self-assembly of libraries of ligands through reversible non-covalent interactions. This approach significantly increases the chemical space within which an optimal ligand set can be found. However, the full potential of this methodology is impeded by current screening techniques which rely on macroscale (mL) trial for all the ligands sets and reaction conditions. Recent advances in droplet-based microfluidics have enabled the effective screening of reaction conditions on a nano- to picoliter scale but have not been applied to screen homogeneous catalysts.

In the schematic diagram of our project depicted in Figure 1, a microfluidic device generates, within nanoliter droplet, arrays of potential catalysts made up of self-assembled ligands around a transition metal. These "catalytic" droplets are the merged with a stream of reactants to form nanoliter-sized reaction vessels which will enable the catalytic activity of the self-assembled catalyst to be evaluated (Figure 2).

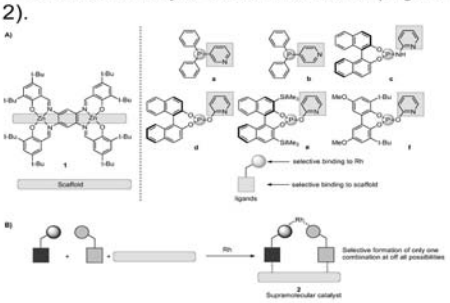

Figure 1. Representative exemple of a a library of self-assembled ligands using the Zn-Pyridine interaction.

Acknowledgement

This research project is carried out in collaboration with Prof. M. T. Kreutzer (TU-Delft) and Prof. M. Bonn (AMOLF). It is financially supported by a Marie Curie Intra-European Fellowship.

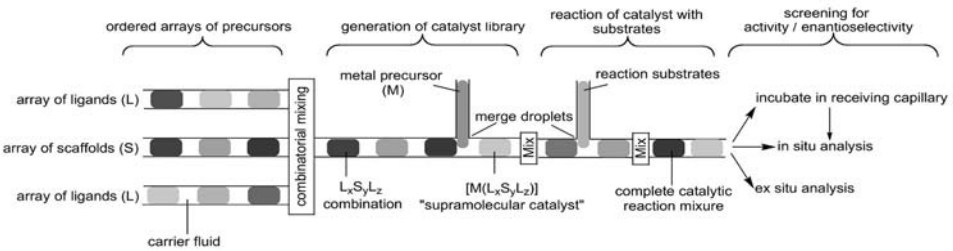

Figure 2. Schematic representation of the microfluidic screening device.

Knowledge-based tools for process systems engineering

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OSPT theme	: Process Systems	**Research school**	: OPST
Supported by	: European Commission, Unilever R&D Vlaardingen, The Netherlands	**Period**	: January 2006 – January 2010

Introduction

Nowadays, the market conditions demand better products at a reduced cost. The complexity of industrial processes requires new techniques for the design of cost-effective plants with flexible control structures. This project aims to develop new model-based techniques for application in process systems engineering.

Scope

The following topics are envisaged:
-integration between design and control: a framework for exploiting the interactions between process design and model-based process control;
-product driven process design, explored by means of an ice-cream case study;
-model reduction: algorithms for development of simplified yet accurate models to be used for the above computationally intensive topics;

Model reduction for processes

The design of both plantwide control structures and optimal dynamic operation require a model of the chemical plant that represents its behavior with sufficient accuracy. In the same time, the complexity of this model should be limited, because the control structure needs repeated solution during a limited amount of time.
This goal can be accomplished by using conventional model order-reduction and model simplification. However, the physical structure of the model is often lost during this process.
We prove the advantage of considering the inherent structure of the process flowsheet when developing reduced-order models to be used during the design of the plantwide control system and for the derivation of the optimal control profiles of a chemical plant. The recommended procedure is to apply the model reduction techniques to individual units of the plant, and then to couple these reduced models. The main advantages of this new approach are: flexibility, ability of retaining the plant nonlinearity, modularity of the reduced model. This procedure has a beneficial effect on the solution time.

Model reduction for products

Further, more complexity emerges when considering a complex product structure. As a case study, the freezing step in the ice cream manufacturing process is studied. Ice cream has a complex structure which includes: air bubbles, fat globules, ice crystals, sugars, proteins etc. The changes that the ice cream suffers in this unit make the freezing a crucial step for the product structuring.
A part of the water in the ice cream mix freezes into ice crystals, air bubbles are whipped into the frozen matrix and stabilized to give a creamy texture to the final product. A first-principles model of the product that takes into account this structure is developed. The model takes into account the essential rate processes and dynamics, as well as the size distribution of the ice crystals and air bubbles. A simple to complex approach is chosen for model implementation. This allows for a gradual verification of the model, as well as for the refinement of the process rate laws. In this way a comprehensive model of the ice cream freezing is obtained. Further, the model is used for application studies. Operational scenarios for product quality control and product design are performed.

Acknowledgement

The financial support of the European Commission (MRTN – CT – 2004 – 512233 – PRISM – Towards Knowledge-Based Processing Systems) and Unilever R&D Vlaardingen, The Netherlands is gratefully acknowledged.

Smart Slurry Systems

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OSPT theme	: Multiphase reactors	Research school	: OSPT
Supported by	: TU Delft	Period	: Oct 2008 – Oct 2012

Introduction

Slurry reactors are examples of three-phase flow systems, which are often used in industry. In these reactors, solid particles can act as catalyst carrier. The gas phase typically contains the reactant that needs to dissolve in the liquid where it can react at the catalyst surface. A well-known example is the Fischer-Tropsch synthesis for producing (bio)fuels. These systems operate at high solids loading, about 25%, at high gas flow rates, giving rise to a complex multiphase flow.

This project aims at developing a methodology for controlling slurry bubble columns in such a way that a desired flow pattern is imposed on the system. By introducing dynamic structuring in slurry bubble columns, modes of operation can be achieved that are out of reach with the current steady-state operation (see Figure 1), which makes it possible to reach a level of efficiency that is not attainable with the current operation.

This project is cooperation between the departments of Chemical Engineering (DelftChemTech) and Multiscale Physics of Delft University of Technology.

Approach

To reach the above goal, we need to be able to detect deviations from the desired set-point in an early stage and take appropriate action to steer the column back to the set-point. We have started first at lab-scale using optical fibre probes. This technique gives direct information about the flow behavior, but is not applicable at industrial scale. Therefore, we have used high-frequency pressure probes in addition. The signals from these probes are more difficult to interpret, but have the advantage that they are very robust and can also be used at industrial scale. To study the flow pattern in high superficial gas velocities we are going to use hot-wire anemometry to measure the liquid velocity. We have started our experiments in both 3-D and 2-D columns.

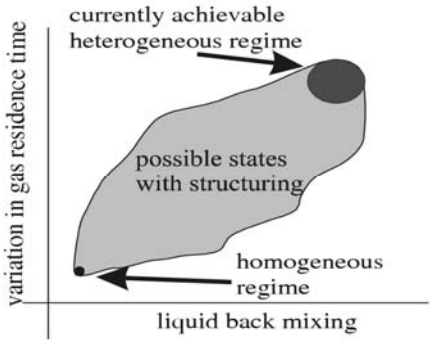

Figure 1. Graphical representation of extended operation modes.

Photocatalytic Oxidation for Drinking Water Treatment in Developing Countries

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OSPT theme	: Green process alternatives	Research school	: OSPT
Supported by	: SenterNovem	Period	: Oct. 2008 – Sep. 2012
Key words	: Drinking water treatment, Photocatalytic oxidation, organic micropollutants		

Introduction

A major challenge facing the developing countries is to provide safe and healthy drinking water, especially in rural areas or areas where drinking water is a scarce resource. Surface water and groundwater contamination is a major environmental problem caused by industrialization and/or agriculture in most of developing countries. Therefore, they need to improve the quality of drinking water. In this concern, advanced oxidation processes (AOPs) (e.g., photocatalytic oxidation (PCO) process) can play an important part in solving this problem.

Problem Definition

Occurrence of organic micropollutants (e.g., pesticides, hormones, pharmaceuticals and industrial chemicals) in surface water and consequently in potential drinking water supplies raises concerns about the safety of the drinking water. The conventional water treatment methods are not sufficient for the destruction of such pollutants, in addition to the formation of carcinogenic and/or mutagenic compounds during the disinfection process. Advanced oxidation processes (AOPs) are very promising methods for the remediation of contaminated surface and ground which contain organic micropollutants especially the non-biodegradable. In some developed countries, photocatalytic AOPs (UV/H_2O_2) are already being used to remove organic micropollutants but these are not suitable for developing countries. We investigate the efficiency of PCO in the removal of organic micropollutants. This looks a more promising AOP for developing countries.

Chemical disinfection has also raised a public health issue: the potential for cancer and reproductive / developmental effects associated with chemical disinfection byproducts (DBPs). Therefore, a combination of disinfection and destruction of the DBPs is proposed using PCO in the presence of solar energy, especially which is available in developing countries.

The use of PCO technology to eliminate organic hazardous chemicals and disinfectant byproducts has attracted considerable interests in recent years. The use of TiO_2 photocatalysts for environmental cleanup has been of great interest since TiO_2 is stable, harmless, and inexpensive and potentially can be activated by solar energy. There are two major problems currently facing the practical application of heterogeneous photocatalytic process: the first one is the separation of catalyst particles when using dispersed catalyst from large water streams and the second is the cost of fixed bed reactors presently used.

Research Aim

The aim of this recently started study is to investigate the efficiency of photocatalytic oxidation in combination with chemical disinfection to produce a safe drinking water, as well as reactor design which makes best use of solar energy.

Optimal Reactor Design for the Thermal Cracking Process

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Introduction

Over the last forty years the thermal cracking technology has developed from an empirical understanding of operations and of the performance of cracking furnaces to on-line use of rigorous models based on first-principles reaction kinetics to optimise plant operations. The models have predictive capability with respect to what is happening in the cracking coils, given the coil configuration and the incoming heat fluxes as well as the feed conditions.

The main issue is whether the fundamental understanding and the reaction kinetic models for steam cracking can be successfully applied to develop new options for thermal cracking units.

Goal Scope

A next step in the development of the thermal cracking process could be that we no longer take the external conditions for granted but try to find the best external conditions and the resulting configurations, exploiting fundamental insights captured in the available first-principles models. That is, that the external conditions are considered as free design decision variables that can be manipulated to find much better cracking performance.

Can we find better (conceptual) designs for the cracking process if we abstract a bit from the current practical limitations and try to identify new routes for development in process operations and in equipment know-how?

Results

To develop new reactor options for thermal cracking of ethane or other light hydrocarbons to lower olefins a fundamental process synthesis approach is taken. Firstly, an optimal reaction path and conditions are targeted, starting from a mechanistic reaction network. Secondly, to implement the optimal reaction path the reactor geometry and equipment are designed. The current results of the research project are related to the development of a targeting approach, for which a new distributive reaction-mixing synthesis model (*d*-RMix) is formulated and applied. The mixing kernel in the model provides freedom to redistribute the reaction mixture along a continuous reaction coordinate to optimize product yield. The model reproduces the results for the Van de Vusse reaction network as obtained by the attainable region theory. When applied to a small reaction network for the conversion of ethane into ethene, it reconfirms the existing result that for this network the plug flow mode at maximum temperature and minimum pressure gives the optimal olefin yield.

Further research

We will continue our research to the fundamentals of the new model, *d*-RMix. The application of the new model to the industrial kinetic scheme, Spyro® will also be pursued.

Acknowledgement

Technip financially supports this project.

Task Based Design Techniques for Crystallisation Processes

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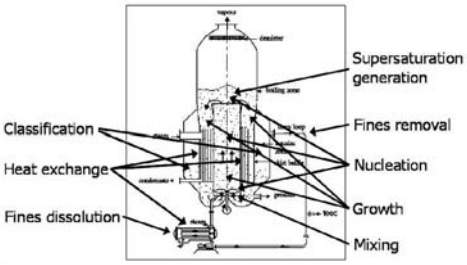
OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: DCSIP, BASF, BP	**Period**	: 10 2005 – 10 2009

Introduction

Crystallisation is the formation of a solid material from a liquid. It is one of the oldest and economically most important separation technologies in chemical industry. Many interacting phenomena occur in industrial crystallizers as shown in the figure below. The complex interplay between the various physical phenomena poses many challenges to the design and operation of crystallisation processes.



Objective

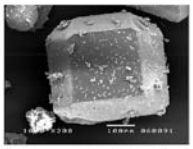
The aim is to identify the basic functions of a crystallisation process, called tasks, and to use them as fundamental building blocks in a design procedure. A two track approach has been followed. First of all experimental facilities are build which are dedicated to isolation of single crystallisation tasks. The aim is to show practical feasibility of the approach. Secondly, optimisation studies demonstrate the increase in flexibility for design and operation.

Experimental

A setup involving a *bubble column* has been constructed to optimize crystal growth. Supersaturation is created by simultaneous cooling and evaporation of the solvent.

The crystals are kept in suspension by the upward velocity of bubbles, eliminating the need for a stirrer or a circulation pump. Seeded batch experiments show that attrition can be minized in contrast to agitated crystallizers. The use of membranes is explored to optimize the generation of supersaturation. A pilot plant setup has been constructed. The results show practical feasibility, but polarization effects reduce the mass flux over the membrane. Finally, ultrasound is used as a tool to isolate and optimize the task nucleation. Experimental results show that utlrasound can be used to generate new particles independent of supersaturation.

Conclusion



The task based design approach is more flexible than current design approaches and creates a wider solution space needed to arrive at innovative crystallisation equipment. Experimental results demonstrate practical feasibility of the approach by the ability to isolsate single crystallisation tasks. Model based optimisation studies show that there is a large increase in flexibility in design and operation of task based crystallisers with novel techniques such as special growth compartments, membranes and ultrasound.

Acknowledgement

DCSIP, BASF and BP

PROBING ACTIVE SITES IN HETEROGENEOUS CATALYSIS USING ATR FT-IR

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OSPT theme	: Multiphase Reactors	Res. school	: NIOK
Supported by	: NWO	Period	: Jan 2007 – Dec 2010

Introduction

To design a chemical reactor, we need a thorough understanding of catalyst behaviour. This means understanding adsorption and desorption for all relevant components and the catalytic reaction time for adsorbed species. For gas phase, some tools to study the above are already available, but for liquid phase, these are still lacking[1]. As many industrial chemical processes are liquid phase, there is significant incentive to develop tools for studying (gas-)liquid phase catalysis.

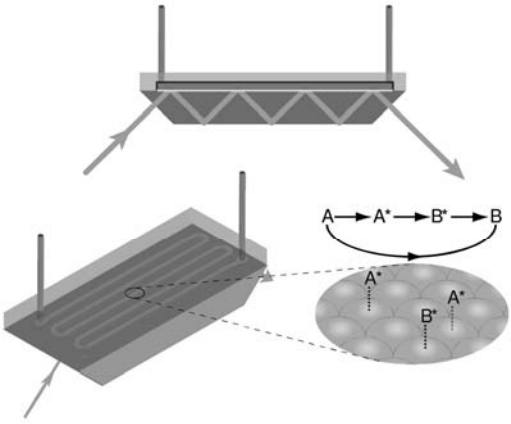

Figure 1: Artist's impression of ATR microreactor

Infrared (IR) spectroscopy is a very suitable method for studying microkinetics, because it allows tracking of functional groups and their interactions with active sites. One IR spectroscopy technique, Attenuated Total Reflection Fourier Transform-IR Spectroscopy (ATR FT-IR), is based on internal reflection of IR light in an IR transparent crystal (see top of Figure 1). It is non-invasive and it probes only a few micrometers from the crystal surface.[2] This means that the technique can be used to study immobilised powders and local conditions around the catalyst are measured.

Microreactor technology is well-suited for determination of catalyst kinetics. The small size of microreactors offers a great measure of control over temperature and flow, as well as the reduction of heat transfer limitations.[3] The reduced size can also be exploited for generation of rapid transients, which opens up new possibilities for study of liquid phase catalysis.

Aim of the project

This project aims to integrate ATR FT-IR spectroscopy with a microreactor for in-situ and operando analysis, to elucidate catalyst behaviour in a qualitative and quantitative manner. To demonstrate the potential of this concept, we will study cylohexanone adsorption on titania, as used in selective photo oxidation as well as noble metal catalysis.

References

1. R. J. Berger et al., Applied Catalysis A-General 342, 3-28 (2008).
2. T. Burgi and A. Baiker, Advances in Catalysis, Vol 50 50, 227-283 (2006).
3. J. deMello, Nature 442, 394-402 (2006).

Acknowledgement

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Furfural production from biomass using green solvents

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OSPT theme	: Energy conversion processes	Research school	: OSPT
Supported by	: TU Delft	Period	: Nov. 2008 – Oct. 2009

Introduction

The decrease in available cheap fossil fuels drives the necessity of exploring feasible alternative routes to supply our modern society with energy carriers and chemicals. Sustainable, biomass-based alternative production methods are therefore getting increased attention. The current biorefinery concept mainly aims at ethanol production from food crops. On the other hand, most of the existing biorefinery processes do not take into account valorization of the natural raw material prior to gasification or fermentation. This feature can be determinant for the economical viability of certain biorefinery units and can also contribute for the development of several sustainable industries free from the oil-dependency.

This collaborative project between the Product & Process Engineering section (DelftChemTech, Applied Sciences) and the Energy Technology Section (Process & Energy, 3mE), presents a new biorefinery process for the production of liquid energy carriers - transportation fuels - based on the coupled production of syngas and the green platform chemical furfural, which is identified as one of the key-platform chemicals for a (near) future biorefinery. To overcome the limitations associated with the furfural current production processes, a new approach is being used based on green solvents. In addition to the development of a technology that is environmentally friendly, the combined use of ionic liquids and supercritical carbon dioxide allows to simplify the pre-treatment of the biomass while increases the yield and the selectivity of the dehydration of C5 sugar (xylose) from the hemi-cellulose part of plant biomass.

Results

The preliminary results obtained so far concerning the dissolution of wheat straw in ionic liquids (Fig. 1) are very promising. In addition to the relative fast dissolution rate of the biomass, the simplicity on the separation and recovery of the pure cellulose from the other biomass components gives confidence in the use of ionic liquids to replace the traditional biomass pre-treatments, such as steam explosion or organosolv.

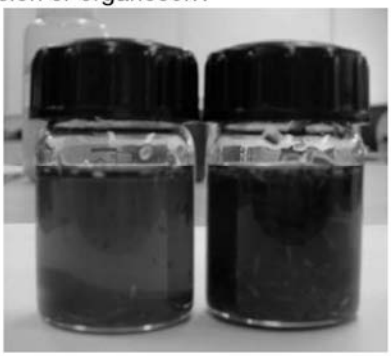

Figure 1. Dissolution of wheat straw in 1-Ethyl-3-methylimidazolium acetate.

Future work

In the next months it is expected to conclude the dissolution studies and to start the work on the new high pressure apparatus.

Acknowledgement

This research project is financially supported by the research centres for Sustainable Industrial Processes and Sustainable Energy of TU Delft.

Structured Packings for Co-Current Gas-Liquid Reactors

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OSPT theme	: GSPT	Research school	: OSPT
Supported by	: STW	Period	: Nov 2007 – Nov 2011

Introduction

Structuring the reaction environment is an attractive way to improve the reactor performance. The increase in reactor performance mainly results from improved heat and mass transfer characteristics of structured flow profiles. Therefore, specifically reactions which are mass transfer limited and/or reactions with large heat effects can benefit from an introduction of structure in the reaction environment.

Multi-scale approach

Different phenomena take place at different length and time-scales. More than often these phenomena cannot be decoupled and have to be taken into account for the assessment of reactor performance. We aim to describe the relevant transport phenomena on reactor scale using a combination of disciplines, including detailed and generalized modeling, and detailed and pilot plant experimental work. This project is carried out in cooperation with Multi-Scale Physics, Catalysis Engineering, and Delft Ingenious Design at Delft University of Technology.

Objective

A thorough understanding of the transport phenomena on all relevant scales of this research and the interaction between the phenomena will aid in the development of a structured reaction environment for multiphase catalyzed reaction systems in tubular fixed bed reactors.

Results

Thus far, we have experimentally shown that several types of structured packings, based on a cross flow geometry, perform much better in terms of heat transfer than randomly packed beds, knitted wire and open foam packings at all investigated gas and liquid flowrates. Furthermore, even higher heat transfer rates were obtained by increasing the isotropy of the system, i.e. by alternating the rotation of the packing elements, which have an anisotropic geometry. Also, it was found that the size of the gap between the packing and the reactor wall plays an important role in the heat transfer.

Current work

Currently, we are investigating the flow profiles in a transparent pseudo 2D set-up in order to study the flow dynamics in an axial reactor cross section. Also, we are investigating the residence time distribution of both the gas and the liquid phase. Finally, a meso-scale model for the assessment of radial heat transport in the tubular fixed bed reactor with structured packings is in development.

Acknowledgement

This research project is carried out with financial support from STW.

Intensified Detection for Microfluidics Bioarrays

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Supported by	: DCSIP	Period	: Dec 2008 – Dec 2009

Introduction

We aim at enhancing mass transfer in microfluidic biosensors, where diffusion is the main limiting step to speed up detection of analytes bound onto surfaces.

In surface-based biosensors, the analyte can be separated from the liquid sample by binding it to a specific receptor grafted on the walls of the capillary. After this binding, the presence of the analyte can be detected by various techniques (fluorescence, infra-red, reflectometry…).

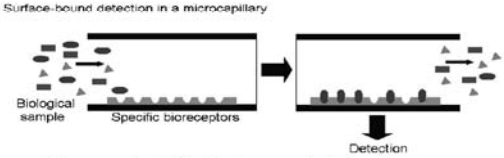

Figure 1. Affinity-based detection on surfaces

However, at microscale dimensions, viscosity rules over the flow regime of liquids characterized by low Reynolds numbers. The laminar flow developing in small capillaries (diameter < 100 microns) prevents the mixing by convection and the homogenization of concentrations in the liquid.[1-3] The migration of molecules to the surface can be very slow and limit the application of microfluidic biosensors, especially for low concentrations (ppm/ppb).

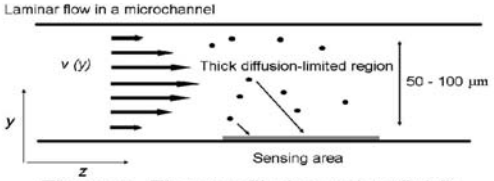

Figure 2. Flow profile in a microfluidic sensor

Approach

With the use of microfluidic devices, surface modification and optical detection techniques, we develop methods to speed up the detection of low-concentration analytes. We want to integrate these methods to existing sensing technologies to provide fast and sensitive analytical systems.

Acknowledgement

This research project is carried out within the framework of the Delft Center for Sustainable Industrial Processes.

References

(1) Squires, T. M.; Messinger, R. J.; Manalis, S. R. Nature Biotechnology 2008, 26, 417-426.
(2) Feldman, H. C.; Sigurdson, M.; Meinhart, C. D. Lab on A Chip 2007, 7, 1553-1559.
(3) Sheehan, P. E.; Whitman, L. J. Nano Letters 2005, 5, 803-807.

Faculty of Mechanical, Maritime and Materials Engineering

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Activities of the Intensified Reaction & Separation Systems Section

Research activities of the IRS group within the department of Process & Energy of the TU Delft focus on intensified reaction and separation systems for the process and energy industries within the framework of sustainability. The interdisciplinary research is aimed at generating fundamental and application-oriented knowledge focusing on locally controlled activation and transport for tailored processes and products. The research addresses Process Intensification approaches in four fundamental domains (spatial, thermodynamic, functional and temporal) and involves a combination of experimental work and modeling studies spanning a broad range of length scales, from molecules to process plants.

Process Intensification

Process Intensification (PI) aims at a paradigm shift in the development of process technology and equipment. PI is the key route towards intrinsic safety, minimal ecologic footprint, effective use of resources and energy and cost-leading technology. Fundamental understanding of the underlying physical principles and the availability of computer-aided design tools enable us for the first time to develop hybrid equipment, integrated processes and miniaturized plants. A core research theme of the IRS group is the integration of alternative forms of energy, such as microwaves, light or ultrasound and the development of appropriate multifunctional reactors, either scaled-up or scaled-down.

Advanced Fluid Separations

The research on fluid separations targets advanced distillation technologies and intensified gas separation systems. By realizing full heat integration within a single piece of equipment our new and patented design for concentric heat-integrated distillation columns (HIDiC) saves up to 75 % energy relative to conventional distillation. In addition, novel technologies for CO_2 capture are developed with a focus on the integrated design of solvents and capture processes as well as (hybrid) membrane separation systems.

Crystalline Product Technology

Most pharmaceuticals and many products of the Fine Chemicals and Food sector are based on crystalline powders with extraordinary high added value but also with very tight specifications. Contrary to most chemicals, crystalline product performance is not merely determined by purity, but also by properties such as crystal size distribution, shape and polymorphism. In industrial practice it remains troublesome to develop crystallization processes for a reproducibly high product quality and with predictive scale-up behavior. A synergetic combination of fundamental crystallization research and crystallization technology development is needed to solve these problems. Our approach is to develop rigorous models of the governing mechanisms at the relevant length scales based on fundamental knowledge. These models are validated using well-defined experiments ranging in size from a droplet under a microscope to a pilot plant of 2000 liter.

Conceptual Design of Reactive Distillation Processes Heated with Microwaves Effects on Thermodynamics and Kinetics

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OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: SenterNovem	**Period**	: May 2007 – May 2011

Introduction

Electromagnetic radiation applied to chemical syntheses has gathered the attention of the scientific and industrial communities in view of possible process intensification. Although the literature regarding intensification effects of microwave radiation (MW) on chemical reactions is remarkably rich, no industrial applications have been reported. In addition to reactions, distillation processes could possibly benefit from MW. Since the two processes (reaction and distillation) separately could possibly be enhanced by MW, the synergy gained by the integration of both operations could be further improved by the application of electromagnetic fields. The objective of this research is to conceptually address the combination of reactive distillation (RD) with MW from an engineering perspective. The heterogeneously catalyzed synthesis of *n*-propyl propionate (ProPro) from 1-propanol (ProOH) and propionic acid (ProAc) was chosen as a test system.

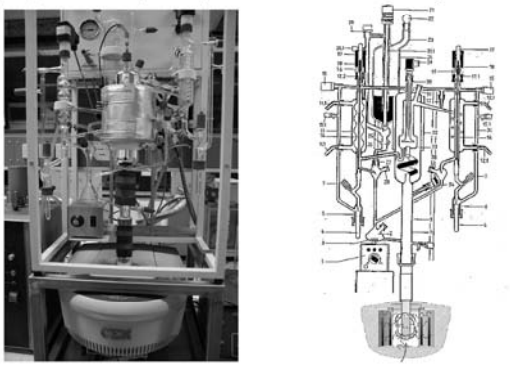

Fig. 1. Glass Fischer Labodest VLE apparatus coupled with a CEM mono-mode microwave cavity for the determination of binary VLE data.

MW radiation and thermodynamics

Theoretical design of RD processes relies in thermodynamic and kinetic data. Thermodynamic data was obtained using a microwave radiated vapor liquid equilibrium (VLE) apparatus to produce VLE curves of the binary pairs showing no difference from curves obtained with the conventionally heated apparatus.

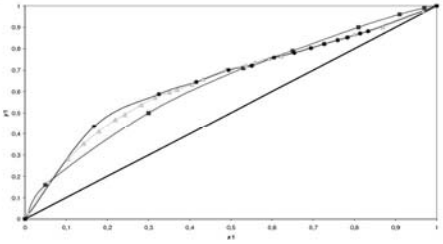

Fig. 2. Binary xy diagram of the binary system ProOH(1)+ProPro(2), (●)this work (microwave heated); (▲)data set 1; (■)data set 2.

MW radiation and kinetics

The commercial reaction is heterogeneously catalyzed using an acidic surface-sulfonated ion exchange resin. Microwaves cannot enhance reactions using ion-exchange resins because the building block of the catalyst is transparent to them. Catalyst selection was based on the material dielectric properties, absorption of electromagnetic radiation and reported reaction results under conventional heating conditions. Reaction kinetics of various metal catalysts will be measured and their behavior examined under microwave radiation in a multimode cavity.

Residue curve mapping (RCM)

The thermodynamic and kinetic data will be incorporated using an analytical tool like residue curve mapping (RCM) to represent concentration profiles at infinite reflux conditions and to envision the feasibility of a specific RD column configuration.

Acknowledgements

The Dutch Ministry of Economic Affairs and SenterNovem are acknowledged for their financial support through the EOS-LT 04033 project grant. This project runs in collaboration with CEM, Uni. Dortmund, Uni. Stuttgart, DSM and Akzo Nobel.

Keywords: Microwaves, Reactive distillation, Process intensification.

Product and process development of Mg-Al layered double hydroxides

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OSPT theme	: IRSS	Research school	: OSPT
Supported by	: TU Delft, Akzo Nobel, Senter Novem	Period	: September 2006 - August 2010

Introduction

Mg-Al layered double hydroxides (Mg-Al LDH) are stacks of magnesium and aluminum hydroxides layers with the interlayer water and anions compensating the charges. A novel method to produce Mg-Al LDH is by hydrothermal synthesis. This method has advantages in its simple processing, no waste production and the formation of two polytype depending on its process condition.

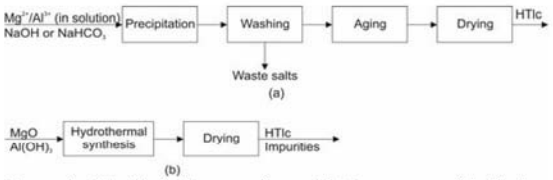

Figure 1: (a) Block diagram of precipitation process (b) Block diagram of hydrothermal synthesis process

The aim of the project is to optimize the synthesis condition of both polytypes and to study the reaction mechanism and kinetics. This project is expected to provide a clear picture on the relation between chemical and physical properties of the Mg-Al LDH to the process conditions and application properties.

Hydrothermal Synthesis

The starting material of this novel method is slurry of aluminum trihydroxide and magnesium oxide in water. The synthesis is performed in an autoclave at 90℃ and 170 ℃ to produce polytype 3R1 and 3R2, respectively. Pre-treatment by grinding is an essential step to increase the reaction kinetics.

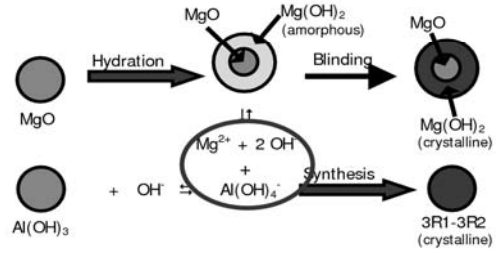

Figure 2: Reaction mechanism

An amorphous brucite layer is formed on the surface of the MgO particles. This amorphous layer slowly converts into crystalline brucite with lower solubility. If the particle size of the MgO is not small enough, the MgO can be blinded by a thin layer of brucite. This process in particular hampers the conversion of brucite and ATH into HTlc at a prolonged exposure to the water before the temperature is increased and reaction takes place.

Polytype Transformation

The Mg-Al LDH polytypes have different layer stacking sequences, with a different interlayer spacing. Polytype 3R2 has a shorter interlayer distance and thus a more compact crystal structure. Since the difference in structure can potentially provide distinct performance characteristics of each polytype, it is of interest to determine the stability of both polytypes at different temperatures and their transformation accordingly.

Polytype 3R1 is stable at lower temperature, while polytype 3R2 at higher temperature. From the study it was found that the transition temperature is at 110 ℃. The transformation of polytype 3R1 to polytype 3R2 is hampered by the carbonate ion in the interlayer. The transformation kinetics from 3R1 to 3R2 above 110 ℃ increases with temperature, and is faster than the transformation from 3R2 to 3R1 below 110 ℃. SEM pictures depicted different shapes of the 3R1 and 3R2 polytype crystals after transformation, so this transformation is solvent mediated. Solid phase transformation has indeed not been observed.

Project Outlook

The project is now focused on the determination of the structure of 3R2 polytype and also on its possible applications.

Acknowledgement

This research project is carried out in cooperation with AkzoNobel. It is financially supported by Senter Novem.

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High throughput experimentation for protein crystallization process design

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OSPT theme	: Separation Technology	**Research school**	:
Supported by	: DRC-LST-SIP	**Period**	: March 2007 – March 2011

Introduction

Novel bio-pharmaceuticals such as monoclonal antibodies (Mab's) and other proteins are increasingly purified and formulated by means of crystallization. Industrial crystallization of proteins is still in its infancy and essentially empirical. The many possible process conditions require substantial experimenting and the result of all labor and costs is too often poor. In addition, other protein-based structures can also be formed, provided that the local degree of supersaturation and the rate-of-change in supersaturation are carefully controlled.

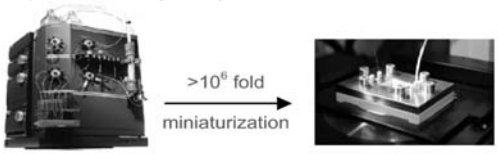
This has led to an entirely new scientific field, with great potential in food, biocatalysis, consumer products and, most importantly, novel pharmaceutical applications. These developments urge for the combined development of High-speed experimental methodologies for the acquisition of relevant thermodynamic and kinetic data for forming protein-based structures, and to extend concurrently the required theoretical framework that is till essentially based on conventional crystallization/precipitation theory.

Recently it has been hypothesized that solution conditions for crystallizing proteins correspond to a slightly negative osmotic virial coefficient (B_{22}). This is a key measure for the interaction between components and can be used for prediction and description of the phase behaviour of proteins.

A novel method to measure B_{22} is by Self-interaction chromatography (SIC) which uses conventional liquid chromatography equipments for quantitative determination of protein self interactions (B_{22}) amenable to high-throughput screening.

Objectives

The aim of this work is to develop a miniaturized, parallel experimental procedure based on the measurement of protein-protein interactions through Self-Interaction Chromatography (SIC) coupled to high-throughput crystallization (nucleation / growth) experiments (HTE).



Conventional SIC — SIC on Microchip

The link between SIC results and HTE screening results will be utilized in developing general design rules for protein crystallization processes. Larger scale crystallization experiments will test the validity of the recommended design rules and will identify scale-up issues. A major fraction of the next generation biopharmaceuticals will be Mab's and the work will also be focussed on these components, as well as on model proteins and industrially relevant technical enzymes.

Acknowledgement

This research project is carried out within the framework of the DRC-LST-SIP programme of the TU Delft.

Design of High Race Algae Ponds based on Computational Fluid Dynamic (CFD)

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OSPT theme	: Process intensification	Research school	: -
Supported by	: SenterNovem, FeyeCon, Ingrepro	Period	: January 2009-January 2010

Introduction

For large scale production of high density biomass of microalgae, an open pond (high raceways algae pond) is still the most suitable among other photobioreactors. Besides its simplicity in control, this pond is relatively cheaper since it mainly uses sunlight for photosynthetic of microalgae. However, the common drawback of this algae pond is lower productivity of microalgae due to un-mixing region (death zone), undistributed sunlight to algae culture, cell sedimentations and shear stress due to hydrodynamic flow. Therefore, this research aims to design and to intensify an open pond based on hydrodynamic flow to overcome problems in the existing one. One of the proposed intensification in this pond is implementation of light distribution system (LEF) which is purposed to distribute the sunlight more inside to the algae culture.

Current state

The computational fluid dynamic (CFD) is being used to simulate the hydrodynamic flow in an open pond (Figure 1). Using this modeling approach, we could identify the un-mixing zones which are the most common problem in the open pond. Moreover, the shear stress due to turbulence was evaluated. The depth culture, and ratio between width and length of pond has been incorporated also in the design of new pond.

The sunlight distribution system (LEF) is evaluated for their optimal spacing and their geometrical effect to hydrodynamic flow.

Future work

The current work will be extended to the evaluation of:

- Particle (cell) settling in the open pond
- Enhancement of CO2 transfer
- Coupling of hydrodynamic flow to growth rate model(photosynthetic) to increase the productivity
- Implementation of LEF (light distribution system) in open pond

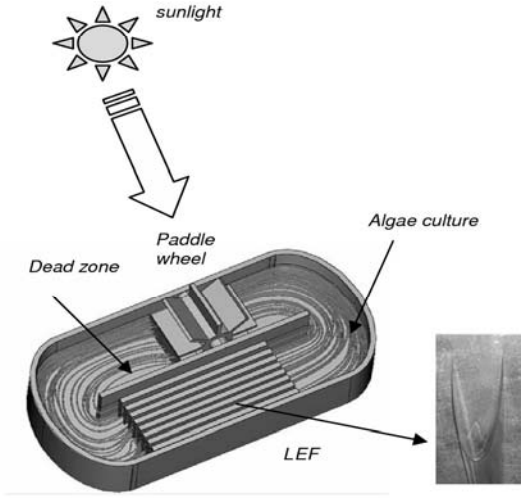

Figure 1. Streamline of velocity field in the open pond implemented with LEF.

Acknowledgement

We acknowledge SenterNovem, FeyeCon and Ingrepro for their financially support and collaborations.

Intelligent Observer and Control for Pharmaceutical Batch Crystallization

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OSPT theme	: Separation Processes	Research school	: OSPT
Supported by	: DSTI	Period	: February 2008 – February 2012

Introduction:

Batch cooling crystallization is an important step in pharmaceutical industry that determines the final product quality. The control of the crystallization process to a large extent is still done with trial and error. This results in large variations in crystal quality. FDA has realised that the lack of understanding and innovation is stifling the progress of process improvement. Hence they have reviewed cGMP and initiated PAT (Process Analytical Technology) initiative, which allows companies to specify a range in conditions they might use to manipulate crystallization towards a stable product quality, using preferably on-line analytical tools and control

Objectives:

The objective of this project is to demonstrate the feasibility of on-line control of seeded batch cooling crystallization in a pharmaceutical plant. The focus will be to rapidly characterize crystallization processes (without a-priori knowledge of the crystallizing systems.) based on combination of data from different online sensors arranged in form of a skid.

Experimental:

Testing of online sensors was carried out on lab and pilot plant scale. Feasibility study of Liquisonic lab probe based on ultrasound, of ATR FTIR and FT NIR probes based on Infra red was carried out. Image analysis algorithm was developed based on images captured by the imaging probe.

Experimental Set-up:

The experimental set up consisted of a 1.2L stirred jacketed glass vessel attached to a thermostatic bath with possibility of external temperature control with help of Pt-100. The probes were inserted in the vessel from the lid. Several experiments were conducted to calibrate the probe, to determine solubility curve, to determine the cloud point and to determine the de-supersaturation curve.

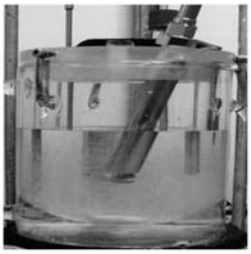

Fig.1: ATR FTIR, FT NIR sensors in crystallizer

Results and Discussions:

Based on the tests conducted Mid and Near Infrared spectroscopic techniques were found suitable for monitoring crystallization processes while technique based on ultra sound failed after nucleation. The image processing algorithm has showed some promising results as shown below but substantial amount of work is foreseen before it could be used in process conditions

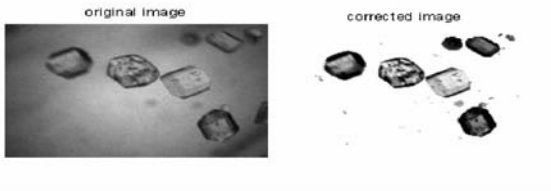

Fig.2: Result of image analysis algorithm.

Acknowledgement:

This research project is carried in the frameworks of DSTI

INFLUENCE OF MICROWAVE IRRADIATION ON POLYESTERIFICATION REACTION AND MEMBRANE SEPARATION

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Introduction

Condensation polymerization processes have a significant importance for the chemical industry. The current industrial production of the polyester resins is performed at high temperature and leads to the generation of contaminated water, which has to be condensed and incinerated. This process is slow with high-energy consumption.

Aims

The main aim of the project is focused on fundamental research to explore the potential options of intensification of polycondensation process. In recent years considerable research efforts have been directed towards applying microwave heating to perform polymer synthesis. There are many studies on the applications of microwave irradiation for the heating of chemical reaction under different process conditions. Additionally the microwave irradiation is a promising alternative energy for mass transport enhancement in membranes and for the controlled membrane synthesis under microwave irradiation.

Experimental:

1) Chemical reaction

This research is focused on microwave selective heating phenomena and its influence on a polyesterification process. As a model reaction a polyesterification reaction of dicarboxylic acid with diol was selected. This reaction is reversible and it is necessary to remove the by-product water from the reaction mixture to shift reaction equilibrium towards the product side. The impact of microwave heating on formation of the by-product, water, and its removal from the reactor is examined.

$$n\ \mathrm{HOOC\text{-}R^1\text{-}COOH} + n\ \mathrm{HO\text{-}R^2\text{-}OH} \leftrightarrow \mathrm{H\text{-}(OOC\text{-}R^1\text{-}COO\text{-}R^2)_n\text{-}OH} + (2n\text{-}1)\ \mathrm{H_2O}\uparrow$$

2) Membrane separation

Membrane science has a leading role in process improvement and it is considered one of the main strategies towards the implementation of enhanced separation technologies. Therefore the second part of the research is focused on the fundamental research on the investigation of influence of microwave irradiation on membrane separation. Series experiments are planned with conventional heating and microwave heating.

Key words: polycondensation, microwaves, membrane separation

Acknowledgements

This research project is carried out in collaboration with CEM Corporation, DSM, Uni. Dortmund and Uni. Stuttgart.
It is financially supported by SenterNovem (EOS-LT 04033 project grant). We also thank Akzo Nobel for the support on this project.

Task Based Design Techniques for Crystallisation Processes

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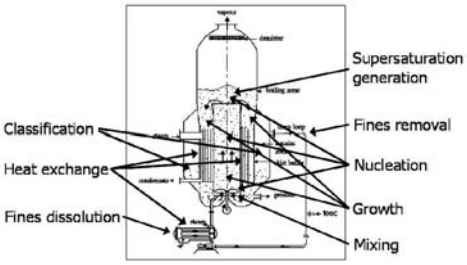
OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: DCSIP, BASF, BP	**Period**	: 10 2005 – 10 2009

Introduction

Crystallisation is the formation of a solid material from a liquid. It is one of the oldest and economically most important separation technologies in chemical industry. Many interacting phenomena occur in industrial crystallizers as shown in the figure below. The complex interplay between the various physical phenomena poses many challenges to the design and operation of crystallisation processes.



Objective

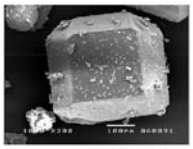
The aim is to identify the basic functions of a crystallisation process, called tasks, and to use them as fundamental building blocks in a design procedure. A two track approach has been followed. First of all experimental facilities are build which are dedicated to isolation of single crystallisation tasks. The aim is to show practical feasibility of the approach. Secondly, optimisation studies demonstrate the increase in flexibility for design and operation.

Experimental

A setup involving a *bubble column* has been constructed to optimize crystal growth. Supersaturation is created by simultaneous cooling and evaporation of the solvent.

The crystals are kept in suspension by the upward velocity of bubbles, eliminating the need for a stirrer or a circulation pump. Seeded batch experiments show that attrition can be minized in contrast to agitated crystallizers. The use of membranes is explored to optimize the generation of supersaturation. A pilot plant setup has been constructed. The results show practical feasibility, but polarization effects reduce the mass flux over the membrane. Finally, ultrasound is used as a tool to isolate and optimize the task nucleation. Experimental results show that utlrasound can be used to generate new particles independent of supersaturation.

Conclusion



The task based design approach is more flexible than current design approaches and creates a wider solution space needed to arrive at innovative crystallisation equipment. Experimental results demonstrate practical feasibility of the approach by the ability to isolsate single crystallisation tasks. Model based optimisation studies show that there is a large increase in flexibility in design and operation of task based crystallisers with novel techniques such as special growth compartments, membranes and ultrasound.

Acknowledgement

DCSIP, BASF and BP

Integrated synthesis and extraction of fatty acid esters from milk fat using supercritical CO_2

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OSPT theme	: Separation Technology	Research school	: OSPT
Supported by	: Senter Novem	Period	: April 2006 – April 2010

Introduction

Fatty acid ethyl esters (FAEE) have a wide range of commercial uses. Medium and long-chain FAEE are used as ingredients in cosmetic and food industry. Short-chain FAEE are used as aromas and flavouring agents. FAEE can be produced by transesterification of natural fats or oils with ethanol (ethanolysis), catalyzed chemically or by lipases (acylglycerol hydrolases). Milk fat is a natural animal fat containing ca. 20 mol% of short-chain fatty acids (C4-C10) and 80 mol% of medium and long chain fatty acids (C12-C18). Milk fat can be converted by ethanolysis into a mixture of FAEE of different chain lengths, which can be separated using supercritical carbon dioxide ($scCO_2$).

$ScCO_2$ is an attractive solvent for the processing of foodstuff, due to its wide availability and lack of toxicity. Its particular properties (gas-like viscosity, liquid-like density) make it suitable both as a reaction and extraction solvent. In addition, it can be separated from solutes by simple depressurization.

Experimental work

Mixtures of FAEE are synthesized from milk fat by lipase-catalyzed ethanolysis, and the lighter FAEE (short-chain) are extracted in-situ by a $scCO_2$ stream (Figure 1). The integrated reactor-separator is operated in semi continuous mode, allowing continuous or cyclic feed of ethanol and $scCO_2$.

The effect of reactants molar ratio, extraction pressure and operation mode were investigated.

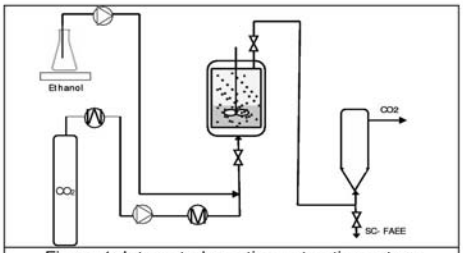

Figure 1: Integrated reaction-extraction set-up

Results

In-situ product removal proved to increase the lipase production rate of FAEE, as shown in Figure 2. The amount and composition of the FAEE extract obtained in the separator varied as function of the extraction pressure. Integration of reaction extraction improved the separation factor of short-chain fatty acids, by a combined effect of the enhanced lipase selectivity and the extraction solvent selectivity.

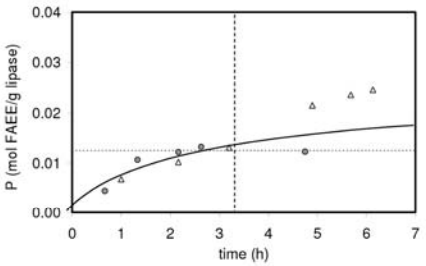

Figure 2: Lipase productivity in a reference ethanolysis reaction (solid line) and in a ethanolysis with in-situ product removal (white triangles).

Acknowledgement

This research project is carried out as a cooperation between TU Delft, Feyecon and Kievit-Friesland Foods, and it is financially supported by Senter Novem.

Model-based Optimal Control of Industrial Batch Crystallization Processes

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OSPT theme	: Separation Processes	**Research schools**	: OSPT, DISC
Supported by	: SenterNovem, BASF, BP	**Period**	: August 2006 – August 2010

Introduction

Batch crystallisation processes are of paramount importance in the production of pharmaceuticals, food and speciality chemicals in the highly competitive chemical industry. Due to low-volume and high-value of such chemicals, interest in the optimal operation of batch crystallisation processes has substantially grown in the recent years.

The control of batch crystallization processes is often a challenging task due to their highly non-linear behavior, plant-model mismatch, irreproducible start-up, unmeasured process disturbances and lack of reliable measurements for the system states. Such limitations often render the use of off-line optimized profiles impractical for industrial applications. This research project therefore aims at the development of model-based optimal control strategies for on-line computation of the optimal operating policy in a seeded batch crystallization process.

Current State

A feedback multilayer control structure has been developed, depicted in Figure 1. An extended Luenberger-type observer is embedded in this framework to account for the plant-model mismatch and enable disturbance handling. The core component of the control architecture is the dynamic optimizer in which a constrained optimal control problem is solved on-line by simultaneous optimization approach. The dynamic optimizer and the observer both make use of a non-linear process model.

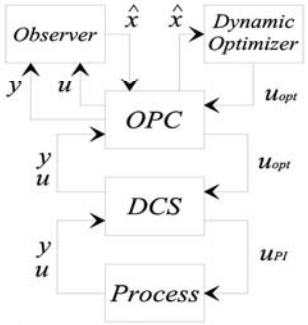

Figure 1: The proposed advanced control structure.

Real-time implementations of the proposed optimal control strategy on a semi-industrial 75-liter draft tube crystallizer have led to a substantial increase of 60% in the amount of crystals produced in a batch while the quality aspects of the product are also sustained. The latter is due to the effective constraint tracking realized by the dynamic optimizer.

Future Work

The current work will be extended to optimal control of an 1100-liter draft tube baffle crystallizer equipped with a fines removal loop that offers an extra degree of freedom to better control the crystal size distribution of the product.

Acknowledgements

The financial support of SenterNovem, BASF and BP is gratefully acknowledged.

Application of Smart moving Process Environment Actuators and Sensors (Smart PEAS) in process industry

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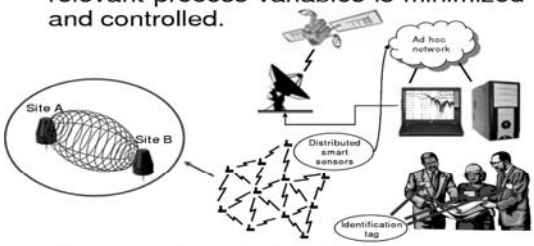
OSPT theme	: Separation Processes	Research school	: OSPT
Supported by	: STW	Period	: Sept.2007– Sept.2011

Introduction

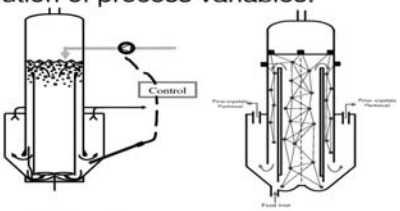
The control of chemical reactions and separation systems is of great importance in the process industry. The presence of spatial distributions of process conditions caused by insufficient mixing or non-ideal flow patterns can have severe effects on the quality of chemical products. Safe operation of chemical processes and a high product quality can be ensured only when the maldistribution of relevant process variables is minimized and controlled.



The current control methods are based on data obtained from a limited number of sensors at fixed positions in the vessel and therefore not capable of fully resolving the problems associated with non ideal mixing. The application of smart sensors can offer a breakthrough in control techniques by enabling the local measurements and the three-dimensional profiling of different parameters inside process equipment. Moreover, smart sensor will provide local data on the actual condition within equipment that is of importance for the validation of process models. In case of UWB-based sensors, the position of sensors can be predicted using e.g. TOA or AOA techniques.

Methodology

The main idea here is to float smart sensors inside the process equipment. Such sensors apply UWB technology to transmit the online data with very low power and to calculate the position of sensors. For the first demonstration the combination of recording sensors with visual tracking techniques can be applied for the offline analysis of spatial distribution of process variables.



Project Objectives

- Investigation of the state of art for smart sensors
- Identification of most promising applications and determining the challenges for sensor implementation
- Development of prototypes of peas for process model validation
- PEAS material hydrodynamic design
- Investigation of the application of recording sensors for off-line analysis
- Investigation of alternative tracking techniques
- Design of an experimental setup for analysis of flow behavior, sensor dynamics and flow model validation
- Process modeling and CFD calculations

Acknowledgement

This project is in cooperation with Siemens, 3UB, TNO, Westfield Business Development, Unilever & NIZO. The financial support of STW is gratefully acknowledged.

Plasma aided crystallisation for high quality nanoparticles

TU Delft

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OSPT theme	: IRSS	Research school	: OSPT
Supported by	: TU Delft, TNO	Period	: June 2008 - June 2012

Introduction

Nanomaterials are at the leading edge of the rapidly developing field of nanotechnology. Nanoparticles have wide variety of potential applications from biology, pharmaceutical industry, electronic industry or military applications. They can have much better properties than bigger particles, since nanoparticles have different chemical and physical properties.

Conventional processes are not suited for nanoparticles production because the quality of the product is low or the particle size distribution is wide. Our research is focused on innovative nanoparticle production processes. Using cold plasma as an external energy source helps in making high quality nanoparticles with equal size. We use non-thermal Dielectric Barrier Discharge (plasma) with evaporative crystallization in order to achieve our goals. However, the cold plasma has more effects than just energy delivery to the solution droplets.

The project is also focused to fundamental understanding of a non-thermal plasma process for synthesis of crystalline organic nanoparticles. This type of technique is applicable to synthesis of nano-sized pharmaceuticals or other materials and reinforcement of

Keywords

Plasma, DBD, evaporation crystallization, nanoparticle

Acknowledgement

This research project is carried out in cooperation with TNO Defense, Safety and Security.

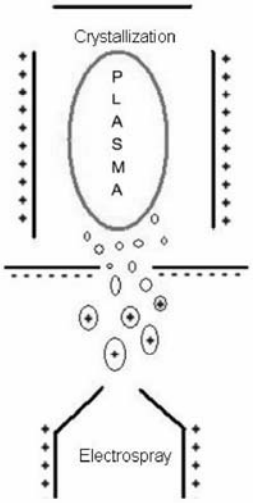

Figure: The operation of the setup

How the setup works

A nebulizer (e.g. electrospray) would create charged mist what would be accelerated to the DBD. Due to Coulomb-explosions the nanoparticles would be created in the plasma. As for the collection an electrostatic collector would be used. It can be done by using grounded metal walls above the plasma part. The grounded collector would attract the charged particles and neutralize them. The walls would be resonated by mechanical vibration or electromagnetic field. Thus the attracted, neutralized nanoparticles could fall down and be stored in the lower region of the collector.

Project Outlook

The project is now focused on the design of a novel setup.

Enhancement of Light Utilization Efficiency Inside of Microalgae Cultivation Systems by Using Novel Light Distributors

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OSPT theme	: Process Intensification	**Period**	: Jan. 2009 – Jan. 2010
Supported by	: SenterNovem, Feyecon, Ingrepro		

Introduction

Global warming due to increased carbon dioxide concentration in the atmosphere is receiving a great deal of attention these days. One attractive option to limit the carbon dioxide entering the atmosphere is biological sequestration of carbon dioxide by using photosynthetic cells including microalgae and bacteria. Since these kinds of cells accumulate large amounts of lipids they are considered as a source of 3rd generation of biofuel. In spite of great interest of microalgal biodiesel the large scale cultivation is limited by low productivity of cells inside of cultivation systems.

The biomass productivity of a microalgae culture in a photobioreactor is a function of light input and photon efficiency. In the conventional cultivation systems one of the major drawbacks for commercial cultivation is the poor distribution of sunlight irradiance inside of cultivation systems which makes photoinhibition and photolimitation phenomena inside of culture and these effects significantly reduce the biomass productivity. In this research project a novel light distribution system for improvement of sunlight utilization inside of cultivation system is proposed to enhance the biomass productivity.

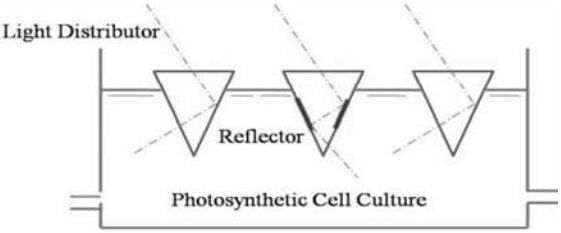

Figure 1: Schematic view of Light Distributors

Current State

In order to avoid the photoinhibition effect inside of cultivation system different distributor designs have been modeled to dilute the sunlight irradiance and then the uniformity of irradiance distribution inside of culture and over the distributors' surfaces was investigated.

Future Work

The sun path on the sky will be modeled and the effects of irradiance variation through the day and the year on distributer design will be investigated and the optimized design and dimensions for a specific location will be proposed. In the final step the effect of light distributors on biomass productivity will be modeled.

Acknowledgement

The financial support of SenterNovem, Feyecon and Ingrepro is highly acknowledged.

Thermodynamics of Hyperbranched Polymers - CO2 - Systems: Facilitating Thermal Separation Processes

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OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: Shell - Global Solutions	**Period**	: 10 2006 – 10 2010

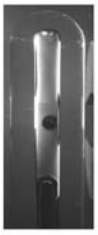
Introduction

Hyperbranched polymers (HBPs) are highly branched, polydisperse, macromolecules that can be synthesized via one-step reactions and have no measurable vapor pressure. The properties of hyperbranched polymers are highly tunable due to the fact, that core and shell groups might be modified individually. Opposed to linear polymers HBPs inhibit a globular shape and are liquids at room temperature. It could be shown that HBPs selectively alter the fugacities in a mixture. Thus, they possess a high potential to being used as process solvents.

Objective

Develop an understanding of the phase behavior of branched molecules. Therefore, determine the influence of molecular weight as well as varying end groups on the phase equilibrium with CO_2. VLE measurements are performed and the thus obtained data is used to develop an equation of state, suitable to describe the properties of branched molecules.

Experimentals



The bubble point pressures of HBP + MeOH + CO_2 (HBP: Polyglycerol Mw = 2000 g.mol-1, Polyglycerol Mw = 5600 g.mol-1) systems with fixed compositions are measured using the Cailletet apparatus. With this synthetic method the phase change due to small increases in pressure is determined visually at constant temperature. The pressure at which the last bubble disappears is the bubble point pressure of the mixture at a given T.

Modeling

The modeling has been done within the PC-Saft framework. Within this equation of state (EOS) molecules are assumed to consist of freely jointed spherical segments. A perturbation has been added to account for the formation of articulation tetramers with fixed angles. This EOS is called bPCP-Saft.

Results

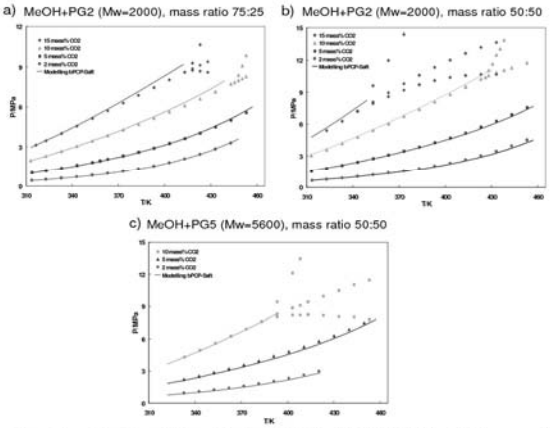


Figure: Vapor-liquid equilibrium data for: a) CO2 + [MeOH+PG2 (Mw=2000), mass ratio 75:25], b) CO2 + [MeOH+PG2 (Mw=2000), mass ratio 50:50], c) CO2 + [MeOH+PG5 (Mw=5600), mass ratio 50:50]. Symbols represent the experimental data with CO2 concentrations (wt%) as indicated. Lines are given by the model bPCP-Saft.

Conclusions

- Decreasing polymer concentrations shift the demixing to higher temperatures
- Increasing polymer molecular weigth shifts the demixing to lower temperatures
- Decreasing MeOH concentration shifts the phase envelope to higher pressures
- An EOS was developed that accounts for the structure of the polymer

Development of new model based crystallization concepts

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OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: BASF, BP, DCSIP	**Period**	: Oct. 2008 – Oct. 2012

Introduction

Many interacting physical phenomena occur in crystallisation processes, involving nucleation, growth, attrition, agglomeration and classification of crystals. The operating conditions and the spatial staging of the phenomena jointly determine the properties of the crystal particles in a non-uniform manner. The complex interplay between the various physical phenomena poses many challenges to the design and operation of crystallisation processes.

The CrysCODE II project

In the CrysCODE II project a task based design procedure is developed as a team effort aiming at improved product quality and more flexible process operation and design. A task is defined as an intentional transformation of matter from a given state to a desired state driven by physical phenomena. One of the key challenges of the project is to isolate single crystallization tasks which make optimization of that particular task possible. In that perspective several experimental setups dedicated to single crystallization tasks will be designed and tested.

Objective

Development of new behavioral models for specific crystallization task which predict the task behavior as function of the process conditions both in terms of the desirable as well as the undesirable crystallization phenomena.

The main specific crystallization tasks that are isolated and modeled are:

- *The growth behavior* – the task crystal growth can be isolated by minimizing the shear stress. One of the most promising setup for minimizing attrition and approaching ideal growth consist of an air lift crystallizer. The growth behavior, the attrition and the supersaturation are functions of process conditions (air flow, temperature, bubbles dimensions, pressure). A model is developed for describing the three - phase flows in the air lift crystallizer and for optimizing the growth function of the process conditions.
- *The nucleation/seed generation* – the task nucleation can be isolated by inducing it at very low supersaturation. One of the most promising tools for inducing and controlling nucleation is ultrasound. The quality of the generated crystals (seeds) can be controlled and optimized by manipulating the power input, the irradiation time, the ultrasound frequency, the temperature and the vessel geometry.

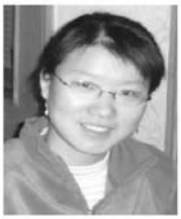
Nikon Optiphot 200 microscope

Pilot scale crystallizer

Acknowledgement

This research project is supported by BASF, BP and DCSIP.

Study for underground separation of sour gases from natural gas



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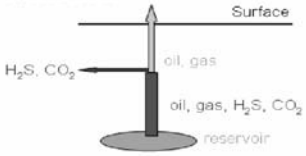
OSPT theme	: Separation Technology	Research school	: OSPT
Supported by	: TNO, Shell, TUDelft	Period	: 02.2006 – 02.2010

Introduction

Crude oil and hydrocarbon gas streams may contain high levels of CO_2 and/or H_2S as contaminants. Opportunities for disposal of the unwanted components include subsurface sequestration of these substances.



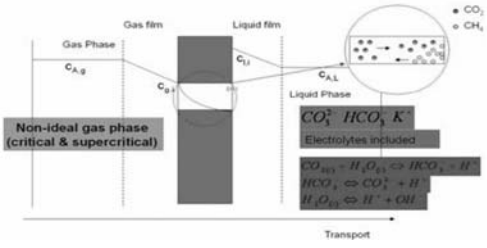
Technologies evaluation

Absorption/desorption processes were elaborated for the treatment of natural gas. The distinct advantage of the fluid processes is the robustness under severe conditions of the reservoir. There are different choices for the solvent selection.

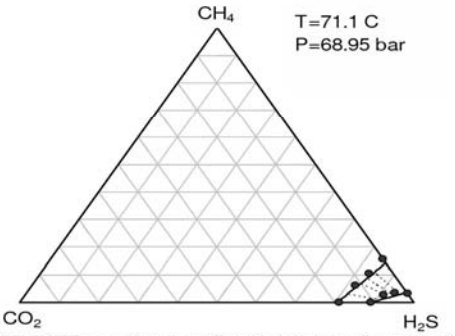
Solvent selection

The use of mildly basic aqueous electrolyte solutions, for example K_2CO_3 aqueous solution as absorbents leads to a balanced absorption as well as desorption behavior under the conditions at hand.

Evaluation of membrane absorption process

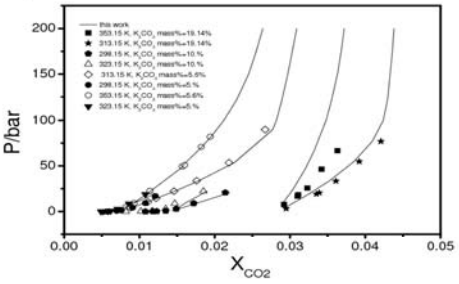


Gas phase containing sour gas at high pressure



PCP-SAFT equation is well suited to describe natural gas systems containing acid gas at elevated pressure.

Vapor-liquid Equilibrium for H_2S/CO_2 in aqueous solution



Peng-Robinsen EOS combined with an extended UNIQUAC model solves phase equilibrium and reaction equilibrium simultaneously.

Conclusions

Membrane absorber appears promising for separation process undergroud. A detailed mass transfer model using a Maxwell-Stefan approach including combined phase & reaction equilibrium is currently being developed.

HIDiC II: Heat Integrated Distillation Column

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OSPT theme	: Process Intensification	Research school	: OSPT
Supported by	: EOS	Period	: March 2009 – August 2010
Project Partners	: ECN, Sulzer, BASF, Bayer Technology Services		

Introduction

Distillation is by far the most important separation technology in the chemical and refinery industry. However, large energy degradation takes place in tge process. High temperature heat is introduced in the reboiler, which is withdrawn at lower temperature from the condenser, resulting in an exergy efficiency of less than 10%. The scope for improvement is evident.

HIDiC

A promising alternative is the Heat Integrated Distillation Column (HIDiC). The idea is shown in Figure 1. The distillation column is divided in two parts, a stripping section (the bottom part of a normal distillation column) and a rectification section. The rectification section is operated at higher pressure (and therefore higher temperature) than the stripping section. Heat coupling between the two columns results in a heat flux from the rectification to the stripping section. The corresponding evaporation in the stripping section greatly reduces reboiler requirements and condensation in the rectification section reduces the condenser requirements.

Two alternative implementations of the HIDiC are being studied, as described in the following sections.

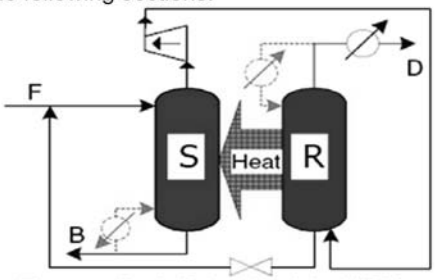

Figure 1: Basic Principle of the HIDiC

Concentric Tray (CT) HIDiC

In the CT HIDiC a concentric rectification column is placed within a concentric stripping section. Heat transfer is achieved by implementation of heat panels on each stripping tray, which are connected to the corresponding tray on the rectifier side. A pilot-scale CT HIDiC (0,8m diameter) was designed and constructed at TU Delft to proof this principle works on semi-industrial scale and to generate essential experimental data for industrial application.

Concentric Tray Column

Plate-Fin (PF) HIDiC

The idea behind the PF-HIDiC (ECN design) is opposite from that behind the CT-HIDiC; instead of adding heat exchange area in a distillation column, distillation is carried out in a plate-fin heat exchanger.

Extensive modelling has shown that this idea should be feasible, with large energy savings being predicted. A bench-scale experimental set-up was designed and constructed as a proof of principle.

Integration of fermentation and crystallization

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Period : Nov 2005 – Nov 2009

Introduction

Research on sustainable processes within B-Basic is focused on bio-based processes to decrease the usage of non-renewable fossil resources. This project aims to design an integrated process where compounds from fermentation processes are obtained using *in-situ* Template Induced Crystallization (TIC) as the separation tool. For this purpose templates have to be screened, a suitable driving force for crystallization has to be created and template separation and regeneration steps have to be designed.

State of affairs

A methodology for template screening was developed and applied, using cinnamic acid (TCA) as the model compound. Interesting templates were analyzed to investigate the governing principle of TIC.

Experiments

Induction times of blank experiments (where no templates were added) were compared with induction times of templated experiments. The induction time of a solution of cinnamic acid was measured upon instantaneous addition of HCl. Properties as zeta-potential and particle size were analyzed.

Results

Fig. 1 shows that TiO_2 templates decrease induction times of cinnamic acid crystallization, which is an indication for enhanced nucleation. Zeta-potential measurements revealed that adsorption of dissociated cinnamic acid takes place before nucleation starts.

Probably a layer of cinnamic acid molecules promotes nucleation of this compound. This was confirmed by measuring induction times of a particle with covalently bonded cinnamic acid molecules (see triangles in fig 1).

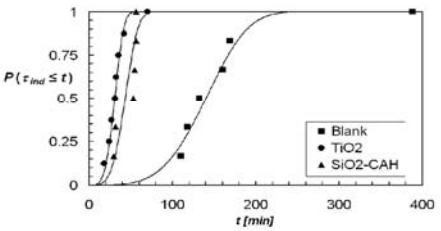

Fig. 1: Squares: Induction time distribution of blank experiments. Dots: Induction times of TiO_2 templated experiments. Triangles: Induction times of particles with covalently bonded cinnamic acid.

Conclusions / Future work

- TiO_2 & SiO_2-CAH particles promote cinnamic acid crystallization.
- Governing principle is that templates should be surrounded by adsorbed or covalently bonded layer of cinnamic acid.
- Future work focuses on creating an in-situ driving force for crystallization.

Acknowledgements

This project is financially supported by the Netherlands Ministry of Economic Affairs and the B-Basic partner organizations (www.b-basic.nl) through B-Basic, a public-private NWO-ACTS programme (ACTS = Advanced Chemical Technologies for Sustainability).

Crystallization in CO_2 post - combustion absorption and stripping

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OSPT theme	: Separation processes	Research school	: OSPT
Supported by	: TNO	Period	: March 2009 – March 2010

Introduction

Due to global warming the separation of CO_2 from gas mixtures will become an increasingly important step in petroleum refining, natural gas processing, and petrochemical manufacturing. Generally, CO_2 is captured by subsequent absorption and desorption. The removal of absorbed CO_2 from a solvent is cost-determining as it is an energy inefficient process performed at increased temperatures using steam. We want to identify opportunities for further energy reduction by generating extra driving forces for the CO_2 release by manipulating the solution characteristics in the desorption process. The absorption process is also investigated since these processes (absorption and stripping) are intrinsically couples through the solvent recycle.

Normally alkanolamides are used as the absorbent (solvent) in CO_2 absorption. Dissolving a crystalline compound X in this solvent can change the CO_2 capacity of that solvent. Compound X can help increase CO_2 capacity in the absorber or decrease CO_2 capacity in the desorber. Upon crystallization of compound X e.g., by changing the temperature, compound X is removed from the solvent and capacity is changed back to near its original value.

Current state

The project started on 1 March 2009. Literature search in the related works is carried out.

Future work

The future work focuses on screening desorption behavior of CO_2 under the influence of a crystallizable desorption agent and screen of CO_2-containing complex crystalline compounds on their ability to enhance absorption/desorption efficiency.

Acknowledgement

The financial support of TNO is gratefully acknowledged.

TU Delft
Process & Energy Laboratory

Microwave Enhanced Ethanol Steam Reforming

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OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: SenterNovem	**Period**	: Dec. 2006 – Dec. 2010

Introduction

A well-working hydrogen fuel cell needs continuous delivery of pure hydrogen. Instead of storing hydrogen on board, an alternative is to produce it in situ from renewable source of energy e.g. bio ethanol. One of the ways is steam reforming.
This research work focuses on the use of microwave radiation for intensification and development of low-temperature steam reforming of ethanol (ESR). Experimental approach is performed in order to compare ethanol conversion, hydrogen selectivity and by-products composition from conventionally heated and microwave processes. Hypothesis of "hot spots" formation at heterogeneous gas phase reactions under microwave conditions is evaluated by continuous measurement of temperature distribution inside the catalytic bed.

Experimental work

Reaction is carried out at atmospheric pressure in a tubular glass reactor in the presence of catalyst. A mixture of $EtOH/H_2O$ is supplied by a pump to the evaporator where it is mixed with carrier gas (Ar) and then vaporized. The temperature of reaction is measured by fiber optic sensors in three places inside the catalytic bed. Products of reaction are analyzed by on-line gas chromatography (Fig.1).

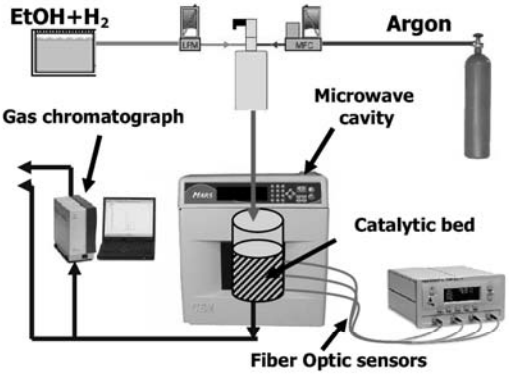

Fig. 1. Scheme of experimental equipment.

Reaction is performed with three potential catalysts for low-temperature ethanol steam reforming:

- Rh/Al_2O_3,
- Rh/CeO_2-ZrO_2,
- Ni/Al_2O_3.

Following parameters which influence the conversion of EtOH and the H_2 selectivity are investigated:

- steam to carbon ratio (S/C),
- gas hourly space velocity (GHSV),
- temperature of catalytic bed

Acknowledgements

The Dutch Ministry of Economic Affairs and SenterNovem are acknowledged for their financial support through the EOS-LT 04033 project grant. This research project is carried out in collaboration with CEM Corporation, Dortmund University and Stuttgart University.

An Alternative Separation Technology: Frictional Diffusion

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Period : April 2006 – April 2010

Introduction

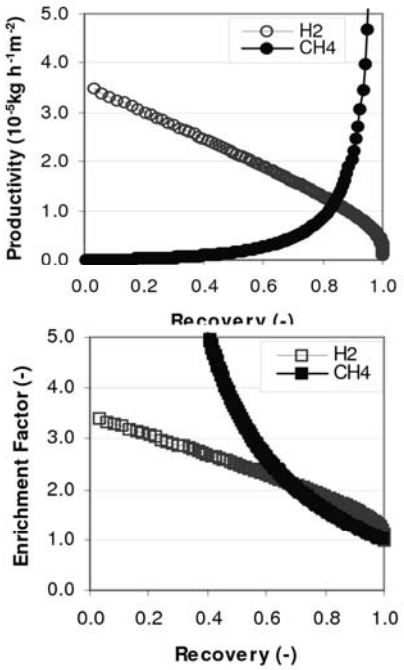
There are cases in which even the most useful separation technologies can not work efficiently. Especially the separation of azeotropic mixtures, which normally requires combination of distillation columns and other additives offer great opportunities to be replaced by alternative processes. Looking for separations using different mechanisms is the motivation for Frictional Diffusion (FricDiff) which is based on difference of diffusivities in a third gas the so-called counter gas.

State of Affairs

The papers published so far on FricDiff all focus on the separation of azeotropic mixtures of alcohol and water. To show this is not the only application of FricDiff, the separation of hydrogen and hydrocarbons is studied here to prove the variability and flexibility of the technology. The system consisting of H_2-CH_4 separation by counter gas H_2O is chosen. For the design of FricDiff module the performance criteria, Enrichment Factor, Recovery and Productivity have been developed.

Conclusions:

- **N**ew sustainable, alternative separation technology based on difference of molecular size of components
- **F**ricDiff can be applicable beyond azeotropic separations.
- **K**ey-performance indicators: recovery, enrichment factor and productivity should be studied concurrently for the optimum design.



Tradeoffs in the design of FricDiff for the separation of H_2-CH_4 by H_2O as a counter gas are shown above. The influence of regarding H_2 or CH_4 as product on the performance criteria is studied.

Acknowledgement

This project is conducted in cooperation with Akzo Nobel, Shell, Purac Biochemie, FIB, Bodec and TU Eindhoven and is financially supported by SenterNovem.

TUDelft
Delft University of Technology

Application of dielectric heating in chemical process applications

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OSPT theme	: Green process alternatives	**Research school**	: OSPT
Supported by	: STW	**Period**	: Feb 2008 – Feb 2012

Introduction

The goal of this project is to provide heat in microreactors through dielectric heating. It is part of a collaborative project with Eindhoven University of Technology, which aims to design, develop and demonstrate a microstructured reactor for chemical synthesis with microwave heating.

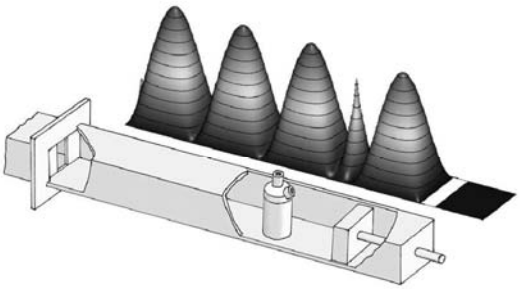
Aim

The primary aim of the project is finding ways to generate heat in microstructured reactors with microwave heating. The goal is to demonstrate a proof-of-principle setup. From a more general perspective, it is intended: to gain understanding on electromagnetic fields in chemical process applications; to investigate manipulation of electromagnetic fields in such applications to control dielectric heating and temperature profile inside process equipment; to investigate the conditions that determine whether conventional or dielectric heating would best be used and, in case of the latter, what type of applicator is most adequate.

Current research

If dielectric heating is chosen for a process application, there are a number of degrees of freedom for the design of the heating system. Which solutions to choose depends on each particular application. These solutions are being categorized, their advantages and disadvantages are described and they are compared with each other and with conventional heating.

To gain insight into the effects of material properties and geometry of a single mode applicator cavity, a simplified cavity has been modelled in Comsol 3.5. One conclusion is that a requirement of uniform heating puts rather limiting constraints on the dimensions of objects in the cavity.



Outlook

- Further analysis of applicator types for electromagnetic energy for process applications
- Calculations on several applicator types
- Experiments with a microwave heated microreactor.
- Evaluation of methods of temperature measurement in a electromagnetic field.

Acknowledgement

This research is supported by the Dutch Technology Foundation STW, applied science division of NWO and the Technology Program of the Ministry of Economic Affairs. It is part of a collaborative project with Eindhoven University of Technology. DSM, IMM, FrieslandCampina, Milestone s.r.l (Italy) and Lionix are acknowledged for their support both financial and in kind.

Precipitation and Melt Crystallization for the selective removal of trace components from aqueous or organic process streams

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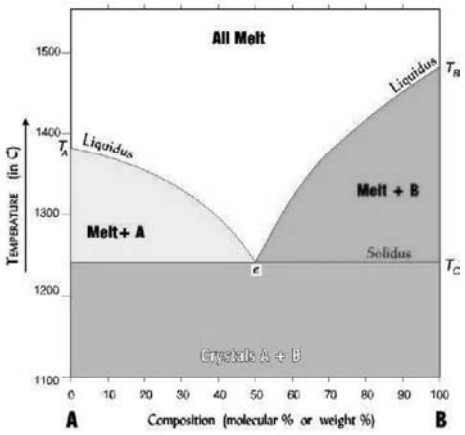
OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: DSTI	**Period**	: Oct. 2008 – Oct. 2012

Introduction:
The project addresses one of the main application domains of separation technology in the bulk chemicals sector: removal of compounds present in ppm concentrations in organic (and inorganic) bulk chemical streams. Five separation techniques (crystallization, precipitation; extraction, distillation, absorbtion; adsorbtion; membrane; ion-exchange) are evaluated.

Objectives:
During my first year process analyses and syntheses will be carried out for use of (melt) crystallization and/or precipitation for the removal of trace impurities.
For the evaluation of (melt) crystallization or precipitation as a potential good solution for removing trace impurities, the costs of the proposed technology must be estimated and then compared with the cost of the other separation techniques involved in the project.

Melt crystallization:
The melt crystallization technique is often applied as final purification technique because of its ability to generate ultra-pure products (99.9+ wt%), especially when wash columns are used for the separation of the pure crystals from the impure mother liquor. The selectivity by which molecules can be built in a crystal lattice can be very large. By this high product purities can be realized. Purities up to 99.99 and 99.999% are often feasible – also in the case of feed stocks containing 20 to 50% impurities. This makes melt crystallization rather unique, as it is usually very difficult to establish these high purities with other physical separation methods (Melt crystallization technology, G.F. Arkenbout 1995).
Melt crystallization differs from other crystallization methods in the fact that the operating temperature is close to the melting temperature of the main component. This enables the use of extra purification methods around the melting temperature, like washing with the pure melts, sweating, etc.

Approach for the first year:
- Binary and ternary phase diagram prediction;
- Pressure influence on phase diagram;
- Laboratory – scale experiments;



Phase diagram of a binary eutectic system.

Acknowledgement
This is a DSTI project.

Faculty of Mechanical, Materials and Maritime Engineering

Research Group:
Apparatenbouw voor de Procesindustrie
(Process Equipment)

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Research activities of the Process Equipment group

The OSPT research activities within the Process Equipment group address fundamental as well as applied product, process and equipment aspects of advanced technologies of (electro-) chemical reactions and separations in the field of (bio-)chemical, food and pharmaceutical technologies. There our roughly three main lines of research:

1) *Supercritical carbon dioxide , ionic liquids as green solvents* for reactions, (anti- or cosolvent) crystallisation, extraction, precipitation, textile dyeing, textile dry cleaning, product formulations.

2) *Advanced (hybrid) crystallisation technologies*, such as simultaneous combined transverse flow (hollow fibre membrane) extraction with (re)crystallisation, or combining transverse flow module ion exchange with (re)crystallisation. Another example is the simultaneous production of very pure water and salt from mixtures by eutectic freezing, also by CO_2 hydrates. Antiscaling is an important subtopic.

3) *Research related to clean energy*, such as solar boilers, hydrogen transport.

Most projects are carried out in cooperation with industrial partners including equipment manufacturers and with other research groups.

EUTECTIC FREEZE CRYSTALLIZATION (EFC)

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OSPT theme : Separation Processes
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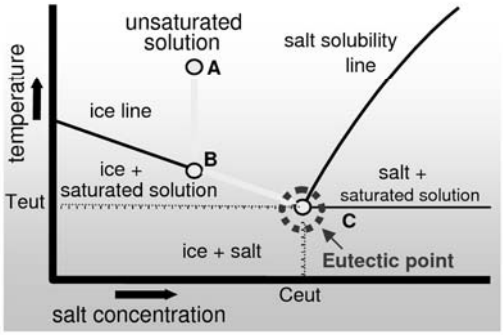
Period : Nov 2007 – Nov 2009

Introduction

Salt solutions can be separated into pure ice & pure salt by EFC. Compared to conventional evaporative or cooling crystallizations, the main advantages of this separation technique are its low energy requirements and high product yield. By cooling the solution up to its eutectic point, ice and salt form simultaneously as two separable solid phases. These solid phases are then separated utilizing the density difference.



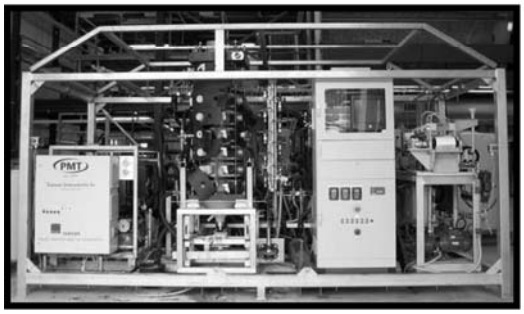
EFC technology was scaled up and a complete mobile skid mounted unit was designed and constructed together with industrial partners, allowing the system to be easily installed and connected to an industrial plant.

Applications

EFC technique can be applied most of the waste and process streams of the chemical industry to recover and separate valuable inorganic salts or to remove the water from the process streams.

Research aim

The main goal of this research is to operate this skid mounted unit, define the optimum working conditions and develop an industrial application for EFC which is both economically and technically more attractive than the previous crystallization & separation techniques. Over the last ten years many potential applications were discovered, many of them unexpected, and investigated. Now wider scale implementation of EFC has the highest priority. For this aim, industrial sodium (bi-)carbonate solution application is being investigated and the feasibility of the process is being evaluated.



Separation of corresponding olefins/paraffins by selective paraffin adsorption

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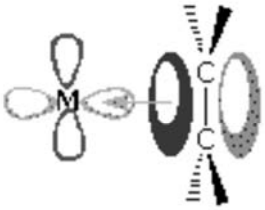
OSPT theme	: Separation technology	**Research school**	: OSPT
Supported by	: TUDelft	**Period**	: -

Introduction

Corresponding olefins and paraffins are difficult to separate because of their similar structure and properties. Conventionally, they are separated by means of distillation, which is very energy-intensive.

An alternative to distillation is selective adsorption, resulting in preferential adsorption of the olefin via π-complexation.

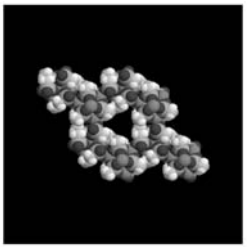


Aim

The aim of this work is to find a material that selectively adsorbs the paraffin (minority compound) instead of the olefin from corresponding olefin/paraffin mixtures.

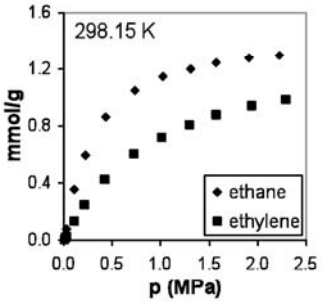
Experimental

The material aluminum methylphosphonate polymorph alpha (AlMePO-α) was tested as selective paraffin adsorbent using a combined experimental – molecular simulation approach.



Results and Discussion

AlMePO-α was found to be able to selectively adsorb the paraffin from both ethane/ethylene and ethyl chloride/vinyl chloride mixtures.



Both ethane and ethyl chloride arrange similarly in AlMePO-α.

Conclusions

Because ethane and ethyl chloride have different size but similar adsorption behavior, it is concluded that the interaction of AlMePO-α with the methyl groups of the paraffins is the key factor detemining the adsorption behavior.

Acknowledgements

Cooperation with MATGAS institute in Barcelona is gratefully acknowledged.

Dyeing of textiles in carbondioxide

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OSPT theme	: Green Process Alternatives	**Research school**	: OSPT

Introduction

Dyeing of textile is a process that consumes huge quantities of pure water. For example dyeing of 1 kg of cotton requires about 100 kg of water. Purification of the resulting wastewater is expensive and requires a lot of energy. Displacement of water by carbon dioxide saves energy and water and produces less waste. Disadvantage of the use of carbon dioxide is the need for pressure equipment, new dying procedures and in the case of natural fibers completely new dying processes.

Aim

The project focuses on three issues:

- The design and building of industrial high pressure equipment for the dyeing of textile.
- The development of new dyeing procedures for synthetic fibers.
- The development of completely new dyeing processes for natural fibers.

Experimental

The dyeing of polyester has been scaled up from 150 ml to 4 l, 40 l and reaching ultimately 100 l. The 100 l dyeing machine was specifically developed for this purpose and is unique for its carbon-fiber reinforcement (low cost, low energy consumption).

figure 1: 100l dyeing machine using carbon dioxide as a solvent.

Polyester can be dyed deeply, evenly and with good color fastness in the 100 l machine. The 100 l dyeing machine shows good performance with respect to critical process parameters.

For natural fibers quantum mechanical simulations are used to understand dye-fiber interactions and to develop dyes that will work in carbon dioxide.

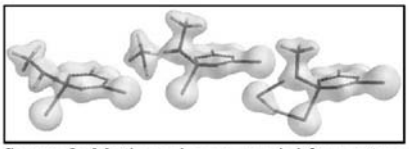

figure 2: Methanol as a model for cotton: Transition states for direct, MeOH- and HCl-assisted substitution of 2,4-dichlorotriazine with methanol.

These simulations resulted in a major breakthrough. Due to the use of new dying procedures and new dyes it was possible for the first time to dye cotton in carbondioxide.

Outlook

- From the 100 l dying machine it is one scale up step to a production machine of 1000 l. This step will have to be made and is underway.
- Other synthetic fibers are under investigation.
- The new dyeing process for cotton is being scaled up and optimised.
- New dyes for cotton in order to fill in the color palette are under development.
- Other natural fibers are under investigation.

Acknowledgement:

This work is carried out in collaboration with FeyeCon.

Dexamethasone controlled release from PLGA particles impregnated in porous metal implants

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OSPT theme	: Products and Processes	**Research school**	: OSPT
Supported by	: DCSIP	**Period**	: Nov 2007 – Nov 2007

Introduction

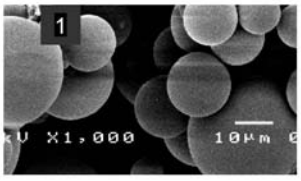
Synthesis of medical combination devices could involve three properties in a single device: device, drug delivery system, and, bioactive agents (DDB). One example of such as a system is a DDB Ti/Mg oxide bone implant which is not yet available. The first step toward realization of this implant would be the encapsulation of an anti-inflammatory drug inside a biodegradable polymer matrix followed by impregnation of the resulting micro/nanospheres into the porous coating of the implants. An anti-inflammatory drug, dexamethasone, is used to suppress inflammation of the tissue surrounding the implants as it is released from poly(lactic-co-glycolic acid) micro/ nanospheres in a controlled manner. PLGA is used in a host of therapeutic devices due to its biodegradability and biocompatibility.

Objectives

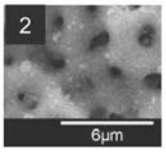
The objectives of the study are twofold: to prepare dexamethasone-PLGA particles with the necessary characteristics (size appropriate to the pore size of the coating, stable during the deposition process, adequate encapsulation efficiency) and to evaluate their compatibility with Ti/Mg oxide and CoCrMo implants based on the in vitro dexamethasone release profiles.

Experiments

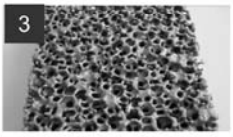
First, dexamethasone-PLGA microspheres were prepared using an emulsification and solvent evaporation technique. Microspheres with diameters less than 30 μm was obtained (see picture 1) and their zeta potential were determined.



To achieve nanosphere size of 200 nm or less, a modified emulsification and solvent evaporation technique will be implemented. Next, the nanospheres will be impregnated into the pores of the Ti/Mg implants (see picture 2) using in situ plasma electrolytic oxidation. The challenge is that the nanospheres loading will be limited due to similar sizes of the nanospheres and the pores (200 nm and 1000 nm, respectively).



The microspheres will need to be coated into the CoCrMo implants that have large openings instead of pores (see picture 3). Suitable coating methods such as vacuum evaporation from aqueous solution at PLGA glass transition temperature or CO2 super-critical anti solvent will be tested in the case of CoCrMo implants.



The final step is the in vitro release study of dexamethasone in PBS under sink conditions. Time release profiles of dexamethasone from both types of implants will be assessed to determine the effectiveness of these implants.

Acknowledgement

This research project is carried out as a cooperation between the Process Equipment Section (Process& Energy Dept.) and the Light Metals Processing Group (Material Science and Engineering Dept.), and it is financially supported by DCSIP TU-Delft.

Cavitation for effective bore well cleaning

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Research grp: Process equipment
OSPT theme: Products and Processes

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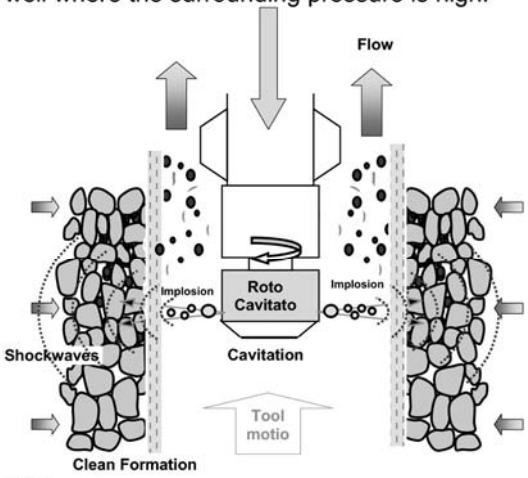
Introduction

The productivity of a deep well (oil, water or gas well) decreases over time. To restore the production the well bore and formation must be cleaned once a while. Use of cavitation is a new cleaning technology. A cavitation tool will make a cavitation (low pressure) bubble that violently implodes due to the higher surrounding pressure. This gives strong shockwaves and suction effects. The shockwave will shake up the dirt/scale/bridges particles inside the formation. These particles will get out the formation/well because the well is producing. The difficulty is to create cavitation deep in the well where the surrounding pressure is high.



Aim

To develop a cavitation tool that creates cavitation in a surrounding pressure up to 300 bar (3 km deep well). Cavitation must be strong enough to create powerful shockwaves that shake up the particles but do not damage the bore well itself. The distance between the imploding bubble and the bore well is important because closer to the well bore face means that the shockwave will travel further into the formation. Too close to the well bore face can damage the well.

Setup

There are now two experimental test circuits.

The 50 bar setup (closed system) exists of a pump, cavitation tool, bypass and a pressure vessel. The vessel, where the cavitation tool is, can be put under a pressure up to 10 Bar. To measure the cavitation effects in surrounding pressure there are windows and pressure sensors in the vessel. The pressure sensors are fast, that they are capable of measure a pressure fluctuation created by the shockwaves. The pump gives a constant flow depending on the pressure drop over the tool. To regulate the flow through the tool can be done with the bypass. The maximum pressure the pump can give is 50 Bar.

The 350 bar setup is similar to the 50 bar setup besides that there the vessel pressure can increase till 300 bar.

50 bar cavitation setup

Cannabis isolation

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Research group	: Process Equipment	**URL**	: www.api.tudelft.nl
OSPT theme	: Separation technology	**Research school**	: OSPT
Supported by	: STW	**Period**	: July 2006 – July 2010

Introduction

Cannabis is one of the oldest known medicinal plant. The active components, called cannabinoids are interesting in medical applications but there use is limited by the poor accessibility in the pure form.
The growing interest in developing new separation methods with supercritical CO2 will be studied within this project.

Aims

- Develop a process for the separation of the major and minor cannabinoids from cannabis in their pure form following GMP guidelines;
- Develop a production method to obtain an extract with the same composition as the cannabis smoke

Separation methods to be developed

- Supercritical Fluid extraction (SFE)
- Supercritical Fluid fractionation (SFF)
- Heated gas extraction
- Centrifugal Partition Chromatography using supercritical CO2 as a solvent (C-CPC)

Experimental

- Experimental set-up available to perform extraction of cannabis material and optimize the process parameters (T,P…)
- Construction of the C-CPC

Investigations

- Thermodynamic studies to define a solvent system able to separate the cannabinoids
- Design and construction of the C-CPC
- Optimization of the C-CPC

Outlook

- Better accessibility of cannabinoids to perform research to find more efficient medicines against chronic pain, multi-sclerosis (MS)…
- Cheaper way of producing pure cannabinoids that can be used as a medicine

Acknowledgement

This research project is in collaboration with the Leiden University, FeyeCon D&I B.V., Farmalyse and Enzyscreen. It is financially supported by the Dutch foundation STW.

Fluid dynamics of supercritical fluids for process and energy applications

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OSPT theme	: Energy conversion process	**Research school**	: OSPT, Burgers Centre
Supported by	: DCSIP	**Period**	: Febr 2005 – Febr 2009

Introduction

Existing Computational Fluid Dynamics (CFD) software relies on the simple ideal gas law for the thermodynamic modeling of the fluid flow. As a result, it fails to correctly simulate the fluid flows for which ideal gas can no longer be assumed: processes that occur close to the critical point (supercritical) and close to and into the two-phase region (dense gas).

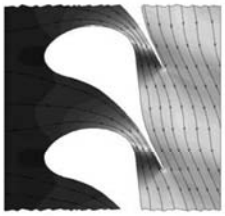
A state-of-the-art fluid dynamic code (zFlow) is currently being developed which is interfaced with a thermodynamic library of highly accurate thermodynamic equations of state (EOS) called FluidProp. This allows for the accurate simulation of fluid flows under highly non-ideal conditions, which occur for supercritical processes and in many turbines.

Objectives

1) Further development of the zFlow CFD code to make it a tool suitable for general dense-gas process simulations with particular emphasis on supercritical fluid flows.
2) Experimental code validation, in particular its ability to correctly simulate dense gas flows.
3) Characterization of peculiar fluid dynamic effects caused by thermodynamic non-ideality in the dense-gas fluid expansions of relevant process and energy technologies.

Modeling results

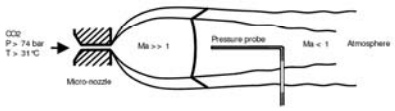
zFlow has been used to study the fluid dynamics and performance of the turbine blades of sub- and supercritical Organic Rankine Cycles, an attractive energy conversion technology for low-grade heat. Results have been published.



The effect of using thermodynamic models of different degrees of accuracy in the fluid dynamic simulation of subcritical and supercritical expansion processes of fluids that differ in molecular complexity and weight have been investigated.

Experiments

For the validation of the code, a scaled-up RESS setup will be constructed which enables one to take measurements in the free-jet formed by the expansion of supercritical CO_2 to atmosphere.



Outlook

In the near future, zFlow will be extended to allow for viscous turbulent simulations. In parallel, the experimental setup will be constructed.

Acknowledgement

This research project is financially supported by the Delft Center for Sustainable Industrial Processes.

Rapid Expansion of Polystyrene using Supercritical CO_2

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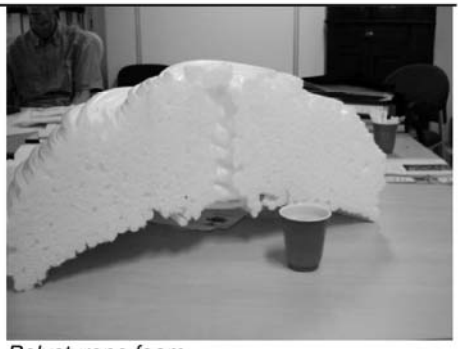
OSPT theme	: Green process alternatives	**Research school**	: TUDelft
Supported by	: SenterNovm	**Period**	: Apr 2006– Apr 2010

Introduction

Polymeric foams are widely used materials (as packaging, insulation, construction and flotation) but the conventional foaming agent (pentane) is known to be expensive, flammable and takes a long time to diffuse out of the foam. 200.000 ton of pentane is used for polystyrene foam production each year. There is a large incentive to replace the pentane with more benign blowing agents (CO2, N2, etc.).

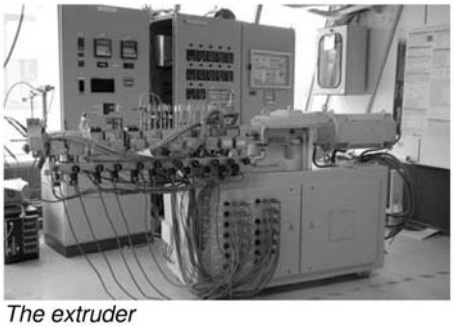


Polystyrene foam

Theory

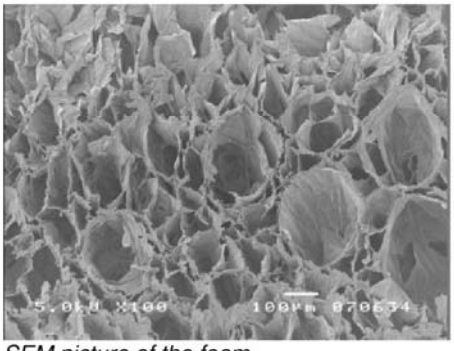
Microcellular thermoplastic Polystyrene foam production employs CO2 in its supercritical state in order to create a swarm of bubbles (cell density: 10^8-10^9cells/cm^3) in the polymeric matrix. The obtained foam exhibits improved mechanical properties, impact strength and toughness compared to conventional foam.

All the main operations(Melting, Pressurization, CO_2 injection, mixing and cooling) are subsequently performed in one extruder. This extruder is a 25ZSK built by W&P. It is a co-rotating double screw extruder. The results



The extruder

- Production of low-cost foams with superior mechanical properties;
- A large reduction in production time
- The environmental effects are much less severe by replacing conventional organic foaming agents.



SEM picture of the foam

Acknowledgement

This project has been made possible with the cooperation of Feyecon and Unidek

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Catalysis Engineering

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The Catalysis Engineering section focuses on novel concepts for creating optimal environments for catalytic reactions on a multiscale level, from Ångstrøms to meters, marrying catalysis with engineering.
The multi-level approach integrates the molecular scale (micro level), the catalyst and reactor (meso level) up to the product and process level (macro level), leading to a rational design of and precision in catalytic operations. Included are elements of nanochemical engineering, utilizing the specific phenomena on the nanometer scale, such as catalysis, (self-)assembly and structuring, and size effects of particles and pores.

The main drivers are on the one hand scientific developments in nanotechnology and on the other hand the societal need for sustainability, where materials' and energy efficiency, environment, renewables and process intensification are key elements.

The main research topics include spatial structuring, multifunctional catalysts and -reaction systems, photo- and electro-catalysis, and multiphase operation. The mission is translated to a number of specific subjects that serve on the one hand as specific examples for the generic approach and on the other hand as contribution to sustainable development.

DDR Membranes in Separation and Catalytic Processes

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Research group	: DCT / The Pore	URL	: www.dct.tudelft.nl/ce
Supported by	: TU Delft	Period	: May 2006 – April 2010

Introduction

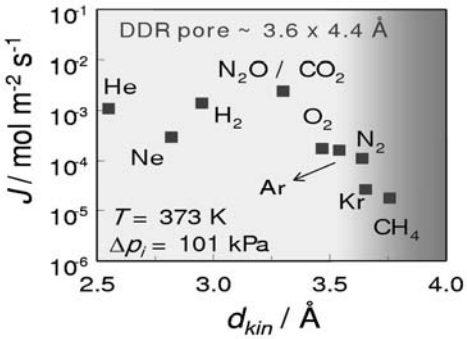
This project is carried out at the Delft University of Technology within "The Pore". The Pore is an interfaculty research group of the Delft Centre for Sustainable Industrial Processes (DC-SIP) and has expertise in principles and fundamentals in design and development, as well as in applications of ceramic microporous and mesoporous membranes and catalysts.

The aim of this project is to investigate what the opportunities are for application of DDR membranes in the chemical industry.

DDR is a zeolite consisting of separate cages connected by 8-ring pores forming a 2-dimensional pore network. Zeolites in general and especially all silica DDR have a high chemical and thermal stability (Calcination @ 973 K!)

Motivation

Recently, very high separation factors (100 – 5000) have been found with DDR membranes for CO_2/CH_4 mixtures combined with high CO_2 fluxes. Molecular sieving effects are very dominant (see figure below) and indicate that separation of many small molecules is possible.

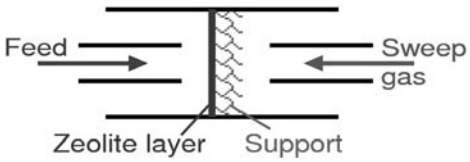


An application of such a membrane could be in situ separation of desired products in an equilibrium-limited reaction. Reactions of interest are *for example* the dehydrogenation of isobutane. Where selective removal of H_2 is anticipated since Isobutane and isobutene will be sterically hindered.

$$i\text{-}C_4 \rightleftarrows i\text{-}C_4^{=} + H_2$$

Experimental work

- Adsorption on DDR crystals
- Single/multi-component membrane permeation (illustrated below)
- Reactive separation



Modeling work

From engineering point of view, a good model description of the mixture permeation is required, preferably based on the single component adsorption and permeation data. Modeling by macroscopic transport models will therefore get significant attention.

Acknowledgement

NGK Insulators is gratefully acknowledged for supplying the membranes and TU Delft for its financial support.

High-throughput kinetic modeling of diesel ultra-deep hydrodesulphurization

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Research group	: Catalysis Engineering	URL	: http://www.dct.tudelft.nl/ce/
Supported by	: Shell and Albemarle	Period	: January 2007 – January 2009

Introduction

Environmental concerns have brought legislations all over the world which attempt to restrict sulfur content of fuels, particularly in the diesel fraction. This issue, jointly with the necessity for upgrading increasingly refractory feedstock is challenging refineries to revamp hydrotreating units, often by enhancing both the catalyst performance and the reactor design optimization. Despite the broad literature in the field of hydrodesulphurization, the knowledge of 'real' kinetic models that explain the behavior under ultra-deep hydrodesulphurization (up to full conversion) of diesel is rather limited. Therefore, precise high-throughput experimentation can give extensive information of such kinetics.

The objective of this project is to design and build a laboratory-scale high-throughput setup and investigate the hydrodesulphurization of model compounds in order to propose real kinetic models for this process. Furthermore, the simulation of the reaction will be carried out in order to estimate the activity and selectivity of the catalyst in conditions different to the ones used.

Experimental

The studies will be undertaken in high-throughput equipment consisted in six identical down-flow tubular reactors (2 mm inner diameter) operating under trickle bed conditions. Fig. 1 shows a detail of the multi-reactor inlet section of the setup.

Approach

The first step is the interpretation of the kinetic data in general, from powder catalyst operating inside the packed reactor. The small scale of the system can create hurdles that are not observed at an industrial scale. Naphthalene hydrogenation over a noble-metal supported catalyst has been chosen as a model reaction to characterize the reactor in combination with hydrodynamic experiments. The data of the high-throughput setup will be compared to the one obtained under similar conditions in a batch reactor (Autoclave).

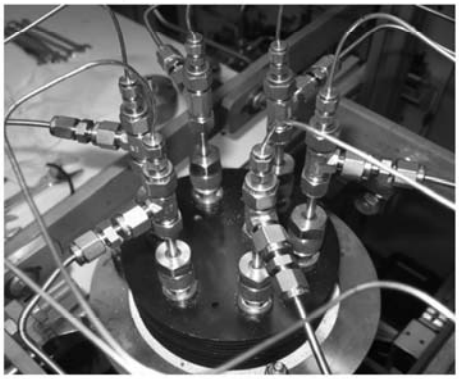


Fig. 1. High-throughput setup.

The second step is to investigate the hydrodesulphurization of several feedstock, analyzing the inhibiting effect of H_2S and N-containing compounds and incorporating all of these, as well of deactivation, to design novel kinetic models for the process.

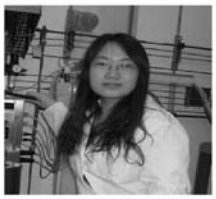
Researchers

Besides the researchers described above also *Nathalie Márquez* works in this research project.

Acknowledgements

This work has been carried out with the financial and scientific support of *Shell Global Solutions* and *Albemarle Catalyst Company*.

Smarter Biomass Conversion



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		Research school	: NIOK
Supported by	:BIOeCON	Period	: March 2007 – March 2011

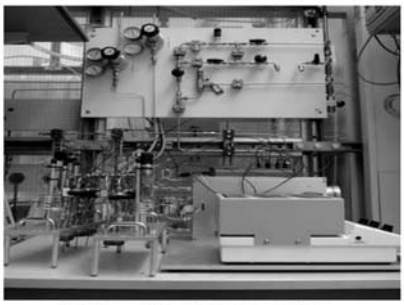
Introduction

The limited availability of fossil fuels, together with social, economical and ecological reasons, has led to the search for alternative sources of energy. Renewable biomass has been considered as a potential solution for the world's increasing demand for energy and ecological awareness. However, because of its high moisture content and low volumetric energetic value, biomass is poorly suited for direct use. By converting biomass into a liquid fuel, problems regarding transportation and storage are eliminated, while the volumetric energetic value is increased.

Biomass can be converted to alternative fuel sources by different techniques such as fermentation, extraction/compression, trans-esterification, pyrolysis gasification, liquefaction, etc.

Most commonly and abundantly available starting material of biomass conversion is wood; it consists mainly of cellulose, hemi-cellulose and lignin.

Experimental setup



Mini-multi-autoclaves setup

In my project, we mainly focus on a smart biomass conversion process, in which several individual, but essential steps are combined in a one-pot approach. Model component will play an essential part in the research. The objective is the conversion of wood to one or more platform chemicals and/or a product that can be easily processed in the oil classical refinery.

Results

A clear picture for wood convert to stable platform chemical and/or fuel

By the combination of hydrolysis, hydrogenation and dehydration in a sequence of conversion steps, we are able to convert wood into a platform chemical which can be easily extracted from the water phase.

Conclusions

- Proof of concept was established
- A combination of two catalysts in a one-pot-approach wood was converted into bulk chemicals
- Cellulose and hemi-cellulose can be solved at mild conditions
- Lignin has the lowest reactivity

Acknowledgement

The financial support by the company BIOeCON is gratefully acknowledged.

Effect of TiO_2 hydrophobicity on the selective cyclohexane photo-oxidation

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OSPT theme	: Green Process Alternatives	**Research school**	: NIOK
Supported by	: NWO-VIDI	**Period**	: June 2006 – June 2010

Introduction

The oxidation of cyclohexane is an important commercial reaction to convert cyclohexane via cyclohexanone into caprolactam, a monomer for nylon-6 production. TiO_2 based catalysts are active in the photocatalytic conversion of cyclohexane, with a high selectivity towards cyclohexanone. However the desorption of this product was found to be limiting, leading to the formation of deactivating species at the TiO_2 surface. Improvements on the performance and stability of TiO_2 in the photo-catalytic liquid phase cyclohexane oxidation are therefore needed. In this work the TiO_2 catalyst has been altered, by anchoring silane groups to its surface, to analyze the effect of hydrophobicity on the catalyst performance on cyclohexane photo-oxidation.

Approach

Silylated TiO_2 materials were synthesized using Hombikat UV100 TiO_2 (anatase) and hexamethyldisilazane (HMDS). The synthesis was carried out in toluene at room temperature for 24 hours in, after which the silylated TiO_2 materials were filtered, washed and dried overnight at 120ºC. The obtained catalysts were characterized by ICP, Si-NMR, TGA and DRIFTS and test for the photo-catalytic cyclohexane oxidation on an *in situ* ATR-FTIR and on a top illumination reactor.

Results and Discussion

Catalyst characterization showed that different silica loadings on TiO_2 were obtained: TiSi8, TiSi10, TiSi12 and TiSi30 (in wt%); and isolated Ti-O-Si$(CH_3)_3$ groups were formed, resulting in an increased surface hydrophobicity. The photo-catalytic testing by ATR-FTIR showed that silylated catalysts have lower formation of surface bounded species (Fig. 1), as well as lower Ti-OH deactivation. The initial rate of cyclohexanone desorption, tested by ATR-FTIR, had an increasing trend with silane content (Fig. 2). The initial reaction rate obtained on the top illumination reactor showed a decrease with low silane loading on TiO_2, followed by an increase for higher silane content (Fig. 2). Silylation has the disadvantage of reducing the OH population, which was determined by DRIFTS and is shown in Fig. 2. The reaction rate is seen to depend mostly on these two parameters and two extreme conditions may be defined:

(1) Low silane loading: $r \sim k_l*[OH]*[C_6H_{12}]_{ads}$

(2) High silane loading: $r \sim k_{des}*[C_6H_{10}O]_{ads}$.

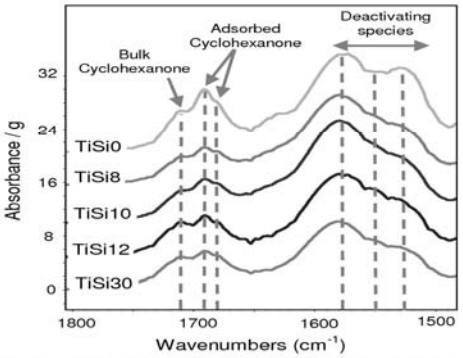

Fig.1. ATR-FTIR spectra after 90 minutes of cyclohexane photo-oxidation on TiSi0, 8, 10, 12, 30.

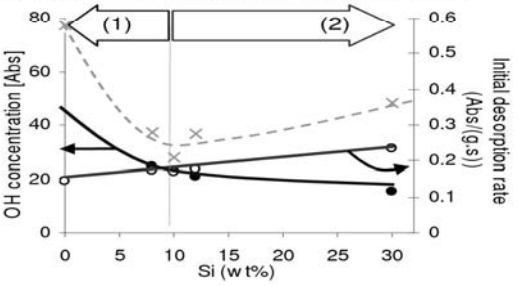

Fig.2. Comparison between OH surface concentration (blue), cyclohexanone desorption rate (red) and initial reaction rate (dashed grey).

Conclusions

Silylation increases the surface hydrophobicity of TiO_2, which improves the desorption rate of cyclohexanone and decreases catalyst deactivation. For low silane content, the reaction rate is dominated by the lower availability of OH active sites, while for higher silane content, the rate is enhanced due to a high rate of cyclohexanone desorption.

Electrocatalytic CO_2 reduction to hydrocarbons

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OSPT theme	: Energy Conversion Processes	**Research school**	: NIOK
Supported by	: Shell Mobility Program	**Period**	: 11/2007 – 11/2011

Introduction

When driving a car, gasoline is converted into energy, carbon dioxide and water. The present research is aimed at reversing this process, i.e. making gasoline from carbon dioxide and water. This will both solve the problem of the CO_2 emissions and the environmental issues associated with sulfur and nitrogen components in gasoline.

$$xCO_2 + yH_2O \xrightarrow{E} C_xH_{2y} + (x+0.5y)O_2$$

Project aim

The primary objective of this research is to improve the current status of electrochemical reduction of CO_2 to hydrocarbons.

In electrochemistry a voltage is applied between a working electrode and a counter electrode. Depending on the material of the working electrode, i.e. the electrocatalyst, different reaction products can be formed.

Copper typically shows the best Faradaic efficiency to CO_2 reduction, but still the undesired decomposition of water into H_2 and O_2 consumes most of the electrons fed to the electrode.

Various options exist to improve the Faradaic efficiency towards CO_2 reduction and to tune product selectivity to long chain hydrocarbons, as outlined below.

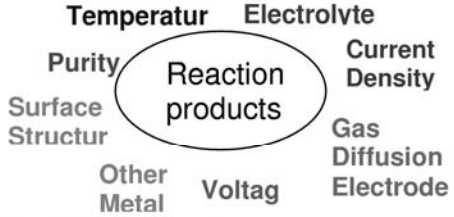

Figure 1: Influencing parameters

Experimental

In the initial stages of the project, the effect of surface structure on the total product formation and distribution was investigated by changing the surface by electrochemical etching in an acidic solution. Also the effect of temperature on the total production was studied.

The reaction was performed in an electrochemical cell, containing a working electrode (cathode, copper plate), a counter electrode (anode, platinum plate) and a reference electrode (Ag/AgCl). Furthermore, a gas inlet system was used to saturate the 0.1M $KHCO_3$-solution (electrolyte) with CO_2.

The voltage was set to -1.65V and the current was registered over time. During eight and a half hours of reaction, a gas sample was taken every 25 minutes and analyzed by gas chromatography.

Results

Figure 2 shows the total production of hydrocarbons after 500 minutes of reaction.

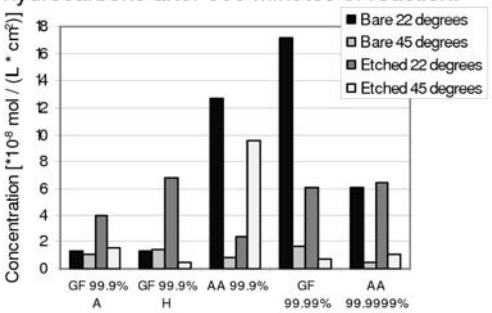

Figure 2: Total production of hydrocarbons after 500 minutes.

Etching sometimes increases and other times decreases the total product formation, depending on the electrode supplier and purity.
Increasing the temperature of the solution decreases the total production of hydrocarbons, the result of a lower CO_2 solubility.

Acknowledgements

Financial contribution of Shell is gratefully acknowledged.

Advanced Materials and Reactors for Photocatalytic Conversion of CO_2 into Fuels

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OSPT theme	: Green Process Alternatives	**Research school**	: NIOK
Supported by	: NSC-NWO	**Period**	: May 2007 – May 2011

Introduction

Convert thermal-dynamically stable CO_2 into valuable hydrocarbons under mild condition by photocatalysis.

$CO_2 + H_2O \rightarrow CH_4 + O_2$
$CO_2 + H_2O \rightarrow CH_3OH + O_2$
$XCO_2 + ½\ yH_2O \rightarrow C_xH_y + (x+2y)O_2$

Approach

The proposed research comprises catalyst development, CO_2 reduction mechanism investigation, and practical photoreactor design, all aiming at highly efficient light harvesting. The photocatalysts should have well designed characteristics, such as large absorption of, preferably, visible light photons, a long lifetime of activated states, a good adsorption of reactants CO_2 and H_2O, and a relatively easy desorption of products (the fuel molecules).

Catalyst development

i) Ti-based mesoporous materials (e.g. Ti-SBA15) have been reported in the literature to be more efficient in the CO_2 reduction reaction than dense phase TiO_2 particles. Titanium-Silicalite-1 (TS-1) is also the candidate for gaseous CO_2 reduction.
ii) Metal organic frameworks (MIL-53, $Cr^{3+}(OH)(O_2C\text{-}C_6H_4\text{-}CO_2)$ materials showed high potential for CO_2 adsorption, which are under investigation for the application of CO_2 reduction.

Operando DRIFTs experiment

Operando DRIFTs (Diffuse Infrared Fourier Transform Spectroscopy) experiments are means to obtain mechanistic information and can be carried out using a three-window cell. Two windows (ZnSe) allow IR transmission, and the third (Quartz) the introduction of UV/Vis light into the reactor. IR signals can thus be collected purging CO_2 and water vapor under UV light irradiation (Hg lamp, $\lambda > 250$nm, 100W). The reaction dome is connected to mass spectrometer. Hydrocarbon production can be detected below ppm range (Fig.1a). As shown in Fig. 1b, different materials (e.g. TiO_2, ZnO and SiC) exhibit different conduction band positions relative to the reduction potentials of CO_2 (carbon monoxide, methane, methanol, formaldehyde and formic acid). The performance of CO_2 reduction can be obtained and helps to figure out the mechanism.

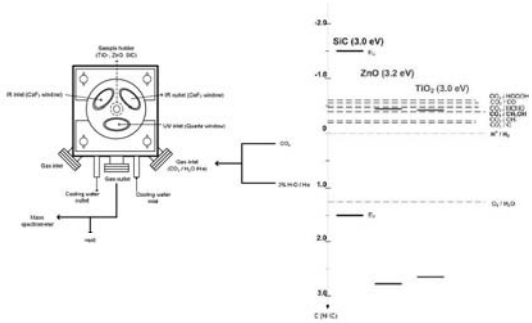

Fig. 1 (a)Three-window cell for DRIFTs
(b) Band position of TiO_2, ZnO and SiC (vs NHE)

Photocatalytic reactor

Another challenge is to design an optimized photoreactor: illumination of active sites and desorption of products need to be maximized. Internally Illuminated Monolith Reactor (IIMR) is built up for gaseous phase CO_2 reduction.

Acknowledgement
Thanks to the financial support by NSC and NWO.

Real time imaging of Heterogeneous Catalyst Reaction

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Supported by	: NIMIC	Period	: August 2008-August 2012

Keywords:
In situ TEM, heterogeneous catalyst, catalyst structure-performance relations

Introduction

The size, shape and detailed surface structure are important properties of a heterogeneous catalyst. They play important roles in the catalytic performance. Even though those properties can be controlled during catalyst preparation, there is no guarantee that the catalyst will remain stable under reaction condition. Both reactants and products can induce changes in the catalyst properties.[1] Therefore in situ study of the relationship between the catalyst structure and reaction conditions is important to improve catalyst performance.

Transmission Electron Microscopy (TEM) is a suitable technique to study the surface properties of catalysts with resolution down to the atomic scale. Recent development of in situ TEM nanoreactors incorporated into the TEM sample holder leads to the possibility of real-time imaging of catalytic reactions. The reactor is build by MEMS technology using window cell design. This design allows in situ TEM observation of the catalytic reaction. A controllable elevated temperature reaction can be reached inside the reactor using a platinum wire heating system. An integrated gas supply system is also build into the reactor, allowing atmospheric pressure in situ reactions, while maintaining the vacuum condition inside the TEM.[2]

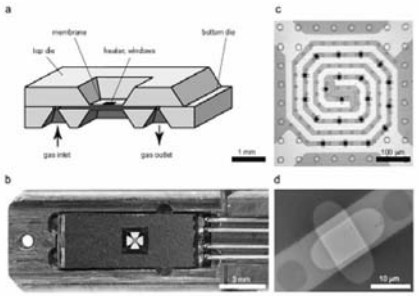

Fig. 1. Cross sectional illustration of nanoreactor device (a), optical image of the integrated nanoreactor (b), optical close up of the nanoreactor membrane (c) and electron transparent window cell design (d)

Objective

In the present research we will study the dynamic changes in the structure and catalytic activity of heterogeneous catalyst using in situ TEM. In order to relate them to previous results, these studies will be compared with traditional ex situ studies on the same reactions and catalysts.

Acknowledgments

This work is supported by NIMIC (Nano Imaging under Industrial Conditions; www.realnano.nl). We acknowledge financial support from Smartmix NWO-Senternovem, Albemarle Catalysts Company BV, FEI Company, and Haldor Topsøe A/S.

References

1. S Helveg, P.L Hansen, Catalysis Today, 111, 2006, 68
2. J.F Creemer, et al, Ultramicroscopy, 108, 9, 2008, 993

Nanostructured TiO_2 Based Materials for the Selective Photo-Oxidation of Hydrocarbons

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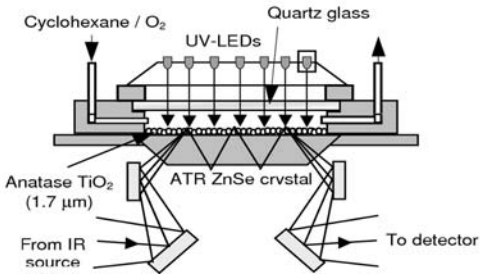
Selective photo-oxidation of cyclohexane

Research on the selective photo-oxidation of cyclohexane to obtain cyclohexanone, an important commercial product used to obtain caprolactam for Nylon-6 production, demonstrated that high selectivity (>90%) can be obtained over TiO_2. Studies have mostly been carried out using pure titania photocatalysts. The strength of adsorption of the oxidation products is largely determining the effectiveness and stability of the photocatalys. Favouring cyclohexanone desorption, and limiting carboxylate and carbonate accumulation on the catalyst surface by modification of titania surface properties is one of the goals of this research.

Photo-oxidation of cyclohexane has been analyzed by means of ATR-FTIR spectroscopy. *In situ* Attenuated Total Reflectance (ATR)-FTIR spectroscopy was used to follow the reaction. It makes possible to detect unstable reaction intermediates and species adsorbed on, or interacting with the catalyst surface. These advantages make this technique very suitable for both kinetic and mechanistic studies of liquid phase selective photo-oxidation.



Metal Organic Frameworks as Quantum Dots for Photocatalytic Applications

MOF-5 is a hybrid metal-organic structure built up from terephthalic acid and Zn oxide clusters. The behaviour of this MOF as a semiconductor has been claimed in several publications, with a band gap around 4 eV, where excitation takes place at the organic linker. These materials are potentially useful for photocatalytic applications.

Although changing the metal in the cluster has been proven not to lead to alterations in the band gap, it is feasible to tune the absorption edge of MOF-5-like structures by changing the organic linker. This may improve the capture of visible light by the organic 'antenna' and to transfer this energy to the inorganic cluster, activating it for catalytic action.

The aim of the project is the development of improved MOF-based photocatalysts. With this purpose, the effect of different linkers on the absorption edge of MOF-5-like structures is being studied and rationalized, and the photocatalytic performance of the materials tested for different reactions.

Operando ATR-IR/Raman set-up

Optimization of a simultaneous ATR-IR/Raman reaction system for operando studies is being carried out.

Acknowledgement

M.D. Hernandez Alonso would like to thank the "Ministerio de Educacion y Ciencia" of Spain for the award of her postdoctoral contract.

Novel reactor concepts for analysis and application of photocatalytic oxidation reactions

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Period : February 2006 – February 2010

Introduction

The design of an efficient reactor for many photocatalytic reactions is still a challenge. An effective illumination of the active sites and desorption of products needs to be maximized. Current photocatalytic reactors often have a low light efficiency, a low surface area for catalyst coating, and suffer from mass transfer limitations in liquid phase applications. Light transmitting reactor modules with parallel channels combined with Taylor flow (Figure 1 a)) operation might provide the optimal reaction environment. Especially when the desorption of the products is rate determining, Taylor flow operation of two liquids can be favorable, in which one is the reactant and the other is a solvent for removal of the product from the catalyst surface.

Approach

The objective of this work is to design a reactor for analysis and application of photocatalytic reactions. We believe that a structured reactor is the best choice.
By an integrated approach of mechanistic studies for catalyst development and novel reactor design the present research aims to improve the current levels of activity of photo-catalytic processes.

Photocatalytic Reactor

A viable option for photocatalytic reactors seems to be a monolith structure of parallel channels. A good thin and uniform layer of catalyst needs to be coated on the monolith channel walls (for example using a washcoat method) in order to avoid diffusion limitations and to ensure efficient light absorption by the catalyst. Tests in a single channel have to be done in order to evaluate the coated catalyst activity and the hydrodynamic profile which delivers the better performance. In each channel two optical fibers are placed to illuminate the catalyst, Figure 1.

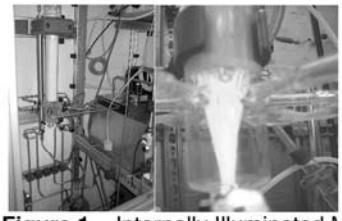

Figure 1 – Internally Illuminated Monolith Reactor with the optical fibers.

The Internal Illuminated Monolith Reactor (IIMR) seems to be a better option when compared with the conventional Optical Fiber Reactors (OFR) because the catalyst is facing the light, Figure 2.

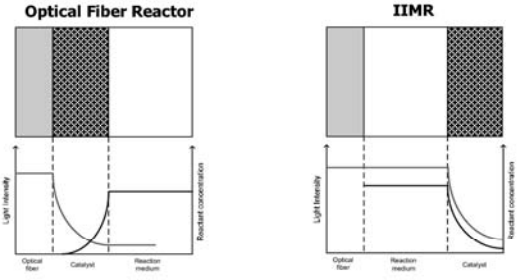

Figure 2 – reactant and concentration profiles in OFR's and in the IIMR.

Acknowledgement

This research project has the financial support of STW.

TUDelft

EUROKIN, a European cooperation initiative on kinetics research

EUROKIN

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OSPT theme	: Multiphase Reactors		www.anaproc.com (consultant)
Industrial members:		Period	: Aug. 1998 –

Aim:

The aim of the EUROKIN network is to produce a toolkit for estimating or measuring kinetic data and interpretation of those data by means of appropriate software routines. It will enable faster and lower cost derivation of kinetically based models, ultimately leading to more efficient commercial reactor design, quicker scale up and more efficient use of raw materials at lower costs. The active work in the Eurokin network will be continued in the coming years.

Consortium:

The EUROKIN Consortium currently consists of 8 European companies (see logos) and 6 academic centres (Delft Univ., Ghent Univ., UCL Louvain-la-Neuve, NTNU Trondheim, CNRS-IRCEL Villeurbanne, and Politecnico di Milano).

Test methods and reactors:

General overviews and other means guide the user through the experimental part of the kinetic investigation:

(1) Selection of a suitable method and test reactor;
(2) Spreadsheets to check for the absence of transport limitations and other phenomena causing non-ideality for various reactor types: (i) fixed beds, (ii) trickle beds, (iii) slurry and other agitated reactors, and (iv) Robinson-Mahoney reactors.

Additionally, we focus on kinetic studies in difficult situations: (i) presence of irreducible transport limitations (special experimental techniques and software); (ii) catalyst deactivation and regeneration, (iii) dynamically operated reactors.

Kinetics software:

EUROKIN also helps the user to with methods and software required for obtaining kinetic expressions. The following items are addressed:

(1) Ab-initio methods;
(2) Complex reaction networks and lumping;
(3) Liquid-phase kinetics;
(4) Computational fluid dynamics (CFD);
(5) Dynamic methods
(6) Reactor modelling for the 'difficult situations' as described above;
(7) Kinetic parameters estimation;
(8) Design of experiments;
(9) Extraction of kinetics from large data sets;
(10) User-friendliness.

Finally, EUROKIN pays attention to the implementation of kinetics (including uncertainties) in plant performance simulations.

Papers

Chemical reaction kinetics in practice: R.J. Berger, E.H. Stitt, G. B. Marin, F. Kapteijn and J. A. Moulijn, *CATTECH*, 5 (2001), p. 30-60.

Catalyst bed dilution: R.J. Berger, J. Pérez-Ramírez, F. Kapteijn and J. A. Moulijn, *Chem. Eng. Sc.*, 57 (2002) 4921-4932, *Applied Catal. A: Gen.* 227 (2002) 321-333, and *Chem. Eng. J.* 90 (2002) 173-183.

Criteria for neglecting radial concentration gradients in coated-wall reactors: R. J. Berger, F. Kapteijn, *Ind. Eng. Chem. Res.* 46 (2007) 3863-3870 and *Ind. Eng. Chem. Res.* 46 (2007) 3871-3876.

Dynamic methods for catalytic kinetics: Rob J. Berger, F. Kapteijn, J.A. Moulijn, G.B. Marin, J. De Wilde, M. Olea, D. Chen, A. Holmen, L. Lietti, E. Tronconi, Y. Schuurman, *Applied. Catal. A: Gen.* 342 (2008) 3–28.

CO_2 oxidative dehydrogenation for hydrocarbons to styrene and olefins

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OSPT theme	: Products and processes	**Research school**	: NIOK
Supported by	: STW/Lummus Technology	**Period**	: Nov 2007 – Nov 2011

Introduction

Styrene and olefins like ethene, propene, butene, and butadiene, are amongst the largest bulk chemicals produced from hydrocarbons and are starting materials for many chemical products and polymers. The dehydrogenation is an endothermic reaction. The current production route is direct dehydrogenation in the presence of steam. Steam has three functions, it delivers heat for the reaction, dilutes the system for a better yield and helps against catalyst deactivation. This process suffers from several disadvantages. It is very energy intensive as it requires large amounts of excess steam, the catalyst is easily deactivated, and it has relatively low conversions due to the thermodynamic equilibrium at the high temperatures that are required.

Other production routes, like oxidative dehydrogenation using oxygen, have been explored for more than 20 years, but without the desired commercial success. This is partly due to explosion risks when using oxygen and low selectivities due to side-reactions.

CO_2 as a mild oxidant avoids the problem of explosion risks, shows high selectivity and conversion at lower temperatures than direct dehydrogenation. This and avoiding the use of steam in the process reduces the energy requirements up to 60%.

CO_2 oxidative dehydrogenation

The use of carbon dioxide instead of steam has three major advantages: the process is more energy efficient, the process is safer, and yield is higher since equilibrium restrictions are overcome. The last advantage is a result of water-gas-shift reactions that are occurring simultaneously with the dehydrogenation reaction.

Compared to the oxidative dehydrogenation using oxygen, this process also has several advantages: It is safer, selectivity is higher, CO_2 provides better temperature control, and it is cheaper.

Reaction conditions for CO_2 oxidative dehydrogenation are 550-600℃, atmospheric pressure and a ratio of CO_2:EB of 5-10.

Objectives

The complete process development is of interest, starting with catalyst development and testing, including reaction kinetics studies and catalyst stability, up to scaling it up to a mini-pilot plant level. To achieve this, I will closely cooperate with the partners, Rijksuniversiteit Groningen and Lummus Technology. My work will mainly focus on the first part, catalyst development and testing. In order to do this, a new six-flow reactor setup has been ordered which will be coupled to a new online-GC for analysis.

Acknowledgement

This research project is carried out within the Green and Smart Process Technologies framework of STW. Partners in the project are RuG and Lummus Technology. It is financially supported by STW and Lummus Technology.

Reactions during CO_2 oxidative ethylbenzene dehydrogenation

$$C_6H_5\text{-}CH_2\text{-}CH_3 + CO_2 \rightleftarrows C_6H_5\text{-}CH{=}CH_2 + H_2O + CO \qquad \Delta H\,(600℃) = 161.1\ kJ/mol$$

$$C_6H_5\text{-}CH_2\text{-}CH_3 \rightleftarrows C_6H_5\text{-}CH{=}CH_2 + H_2 \qquad \Delta H\,(600℃) = 124.9\ kJ/mol$$

$$H_2 + CO_2 \rightleftarrows H_2O + CO \qquad \Delta H\,(600℃) = 36.2\ kJ/mol$$

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Delft University of Technology

CE

Hydrodynamics of multiphase packed-bed microreactors

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Introduction

Miniaturization of catalyst performance testing is primarily motivated by the elimination of temperature and concentration gradients in the catalyst bed. Since the bed diameter decreases the transport phenomena outside the catalyst particle will alter. A six-flow microreactor unit ($L_{reactor}$ = 15 cm, d_{tube} = 2 mm, $d_{particle}$ = 100μm) was built to test the new catalyst formulations for deep desulphiding.

Back mixing, hold-up, and residence time can be very different in micro-packed beds. In these systems (Re~1, $d_{particle}$ < 100μm) capillary forces are dominant. Established correlations are based on large-scale trickle beds (Re>1, $d_{particle}$ ~1mm), where inertia and gravity play a prominent role and, therefore, those cannot be used for these micro-packed beds. One of the objectives of the research is to describe the intricate interplay of diffusion, gas-liquid interaction, and convection for the surface tension-dominated low Reynolds-number flows in these small packed bed systems.

From a design perspective it is vital to determine the extent of the reactant dispersion, especially at high conversion in small reactors. Moreover, it is instructive to know the difference between the residence time of the gas and that of the liquid: stripping of reactants and products can significantly impact conversion levels and mask the proper interpretation of kinetic experiments.

Objective

The ultimate goal is full understanding of the hydrodynamics and true reaction kinetics in micro-packed beds for (deep) hydrodesulphurization.

Experimental program

The starting point was liquid-liquid diffusion coefficients determination of hydrocarbon molecules, typical of hydrodesulphurization reactions, at high temperature. A correlation with an average AAD < 5% was established. Transient times and stability studies in the multiphase micro packed bed showed that the feed section volume has a strong effect in the transient time, therefore, this section should be as small as possible, and that due to very strong capillary forces, the liquid saturation of the bed is very high (>0.5), leading to very stable hydrodynamic conditions with no influence of start-up procedures.

RTD studies at room conditions for low Re numbers indicated low gas-liquid interaction with limited effect of molecular diffusivity on dispersion and very similar dispersion behavior to comparable liquid phase systems.

RTD curves with volatile tracers, to evaluate the reactant evaporation effects on the hydrodynamic parameters, indicated that the major effect is in the reduction of the residence time for the volatile compound.

Visualization experiments in micro fabricated packed beds are being performed to gain insight in the flow patterns that prevail when capillary forces are dominant.

Acknowledgement

This research project is supported by the Programme Alβan, the European Union Programme of High Level Scholarships for Latin America, scholarship no.E04D028997VE.

Keywords: hydrodynamics, multi-phase, packed bed, high-throughput.

Fluid Catalytic Cracking: Evaluation of Commercial Catalysts in a Microriser Reactor

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OSPT theme	: Products and Processes	URL	: not available at the moment
Supported by	: BASF Catalysts, USA	Period	: May 2008 – April 2010

Introduction

Fluid catalytic cracking (FCC) is one of the important and efficient refinery processes for the conversion of heavy oils to high value light products such as gasoline, middle distillates (diesel), and light hydrocarbons (C_1-C_4). Due to the stringent environmental regulations and changing product specifications, FCC catalysts and operations are being continuously modified or developed to meet their requirements. Different types of catalytic reactors are employed for FCC process at laboratory scale. Of these, once-through microriser reactor was found to be one of the promising reactors that simulates the actual riser hydrodynamics and was capable of generating realistic data for commercial FCC applications. Specifically, studies on increasing propylene production and reducing gasoline sulphur in FCC have received increasing attention due to their great demand.

Objectives

The current project aims at studying several aspects in a FCC process. The present work will be carried out in three phases. The first phase would be studying different gas oil feeds and commercial catalysts (E-cat) under various operating conditions (temperature, contact time, and Catalyst-to-Oil ratio) to understand the FCC performance in a microriser. This data will then be compared with the pilot plant circulating riser unit (CRU) data to benchmark the microriser and also to understand the differences between these reactors, if any. The second phase of the project would focus on enhancing the current knowledge of the light olefin or LPG olefin chemistry in a FCC process by varying the ZSM-5 content in the catalysts. In the third phase, we would also like to study one of the most important FCC aspects, the sulphur chemistry and kinetics, which is much less understood. In order to gain more insight into the sulphur chemistry, the conventional gas oil feeds and also the synthetic mixtures made from zero sulphur feeds doped with various sulphur containing hydrocarbons would be studied in a microriser.

Experimental

The typical operating variables for fluid catalytic cracking of gas oils in a microriser are: temperature (530-580 °C), catalyst-to-Oil ratio (2-7), and contact time (1-5 s). The gas oil cracked stream is generally classified into gasoline, light cycle oil (LCO), heavy cycle oil (HCO), and dry gas (H_2, C_1-C_4). Furthermore, the coke formed during cracking on the spent catalyst is measured using a LECO analyzer. Based on the experimental data obtained, we would understand the effect of various factors on product distribution.

Acknowledgement

The TU Delft and the financial support from BASF catalysts, USA for carrying out this work are gratefully acknowledged.

Keywords: FCC, olefins, sulphur

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Particle Technology Activities in the Nanostructured Materials Section

The Nanostructured Materials Section at DelftChemTech dedicates most if its research to producing and characterizing new nanostructured materials based on particles and polymers. Processes for particle production are developed with the goal of obtaining particulate products, which are well defined concerning their composition, grain size, as well as surface and bulk morphology. Methods have been or are being developed that characterize these particles on-line, i.e. with a short time delay. Particle deposition techniques for production of highly porous networks and for imbedding particles into polymers are being developed. Fast screening of the particles with respect properties like catalytic activity or hydrogen storage capacity, while their composition and size are continuously changed, is expected to lead to the discovery of new materials for technical applications.

The research on electrospray particle production and its scaling up is forming important bridges to processes in biotechnology. Methods are being developed that produce nano-particles of complicated organic compounds for use as medicines and as new materials for diagnostics. The selective detection of specific micro-organisms on-line by fluorescence and mass spectroscopy has attracted attention worldwide.

This research is accompanied by extensive activities in numerical and theoretical modelling of particle systems such as granular materials. The main direction here is finding the transition between the microscopic and the macroscopic description. This work is of practical importance, because about 70 percent of all products from chemical or pharmaceutical industry occur in a powder or granular state or go through such a state in the process of production.

NanoGrinding of Food Products

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OSPT theme	: Nano-Technology	Period	: February 2006 – February 2010

Introduction

Nanogrinding of Food Products consists in making nanoparticles with a simple ball mill. We foresee an strong improve of product efficiency simply by reducing the particle size. Indeed, by doing so, we increase dramatically the surface area. In other words, products will be much more available and therefore, more efficient.

Nanogrinding – Technical aspects.

Diagram representing an horizontal ball mill from Bachofen, Basel, Switzerland.

Grinding media consists of 0.3 to 0.8mm zirconium-, glass-, plastic-, etc beads.
Rotation speed ranges from 2000 to 6000 rpm.
System is cooled with water (about 16°C).
Time ranges from 15 min up to several hours.

Sub micron grinding – Modeling.

The curve of the evolution of the particle size in time (transformed in a cumulative graph) are fitted with an exponential function:

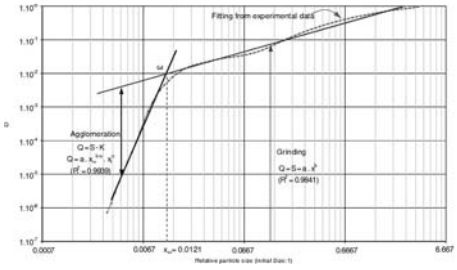
$$R_i(t) = R_i^0 \cdot \exp(K_i \cdot t)$$

The selection and breakage function are defined as follow

$$S_i = -K_i ; \; b_{ij} = \frac{S_{i-1} - S_i}{S_j}$$

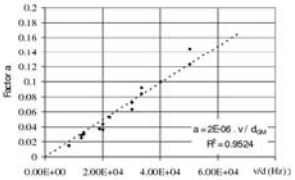
The model becomes therefore defined by

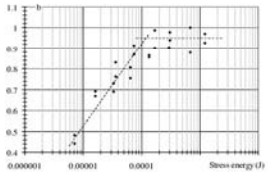
$$\begin{cases} \text{If } x_i > x_\omega ; Q_i = S_i = a \cdot x_i^b \\ \text{If } x_i < x_\omega ; Q_i = S_i - K_i = a.x_\omega^b - c \cdot x_i^c \end{cases}$$



- Parameter a: Frequency factor

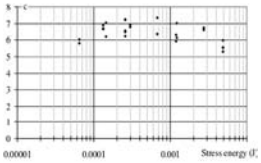
Function of the number of impacts per unit of time





-Parameter b: Breakage efficiency

b is linked to the energy required for breakage



- Parameter c:

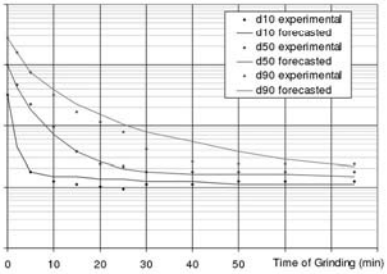
Agglomeration efficiency

c is equivalent to b but for agglomeration

- Xω is the equilibrium point

Model Evaluation and application:

➔ Correct forecast of particle size evolution for random chosen operating conditions.



Acknowledgement

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DSM and TUDelft-NMS are hosting this project and providing all material support.

Nanoparticulate Hydrogen Storage

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OSPT theme	: Energy Conversion Processes	Research school	: OSPT
Supported by	: SenterNovem; Delft Institute for Sustainable Energy (DISE)	Period	: Sept. 2005 – August 2009

Introduction

The successful introduction of hydrogen powered vehicles is not possible without a good method for on-board hydrogen storage. Current methods are hampered by low capacity (high pressure gaseous H_2), high energy consumption (liquid H_2), and safety considerations.

One alternative for hydrogen storage are metal hydrides. These are metals or intermetallic compounds that react reversibly with hydrogen, forming stable compounds with hydrogen volume densities often exceeding liquid H_2.

Metal hydrides however still suffer from a number of drawbacks: (1) low weight percentage of hydrogen, or (2) high required temperature for the release of hydrogen, or (3) slow hydrogen uptake/ discharge kinetics.

This research focuses on the production of new metal hydride storage materials with more favorable properties. This not by using the more conventional ball milling process, but with aerosol-based nanoparticle production and handling processes.

Methods

Nanoparticles are produced using a spark generator. A capacitive discharge between electrodes of the desired material causes a small amount of material to evaporate. Carried away by a carrier gas stream, the material condenses to form nanoparticles. By using two different electrodes, compacted or alloyed electrodes nanoparticles consisting of two different materials (mixed on an *atomic* scale) can be produced. In this way many different interesting materials for hydrogen storage can be obtained. Subsequently the gas containing the particles is accelerated using a low pressure impaction nozzle and directed at a substrate. Due to their inertia the particles hit the substrate. Upon contact the particles stick to the substrate and each other because of localized heating due to the kinetic energy. In this manner a stable but highly porous layer is obtained, in which many of the original properties of the nanoparticles are maintained.

The process is very flexible with regard to the materials used; the treatment of the particles in the gas phase, and nanoparticles of a very well defined nature can be obtained.

The small size and high porosity of the obtained layer of the produced nanoparticles allows for good uptake and discharge kinetics. Initial results seem to indicate some favourable thermodynamic effects occurring as a result of the small particle size.

The formation of layers allows for stable application of the produced nanoparticles. The obtained layers can then be further modified.

Acknowledgement

This research project is financially supported by SenterNovem and the Delft Institute for Sustainable Energy (DISE).

Characterization of Coating Formulation and Process Manufacturing Understanding as Tool for Determination of Coating's Strength

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OSPT theme	:	**Research school**	: OSPT
Supported by	: DSM – Marie Curie	**Period**	: April 206 – April 2010

Introduction

When we apply a coating onto a particle we need to guarantee that the product has sufficient chemical stability and physical strength to survive the thermal, mechanical and humidity stresses encountered during manufacture, packaging, distribution, storage, and use. The design of a commercial manufacturing process that meet all of these requirements require the careful characterization of the coating formulation, and the development of in depth understanding of how its properties impact the ultimate performance of the drug product.

Experiments and Results

Thus a "quality by design" approach will then result in an in-depth understanding of the interactions of the several variables such as raw materials, drug substance, manufacturing and environmental conditions, etc. and facilitate manufacturing of a product The general aim of this is to obtain the desired quality-functionality of the coating starting from the complete knowledge of the coating polymer. With these ideas in mind, we use both a different investigation criteria and a different setup for carrying out alternative raw material characterization and fluid bed coating experiments, which encompass the advantages of the afore-mentioned approach. Polymer-coated particles have been produced by top-spray fluid bed coater and both morphology and resistance to attrition have been analysed using Scanning Electron Microscope, SEM and Repeated Impact Tester, RIT respectively. Coating thickness, coated particles storage conditions and physical aging effects have been assessed. The coating thickness is found to be extremely relevant in raising the resistance to attrition. Thicker the coating and more resistant is the coated particles against attrition. This improvement is found to be more and more relevant while impact energy is increasing. The storage temperature is not influencing the morphology whereas is strongly affecting the resistance to attrition. Coated particles stored at -18 ° were found to be more resistant to attrition then ones stored at room conditions. Such differences, negligible at low energies (low numbers of impacts) increase as soon as the number of impacts and thus the energy rise.

The coated particles, stored at ambient conditions, were subsequently aged in vacuum oven and the effect of aging steps was evaluated in terms of resistance to attrition. In aged coated particles were found a wasting in resistance to attrition directly proportional to the aging time. Moreover, the aging process was found to affect the breakage mechanism experienced by the coated particles during impacts tests. The common attrition mechanism was found to be layer fatigue. Using the equation proposed by Tavares and King [49] as starting point, a new equation has been developed in order to fit to the resistance to attrition data. The equation takes into account the number of impacts, the velocity of the impacts, the coating thickness, the coefficient of restitution, e, of the coated particles and the mass specific fracture energy, $E_{f,m}$. This equation has been successfully applied for different coating materials and different coating thicknesses.

Acknowledgement

This research project has been first financially supported by Marie Curie Biopowders network and by DSM Food Specialties now.

Multiple Hole-based Electrospray System

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OSPT theme	: Separation Technology	Period	: September 2006 – August 2010
Supported by	: MicroNed		

Introduction

A high production rate of monodispersed like droplets by electrohydrodynamic atomization (EHDA) from a single nozzle is limited by the fact that the expected droplet diameter is mainly a function of the flow rate. Outscaling of EHDA by using multiple nozzles is possible. However, factors such as electrical interference between the neighbouring sprays, and liquid flow rate variations from nozzle to nozzle are problems to overcome for industrially acceptable stable systems (Tang and Gomez, 1996; Bocanegra et al., 2005).

Providing a uniform flow rate and a uniform electric field to each nozzle is essential for getting uniform droplet from an outscaled electrospray assembly. Bocanegra et al. (2005) reported that multi-hole electrosprays provided no large dispersion in the droplet size distribution from nozzle to nozzle when the flow rate throughout each hole was the same.

Method

The performance of a line array of adjacent electrospray holes is studied in an attempt to optimise the design of a multi-hole electrospray system. The test system is shown in Fig. 1.

The reservoir is made of Delrin®. The HV is applied to the liquid. The ejector plate is made of Delrin®, Teflon®, or brass and is to test the effect of hydrophobic and hydrophilic surfaces of the sprayed solution. An advantage of an insulator/hydrophobic is that it enhances the local field at the emission point

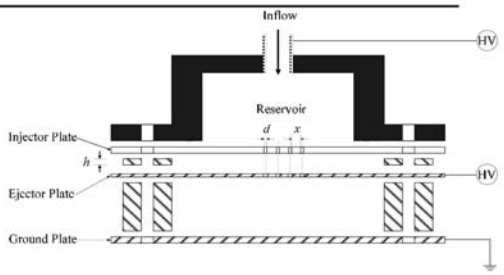

Figure 1. Schematic of the multi-hole electrospray atomiser.

The different solutions were a mixture of ethanol and ethylene glycol and pure ethanol. The flow rates were varied between 0.1ml/hr and 5 ml/hr.

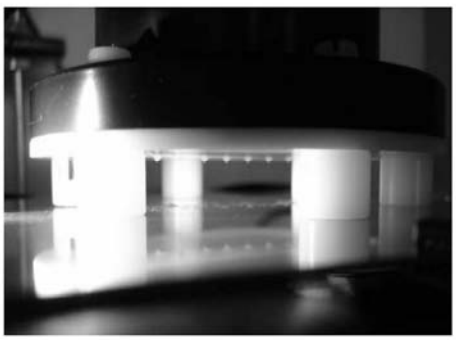

Figure 2. A multi-hole electrospray

Figure 3 illustrates a working multi-hole (8 jets) in line electrospray.

Acknowledgement

This research project is carried out within the framework of the MicroNed. It is financially supported by MicroNed.

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Activities of the Engineering Thermodynamics Chair

The description, prediction and optimization of process fluids is of key importance for the further development of chemical processes and energy technology. Within this goal, the tailoring of physical properties of process fluids allows for rigorously optimizing their performance. The analysis of energy and matter streams in conversion processes and a systematic process analysis/optimization are seen as a basis towards the development of more efficient processes. Therefore, within the chair of Engineering Thermodynamics the three central disciplines are Thermodynamics of complex mixtures, Molecular Simulation and Heat Pumps. The field of irreversible Thermodynamics provides a systematic methodological framework to optimize processes through minimizing the appropriate entropy production. Summing up, the group is equipped with a toolbox of Molecular Simulation, Theoretical Fluid Theories and entropy minimization, giving the knowledge to tackle problems at macroscopic or at microscopic scale as required.

Lines of Research

In the Engineering Thermodynamics group we work on the design of process fluids enabling efficient chemical processes and energy technology. Further, we focus on interfacial behavior. Molecular Thermodynamics is the basis for the theoretical developments. And our comprehensive laboratory allows for systematic experimental work.

The central disciplines of the Engineering Thermodynamics chair are:

- Thermodynamics of Complex Mixtures (theoretical: Molecular Fluid Theories)
- Thermodynamics of Complex Mixtures (experimental)
- Molecular Simulation
- Refrigeration & Heat Pumps
- Irreversible Thermodynamics

The different lines of research are closely interconnected and the toolbox which is used to work on these subjects is narrow – the toolbox is given by Experiments, Molecular Simulations, Fluid Theories from Statistical Mechanics, and Entropy Minimization by Irreversible Thermodynamics. The field of Irreversible Thermodynamics provides a systematic methodological framework to optimize processes through minimizing the appropriate entropy production.

Thermodynamics of Mixtures

Fascinating new materials have recently emerged as solvents for process industries, such as hyperbranched polymers, or (ionic) Liquid Crystals. It was shown that carbon dioxide for example shows a step-change of solubility in Liquid Crystals over variation of temperature. These solvents can be tailored to a specific task. In the interplay between theoretical, experimental and computational thermodynamics lays the appeal and the potential for innovative research in this field.

Molecular Simulation

Molecular Simulation has emerged as a powerful tool in molecular thermodynamics. It is possible to represent real components in terms of classical force fields to such an extend that reliable predictions are not only possible for structural properties but also for phase equilibria and transport properties. Therefore, this offers an elegant way to predict equilibria of yet unknown components and therefore the tool of choice for the structural optimization of complex solvents. Molecular Simulations also play a key role in the development of fluid theories and the understanding of transport processes.

Refrigeration and Heat Pumps

Refrigeration plays a major role in the food industry. Industrial waste streams even if existing at fairly low temperatures might inhibit substantial amounts of energy. Thermodynamic cycles allow for upgrading of these energy flows to higher temperature levels. Energy storage systems allow for compensation of the mismatch between availability of low temperature energy streams and demand for higher temperature energy streams. The analysis of energy and matter streams in conversion processes making use of thermodynamic cycles, energy storage systems and entropy minimization techniques allows for their systematic optimization.

Irreversible Thermodynamics

The field of Irreversible Thermodynamics can be used to systematically improve processes through minimizing entropy production and can thus be used as a tool within the areas of conceptual process design and equipment design. The minimization of entropy offers a systematic methodological framework to improve processes; particularly it offers a conceptual scheme to evaluate processes towards their sustainability. Irreversible Thermodynamics can be applied on all scales, from microscopic views to the point of the design of large scale units.

Enclosure 1

Simulation of Adsorption of Benzene and Propylene in MOR-type Zeolites

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OSPT theme	: simulation	**Research school**	: OSPT
Supported by	: NWO	**Period**	: 04.2005 – 04.2009

Introduction

Cumene (isopropylbenzene) is an important bulk chemical used mainly for the production of phenol. Recently, there is a growing interest in performing this reaction inside zeolite pores in such a way that the B/P ratio is close to one in the reaction feed but very large near the acid sides inside the zeolite. This will avoid the use of large benzene recycling streams. To operate such a process detailed knowledge on the microscopic sitting of benzene and propylene is necessary. In this work, molecular simulation is used to investigate the sitting of propylene and benzene inside MOR- and MFI-type zeolites. It is shown that the adsorption of benzene and propylene is strongly influenced by the zeolite topology.

Methods

We performed Monte Carlo simulations in the grand-canonical ensemble using the Configurational bias Monte Carlo technique. The hydrocarbons are described using a united-atom model. Intra-molecular bond-stretching and bond-bending potentials are included for the hydrocarbons. Intermolecular interactions as well as interactions of the hydrocarbons with the zeolite are described by Lennard-Jones potentials. Interaction parameters between the hydrocarbons and the zeolite are chosen such that the simulations reproduce experimental pure-component adsorption isotherms.

Results and Discussion

In Fig. 1, we have plotted the adsorption isotherms of benzene, propylene and 50/50 mixtures of benzene/propylene in zeolite MOR. In MOR-type zeolite, the adsorption of propylene is strongly suppressed in the benzene and propylene mixture due to the larger heat of adsorption of benzene (B/P=100). Adsorption takes only place in the (large) main channel and not in the side pockets (Fig 2, left).

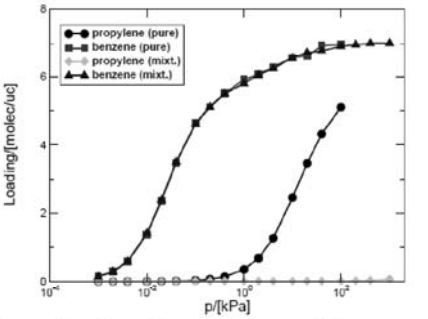

Figure 1. Adsorption isotherms of benzene, propylene and 50/50 benzene and propylene mixtures in MOR-type at 320K.

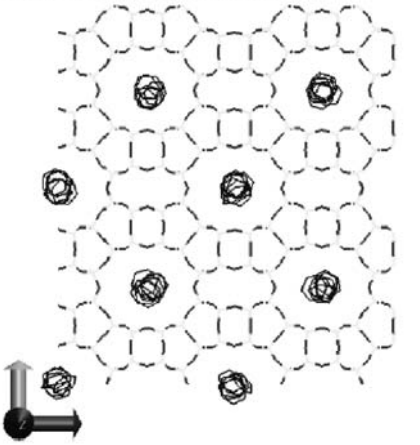

Figure 2. Adsorption of benzene and propylene mixtures at p = 100 kPa and T = 320K. In MOR only benzene (blue) is adsorbed.

Conclusion

MOR-type zeolite has a high selectivity towards benzene in the benzene and propene mixture due to its 1D pore system.

Acknowledgments

This work is supported by the Dutch ACTS/ASPECT program.

Understanding the Adsorption of Water in Metal-Organic Frameworks

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OSPT theme	: Porous materials	**School**	: OSPT
Supported by	: EuroSim	**Period**	: 05 2008 – 06 2010

Introduction

Molecular simulations were performed to study the adsorption behavior of water in the Metal Organic Framework Cu-BTC. The force field was adjusted to reproduce the experimental adsorption isotherm. Henry coefficients, energies, entropies and enthalpies of adsorption were calculated using this force field at different adsorption sites.

Objective

Developing a new force field able to reproduce the adsorption of water in the Metal-Organic Framework Cu-BTC, and that allows the understanding of water behaviour in this type of materials.

Simulation details

The system was modelled using force field parameters taken from the literature. In order to reproduce the experimental adsorption isotherm, the partial charge of the framework atoms had to be increased respect to the values obtained using quantum-chemistry calculations.

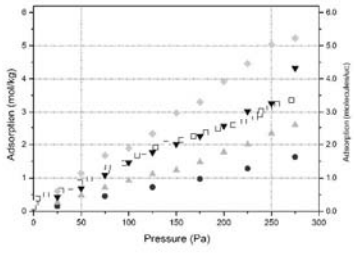

Figure 1. Adsorption isotherms of water in Cu-BTC at 295 K. Open squares, experimental data2; circles, original charge set; triangles up, triangles down and rhombus, original charge set increased in one 2%, 4% and 6% respectively.

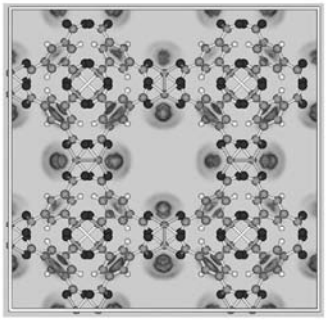

Figure 2. Location of water molecules adsorbed in Cu-BTC at 295 K and low loading. Water preferentially adsorbs close to the Cu atoms of the structure.

Results

The new force field is able to reproduce the experimental adsorption isotherm, as shown in Figure 1. The new parameters were used to identify the preferential adsorption sites. Water adsorbs preferentially close to the Cu atoms of the structure as shown in Figure 2. This preference is totally different to other molecules without dipole moment. This effect is due to the fact that the Henry coefficient or water at the preferential adsorption site is four orders of magnitude larger than in other adsorption sites.

Conclusions

Water has a large affinity for the metal centres of Cu-BTC. This is due to the strong electrostatic interaction between this molecule and Cu. This particular behaviour could be further exploited for the separation of water from other compounds.

Determining the Thermodynamic Behavior of Mixtures for Down-Hole Processing:

Modeling of Electrolyte Solutions Using the MSA Coupled with the PCP-SAFT EOS

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Supported by	: TUDelft, TNO, Shell	**Period**	: 02.2007 – 02.2009

Introduction

The down-hole conditions of high temperature and pressure along with the presence of water and ionic species makes such a description a non-trivial task. The underlying models have to account for the polar and associating molecular interactions with water and they have to adequately consider the presence of electrolytes and their influence on the acid gas (CO_2, H_2S) solubility.

The thermodynamic modeling of electrolyte systems is challenging because an ion–specific approach is needed. The model is combination of equation which describes the non–electrostatic short range repulsive and attractive interactions (G^E model or equation of state (EOS)) and the theory accounting for the long–range Coulombic interactions present between the molecules (Debye-Hückel theory, mean spherical approximation (MSA), etc.).

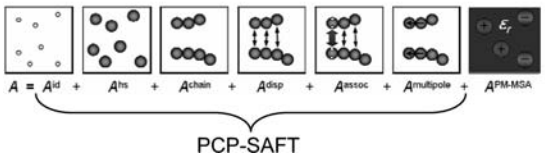
Goals

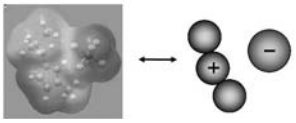
The project aims:

- to develop thermodynamic model derived from Statistical Mechanics which well describes phase behavior of complex mixtures, in particular electrolyte solutions, at wide range of T and P;
- to use the PCP-SAFT EOS to describe the non-electrostatic interactions between ions and dipoles;
- to apply the primitive MSA (PM-MSA) to account for the long-range Coulombic interactions.

Model Description

The ionPCP–SAFT model is used to correlate and predict the solubility of CO_2, ethylene and other gases in ionic liquid mixtures over a wide range of conditions. In this model, the molecules are chains of segments and the Helmholtz energy is the sum of ideal gas contribution, hard-chain term, dispersive part and contribution due to association, polar interactions and MSA term accounting for ionic interactions:

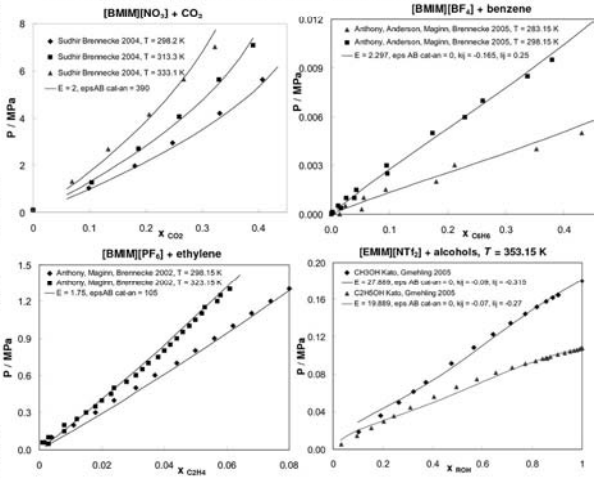




The ionic liquid mixtures are considered as highly asymmetric. Thus the modeling of phase equilibria of ionic liquid (IL) systems using ionPCP-SAFT EOS is performed in order to verify the applicability of this model to such complex electrolyte mixtures.

Results and Discussion

Primitive MSA coupled with PCP-SAFT EOS describes ionic liquid / gas and ionic liquid / alcohol systems very accurate. Good agreement between the experimental results and the model is obtained.



Vapor-liquid equilibria of IL + gas or alcohol systems at different temperatures. Comparison of the ionPCP-SAFT EOS to experimental data.

Conclusion

PM-MSA + PCP-SAFT = ionPCP-SAFT equation of state is a powerful tool for thermodynamic description of electrolyte solutions.

Acknowledgement

This research project is carried out within the framework of the ISAPP project. It is financially supported by TNO and Shell.

Dehydration performance of a hydrophobic DD3R membrane

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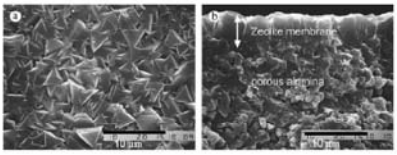
Supported by	: DC SIP	**Period**	: 8-2004 – 02-2009

Introduction

The dehydration performance of an all-silica DDR membrane (NGK Insulators, Japan) has been studied in pervaporation mode. Although the zeolite is hydrophobic, the small pore size allows for selective water separation by molecular sieving.

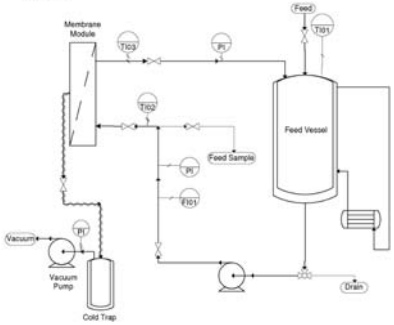


Aims

- Determine the dehydration performance of DD3R zeolite membranes
- Model the mass transport using Maxwell-Stefan type of equations

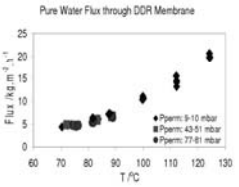
Approach

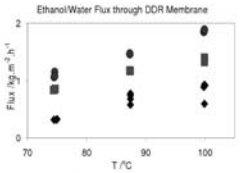
- Pervaporation mode
- Temperatures up to 150 °C
- Pressures up to 16 bar
- Traced permeate tubing, allowing higher permeate pressures
- Flux is insensitive to feed pressure, indicating no viscous flow contribution.

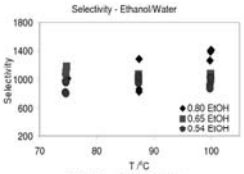


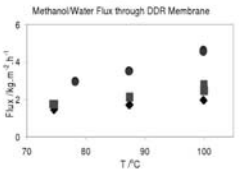
Results

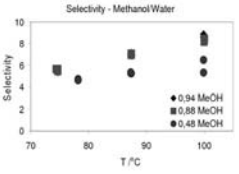
- High water flux
- Arrhenius type temperature dependence.
- Methanol flux insensitive to temperature











Conclusions

- Pure water fluxes up to 20 $kg.m^{-2}.h^{-1}$ were measured.
- Selectivities for water in ethanol and methanol are respectively 1400 and 9.
- The flux and selectivity increases with temperature.
- Presence of ethanol and methanol decreases the water permeance
- Presence of water decreases ethanol permeance, but does not effect methanol permeance

Acknowledgements

We acknowledge Rainier Maldonado Blanco and Jos Nijenhuis for their experimental work.

Thermodynamics of Hyperbranched Polymers - CO2 - Systems: Facilitating Thermal Separation Processes

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OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: Shell - Global Solutions	**Period**	: 10 2006 – 10 2010

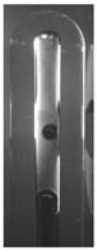
Introduction

Hyperbranched polymers (HBPs) are highly branched, polydisperse, macromolecules that can be synthesized via one-step reactions and have no measurable vapor pressure. The properties of hyperbranched polymers are highly tunable due to the fact, that core and shell groups might be modified individually. Opposed to linear polymers HBPs inhibit a globular shape and are liquids at room temperature. It could be shown that HBPs selectively alter the fugacities in a mixture. Thus, they possess a high potential to being used as process solvents.

Objective

Develop an understanding of the phase behavior of branched molecules. Therefore, determine the influence of molecular weight as well as varying end groups on the phase equilibrium with CO_2. VLE measurements are performed and the thus obtained data is used to develop an equation of state, suitable to describe the properties of branched molecules.

Experimentals



The bubble point pressures of HBP + MeOH + CO_2 (HBP: Polyglycerol Mw = 2000 g.mol-1, Polyglycerol Mw = 5600 g.mol-1) systems with fixed compositions are measured using the Cailletet apparatus. With this synthetic method the phase change due to small increases in pressure is determined visually at constant temperature. The pressure at which the last bubble disappears is the bubble point pressure of the mixture at a given T.

Modeling

The modeling has been done within the PC-Saft framework. Within this equation of state (EOS) molecules are assumed to consist of freely jointed spherical segments. A perturbation has been added to account for the formation of articulation tetramers with fixed angles. This EOS is called bPCP-Saft.

Results

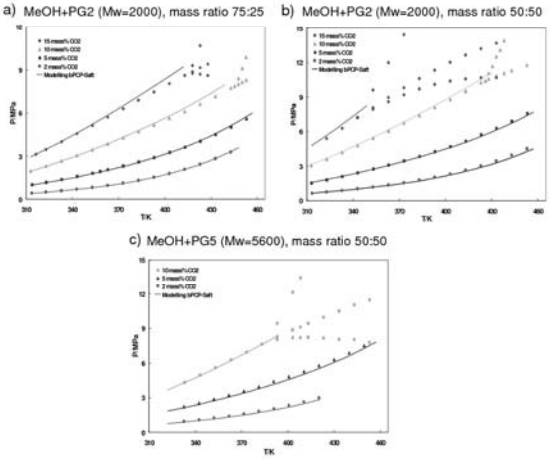


Figure: Vapor-liquid equilibrium data for: a) CO2 + [MeOH+PG2 (Mw=2000), mass ratio 75:25], b) CO2 + [MeOH+PG2 (Mw=2000), mass ratio 50:50], c) CO2 + [MeOH+PG5 (Mw=5600), mass ratio 50:50]. Symbols represent the experimental data with CO2 concentrations (wt%) as indicated. Lines are given by the model bPCP-Saft.

Conclusions

- Decreasing polymer concentrations shift the demixing to higher temperatures
- Increasing polymer molecular weigth shifts the demixing to lower temperatures
- Decreasing MeOH concentration shifts the phase envelope to higher pressures
- An EOS was developed that accounts for the structure of the polymer

Thermodynamic Properties of Nanocrystal-Surfactant Systems

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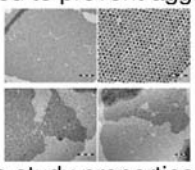
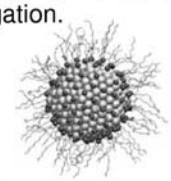
INTRODUCTION

Gold- and semiconductor colloids with controlled size and shape (nanocrystals) are of growing importance in the fields of optics, electronics, catalysis, ceramics, magnetic storage and biophysics.
They can self-assemble in a range of different 2D and 3D superstructures. Properties of these assemblies often depend on (organic) capping molecules used to prevent aggregation.

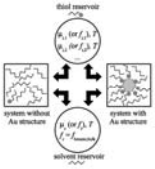




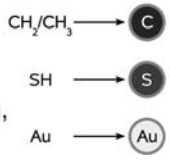
We study properties of capping layers on single gold NCs using computer simulations. These properties are can hardly be accessed by experiments, but are crucial for understanding of formation of lattices.

MODEL and METHODS

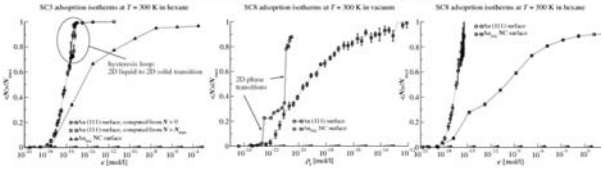
• Advanced Monte-Carlo in the μVT ensemble. Chemical potential μ is related to concentration via Henry's law.



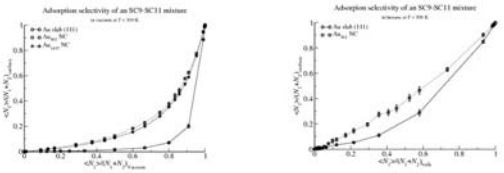
• United atom model with itermolecular Lennard-Jones interactions and intramolecular bond strech, bending and torsion



RESULTS – ADSORPTION ISOTHERMS



RESULTS – ADSORPTION SELECTIVITIES



CONCLUSIONS

There is a difference in adsorption behavior of surfactants to flat Au (111) surfaces compared to NC surfaces.

Compared to flat Au (111) systems:

• adsorption on the NC starts at higher concentrations;
• the range of adsorption is wider for NCs;
• no coverage dependent 2D phases on the NC at room temperature;
• reduced NC adsorption selectivity.

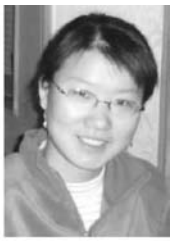
⇒ Tail-tail interactions are weaker in NC systems

The solvent effects are:

• competition in adsorption between surfactants and solvents;
• reduction of attractive interaction between aliphatic tails.

⇒ The solvent cannot be neglected in molecular simulations

Study for underground separation of sour gases from natural gas



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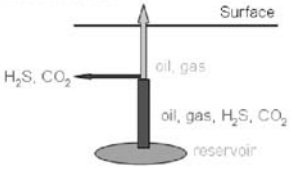
OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: TNO, Shell, TUDelft	**Period**	: 02.2006 – 02.2010

Introduction

Crude oil and hydrocarbon gas streams may contain high levels of CO_2 and/or H_2S as contaminants. Opportunities for disposal of the unwanted components include subsurface sequestration of these substances.



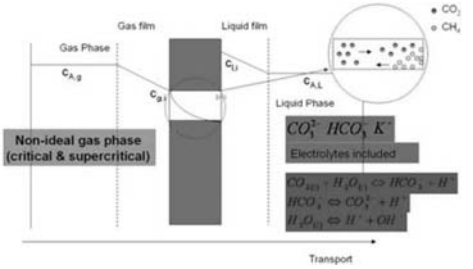
Technologies evaluation

Absorption/desorption processes were elaborated for the treatment of natural gas. The distinct advantage of the fluid processes is the robustness under severe conditions of the reservoir. There are different choices for the solvent selection.

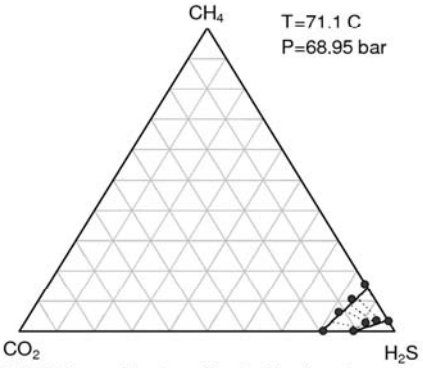
Solvent selection

The use of mildly basic aqueous electrolyte solutions, for example K_2CO_3 aqueous solution as absorbents leads to a balanced absorption as well as desorption behavior under the conditions at hand.

Evaluation of membrane absorption process

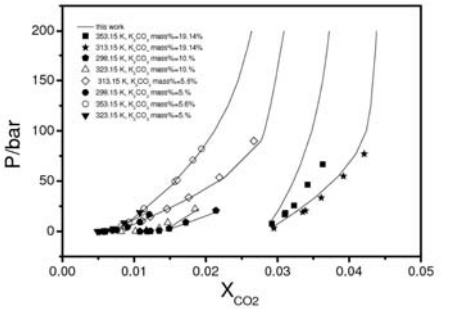


Gas phase containing sour gas at high pressure



PCP-SAFT equation is well suited to describe natural gas systems containing acid gas at elevated pressure.

Vapor-liquid Equilibrium for H_2S/CO_2 in aqueous solution



Peng-Robinsen EOS combined with an extended UNIQUAC model solves phase equilibrium and reaction equilibrium simultaneously.

Conclusions

Membrane absorber appears promising for separation process undergroud. A detailed mass transfer model using a Maxwell-Stefan approach including combined phase & reaction equilibrium is currently being developed.

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Activities of the Delft Center for Systems and Control

The relevant trends in process industry could be summarized as: better profitability, increased flexibility, and the incorporation of sustainability. The vision of DCSC is to support these trends from an *operational point of view*. The central paradigm for achieving this is *model-based control and optimization*. It provides a framework for feedforward and feedback strategies and it can handle all kinds of models, objectives and constraints. The research focuses on three areas:

1. Modeling

The area not only includes modeling but also estimation, validation, identification and reduction. The idea is to get a dynamic model that is sufficiently accurate at an acceptable computational effort. It might be necessary to deal with model uncertainty explicitly. Some research examples in this area are:

- System identification of hydrocarbon reservoirs (Van Doren, Van den Hof, Jansen and Bosgra).
- Automated model calibration in industrial process control (Bombois and Van den Hof).
- Block structured based model reduction (Naeem, Bosgra and Huesman).
- Closed-loop identification (Van den Hof, Bombois).
- Identification of nonlinear (LPV) models (Toth, Heuberger, Van den Hof).

2. Control/optimization

If an adequate model is available then it can be used for model-based control and optimization. However to enable feedback state estimation is necessary, and both estimation and control require solving optimization problems in real-time. A few research examples in this area are:

- Model predictive control of industrial crystallizers (Mesbah, Van den Hof, Huesman and Kramer).
- Economic dynamic process optimization (Huesman, Bosgra and Van den Hof).
- Grey-box modeling and plantwide integrated control of water purification processes (van Schagen, Babuška and Scherpen).
- Balancing long term economic optimal strategies and short term production targets in hydrocarbon reservoir management (Van Essen, Van den Hof, Jansen and Bosgra).

3. Interface design and control

The ultimate design of innovative and highly efficient process systems, requires the involvement of aspects of operation and control in its design phase. New developments in process intensification focuss on process systems in which intensified levels of sensing and actuation of process variables occurs. This provides new challenges for dynamic operation and optimization of processes by using model-based control strategies.

Multi-scale System Optimization of Oil and Gas Production

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OSPT theme	: Process Engineering	**Research school**	: DISC, OSPT
Supported by	: ISAPP	**Period**	: February 2006 - February 2010

Introduction

This PhD project concerns the application of system optimization techniques to the life cycle of oil and gas production. It is aimed at the development of a strategy to decompose the problem into sub-problems at different time and spatial scales, methods to optimize the individual subsystems and methods to manage the interrelationships between the subsystems taking into account uncertainty in the geology and the business conditions.

Project Description

Figure 1 depicts the main processes in the Exploration and Production (E&P) life cycle. Decision-making and optimization during development of an oil field and the production phase involves sub-process elements at various time and spatial scales, in particular Production Management, Reservoir Management and Portfolio Management, as indicated in Figure 2. Due to the difference in time and spatial scales,

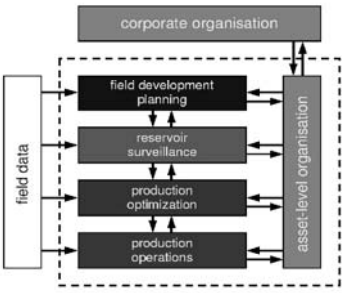

Figure 1: ***main processes in the E&P life cycle.***

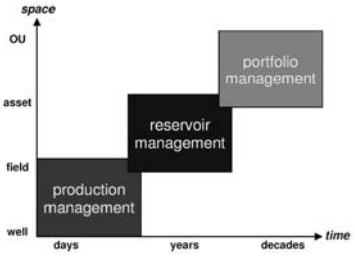

Figure 2: ***Sub-process elements of oil production.***

these elements operate under different objectives and constraints, while many of the decision variables within the different management layers cannot be separated. In many cases, this results in contradictory and generally sub-optimal operational strategies over the production life of an oil field.
The aim of this project is to go from a silo-structure, where every process element is optimized independently to a more integrated structure, where decision-making is carried out to result in optimal life-cycle performance. The main focus is on integrating Production Management and Reservoir Management. A hierarchical control structure is used to address the different multi-level objectives and constraints.

Acknowledgement

This research was carried out within the context of the Integrated Systems Approach to Petroleum Production (ISAPP) knowledge centre. ISAPP is a joint project between Delft University of Technology, Shell International E&P and TNO.

Model-based Optimal Control of Industrial Batch Crystallization Processes

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OSPT theme	: Separation Processes	**Research schools**	: DISC, OSPT
Supported by	: SenterNovem, BASF, BP	**Period**	: Aug. 2006 – Aug. 2010

Introduction

Batch crystallisation processes are of paramount importance in the production of pharmaceuticals, food and speciality chemicals in the highly competitive chemical industry. Due to low-volume and high-value of such chemicals, interest in the optimal operation of batch crystallisation processes has substantially grown in the recent years.

The control of batch crystallization processes is often a challenging task due to their highly non-linear behavior, plant-model mismatch, irreproducible start-up, unmeasured process disturbances and lack of reliable measurements for the system states. Such limitations often render the use of off-line optimized profiles impractical for industrial applications. This research project therefore aims at the development of model-based optimal control strategies for on-line computation of the optimal operating policy in a seeded batch crystallization process.

Current State

A feedback multilayer control structure has been developed, depicted in Figure 1. An extended Luenberger-type observer is embedded in this framework to account for the plant-model mismatch and enable disturbance handling. The core component of the control architecture is the dynamic optimizer in which a constrained optimal control problem is solved on-line by simultaneous optimization approach. The dynamic optimizer and the observer both make use of a non-linear process model.

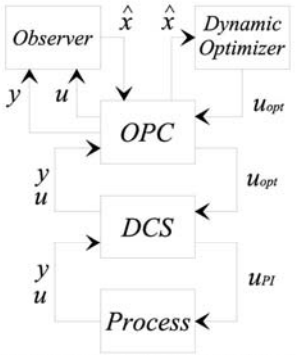

Figure 1: The proposed advanced control structure.

Real-time implementations of the proposed optimal control strategy on a semi-industrial 75-liter draft tube crystallizer have led to a substantial increase of 60% in the amount of crystals produced in a batch while the quality aspects of the product are also sustained. The latter is due to the effective constraint tracking realized by the dynamic optimizer.

Future Work

The current work will be extended to optimal control of an 1100-liter draft tube baffle crystallizer equipped with a fines removal loop that offers an extra degree of freedom to better control the crystal size distribution of the product.

Acknowledgements

The financial support of SenterNovem, BASF and BP is gratefully acknowledged.

Non-linear model reduction for large scale process models using input-state Hammerstein structure

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OSPT theme	:	**Research schools**	: OSPT, DISC
Supported by	: EU (ProMATCH)	**Period**	: June 2006 – June 2010

Introduction

Mathematical models of DAE or PDE form are used for the representation of different processes. The mathematical models are typically nonlinear as are the real processes. The mathematical models are generally very large for industrial processes, consisting of large number of differential algebraic equations and usually dynamic libraries for thermodynamic properties. So, the mathematical models for typical chemical processes are large and computationally inefficient. Low order models, with reduced order, reduced complexity and satisfactory accuracy are essential for online applications.

There are different perspectives of model reduction, for instance, balancing and truncation, projection based model reduction or block structure model reduction. In this research, the focus will be on approximating original model of process systems using block structures. Hammerstein structures have been used so far to approximate the process's mathematical model.

Current State

I/S (input-state) Hammerstein structure has been developed (Fig. 1) to approximate NL process within defined "*operating domain*". The process of defining operating domain is known as "*input design*" and is prerequisite for the model reduction methodology. It is shown in this research that I/S Hammerstein structure can be derived from Taylor series under few assumptions. I/S Hammerstein gives good approximation of the original system. I/S Hammerstein structure provides opportunities for model reduction in sense of lowering the computational load.

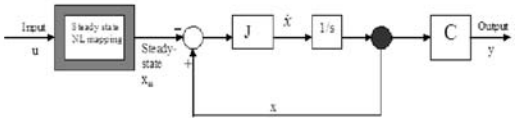

Figure 1:Input-State Hammerstein structure.

The accuracy of the approximation model has been improved up to second order. The methodology has been applied to a high purity distillation benchmark and satisfactory results are obtained as far as approximation is concerned. State and Jacobian order reduction up to 70% has been achieved for high purity distillation problem.

Future Work

In future it is planned to investigate computational time reduction of reuced model and to compare the computational time for reduced order model with original NL model in efficient environment (C++). Further state order reduction is to be investigated. The methodology is to be implemented on other applications.

Acknowledgements

This work was supported by the European Union within the Marie-Curie training Network PROMATCH under the grant number MRTN-CT-2004-512441.

Model Structure Analysis for Model-Based Operations of Hydrocarbon Reservoirs

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OSPT theme	: Process engineering	**Research school**	: DISC, OSPT
Supported by	: Shell, SenterNovem	**Period**	: November 2004-January 2009

Introduction

This PhD project concerns the model structure analysis of large-scale physical models as are used for model-based operations of hydrocarbon reservoirs. The goal of model-based operation is to optimize the performance of the hydrocarbon reservoir (including the wells and the surface facilities) based on long-term predictions of the fluid flow behavior in the subsurface reservoir rocks. Performance can mean a higher net present value of the reservoir or a higher ultimate recovery. The reservoir model is large-scale (possibly contains after spatial discretization millions of states and parameters), nonlinear and has multiple inputs and outputs. The states and parameters are estimated from measurements such as flow rate and pressure measurements in well.

Project description

Aspects that play a role in model structure analysis of large-scale physical reservoir models are the notions of identifiability structural identifiability, controllability and observability. The notions of identifiability and structural identifiability are related to the parameters, and the notions of controllability and observability are related to the states. In this work the notions of identifiability and structural identifiability are quantified.

Furthermore, the model structure of the large–scale physical models is approximated, where the physical interpretation of the parameters is preserved. The controllability and observability properties of the model are quantified, showing which (combinations of) states are most controllable and observable, and in addition which (combinations of) states are most relevant for the input-output behavior.

Acknowledgement

This research has been conducted in the framework of the ``Integrated System Approach Petroleum Production'' (ISAPP) program. The knowledge center is a long-term co-operation of TNO, Shell and Delft University of Technology to increase hydrocarbon recovery through the application of innovative reservoir development and management technologies. Financial support has also been provided through the ``Virtual Asset Learning and Understanding Environment'' (VALUE) program, which is sponsored by Shell and SenterNovem.

Model-based control of the hydrodynamics of bubble columns

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OSPT theme	: Multiphase Reactors	**Research schools**	: DISC, OSPT
Supported by	: DCSIP	**Period**	: January 2006–January2010

Introduction

Over the last few decades, much effort has been directed towards developing different techniques for control of fluid flows, i.e., hydrodynamics. This growing academic interest is encouraged by a wide range of industrial applications. The goal of flow control is to lower the operational expenses and improve the process performances.

Aim of the project

The project aims to develop a methodology for controlling fluid flow in bubble columns, which are frequently used for wastewater treatment, bioprocess transformation and production of petroleum substitutes (i.e., Fisher-Tropsch synthesis). An essential part of the development is to obtain a model in its simplest form retaining sufficient physical and mechanical phenomena. This model-based approach requires state estimation with an acceptable computational effort and sufficient accuracy.

Results

In carrying out the investigation, we addressed the problem of stabilizing fluid flow using macroscopic flow variables. ***Figure 1*** and ***2*** illustrate the macroscopic observation of a single fluid in a cavity and the control performances obtained by tuning the control parameters. The results have shown that the complexity of control design for fluid flow can be considerably reduced by accounting different observation levels.

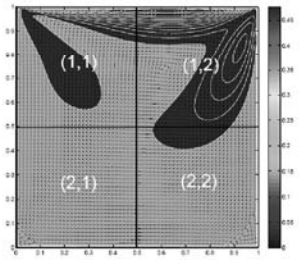

Figure 1. *Macroscopic energy distribution of the lid-driven cavity case*

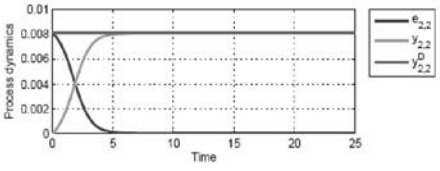

Figure 2. *Feedback control of the lid driven cavity case for Re = 100*

Future work

Using the previous findings, the future work will addressed the following research problems:

- Macroscopic modelling for two-phase flow (i.e., bubble columns),
- Mixing criteria and different operational modes, and
- Controllability analysis and feedback control design based on macroscopic observation

Acknowledgement

This research project is financially supported by the Delft Center for Sustainable Industrial Processes.

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Nano-Organic Chemistry

The new chair of Nano-Organic Chemistry at TU Delft focuses on research and education related to the design, synthesis, characterization and self-assembly of (bio)organic molecules and macromolecules to nano-sized architectures, thus exploiting the opportunities for inserting (bio)chemical functionality in these systems. The modification and optimisation of supramolecular interactions may deal with organic systems, and also with hybrid organic/inorganic concepts. Chemical surface modification of different supporting materials, i.e. patterned silicon, silicon nanowires, glass etc., is applied to develop highly sensitive and selective chemical sensors and also for obtaining biofunctionalised micro-channels in capillaries and microreactor devices. In addition new amphiphilic block copolymers are designed for the spontaneous formation of designed nanocapsules. These capsules are of interest for delivery and diagnostic purposes and can be used as microreactors. The research is fundamental in nature but always with a clear focus on possible applications.

Eindhoven University of Technology

Faculty of Chemical Engineering and Chemistry

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Environmental Technology Group

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Research Activities

A. Thermochemical biomass conversion

A1. Biomass torrefaction for the production of biofuels from wastes
A2. Biomass gasification: in-bed measures for gas conditioning and cleaning
A3. Mechanism of tar removal in gasification systems

B. Evaluation of conversion technologies biomass-to-biofuels

B1. Decision Support System waste-to-biofuels for the Province of Friesland
B2. Optimal conversion technologies waste-to-biofuels

TU/e Biomass upgrading by torrefaction for the production of biofuels

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OSPT theme	: Green process altern.	**Research school**	: OSPT
Supported by	: ECN	**Period**	: Oct.2006 – Oct.2010

INTRODUCTION

Torrefaction is a thermal pre-treatment technology to make biomass more suitable for co-firing and gasification applications. Due to distinct differences between the properties of coal and biomass co-firing has turned out to be rather difficult. The main principle of torrefaction is the removal of oxygen from the biomass, to become more coal liked. Torrefaction operates at 200 to 300ºC under atmospheric conditions. Other names are roasting, wood cooking and slow pyrolysis.

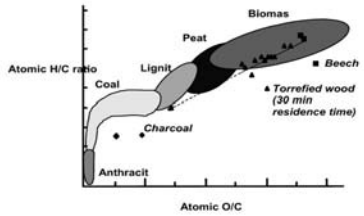

Fig 1. Composition wood and torrefied wood in Van Krevelen Diagram

OBJECTIVES

The project focuses on torrefaction of various biowastes which can be used as a potential feedstock for the production of electricity and biofuels. Typical streams of biowastes are refuse derived fuel (RDF), solid recovered fuel (SRF), trockenstabilat (and demolition wood).

The emphasis of the project is on:

- Mechanism & intrinsic kinetics of non-woody biomass
- Overall reaction enthalpy
- Influence of external heat & mass transfer
- Relation between biomass properties & torrefaction conditions, product quality and gas characteristics.
- Some aspects of characteristics of product quality (dust forming and biological degradation).

The torrefaction experiments will be carried out with a fixed bed reactor and/or thermogravimetric analysis. Also torrrefaction can be integrated with gasification using the process simulation program Aspen Plus.

SETUP

Fig 2. Biomass torrefaction setup

ACKNOWLEDGEMENT

The project is granted by the Dutch Agency for Energy and the Environment SenterNovem within the EOS research programme. The financial contribution of the Energy Research Center of the Netherlands (ECN) is also acknowledged.

DSS Decision Support System
Biowaste-to-Biofuels

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OSPT theme	: Green process altern.	**Research school**	: OSPT
Supported by	: Cartesius Institute	**Period**	: Nov 2006 – Nov 2010

INTRODUCTION

According to the Dutch Sustainable Energy Policy, 10% of the primary energy supply in 2020 should be delivered by renewable energy, and about 50% of this target is to be achieved by biomass and (bio)wastes. Friesland is located in the north-east of the Netherlands, and traditionally this area accounts for a great amount of biomass and biowastes from different sources.

However, biomass has some limitations. Its lower energy density results in higher logistics costs and additional pre-treatment steps are required. Moreover biomass technologies (biochemical & thermochemical) are not optimized yet. Hence, further research is needed to increase its efficiency as well as reduce their economical and environmental impact.

AIM OF THE PROJECT

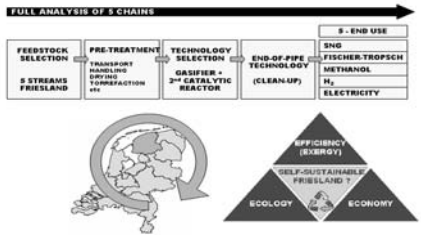
The aim of the project is dual:

1. Determine which biowaste streams of Friesland are more attractive for biofuels production via thermochemical conversion.
2. Define an **Own Accounting Method (multidimensional)** in order to assess sustainability of any production chain.

RESEARCH PLAN

In this project 5 different biowastes and 5 different production chains, including end-of-pipe cleaning treatments, will be selected, optimized and evaluated in terms of **economy, ecology and efficiency**.

The project will end in a DSS (Decision Support System) which may be used for strategic decisions of the involved companies and for regional policy making. The final outcome will be a **Master Plan "Biowaste-to-Biofuels"** for Friesland.



METHODS

Several accounting methods will be use to assess the sustainability of all chains:

Unidimensional Methods (Separate Analysis)	
EXERGY	Exergetic efficiency study
LCA	Environmental impact study
LCC	Economic impact study
Multidimensional Methods (Economy + Ecology + Efficiency)	
EEA	Extended Exergy Analysis
CExC	Cumulative Exergy
TE	Thermo-Economics
Own method	Ecology+Economy+Efficiency

PROGRAMS

The 5 different production chains will be modeled in Aspen Plus and Aspen Icarus for the calculation of exergy efficiency and economic impact respectively. These 5 production chains are:

1. SNG (synthetic Natural Gas)
2. Methanol
3. Fischer-Tropsch
4. Hydrogen
5. Heat & electricity

RESULTS

Economical, social, ecological & efficiency results will be presented either separately and integrated in 1 multidimensional value which will include all this 4 parameters.

EEA	**EE = FE + CEE + LEE + ERE**
FE	**Feedstock exergy** CExC of the feedstock
CEE	**Capital equivalent exergy** Short & long term investment
LEE	**Labor equivalent exergy** Labor & social accounts
ERE	**Environmental Remediation Exergy** Reach 0 environmental impact

SPONSORSHIP

The 4-year PhD project is conducted within the Environmental Technology group at TU/e and is sponsored by Cartesius Institute in Friesland.

In-bed measures for gas conditioning and cleaning

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Period : Nov. 2007 – Nov. 2011

INTRODUCTION

In the Netherlands annually almost 3,300 PJ of primary energy is consumed for the production of electricity, heat, transportation fuels, chemicals and other products. Natural gas consumption represents almost 50% of this Dutch (primary) energy consumption. The substitution of natural gas by a renewable equivalent is an interesting option to reduce the use of fossil fuels and the accompanying greenhouse gas emissions, as well as from the point of view of security of supply. The renewable alternative for natural gas is the so-called Synthetic Natural Gas (SNG). The conventional route for SNG production is based on gasification of biomass to syngas and the subsequent methanation of syngas to SNG.

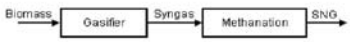

Fig 1. Conventional route for SNG production

OBJECTIVES

It is desired that the syngas contains, already, a high initial yield of methane as the subsequent methanation step involves a substantial efficiency loss. Besides this, and because the methanation is a catalytic reaction, there is a risk of catalyst deactivation due to carbon formation. This problem can arise as the result of the presence of tars. The goal of this project is to produce syngas streams with high methane yields and reduced tar content, acting inside the gasifier

METHOD

Two different routes were chosen:

- Test of bed additives in order to drive the reactions inside the gasifier to the production of methane and depletion of tars.
- Understand the formation of methane from the biomass in the gasification process.

Model gas mixtures will be used in a fixed-bed reactor to test some additives/catalysts. After this, the most successfully developed additives will be tested in real conditions.

SET-UPS

Fig 2. Fixed-bed reactor setup.

Fig 3. Biomass gasifier setup

ACKNOWLEDGEMENT

The research is carried out in cooperation with ECN, UT, TUD and BTG.

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Activities

Our research is aimed at increasing the understanding of molecular transport phenomena, in order to improve existing and possibly develop new separation and reaction processes.

An important theme is the description of fluid multicomponent transport, with a special focus on meso- and macropores. We are strengthening and extending the foundations of the new theory we presented in 2005, both by direct mathematical approaches and molecular simulations. Next to working on first-principle theory we also perform gas mixture permeation experiments in capillaries and mesoporous membranes. We performed first successful experiments and theoretical analysis of the use of an inert gas to separate alcohol-water vapors in very coarse membranes, and will extend research on this “Fricdiff” approach.

TU/e Separation of azeotropic alcohol-water mixtures with FricDiff

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OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: SenterNovem	**Period**	: Oct. 2005 – Sept. 2009

Introduction

A mixture of gases or vapors can be separated when it is forced to diffuse through an auxiliary gaseous or vaporous component (the sweep gas). In this case differences in relative rates of diffusion of the mixture components in the sweep gas are exploited to achieve a separation. This principle forms the backbone of the FricDiff separation process.

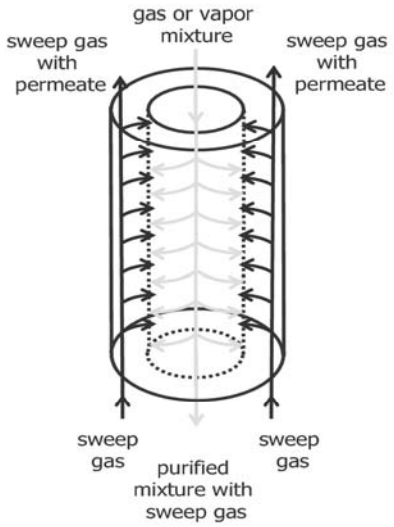

Figure 1. A tubular FricDiff-module with in- and outlet streams. The module consists of two concentric tubes of which the inner tube is porous.

A typical FricDiff-module is shown in Figure 1. It consists of two compartments separated by a non-selective macro-porous screen. Through the compartments the feed mixture and inert gas flow co-currently or counter-currently. Material is selectively exchanged through the porous screen, mainly by diffusion. The porous screen can be made of a robust and relatively cheap material, like stainless steel.

Aim of the project

In this project, the applicability of FricDiff for the separation of azeotropic mixtures of alcohols and water is studied using CO_2 as the sweep gas. This is done by a combination of numerical simulations and experimental work using a lab-scale set-up. The incorporation of FricDiff in existing chemical processes is also studied.

Scope of the work

Detailed numerical models for the FricDiff-module are developed in the programs Aspen Custom Modeler and Comsol Multiphysics. These models are used to study various influences on the separation process, including:

- Process conditions;
- Geometry of the module;
- Characteristics of the porous barrier;
- Concentration polarization;
- Partial condensation of alcohol and water within the module.

The numerical results are partially validated with experimental data. Finally it is examined if conventional separation processes for isopropanol-water and ethanol-water mixtures, which use distillation and are energy-intensive, can be improved by application of FricDiff. The software package Aspen Plus is used for this purpose.

Acknowledgement

This research is financially supported by SenterNovem and is performed in cooperation with Akzo Nobel Chemicals, Purac Biochem, Shell, Bodec Process Technology, FIB Industriële Bedrijven, MolaTech and TU Delft.

TU/e Removal of trace components from organic and aqueous streams by adsorption

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OSPT theme	: Separation Processes	**Research school**	: OSPT
Supported by	: DSTI	**Period**	: June 2008 – May 2012

Introduction

The process industry is confronted with different separation problems, where impurities in small concentrations have to be removed from different organic or aqueous matrices under diverse conditions. Separation processes cause the main part of the energy consumption in process industry.

The most applied separation principle at the moment is distillation, which is shown to be a reliable and robust unit operation. However, distillation possesses important drawbacks in the form of its poor energy efficiency and selectivity when impurities have to be removed, which resemble the main compound in their physical and chemical properties. Furthermore the limited stability of organic bulk chemicals at elevated temperatures can cause extra limits for the use of distillation.

Aim of the project

The objective of this project is to find new separation processes based on adsorption to reduce compounds with concentrations of 100-10'000 ppm in organic or aqueous streams to 1-50 ppm. Six industrial partners defined six different separation problems. Prospects and limitations of adsorption regarding trace removal are investigated.

The different combinations of adsorbents and techniques (e.g. column processes, countercurrent adsorption, simulated moving bed) will be investigated both by experiment and simulation. Integration of this knowledge with a process model for at least part of the production plant will be done.

The new processes should cause a significant reduction in energy consumption and capital costs.

Recent work

For the different streams (product streams or wastewater streams) in a first step selective adsorbents were identified. In a second step isotherms for the removal of the trace from the organic or aqueous solutions were determined on the basis of batch experiments for the relevant concentration range.

Figure 1: Batch experiments in shaking bath at fixed temperature

Acknowledgement

This is a DSTI project.

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Activities

The research activities can be divided in two subprograms: processes in which conventional organic solvents are replaced by "green" alternatives (*clean solvents technology*) and concepts for the integration of unit operations (*process intensification*). The enabling technologies used throughout the program focus on membrane separations, supercritical processes, ultrasound applications and surfactants systems. As hydrodynamics often determine equipment performance, new experimental and modeling methodologies are developed in this field to support the other activities. A characteristic feature of most projects is the integration of the entire chain of knowledge between molecular aspects and the final process.
In the subprogram *Clean Solvents Technology* the main focus is on exploring the potential of supercritical carbon dioxide (scCO2) as well as aqueous surfactant systems. To allow the solubilization of polar and charged components in scCO2, the application of supramolecular structures (reverse micelles and unimolecular dendritic micelles) is explored for the development of novel concepts for extraction and catalysis. Supercritical carbon dioxide usually is a poor solvent, thus offering specific advantages for its application in polymer systems. The use of scCO2 is explored for polymerization reactions as well as for polymer processing operations. The potential of aqueous surfactant systems is studied for homogeneous catalysis emphasizing on oxidation reactions.
The objective of the subprogram *Process Intensification* is to maximize the output of a process with respect to the desired product, using the minimum amount of energy required and without the generation of waste. This is pursued by the integration of unit operations, including reactors and separators. As this integration often cannot be performed in conventional processes, new concepts for equipment are being developed. A central theme is the use of membrane reactors for the selective removal of one of the reaction products from equilibrium reactions.

Residual Monomer Reduction in Polymers using Supercritical CO_2

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OSPT theme	: Green Process Alternatives	**Research School**	: OSPT
Supported by	: SEP	**Period**	: Oct 2005- Nov 2009

Introduction

Existing techniques for residual monomer reduction:

- steam stripping (energy intensive)
  - final residual monomer level not low enough
- introduction of initiator to speed up polymerization
  - product properties may change

Novel approach: extraction with (sc)CO_2:

- improved partitioning
- much lower resistance against mass transport

Extraction equipment:

The system studied is the extraction of styrene from polystyrene (PS) latexes, see **figure 1**. Latex droplets (~250 µm) are dispersed in (sc)CO_2. The latex droplets contain submicron polymer particles.

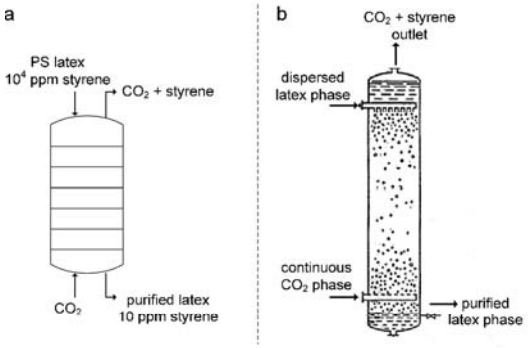


Figure 1. a: Process Flow Diagram of the extraction process, b: Spray tower as extraction column (R. E. Treybal, *Mass transfer operations*, 2nd ed. , 1986)

Research aspects

The key parameter in liquid-liquid extraction is the partition coefficient of the monomer K_s:

$$K_s = \frac{[styrene]_{CO_2}}{[styrene]_{polymer}} \left(\frac{kg_{polymer}}{kg_{CO_2}} \right)$$

K_s is deduced from phase behavior calculations and experiments on the monomer/polymer/(sc)CO2 system (M. Görnert, G. Sadowski, *Macromol. Symp.*, **2007**, 236-242). In cooperation with Prof. G. Sadowski, TU Dortmund, the PC-SAFT Equation Of State was chosen to perform these calculations. Result: K_s is strongly dependent on pressure and temperature.

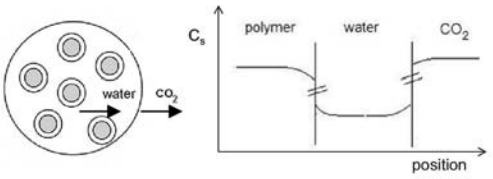
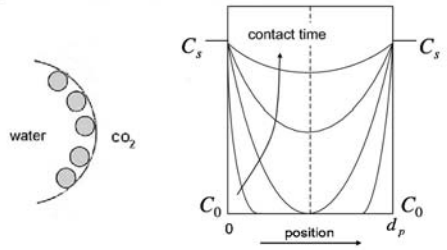


Figure 2. Mass transfer in series



$$D_s^{PS} = 10^{-15}\frac{m^2}{s} \xrightarrow[plasticizing\ effect]{} D_s^{PS} = 10^{-12}\frac{m^2}{s}$$

Figure 3. Shuttle effect (A.A.C.M. Beenackers, W.P.M. Van Swaaij, *Chem. Eng. Sci.*, **1993**, 48, 18, 3109-3139)

Decrease residual monomer level with a factor of 10 (dp = 100 nm):

$$D_s^{PS} = 10^{-15}\frac{m^2}{s} \rightarrow t = 0.4s$$

$$D_s^{PS} = 10^{-12}\frac{m^2}{s} \rightarrow t = 4*10^{-4}s$$

For the shuttle effect to dominate mass transfer, only a small fraction (θ) of the (sc)CO_2-water interface has to be occupied with polymer particles.

When the shuttle effect is dominating mass transport, i.e. at θ≥0.1, a column volume of 9 m^3 is satisfactory to obtain a latex product with 10 ppm styrene!!

Acknowledgements

This research project is financially supported by Stichting Emulsion Polymerization (SEP).

Membrane Reactor Technology for Catalytic Reactions in Supercritical Fluids

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Scope

The current research focuses on finding and developing environmental friendly alternatives to existing chemical production processes by combining membrane separation and supercritical fluid technology.

Reactions in $ScCO_2$

Supercritical carbon dioxide ($scCO_2$) has been established as a viable and environmentally benign alternative medium for catalytic reactions, offering: a high solubility for permanent gases and convenient possibilities for separation.[1]
CO_2 and toluene were compared as solvents for the rhodium catalyzed hydroformylation of 1-octene with carbon monoxide and hydrogen as gaseous reactants and nonanal and 2-methyl-octanal as the main aldehyde products.[2]

CO_2 as Reactant

Besides as a solvent CO2 can be used as a feedstock in the synthesis of carbonates and urethanes.[3] When the equilibrium conversion is low, the removal of water is important.

Future Membrane Reactor Applications

Integrating membrane separation with catalytic reactions could provide means to omit multiple conventional separation steps. In this manner the energy efficiency of a production process might be increased.

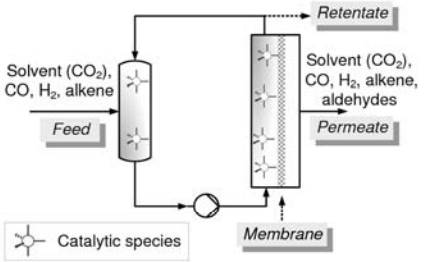

Figure 1. Membrane reactor concept for continuous homogeneous catalysis.

Homogeneous catalysts are often more active, selective, and expensive than their much wider applied heterogeneous equivalents. Their application, however, is impeded by the difficult separation from the products.[4] Through the application of ceramic membranes it is possible to separate a homogeneous catalyst at high-pressure conditions.[5]

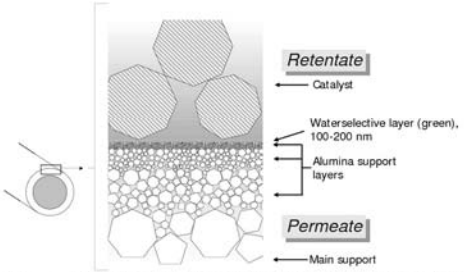

Figure 2. Schematic representation of the integration of membrane and catalyst for the case of esterification reaction.[6]

In equilibrium reactions where water is produced "catalytic" ceramic membranes can be employed to remove water and thus enhance the conversion.[6]
The development of membranes for water removal and separation of homogeneous catalysts is focused on stability and separation performance. The research effort is multidisciplinary in character involving material science, inorganic and organic chemistry, catalysis, and process technology.

References

[1] E.J. Beckman, J. Supercrit. Fluids 2004, 28, 121.
[2] A.C.J. Koeken et al., Adv. Synth. Catal. 2006, 348, 1553.
[3] T. Sakakura et al., Chem. Rev. 2007, 107, 2365.
[4] B. Cornils et al., in Multiphase Homogeneous Catalysis, Vol 1, (Eds.: B. Cornils, W.A. Herrmann, I.T. Horváth, W. Leitner, S. Mecking, H. Olivier-Bourbigou, D. Vogt), Wiley-VCH, Weinheim, 2005, p. 3.
[5] L.J.P. van den Broeke, et al., Angew. Chem. Int. Ed. 2001, 40, 4473.
[6] T.A. Peters et al., Appl. Catal. A, 2007, 317, 113.

Acknowledgements

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- EET grant EETK01115 SenterNovem
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- Arkema Vlissingen BV (development and synthesis of phosphine ligands).

Polymer microsphere production by membrane emulsification

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Introduction

The ability to produce well-defined monodisperse polymer particles appears to be a major driver for innovation in polymer products. Potential applications for these particles are in the field of printer toners, contrast agents for medical imaging and particles for controlled release or controlled dissolution patterns in drug formulations. Especially in the particle size range between 0.5 and 10 µm no current technology is able to produce this type of particles with a narrow particle size distribution. Moreover, particles consisting of polymer blends or containing functional (solid) additives are often required. Production is virtually impossible with existing techniques such as suspension polymerization. In this study, emulsification using micro-engineered membranes is applied for the production of polymer particles in the micrometer range with a narrow size-distribution.

Objective

The objective of emulsification experiments is to develop a proper relationship between the recipe and process parameters and the particle size (distribution) as well as the morphology of the particles produced. The final aim is to produce dispersed solid particles. This will be done by formation of monomer droplets by membrane emulsification with subsequent polymerization or by droplet formation of concentrated polymer solutions or melts.

Results

The undesired emulsion polymerization process reported in literature[1] was completely suppressed by optimizing initiation conditions. Figure 1 shows suspension polymerization particles covered with smaller particles from emulsion polymerization. Figure 2 shows how we can now produce polymer particles without loss of monomer.

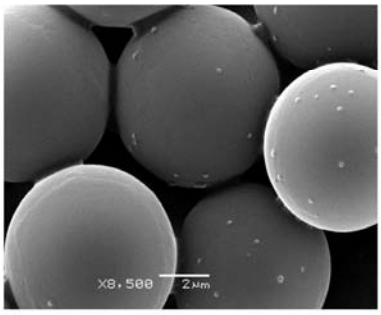

Figure 1. suspension polymerization particles covered with smaller particles from emulsion polymerization.

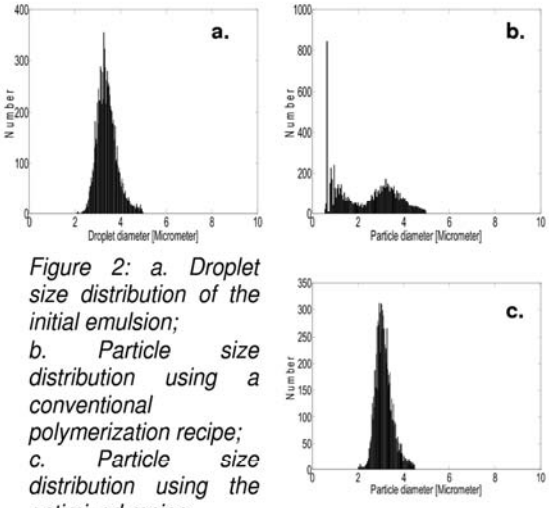

Figure 2: a. Droplet size distribution of the initial emulsion; b. Particle size distribution using a conventional polymerization recipe; c. Particle size distribution using the optimized recipe.

Reference:

(1) Ma, G.; Li, J. *Chem.Eng.Sci.*,2004, *59*, 1711-1721.

Acknowledgement

This project is financially supported by MicroNed.

Molecular Weight Control in Emulsion Polymerization by Catalytic Chain Transfer: Aspects of Process Development

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Introduction

The molecular weight distribution (MWD) governs the end use properties of polymeric materials, e.g. coatings. Molecular weight control is therefore a key issue in polymer production. Catalytic chain transfer (CCT) has proven to be a promising technique to control the MWD. The use of cobalt complexes as catalytic chain transfer agents (CCTA) has been demonstrated to be very effective.

CCT Mediated Emulsion Polymerization

The heterogeneous nature of the emulsion polymerization system has some important implications for the application of CCT.

- Partitioning of the CCTA
- Decomposition in the aqueous phase
- Mass transport of the CCTA

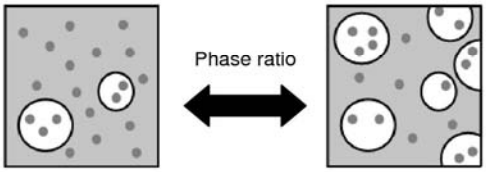

Figure 1. Effect of the phase ratio on CCTA partitioning

The phase ratio (ß) and the partition coefficient (m_{Co}) govern the catalyst concentration at the locus of polymerization and consequently determine the degree of polymerization (DP_n) of the polymer formed.

$$DP_n = \left\{ \frac{V_M C_{M,p}}{C_T} \frac{1}{N^0_{Co,0}} \left(\frac{m_{Co}\beta + 1}{m_{Co}(\beta + 1)} \right) \left(1 + \frac{1}{\beta} \right) \right\} \exp(k_{dca} t)$$

Some decomposition (k_{dea}) of the CCTA can occur during the course of the polymerization, resulting in a poorly defined MWD.

The application of CCT in emulsion polymerization also has severe implications for the course of the emulsion polymerization process.

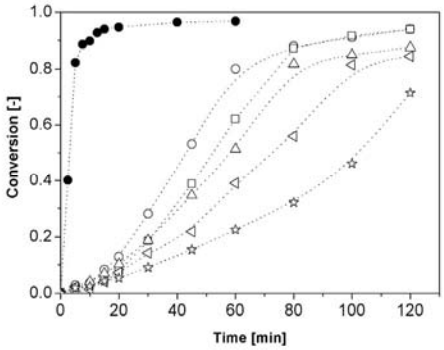

Figure 2. Effect of the addition of a CCTA on the course of the emulsion polymerization. Closed symbols: no CCTA. Open symbols: CCTA and varying surfactant concentrations.

When compared to a conventional emulsion polymerization (●) the addition of a CCTA severely reduces the rate of polymerization (○). Presence in the aqueous phase affects the rate of radical entry, whereas presence in the polymer particles increases the rate of radical exit. The net result of these aforementioned processes is a reduction of the average number of radicals per particle and consequently a reduction of the rate of polymerization.

Conclusions

Thorough understanding of the application of CCT in emulsion polymerization is a prerequisite to achieve proper control of the MWD.

Development of ion-selective thermo-reversible polymers

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OSPT theme	: Green process alternatives		
Supported by	: SenterNovem	**Period**	: April 2006 – April 2010

Introduction

Hardness ions like calcium and barium cause problems in many processes by forming unwanted salt depositions. For different applications, ranging from household applications like laundry and dish washing to drinking water processes, softening of water streams is essentially. The current technology to bind multivalent cations commonly is based on the use of ion exchange resins. Regeneration of these resins typically involves consecutive washing steps with acid or caustic, leading to a large amount of waste salts.

Objective

This project focuses on the development of a new softening technology where regeneration of hardness ions occurs by a change in temperature. In this project hydrophobic polystyrene (PS) and more hydrophilic poly(di-ethyleneglycolacrylate) (PDEGA) are used. PDEGA shows a Lower Critical Solution Temperature (LCST) around 38 °C.

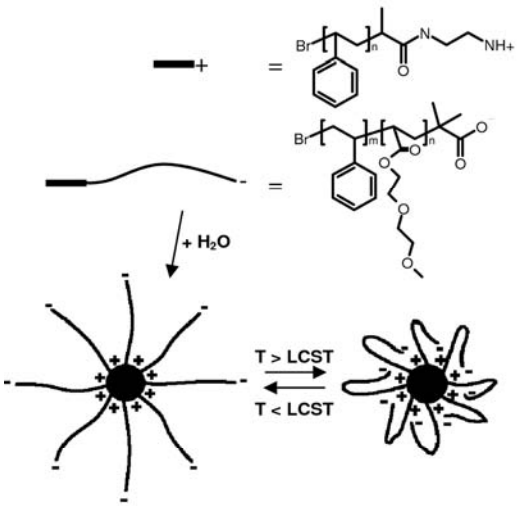

Fig 1. Schematic overview of the thermoresponsive PS-PDEGA system.

Micelle Formation

As a result of the hydrophobic and hydrophilic blocks, mixed micelles with a PS core can be formed (fig 1). Here, the PDEGA-block is provided with a negative charge (carboxylic acid) and the PS-chain with a positive charge (amino group). At a temperature below the LCST, the PDEGA-chains are stretched and the negative charges will be able to bind multivalent hardness ions. Above the LCST, PDEGA-chains will collapse, charge compensation will take place and hardness ions are released. CryoTEM pictures show that micelles in water can be formed with a PS-core of approximately 20 nm (fig 2).

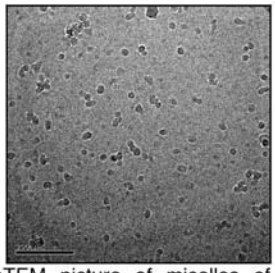

Fig 2. CryoTEM picture of micelles of a 1.3 wt% solution of PS-b-PDEGA in water.

To determine the LCST, UV spectroscopy is used. The optical transmittance of a 1.3 wt% PS-b-PDEGA solution as a function of temperature is shown in figure 3. Clearly, a sharp transition occurs at 38 °C, within a 1.5 °C range.

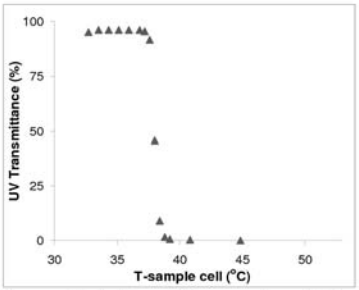

Fig 3. The optical transmittance of a 1.3 wt% PS-PDEGA solution in water as a function of temperature.

Acknowledgement

This project is carried out in cooperation with Wageningen University and Afira B.V. It is financially supported by SenterNovem.

On-demand drug delivery induced by a magnetic field

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Introduction

The pharmaceutical industry asks for prolonged and better control of drug administration to allow for more effective therapies. Highly potent, but often toxic drugs, as used in chemotherapy, require a certain amount of drug released in a specified time interval at a specific site in the human body. A polymeric implant containing drugs can be used to create on-demand release by use of an external trigger.

Aim of the project

The focus of this project is to create a polymeric drug delivery system, which can be switched on and off by use of a magnetic field, see Figure 1.

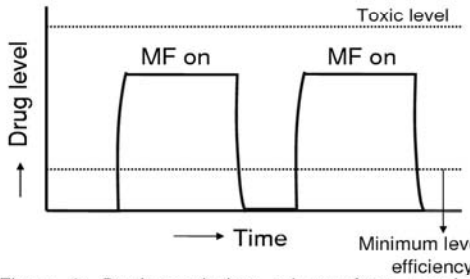


Figure 1: On-demand drug release from a polymeric implant

Approach

Both *in vitro* and *in vivo* research has proven that by heating the implant from below to above its glass transition temperature, the diffusion coefficient of the drugs increases significantly.[1] To induce drug release, superparamagnetic iron oxide nanoparticles (SPION), imbedded in the implant, are heated by the magnetic field.

Experimentally

SPION are incorporated in poly(methyl methacrylate) matrix by freeze drying a PMMA latex containing iron oxide and subsequent compounding. The resulting cylindrical bars are coating with poly(butyl methacrylate-co-methyl methacrylate) containing 5 wt% ibuprofen as a model drug. Heating and release experiments are performed.

Results

The temperature increase is sufficient to exceed the glass transition temperature of the polymer and can be controlled using the magnetic field strength, Figure 2.

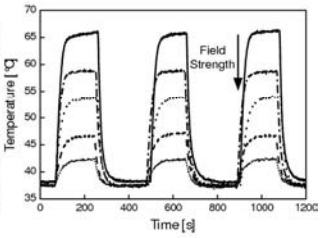
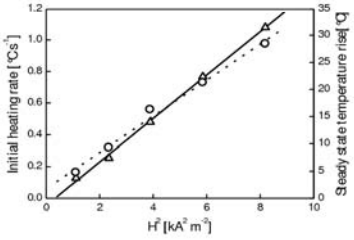
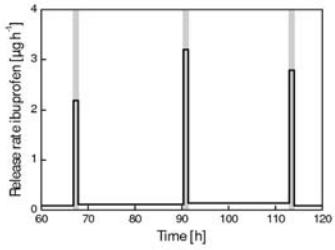


Figure 2: Heating of PMMA core containing SPION



An AC magnetic field can be used as a trigger for on-demand drug delivery from a polymeric implant, Figure 3.

Figure 3: On-demand release using a magnetic field



References

[1] H. Bruinewoud *et al.*, PCT WO 113422 A2, 2004

Acknowledgement

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TU/e Energy efficient sonochemistry

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Introduction

Cavitation is the growth and subsequent violent collapse of a cavity in a liquid under influence of a pressure field. It can be induced using:

- Ultrasound (US)
- A hydrodynamic constriction(Venturi tube)

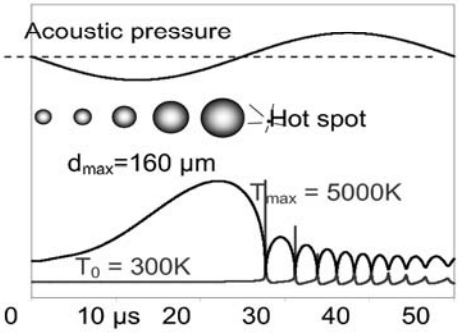

Figure 1: theoretical description of 20 kHz cavitation with Rayleigh-Plesset equation

The cavitation event generates high pressures and temperatures (up to 200 bar and 5000K respectively). Under these conditions, pyrolysis of components in the bubble can take place and radicals are formed. The radicals can further react in e.g. polymerizations or breakdown of organic pollutants in water.

The efficiency of sonochemistry is low, in the order of $\mu mol.L^{-1}.min^{-1}$. One of the reasons for this is the sound reflection by generated bubbles. The bubbles closest to the sound source shield other bubbles.

Goal of the project

The goal of the project is to increase sonochemical efficiency.

Miniaturization

One way of accomplishing this is by miniaturization: shielding can be reduced by manipulating single bubbles with US in microchannels. Hydrodynamic cavitation can improve in microchannels because of faster recovery times [1].

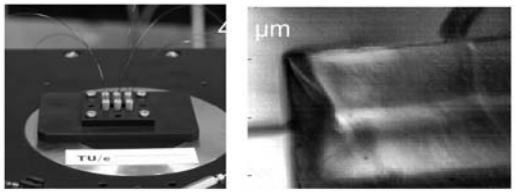

Figure 2: µ-hydrodynamic cavitation set-up

Frequency-effects

The sound frequency has an impact on bubble dynamics, and therefore on temperature and pressure, and radical formation. High frequencies (100 - 1000 kHz) generally give higher chemical conversion [2].

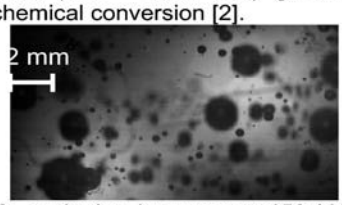

Figure 3: cavitation in water at 450 kHz, 50W. Out of plane vibration

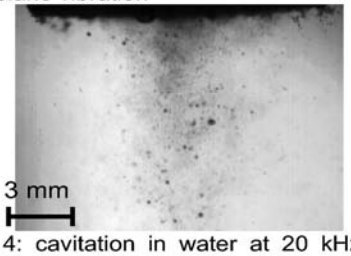

Figure 4: cavitation in water at 20 kHz, 50W. Vibration in vertical direction

Both systems in the figures above operate at resonance. Changing the frequency requires changing the equipment design for optimal results.

References

[1] S. Arrojo, Y. Benito, Ultrason. Sonochem. 15(3) (2008) 203-211
[2] D.G. Wayment, D.J. Casadonte, Ultrason. Sonochem. 9 (2002) 189-195

Acknowledgement

This project is funded by STW.

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Activities

The research of the group focuses on understanding and controlling the interaction of transport and reaction processes in the realization and testing of chemical reactors for a wide range of applications and processes. Research projects are carried out in three areas, viz. "*microstructured reactors and devices*", "*structured multiphase reactors*", and "*reaction mechanisms and kinetics*".

The research area of "*microstructured reactors and devices*" focuses on the development of microchemical systems that provide intricate geometries with characteristic length scales of tens to hundreds of micrometers for optimum mixing, mass and heat transfer, (catalytic) reaction, and product separation. The challenge is to explore the potential benefits of these miniaturized chemical systems in terms of e.g. productivity, selectivity, energy efficiency, new reaction pathways, safety, and environmental benign manufacturing. A particular innovative aspect is to take benefit of microfabrication technologies for integrating sensors and actuators for process monitoring and control. Areas of application include, amongst others, complex chemicals synthesis, catalyst development and screening, fuel processing and hydrogen production, and product separation.

The research area of "*structured multiphase reactors*" focuses on the development of catalytic three-phase reactor systems for a range of applications, varying from Fischer-Tropsch synthesis or water purification to oxidation and hydrogenation reactions in the fine-chemistry and pharmaceutical industries. A particular focus is on the use of meso-structured, solid foam-based materials as catalyst supports to significantly improve reactor performance. A recent line of research explores the potential of a new generation of intensified reactors exploiting rotating motion to induce high shear flow conditions mimicing high gravity conditions that provide excellent heat and mass transfer.

In the research area "*reaction mechanisms and kinetics*", (transient) kinetic and mechanistic studies are performed to identify the relevant (elementary) reaction steps and to quantify the kinetic rate coefficients that are used in supporting modeling studies. Areas of application include Fischer Tropsch synthesis and sorption enhanced reforming of methane.

Microfluidic Methods for Production of Structured Multiple Emulsions

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OSPT theme	: Multiphase reactors	**Research school**	: OSPT
Supported by	: TU/E MiTS Project	**Period**	: Jul. 2008 – Jul. 2010

Introduction

Emulsions (one fluid dispersed in another immiscible fluid) are widely used in many practical industrial processes such as pharmaceuticals, cosmetics and foods to control the targetable delivery and sustained release of active ingredients. In microfluidic systems, as shown in Fig.1, emulsions can automatically form when two immiscible liquids meet at a cross junction. The control takes place at the level of a single droplet. Compared with traditional methods with mixing by sonification or stirring, the microfluidic methods provide better controllability and reproducibility and higher entrapment efficiency. The objective of the project is to develop versatile microfluidic methods for production of structured multiple emulsions.

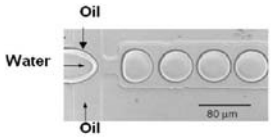


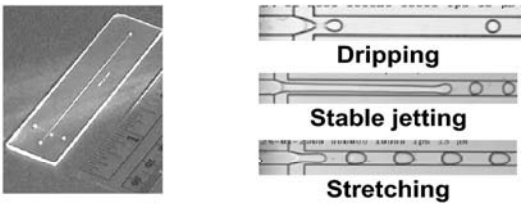
Fig.1 Emulsion formation in a cross junction[1]

Scope of the research

The novel intended microfluidic method will be developed by using microchannels with structured geometries such as co-flowing, flow-focusing and cross-flowing. In order to develop a microfluidic-on-chip system with perfect performance, several key problems should be resolved. For instance, the basic mechanism for emulsion formation should be studied; the flow map at different operating conditions should be developed; the design rules for this kind of device should also be explored. Besides the emulsion production methods in microfluidic devices, detecting and sorting of the byproduct are necessary. In order to meet the requirements of high resolution and fast response time, optical detecting unit will be developed. Sorting methods including both the passive sorting controlled by channel geometry and liquid flow rate and the active sorting controlled by microactuators will also be investigated.

Consecutive splicing structures of flow-focusing will be developed to control the structures, frequencies and sizes for production of multiple emulsions. Droplet traffic units will be explored to regulate the spacing between the primary emulsions so as to control the shell thickness of the multiple emulsions. The final output of this project is expected to be a versatile microfluidic chip, using which the emulsion generating, detecting and sorting can be well performed; the structures, frequencies and sizes of multiple emulsions can be well controlled.

Intermediate results



(a) Chip (b) Operational regimes

Fig.2 Chip used for experiments and resultant operational flow regime

The chip used is shown in Fig.2a, the operational flow regimes include dripping, stable jetting and stretching. In these flow regimes, droplet size and formation frequency can be well controlled through adjusting the flow conditions and fluid properties.

Acknowledgement

The work is part of the MiTS project funded by the Eindhoven University of Technology.

[1] M. Joanicot, A. Ajdari, Science, 309 (2005) 887-888

TU/e

Flow and Heat Transfer Modeling of Continuous Annular Electro-Chromatography (CAEC)

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OSPT theme	: CAEC	**Research school**	: OSPT
Supported by	: EU	**Period**	: Sep.2008–Aug.2010

Project Description:

Capillary electro-chromatography is a very powerful tool for the separation of complex mixtures with chemically similar compounds since it combines the high separation efficiency of capillary electrophoresis with the applicability of high performance liquid chromatography (HPLC) to a wide range of both neutral and charged components. So far, this technology has been applied exclusively for analytical purposes since the small column dimensions limit the productivity to a few millilitres per day. Moreover, continuous annular chromatography, as the only continuous chromatographic technique that fulfils the high demands raised by modern biotechnological production, has been transferred from research laboratories to fully developed industrial process scale.

The proposed integration of these two innovative technologies will increase the productivity of electro-chromatography by several magnitudes whilst maintaining an efficiency of more than 100,000 theoretical separation stages per meter. This breakthrough in productivity will provide potential for tremendous process intensification in chemical, biochemical and pharmaceutical industry. The resulting continuous annular electro-chromatography (CAEC) technology will thus extend the range of application towards a small-scale production of extremely high-value-added products like pharmaceuticals for clinical trials early on in the development stages. As a fully continuous technology, CAEC is optimally suited to transform production processes from batch to continuous operation.

Scope of the Research:

As one participant of the recently approved 7th Framework Programme in CAEC, TU/e is responsible for the flow and heat transfer modeling of the continuous annular electro-chromatography (CAEC) device. Main issues are the equal distribution of the inlet feed flow, the electrical-driven flow in a porous media, and the heat management to suppress hot spot formation. In addition, TUE will model the flow in the outlet to assess a proper uptake of the product stream and to ensure a fast signal response and a high accuracy for sensing the product composition.

Cooperation: University of Dortmund, University of Kaiserslautern, Graz University of Technology, Institut für Mikrotechnik Mainz GmbH, Microinnova Engineering GmbH, Novartis Pharma AG, Galilaeus Oy

TU/e Microwave Enhanced Microprocessing in large-scale Fine Chemical Synthesis

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OSPT theme	: Multiphase reactors	**Period**	: Sept. 2008 – Aug.2012
Supported by	: STW		

Introduction

Microstructured reactors are nowadays regarded as a separate class of chemical reactors with their specific characteristics such as improved heat and mass transfer and well tuned residence times. Recently there has been lot of work going on microwave assisted organic synthesis as well, suggesting the realization of microwave heating as an enabling technology to perform high-speed synthesis with better process selectivity and product yield. The integrated concept of both these technologies, microstructured reactors and microwave heating, is expected to lead to significantly better processing issues, such as a better heating in terms of heating speed, precision of temperature ramping, heat transfer efficiency, a higher selectivity due to a better definition of residence time and temperature ramping by a fast heating up and quenching, and a smooth transient operation due to the ability of microwaves to induce spatially strongly varying properties for a short time, i.e. to have catalyst hot spots on the wall of the microreactor. Thus the goal of this process intensification project is to design, develop, and demonstrate a microstructured device for chemical synthesis and multiphase flow handling in which microprocessing and microwave heating will be integrated in one flow through reactor.

Objective

It has been the biggest challenge of (particularly) the chemist, to survey the microwave effects in a fair manner by means of kinetic study of organic chemistry and assign microwave effect factors to reactions for industrial applications. Reactions to be studied are of interest for the fine-chemical industry, with strong potential for up-scaling. Typical products are used in pharmaceuticals and cosmetics and have high quality demands, such as purity and stability. The biphenyl ether synthesis can be used as model reaction in this project.

Scope of the work

This project is divided in three sections namely, investigations of microwave assisted organic chemistry, process intensification issues associated with the usage of microwaves as a heating medium, and design, development and performance studies of integrated microwave microreactor system. First two sections will be investigated by PhD participants working consecutively at TU/e & TU Delft respectively, while the third section will be investigated in this PhD-project. In this section, chemistry optimization and microwave effects will be investigated, where also the potential for upscaling is part of this project. As mentioned this chemistry regards high additive value chemicals that should promise fast rate of return concerning investment and operational costs of micro-processing.

Acknowledgement

The financial support by Dutch Technology Toundation (STW), DSM, Friesland foods, Milestone, IMM, and LioniX is gratefully acknowledged.

TU/e Development of Mo_2C/Mo catalytic coatings for the WGS reaction in a combined microstructured reactor/heat-exchanger

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OSPT theme	: Comp. Exp. Chem. Eng.	**Research school**	: OSPT
Supported by	: NWO, RFBR	**Period**	: May 2006 – May 2010

Introduction

For portable and transport applications, the most convenient and economical way of hydrogen production is on-board reforming of hydrocarbon fuels in a fuel processor (FP) combined with a fuel cell (FC) stack, forming an integrated power supply device. In the reforming of gasoline or natural gas, a hydrogen-rich gas is produced with a carbon monoxide concentration of 10-12 vol.% Because CO is a poison for a proton exchange membrane FC catalyst, the water gas shift (WGS) reaction is used to reduce its concentration to below 1 vol.%, increasing H_2 yield.

Research scope

The work is focused on the development of new generations of highly active and stable catalytic coatings for the WGS reaction by application of high-temperature electrochemical synthesis in ionic melts. A detailed kinetic study will be performed on the most promising coatings. Based on the result of the kinetic study, a microstructured reactor/heat-exchanger (MRHE) will be designed to further enhance reaction yields by allowing the reactant stream to follow optimal reactant temperature profiles.

Experimental

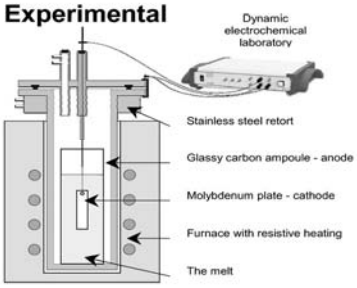

Figure 1. The electrochemical set-up for coating deposition.

The Mo_2C coating was obtained by galvanostatic electrolysis from a NaCl-KCl-Na_2MoO_4-Li_2CO_3 melt at 1123 K (Figure 1). The coatings were stable for more than 500 hours on stream at 631 K in a mixture containing 0.5 vol.% CO, 1.5 vol.% H_2O and 40 vol.% H_2, balanced by He.

A novel microstructured reactor/heat-exchanger containing eight sections with a cross-section of 10 mm x 10 mm and a length of 100 mm has been designed and constructed (Figure 2). Each section of the reactor contains flat, perforated Mo plates and Mo wires with a diameter of 250 □m and a length of 100 mm coated with a porous Mo_2C layer.

In the MRHE, the reactant flow follows an optimal temperature profile. This profile is created by a counter-current flow of the fuel cell anode gas in two cooling pipes. The anode gas is additionally fed from two ports located in the side wall of the assembly to reach the required temperature profile. The present design allows to reduce the catalyst volume by a factor of 2.2 as compared to an isothermal operation.

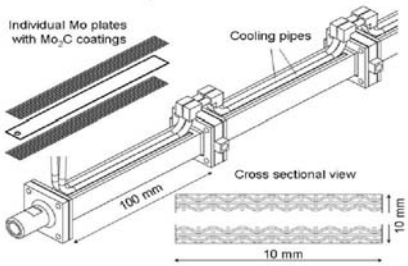

Figure 2. A schematic view of the microstructured reactor/heat-exchanger for the WGS reaction.

Acknowledgement

The financial support by the Netherlands Organization for Scientific Research (NWO) and by the Russian Foundation for Basic Research (RFBR) is gratefully acknowledged.

Microreactor phase transfer catalyzed alkylation of benzyl cyanide

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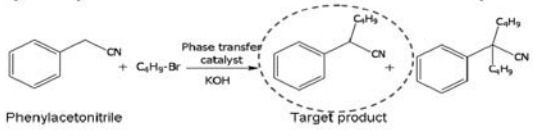
OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: NWO	**Period**	: June 2007 – June 2011

Introduction

Phase transfer catalysts can penetrate the interface of two immiscible phases and transfer chemical species into the phase in which reaction takes place, enabling rapid reactions between otherwise non-reacting reactants. The combination of the phase transfer catalysis and microreactor technology will eliminate the mass transfer limitation which is the main drawback of many phase transfer reactions, thus increasing reaction rate per unit reactor volume and selectivity.

Experimental

Alkylation of phenylacetonitrile is chosen as a test reaction to study the influence of hydrodynamics on conversion and selectivity.



Different flow regimes can be realized in the L/L flow in a microchannel. An optimum flow regime for the mass transfer will be determined.

Results

In a Y-mixer microreactor with varying flow ratios of the aqueous (KOH, quaternary ammonium salt as a catalyst) and organic (Benzyl cyanide, butyl bromide) phases, the size of the liquid slugs influences the conversion (Figure 1).

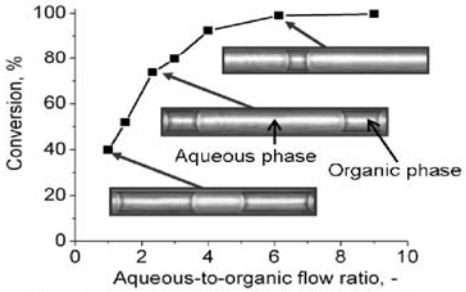


Figure 1: Conversion as a function of slug size.

The conversion increases from 39.9% to 99.7% as a result of a 23% larger slug interfacial area when the aqueous-to-organic phase flow ratio is raised from 1.0 to 6.0 at the same residence time. The larger interfacial area significantly promotes catalyst phase transfer but decreases selectivity due to the simultaneous increase of the rate of the consecutive reaction to the dialkylated product. This gives an optimum flow ratio of 2.3 at which the productivity is maximal (Figure 2)

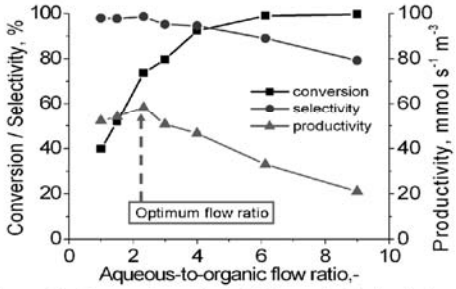


Figure 2: Conversion, Selectivity and Productivity as a function of the aqueous to organic flow ratio.

Conversion in the microchannel is significantly larger than in a stirred reactor (Figure 3).

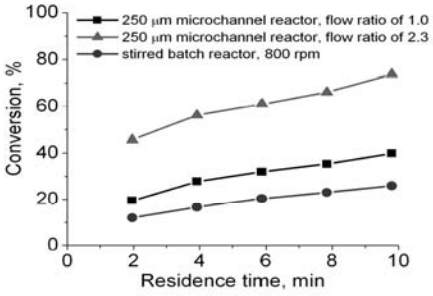


Figure 3: Conversion in microreactor vs the stirred batch reactor

Acknowledgement

This research project is carried out within the framework and financial support NWO.

Smart Micro Reactors

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: MicroNed, LioniX	**Period**	: March 2006 – March 2010

Introduction

The most recent trend in the design of three-phase catalytic microreactors focuses on the use of structured catalyst supports, i.e. a structured geometry with e.g. a metal deposited on the surface. However, because of the high mass transfer in micro reactors, more catalytic surface is required. Therefore, a catalytic support layer based on carbon nanofibers (CNF) can be deposited on the microstructured support body to enlarge the surface area-to-volume ratio.

Objective

The objective of the PhD-project is to develop and demonstrate a micro-structured three-phase microreactor with a catalytic support layer based on CNF.

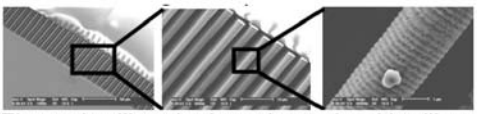

Figure 1: pillared micro channels with pillars of 3 μm in diameter and 50 μm in height.

This microreactor may serve as a tool for developing selective and environmentally benign routes in the production of fine chemicals and can be used as a production device due to favorable scale out properties.

Experimental

In order to be able to properly design and control such a micro-structured system, a comprehensive under-standing of the hydrodynamics in the three-phase microchannels is required. The following hydrodynamic quantities will be determined as a function of gas and liquid flow: liquid hold-up; pressure drop; flow regimes and transitions; gas-liquid and liquid-solid mass transfer; overall gas-liquid-solid mass transfer. Fast reactions will be carried out in a pillared microreactor of 1 mm x 50 μm x 6.6 cm and pillars of 3 μm in diameter (Figure 1).

Results

For a pitch larger than 17 μm, the flow pattern is hardly influenced by the pillars (Figure 2). However, the catalytic surface is increased with a factor 2.

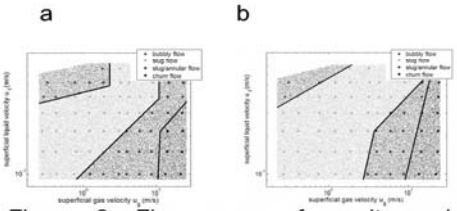

Figure 2: Flow maps of a nitrogen/water system in a) empty channel b) pillared channel with pitch of 27 μm.

For a pitch smaller than 17 μm, different flow patterns are observed with larger gas-liquid interface areas as can be seen in Figure 3.

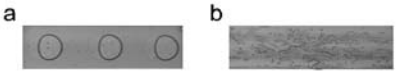

Figure 3: Flow patterns of 3.1 m/s nitrogen and 0.3 m/s water in a) an empty channel b) a pillared channel.

Acknowledgement

This research is carried out in co-operation with prof.dr.ir. L. Lefferts (CPM, UT), prof.dr. J.G.E. Gardeniers (MESA$^+$, UT) and is financially supported by MicroNed and LioniX.

TU/e Spinning Disc Reactor

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Research group	: ST/SCR	**URL**	: www.chem.tue.nl/scr
OSPT theme	: Multiphase reactors	**Research school**	: OSPT
Supported by	: STW, Akzo Nobel, DSM, Organon, TNO, Alfa Laval	**Period**	: Oct. 2006 – Oct. 2010

Introduction

Mass transfer is often the rate limiting step in multiphase reactions. The spinning disc reactor is a new concept in which the gas-liquid and liquid-solid mass transfer is enhanced significantly.

The rotor-stator spinning disc reactor consists of a rotating disc (rotor) and a static disc (stator). The rotation causes a large shear force in the fluid in the small gap between the discs (10^{-3} m). This force breaks up gas bubbles and increases the gas-liquid interfacial area a_L. The high velocity gradient and the high turbulence renews the gas-liquid interface rapidly; resulting in a high mass transfer coefficient k_L. Therefore, a high value of the volumetric gas-liquid mass transfer coefficient k_La_L is expected. The high turbulence also implies high liquid-to-disc mass and heat transfer. In addition, in a rotor-stator system a flow perpendicular to the disc develops. This increases the liquid-to-disc mass and heat transfer even further. The heat resulting from a fast exothermic reaction can thus be easily removed by cooling of the disc.

Objective

Flow regimes, gas bubble size and velocity, and gas-liquid and liquid-to-disc mass transfer are investigated as a function of rotor-stator distance, gas and liquid flow rates and rotational disc speed. The reactor performance is compared to existing multiphase reactors.

Experimental

A rotor-stator spinning disc reactor, with a maximum rotational speed of the rotor of 1700 rotations per minute (rpm) is used. Gas and liquid enter the reactor from the top (see Figure 1). On the top of the rotor a liquid film is present; the gas is present above this film as a large bubble with a diameter of approximately 90% of the diameter of the rotor. Small gas bubbles are sheared off from this large gas bubble. The region surrounding the rim of the rotor and the region between the rotor and the bottom disc are filled with liquid with small bubbles (diameter typically less than 1 mm) dispersed in the liquid, as can been seen in Figure 2.

Results

The volumetric gas-liquid mass transfer coefficient increases, with increasing rotational disc speed and increasing gas flow rate, up to 4.9 $m_{Liquid}^3\ m_{Reactor}^{-3}\ s^{-1}$. This is 40 times higher than, for example, at similar conditions in a conventional multiphase reactor like a bubble column. The rotor-stator spinning disc therefore show a large potential for mass transfer limited multiphase reactors.

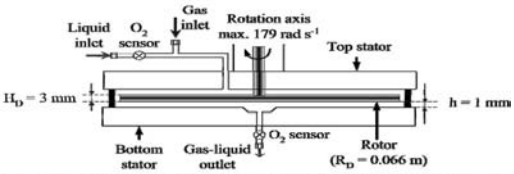

Fig.1 Schematical drawing of the experimental setup. The gas and liquid are combined in a T-junction, the resulting gas-liquid flow is fed through the inlet at the top

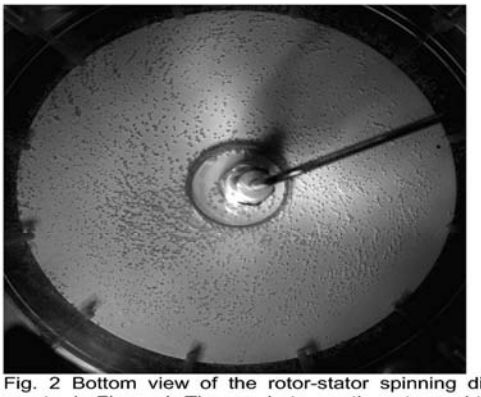

Fig. 2 Bottom view of the rotor-stator spinning disc reactor in Figure 1. The gap between the rotor and the bottom stator is filled with liquid with small gas bubbles.

DeMiR- Design of Micro/Milli-Reactor For Large Scale Processing

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OSPT theme	: Multiphase reactor	**Research school**	: OSPT
Supported by	: STW	**Period**	: August 2008 – August 2012

Introduction

The aim of this project is to develop a generic design methodology for selecting and designing the best scale of reactor operation, either "micrometer-scale" or "millimeter scale", for G/L and L/L catalytic reactions and multiphase food processing systems. Scaling rules will be developed and the window of operation will be defined for micro/milli-reactor systems with large throughputs that are typical for the production of bulk chemicals or food products, in the range of m^3/h and m^3/min for liquids and gases, respectively.

Research focus

Usually lab scale research in microreactor aims to optimize a reaction system for a single channel. However, going from single to multichannel system a need for uniform flow, catalyst loading and heat distribution in each channel is essential.

Experimental setup

The first objective will be to develop a robust flow distributor design for multiphase (G/L) micro/milli reactor. In multiphase system the problem of cross talk between channels is critical. An un-proper distributor design can results in channels filled only with liquid and others with gas. To prevent the cross talk, a pressure drop barrier is inserted before the mixer unit. This pressure drop barrier will be approximately one order of magnitude larger than the reaction channel pressure drop. Therefore any fluctuations in the downstream unit (mixer and reaction channel) will not affect flow distribution in the upper stream.

The first experimental setup made from capillaries and pipe fitting. In this setup the capillary dimensions and the operating conditions will be varied to achieve uniform flow distribution, prevent the cross talk between channels and minimize the pressure drop barrier. Other knowledge to be gained is the maximum downstream pressure fluctuations and the fabrication imprecision allowed in the pressure drop regulation unit.

The flow distributor and window of operations will be extracted from the knowledge achieved in the capillary experiment. Utilization of this knowledge will be in the prototyping of the final pilot scale micro/milli multiphase reactor, cf figure 1.

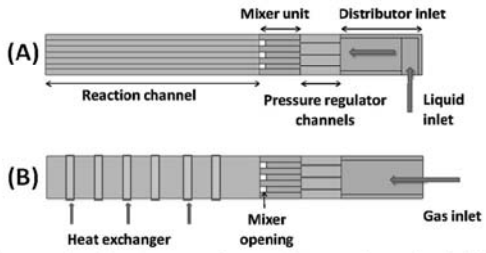

Figure 1. *Prototype of a pilot scale micro/milli multiphase reactor plate. (A) plate top view, (B) plate bottom view.*

Expected result/utilization

The first part of the project seeks to extract general design rule on multiphase flow distributor. Afterward tenths of channels will be fabricated in a single plate aiming to proof the potential reactor layout. Afterward a model reaction will be tested along with catalyst coating incorporated in the potential reactor prototype. Knowledge on the catalyst and heat distribution will be achieved on that stage. Finally, a feasibility study and reactor evaluation in comparison with other reactors will be done.

Acknowledgement

This research project is carried out within the framework of the Green & Smart Process Technologies programme STW-GSPT.

Development of a Novel PEMFC Cathode Electrode

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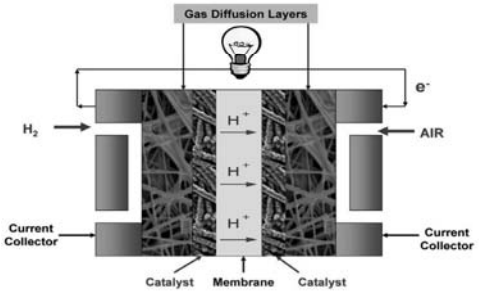
OSPT theme	: Energy Conversion	**Research school**	: NIOK
Supported by	: ECN	**Period**	: Nov. 2007 – Nov. 2011

Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) are electrochemical energy converters transferring the stored energy in hydrogen (H_2) into the electrical energy by means of a catalytic process of H_2 oxidation and O_2 reduction. A PEMFC unit, called Membrane Electrode Assembly (MEA) composed of two gas diffusion layers, catalyst layers and a proton exchange membrane (nafion).



Potential problems in PEMFC are ineffective catalyst utilization, water management, ohmic energy losses on electrodes because of resistances and oxygen reduction difficulties in anode. The main objective of this project is to develop a CNF integrated cathode electrode which is more controlled and highly accessible and to model the transport kinetics on oxygen adsorption and reaction steps.

Tasks

In the development of FC electrodes, following studies will be under research progress:

1. CNF will be grown on silica support and Platinum (Pt) will be depositied on CNF grown silica support.
2. CNF growth with carbon monoxide will be performed and pure CNF will be obtained by using caustic treatment.
3. CNFs will be grown on Carbon paper by using wetness chemical impregnation of nickel and nickel nanoparticle preparation by using hydrazine reduction agent. Nickel deposition on graphite disks will be a parallel model study.
4. Electrical field growth studies will be performed to obtain more controlled CNF surfaces on Toray paper and graphite disks.
5. Pt will be formed on CNF coated Toray and graphite disks and the loading performance studies will be carried out.
6. A cooperative study between Nedstack Company is an ongoing project to explore the reasons for decreasing lifetime of MEA stacks.

Expected results, utilization

Carbon disks and Toray paper integrated Pt-CNF will give better electron conductivity with respect to Pt deposited activated carbon substrates. Effective catalyst usage and comparable surface area of CNFs with respect to activated carbon substrates will contribute to the total efficiency of the PEMFC. These electrodes can be used as catalysts for effective oxygen decomposition at the cathode side of the PEMFC as well as at the anode side.

Acknowledgement

This research project is financially supported by ECN.

TU/e

Direct Epoxidation of Propene in a Microreactor

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT and NIOK
Supported by	: NWO	**Period**	: Sept. 2008 – Sept. 2012

Introduction

Propene oxide is a major bulk material used in chemical industry. The main processes in operation, the chlorohydrin process and the hydroperoxide process, are both complex and have a number of disadvantages. A direct process for the epoxidation is not yet available for propene.

This project intends to develop a clean, simple, and energy efficient process for the safe production of propene oxide in a microreactor system containing a gold-titania based catalyst. Gold catalysts on titania-containing supports for the epoxidation utilize a mixture of hydrogen and oxygen to perform the epoxidation. Even though these catalysts are highly selective (selectivities of over 99% are not uncommon), a major problem is that the conversion levels remain low, typically up to 1 %. The only side product in this reaction is water, which ideally is produced in a 1:1 ratio with propene oxide. One of the limiting factors in research into this system so far, is that the usage of both hydrogen and oxygen as well as propene necessitates the use of relatively low concentrations (up to 10 vol% of each) to assure that one operates outside of the explosive region. Working with higher concentrations could result in an explosion if ignited or in case the temperature control is insufficient for this highly exothermal reaction. Microreactors have an excellent potential for carrying out this reaction safely using a gas mixture which would be inside of the explosive region.

Experimental

The first-generation microreactor system is devised basing on a packed-bed capillary reactor with products analysed by an Interscience Compact GC station. Gold catalysts are prepared using the deposition-precipitation (DP) method and the size of gold particles is usually well controlled under 5 nm according to statistics by transmission electron microscopy (TEM) graphs. X-ray fluorescence (XRF) analysis is used to determine the gold loading on the catalysts (generally 1%) and the probable presence of contaminants (e.g., chloride). Activity tests under normal operating conditions are performed with typically 0.3g of catalyst in a conventional tube reactor, whose results are set to be compared with those obtained from the capillary reactor operated in the explosive region.

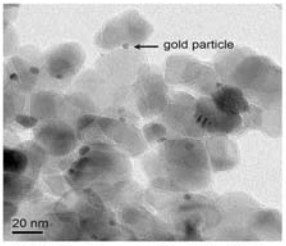

Figure 1. TEM micrograph of Au/TiO_2 catalyst

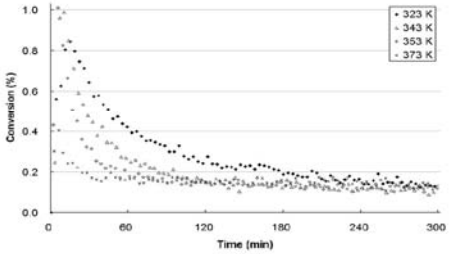

Figure 2. Time-on-stream performance of 1wt% Au/TiO_2 catalyst for direct epoxidation of propene in a tube reactor (P = 1100 mbar, 10 % H_2, O_2, C_3H_6 in Helium, GHSV = 9000 h^{-1})

Objective

- Design and construction of the first generation microreactor for epoxidation,
- Gold catalysts preparation in microreactor,
- Further optimization and kinetic studies of gold catalysts in the micro system.

Acknowledgement

NWO is kindly acknowledged for the financial support to this research project.

TU/e Optimized Sorption Enhanced Autothermal Reforming of Natural gas

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: SenterNovem	**Period**	: Sep.2005 – Sep.2009

Introduction

Steam reforming of methane is the most vital reaction route to convert methane into hydrogen as a pollution-free primary energy carrier. An advanced technique for hydrogen production with in situ carbon dioxide capture is under development in our laboratory using an efficient catalyst-sorbent system.

Motivation

A molecular reaction mechanism and an intrinsic kinetic model are to be developed for catalytic reforming of methane with steam over Rhodium supported Ceria – Zirconia catalyst in a laboratory-scale fixed-bed tubular reactor in the temperature range of 475 to 800 °C and at a pressure of 1.5 bar.

Intermediate Results

- The kinetic experiments show a positive overall reaction order for methane of 0.59 and 0.69 at 475 and 575°C, respectively (Fig. 1).
- The methane reaction rates show a non-monotonic dependency on the steam partial pressure. The reaction order for steam depends on temperature and composition. At 475°C, it is 0.43 at a steam partial pressure lower than 11.2 kPa and reduces to 0.28 above this pressure. The same is observed at 575°C, the order reduces from 0.59 to 0.19. At temperatures higher than 700°C, the overall rate of reaction has a positive order less than 1.0 at a steam/carbon ratio below 2 and a negative order at higher steam/carbon ratios.
- The water-gas shift reaction is suppressed at high temperatures above 575°C and at low steam partial pressures at a steam/carbon ratio below 1.5. H_2 and CO_2 inhibit methane reforming at all investigated conditions of partial pressure and temperature. H_2 reduces the oxidization state of ceria, while CO_2 competes with steam on oxidizing the reduced ceria sites at temperatures below 700°C.
- Two distinct sites are thought to be responsible for the dissociative adsorption of methane and steam on the catalyst surface. Methane is dissociatively adsorbed on the rhodium sites. Steam is dissociatively adsorbed on the ceria support with insignificant dissociative adsorption on rhodium at temperatures below 700°C.

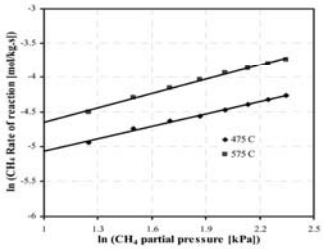

Fig. 1 : reaction order in terms of methane

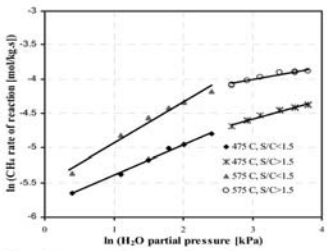

Fig. 2: reaction order in terms of steam

Acknowledgement

The project is performed in collaboration with Energy Research Center of the Netherlands (ECN) and Jacobs Consultancy Nederland. The financial support by SenterNovem is gratefully acknowledged.

TU/e

Solid acid foams for a reactive extraction process for 5-hydroxymethyl furfural (HMF)

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OSPT theme	: Multiphase Reactors	**Research school**	: NIOK
Supported by	: Catchbio, Avantium	**Period**	: Feb 2009 – Jan 2013

Introduction

To achieve future fuel & chemical demand of modernized world, Biomass is the most sustainable and abundant alternative. 5-Hydroxymethyl furfural (HMF), which is produced by aqueous phase dehydration of sugar (Fig. 1) with acid catalyst, posses good fuel properties. HMF can also be a prime building block for future bio-refinery.

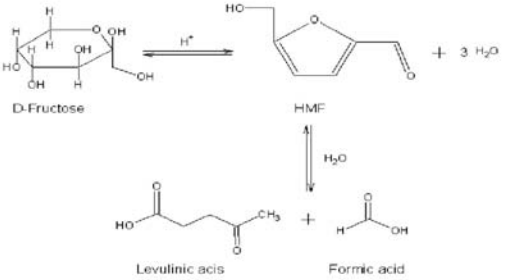

Fig. 1 aqueous phase dehydration of sugar to HMF. HMF further undergoes rehydration to give levulinic acid and formic acid if not removed from aqueous phase

However, if HMF is not removed from aqueous phase, it rehydrates to give Levulinic acid and formic acid and also polymerizes. This not only reduces final selectivity of HMF but also deactivates the catalyst. In last decade intensive research has been done on extracting HMF with the help of an organic phase and searching a viable catalyst. Most research regards to homogenous catalysts which increases the separation cost of product. Heterogeneous catalysts proposed are still not able to achieve high selectivity for glucose feed. Therefore the industrialization of the process is still not possible.

Approach

Solid foam (Fig. 2) provides maximum surface area compared to other packings like rasching rings, intalox saddles, etc. High surface area ensures high rate of reaction and also high mass transfer for the extraction. Also solid foam material ensures high voidage, which helps for effective flow of liquid through column and less pumping cost.

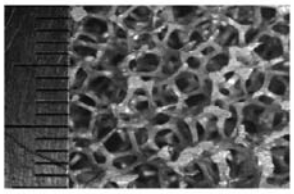

Fig. 2 image of solid foam packing, the graduated markings are in mm, specific surface area 1080 m^2_S m^{-3}_P

Process integration of reaction and extraction will increase selectivity towards desired HMF and use of acidic solid foams will improve rate of formation of HMF.

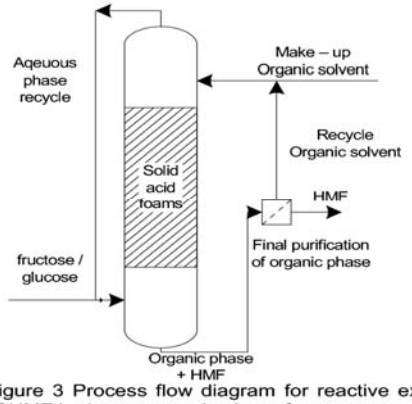

Figure 3 Process flow diagram for reactive extraction of HMF in denser organic phase from aqueous phase

Acidic catalyst could be supported on foam packing and counter current extraction column can be run as explained in Figure 3. Organic phase is fed from top (if it is denser than water) and will extract HMF from aqueous phase which is moving upwards.

Acknowledgement

This research project is carried out within the framework of CatchBio. It is financially supported by Avantium Technologies.

TU/e Microwave Enhanced Microprocessing in large-scale Fine Chemical Synthesis

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OSPT theme	: Multiphase reactors	**Research school**	: OSPT
Supported by	: STW	**Period**	: Aug 2008 – Jul 2012

Introduction:
Miniaturization of process equipment should bring about dramatic changes in the chemical industry in terms of structuring, intensification, and modelling of processes which will allow progress towards the control of every molecular transformation. Therefore microstructured reactors are nowadays regarded as a separate class of chemical reactors with their specific characteristics such as improved heat and mass transfer and well tuned residence times. Recently there has been lot of work going on microwave assisted organic synthesis as well, suggesting the realization of microwave heating as an enabling technology to perform high-speed synthesis with better process selectivity and the product yield. The integrated concept of both these technologies, microstructured reactors and microwave heating, is expected to lead to significantly better processing issues, such as a better heating in terms of heating speed, precision of temperature ramping, heat transfer efficiency, a higher selectivity due to a better definition of residence time and temperature ramping by a fast heating up and quenching, and a smooth transient operation due to the ability of microwaves to induce spatially strongly varying properties for a short time.

Objective:
Thus the goal of this process intensification project is to design, develop, and demonstrate a micro-structured device for chemical synthesis and multiphase flow handling in which microprocessing and microwave heating will be integrated in one flow through reactor. The project aims at establishing the technological scope and limitations of microwave enhanced microprocessing for large scale synthesis of fine chemicals and pharmaceuticals in microstructured reactors.

Scope of the work:
This project is divided in three sections namely, investigations of microwave assisted organic chemistry, process intensification issues associated with the usage of microwaves as a heating medium, and design, development and performance studies of integrated microwave microreactor system. While first two sections will be investigated by other two PhD participants working consecutively at TU/e & TU Delft respectively, the third section will be investigated by above said PhD participant. In this section, after the comparison of microwave heating with conventional micro heat exchanger, an integrated microwave microreactor system will be designed and developed. In particular combined with temperature ramping, the effect of microwave heating on solid catalyzed processes will be investigated.

Acknowledgement:
The financial support by Dutch Technology Foundation (STW), DSM, Friesland foods, Milestone, IMM, and LioniX is gratefully acknowledged.

TU/e

Development of advanced mesostructured substrates for fine chemicals synthesis

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OSPT theme	: Multiphase reactors	**Research school**	: OSPT
Supported by	: NWO-RFBR	**Period**	: Sept. 2006– Sept. 2009

Project description

Microreactors have a large potential in development of very selective and environmentally benign routes for the production of fine chemicals and pharmaceuticals, because full selectivity control can be achieved by total structure uniformity at multiple length scales. First of all, on the nanoscale by using appropriate mesoporous coatings and by obtaining (bi-)metallic clusters with a narrow particle size distribution. Then, on the microscale by synthesizing only a thin (500-1000 nm) coating support layer on the walls of reaction channels to avoid long diffusion pathways in the macropores. Finally, on the macroscale, by providing the same residence time and reaction conditions in every microchannel in a microfabricated reactor. The proposed research is aimed at the development of new types of stable catalytic mesoporous coatings for efficient fine chemicals synthesis under controlled conditions. The unique characteristics of mesostructured materials, namely high pore volume and surface area combined with narrow pore-size distribution, make them particularly suitable for various fine chemicals synthesis processes. Potentially most stable coatings are sol-gel derived crystalline (or amorphous) silicon and transition metal (preferably titanium) oxides. Synthesis of the latter materials is complicated by moisture sensitivity of the required precursors. Moreover, at present there is insufficient knowledge concerning optimal synthesis conditions and optimal coating properties for incorporation of (bi-) metallic catalysts. New sol-gel chemistry strategies for coating synthesis, starting from newly developed precursors, will be developed in combination with the evaporation induced self-assembly (EISA) method. Various experimental techniques will be used and developed to obtain insight in physical and chemical phenomena that determine the catalytic performance as well as the stability of the coatings. Pore morphology and internal surface features of mesoporous coatings will be modified to achieve a good binding of active catalysts with the support. This will create a high surface area available for reactant adsorption. In turn, this will allow efficient operation of wall coated microstructured reactors in various catalytic reactions.

In the second part of the project, we will focus on understanding the influence of catalyst crystallite size effects, type/stoichiometry of bimetallic (Pt-Sn, Ru-Pt and Rh-Sn) clusters on the kinetics of citral hydrogenation. The bimetallic nanoparticle catalysts are discrete anchored clusters, prepared by the gentle decarbonylation of the parent, mixed-metal precursor anions. They will be inserted along with their counterions into a mesoporous support. The mesoporo-encapsulated clusters will be activated by heating in vacuum. The diameter of the resulting, well-dispersed, isolated and anchored bimetallic nanoparticles is in the range of approximately 1-2 nanometers.

The catalytic coatings will be tested in the heterogeneously catalyzed hydrogenation of citral to the corresponding unsaturated alcohols which represent a broad class of industrially relevant compounds useful in the specialty, pharmaceutical and other high-value sectors of the chemicals. Long term performance of catalytic coatings will be evaluated.

TU/e Micro separation technology

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OSPT theme	: Separation Technology	**Research school**	: OSPT
Supported by	: NWO	**Period**	: April 2007 – April 2011

Introduction

Microreactor technology has been developed for a variety of unit operations such as mixers, heat exchanger, and chemical reactors. Due to features such as the enhanced driving force induced by difference in T, P and C in the microfluidic system, higher contact area to-volume ratio, and minimization of unit-processing hardware, microreactor technology has received increasing attention giving way to new research fields of **Microfluidics** and **Microseparation technology**.

The combination of a microreactor with a micro separator should result in a compact production system, which is useful. Since the use of conventional separation units with micro reactors will undermine the advantages the microreactor has. However, only a few studies have reported on microseparation devices and suggested that two or three orders of magnitude size reduction is possible by comparison with conventional operations.

Objective

This research therefore will focus on the microseparation units. The investigation in micro separation technology will deal with miniature devices using extraction, diffusion processes (absorption) for gas-liquid separation and affinity separation for liquid-liquid separation.

Partition wall separator

This microreactor type will be investigated for gas-liquid absorption process. As shown in Figure 1 the liquid stream of an aqueous amine solution is used to absorb the CO_2 from gas stream of N_2/CO_2 mixture. The capillary pressure in a perforated wall separates the gas and liquid streams and mass transfer occurs in a stagnant liquid film. In this reactor the challenge is to keep the pressure drop difference between the gas and liquid sides below capillary pressure.

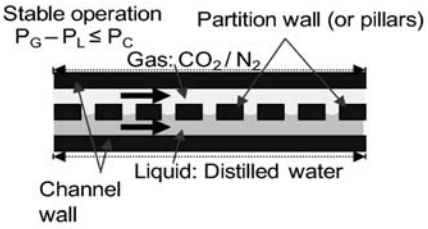

Figure 1: *Absorption of CO_2 by Water from CO_2/N_2 mixture in a flow of gas and liquid streams in two parallel channels separated by membrane walls.*

Affinity separator

For liquid–liquid separation the selective modification of channel walls will be investigated. Fig. 2 shows the separation on aqueous/organic emulsion in the coated channel. The difference in affinity for walls for two liquids should be able to maintain the layer flow. The challenge in this case is to maintain the parallel flow pattern and to avoid the Taylor flow in any case.

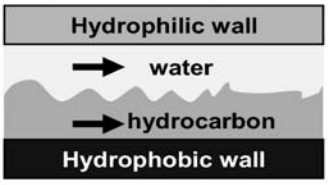

Figure 2: *Separation of Aqueous/Organic solution in micro channel coated with different affinity material on top and bottom of channel.*

In both prototypes the effect of dimensions (channel and partition walls) on separation quality (Mass transfer) will be investigated.

Acknowledgement

This research project is funded by NWO.

Rotating Foam Reactors

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: STW	**Period**	: Dec 2006 – Nov 2010

Introduction

Open cell foams find application in several fields, such as heat exchangers or deep bed filters. However, there is a growing interest for their application as catalyst supports due to high porosity, specific surface area and open structure leading to good mass and heat transfer properties. Various materials (ceramic, metal, carbon) and pore structures can be produced, enabling a broad range of hydrodynamic, mechanical and thermo-dynamical properties.

Objective

New reactor types for gas-liquid-solid reactions are developed. Currently these reactions, such as hydrogenations or oxidations, are performed using slurries of fine catalyst particles. They are dispersed in the liquid and need to be separated from the mixture after reaction.
Furthermore can agglomeration of the particles lead to mass transfer limitations, especially at higher liquid viscosities.

The idea is to immobilize the catalyst on porous structures, which are integrated parts of the reactor, such as rotating blocks or stirrer blades. This allows an easy separation of catalyst from the reaction mixture. In addition to the role as catalyst supports, the rotation of the foams should provide shear forces to break up gas bubbles and lead to a good mixing of reactants.

Procedure

A lab scale three phase reactor is used, allowing the study of different types and shapes of foam structures.
Measurements are performed in order to investigate the hydrodynamics, the mass transfer and the catalytic performance of the systems.
Various foam designs are tested and compared to a Rushton stirrer, which is used in the fine chemical industry.
The reactor performance using a model reaction is investigated and the application for batch processes in fine and pharmaceutical chemistry is studied.

Acknowledgement

The project is financially supported by Dutch Technology Foundation STW.

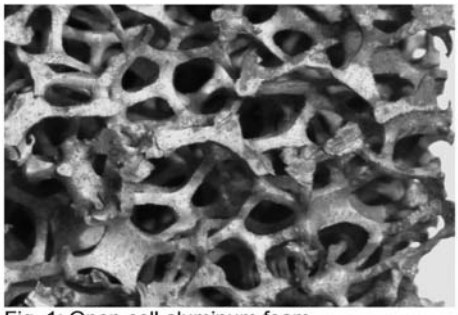

Fig. 1: Open cell aluminum foam.

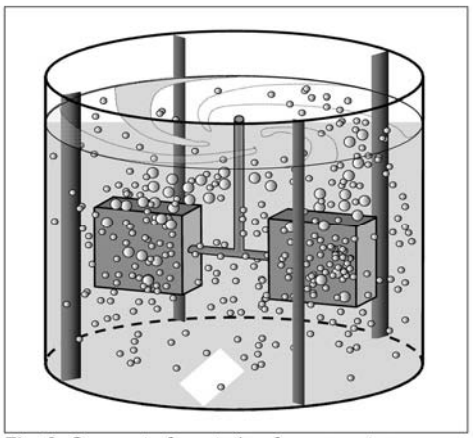

Fig. 2: Concept of a rotating foam reactor.

Hairy Foam Catalysts: towards control at the catalytic site

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OSPT theme	: Comp.Exp.Chem.Eng	**Period**	: June 2005 – May 2009
Supported by	: STW, Akzo Nobel, DSM, Shell, Basf, Stork, Recemat		

Introduction

The objective of the project is to develop a new type of structured catalyst support, consisting of carbon nanofibers (CNFs) grown on solid foam. Solid foams are the inverse of a packed bed; the void space and the packing have exchanged position. Similarly, entangled CNFs are the inverse of a porous catalyst particle. So, the targeted composite material will be the inverse of a packed bed of porous catalyst particles. This new and original approach integrates the design of catalyst support on micro and macro scale. This new type of structured catalyst support enables full control at the catalytic site, by diminishing diffusion resistances, and allows an optimal balance between pressure drop, mass transfer and catalytic reactivity.

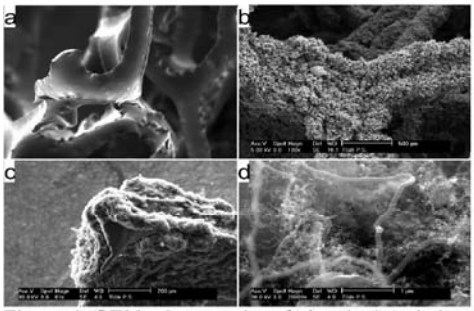

Figure 1: SEM micrographs of a) reticulated vitreous carbon (RVC); b) CNF grown on RVC; c) SEM detail of CNF layer on RVC; d) detail of CNF.

Procedure

Layers of entangled carbon nanofibers have been prepared on the surface of solid carbon foams (Hairy Foam) by catalytic ethylene decomposition. First, the solid carbon foam was coated with nickel. The nickel was deposited by homogeneous deposition precipitation using the decomposition of urea. The effect of nickel loading on fiber diameter and morphology, CNF coverage, and fiber layer thickness has been studied using SEM and N_2-physisorption.

Next palladium was deposited on the obtained Hairy Foam. Hereto the surface of the Hairy Foam was oxidized in order to produce oxygen anchoring groups to facilitate the deposition of palladium. The palladium was deposited on the oxidized Hairy Foam by the ion exchange method.

The obtained Pd/Hairy Foam catalyst has been tested using the liquid phase oxidation of sodium formate. Oxygen was dissolved in aqueous sodium formate using a semi-batch gas-inducing stirred tank reactor. The oxygen saturated liquid was recycled through a Pd/Hairy Foam packed bed reactor. The inlet and outlet O_2-concentration of the packed bed have been measured using optical oxygen sensors. The liquid flow rate, PPI number (pores per inch), and CNF synthesis temperatures have been varied.

Results

The surface area increased from 0.12 $m^2_{support}$ $g^{-1}_{support}$ for RVC foam to 146 $m^2_{support}$ $g^{-1}_{support}$ for Hairy Foam. A nickel conc-entration of 0.5 wt% (g_{Ni} g^{-1}_{RVC}) results in fibers with a diameter of 30-90 nm. Increasing the nickel concentration resulted in a fiber diameter of 30-1100 nm. Complete CNF coverage has been obtained for a nickel deposition time of at least 240 min and a nickel concentration of at least 2.5 wt% (g_{Ni} g^{-1}_{RVC}) [1].

The observed overall reaction rate coefficient, k_{ov}, using 45 and 60 PPI Hairy Foam/Pd catalyst is approximately the same as the mass transfer coefficient predicted by Onda's correlation for packed beds[2] with particle diameters ranging from 0.41 mm to 1.2 mm (k_{ov} up to 0.3 m^3_l m^{-3}_r s^{-1}). Overall rate coefficients up to 0.9 m^3_l m^{-3}_r s^{-1} have been obtained for the 20 PPI Hairy Foam/Pd catalyst.

The results show that Hairy Foam catalyst can obtain similar or higher liquid to solid mass transfer rates as packed beds of spheres. The high voidage of the Hairy Foam combined with the high mass transfer rates results in an efficient used of the reactor volume when applying Hairy Foam as a catalyst support.

1) P.W.A.M. Wenmakers, J. van der Schaaf, B.F.M. Kuster, J.C. Schouten, J. *Mater. Chem.*, **18**, 2426-2436, (2008)
2) K. Onda, *J.Chem.Eng.Jap.*,**1**,56-62 (1968)

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Activities of the Thermo Fluids Engineering Division

Experimental, theoretical and numerical research is carried out on fluid flows, heat- and mass transport processes and combustion. Hence, the division is also an active member of the J.M. Burgers Centrum Research School for Fluid Mechanics. The general goal of the research in the OSPT- programme is the development and functional implementation of computational models and advanced experimental techniques, for the sake of analysis of energy technology systems, combustors and process equipment and the design of it. Within this rather broad and general scope, the following selection of major research areas has been made.

a) Biomass
One of the main issues of interest is the reduction and combustion of biomass in fixed bed and fluidised bed gasifiers. The studies involve for instance the physical and chemical characterisation (global C, H and N-kinetics) of biomass fuels, the development of flame front models propagating in fixed biomass beds and models for the nitrogen chemistry inside and above the fuel bed. Besides the problem of tar production in small-scale fixed bed gasifiers is a topic of research. Reduction possibilities evaluated are thermal cracking, partial oxydation and recycling of pyrolysis gas. Finally, the behaviour of aerosols in a small scale biomass combustion furnace is analysed. The applicability of several turbulence modelling techniques to the problem at hand is evaluated.

b) Heat exchangers

Enhancement of heat and mass transfer in the process industry depends critically on our knowledge and understanding of issues like fouling and dropwise condensation. These two topics are studied, in our laboratory but also with numerical modelling. Based on the improved understanding design recommendations have been generated and tested, such as new types of condensors in which dropwise condensation is promoted. Demixing of gasses can be established with the combination of isentropic expansion and condensation. The competition between mass transport to the wall, ending in condensation or desublimation, and cooling of the bulk phase, possibly leading to homogeneous nucleation, is of special interest to us. Drainage off a condenser plate has been studied under near-critical conditions with dedicated experiments. Experiments have been designed to try to explain the large difference in heat transfer between filmwise and dropwise condensation. In particular in refuse waste incinerators and biomass equipent, particulate fouling occurs at heat exchange surfaces. The fouling layer reduces the heat transfer rate and lead to inefficient operation. Both the deposition process and the removal mechanism are studied. Finally, the combination of heat exchangers with solar cells in so-called combi-panels is analysed.

c) Rotational particle separator

The technique of the Rotational Particle Separator (RPS), an alternative to existing methods of separating solid and liquid particles, is expanded further. The design, construction and testing of a liquid-liquid separator for offshore applications is carried out in cooperation with Shell Exploitation b.v. The results of the project with the liquid-liquid separator are being used in a new design project for a gas -liquid seperator with CDS engineering b.v. Also the viability of the RPS for application in the Esso cathalytic cracking unit is investigated. A more recent development concerns the upgrading of natural gas contaminated by CO_2/ H_2S. A significant part of global reserves of natural gas suffers from this problem. A new concept is being developed involving the RPS. A scaled-down unit was built by Shell.

Numerical calculation of gas mass flow rate through valves at pressures up to 3600 bar

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OSPT theme	: Comp. & Exp. Chem. Eng.		
Supported by	: BASF SE, Germany	**Period**	: May 2005 – Sept 2009

Introduction

Presently the mass flow capacity and valve characteristics of high-pressure safety and control valves cannot be predicted with satisfying accuracy in the range from 250 to 3600 bar. In this range, neither calculation standards, nor test rigs are available. Consequently, the operating reliability of such valves (figure 1) will be sufficient only after expensive and time-consuming empirical validation at low pressures resulting in over-dimensioned geometries.

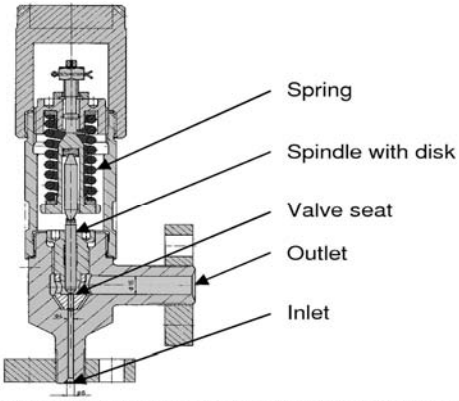


Figure 1: Overview of a high-pressure safety valve

The aim of the project is to develop a numerical model of sufficient predictive capacity that allows the calculation of mass flows, and operating stabilities of high-pressure safety valves at operating pressures above 250 bar. In order to validate this model, experiments with these valves will be carried out at the unique ultrahigh pressure test-rig of BASF for pressures up to 3400 bar. As a result, the number of high cost experiments will reduce, the reliability of safety valves in existing process systems will improve, and valves in future applications will be optimised.

Methodology

The numerical model is based on time dependent Navier Stokes equations, and is extended to account for real gas effects, condensation, and separation of the choked gas flow. The commercial CFD code ANSYS CFX 11.0 is chosen to determine the suitable numerical parameters stepwise from 1D inviscid to a 3D real gas model.

Results

For a critical compressible flow, a model reduction to 2D axisymmetric is valid. At low disk lift, where the disk height h compared to the seat diameter d_0, $h/d_0 < 0.25$, the empirically determined correction factor for the mass flow rate, the discharge coefficient K_d and the numerically calculated value agree with 7% (figure 2). At higher disk lift, the numerically calculated mass flow rate over-predicts the experimental value up to 19%.

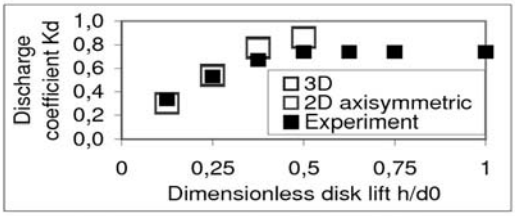


Figure 2: Comparison of fixed valve lift (7 bar air)

Outlook

Both the accuracy of the experimental data and the accuracy of the numerical model is questioned. Since only the inlet flow determines the mass flow rate, it is focused on the boundary layer development at large disk lift.

Acknowledgement

This project is carried out in cooperation with and financially supported by BASF SE, Ludwigshafen in Germany.

TU/e Technische Universiteit Eindhoven University of Technology

Condensed Rotational Bulk Separation

G.P. Willems, J.J.H.Brouwers and M. Golombok

Introduction

Novel method for bulk separation of gas mixtures:

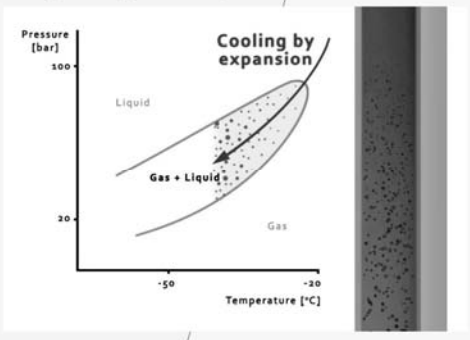
- The mixture is cooled to a temperature at which one of the components condenses to micron sized mist-particles
- These particles are subsequently removed by rotational particle separation.

Advantages:

- Compact / inexpensive equipment
- Low energy costs

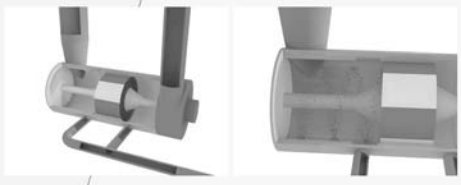
Condensation by expansion

Below the phase diagram of a CH_4/CO_2 mixture can be found:

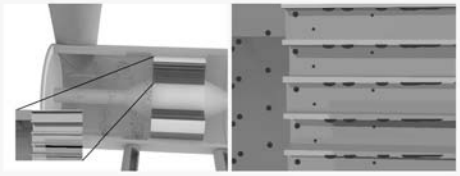


Droplets are formed by isentropic / isenthalpic expansion or isobaric cooling.
The liquid CO_2 droplets contain a small amount of dissolved CH_4. The exact thermodynamical equilibrium concentration depends on the process conditions.

Centrifugal droplet removal by RPS



When the droplets have grown to a size of a few microns, the droplets are fed into the Rotational Phase Separator.



The gas enters the small channels where a large centrifugal field forces the small particles into a thin film.

This film leaves the filter element where big droplets are formed. These big droplets are collected and drained from the equipment, remaining in liquid state.
Because the CO_2 is harvested in a liquid form, no compression costs or additional cooling costs have to be made. This results in relative cheap subsurface storage / enhanced oil recovery possibilities.

Results

Proof of principle on lab scale: Shell Global Solutions.
A preliminary full scale separator has been designed, an impression can be found below.
An equivalent full scale atmospheric prototype is designed, build and will be tested in the TU/e lab.

Conclusions

1. Small scale test results are in agreement with thermodynamic predictions
2. Scale up initiated

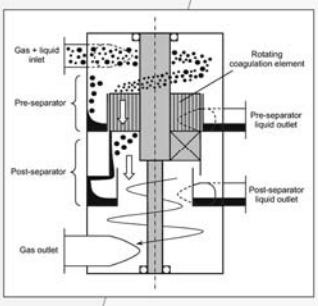
TU/e Technische Universiteit Eindhoven University of Technology

Condensed Rotational *Test Setup*

J.P. Kroes, G.P. Willems, J.J.H. Brouwers, M. Golombok

Introduction

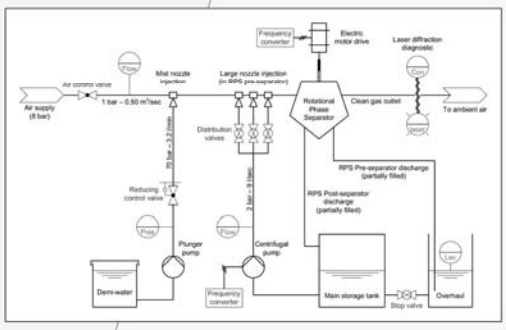
A new method for bulk separation of gas mixtures has been developed, based on rotational separation. An optically accessible prototype is built.



At the TU/e laboratory, the prototype is tested in an atmospheric test rig, with air and water as working fluids. In the real application, pressures are in the range of 10-30 bar and fluids are methane and carbon dioxide (or hydrogen sulfide).

Up to 0.5 m^3/s of gas flow can be provided to the unit. In terms of volume flows this is comparable to a 80 MMscuf/day field application (ca. 4 wells). The test setup is meant to proof and test two operational aspects:

- Liquid removal capacity
- Droplet separation efficiency



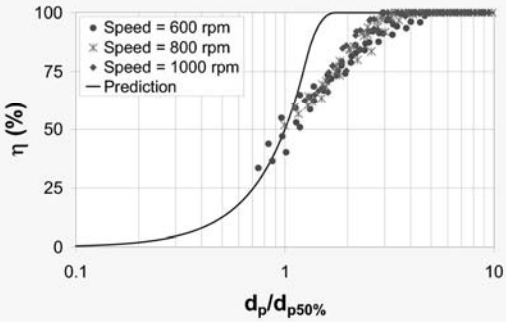
Liquid removal capacity

Within the separator, separated liquid is collected in a so-called post-separator. The capacity of the post-separator volute is put to the test by forcing a large liquid load (0.01 m^3/s) through the unit. At 0.5 m^3/s of gas flow, this load is comparable to ca. 40 mole% of liquid contaminant.

Separation efficiency

In reality, condensed gas droplet sizes are in the range 1-10 μm. This is simulated by injecting a relatively small amount of water (3 l/min) at the prototype inlet using high pressure mist heads.

Using laser diffraction diagnostics, both droplet concentrations and droplet size distributions are measured in the gas flow exiting the unit. Separation efficiency curves can be derived from these measurements at varying airflow and rotational speed.



Results & prospects

1. The post-separator capacity is sufficient at high liquid loads. A mathematical model of the hydrodynamics is under development.
2. Separation measurements have shown that predictions of the design parameter $d_{p50\%}$ are correct. This is the droplet diameter separated with 50% efficiency. On the other hand, efficiencies on the order of 100% are obtained only at four times $d_{p50\%}$, which is higher than expected.

Radical Tar conversion by Flame-Generated-Radicals

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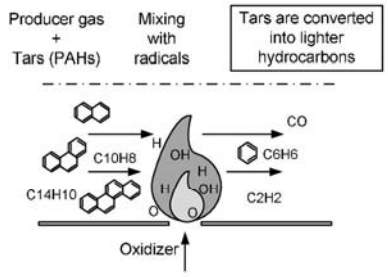
OSPT theme	: Energy Conversion Processes	**Research school**	: OSPT
Supported by	: ECN, SenterNovem	**Period**	: September 2006 – August 2010

Background

* Reduction or decomposition of tar in biomass derived fuel gas → bottleneck in small-scale biomass gasification.
* Tar is made up of Polycyclic Aromatic Hydrocarbons (PAHs) consisting of fused aromatic rings.
* Past experimental results have shown partial combustion as an effective way to convert tars in biomass derived fuel gases.



Objective

Execute a fundamental study of the working mechanisms behind the process of partial combustion. With this knowledge it is possible to optimize the process conditions and the reactor geometry.

Approach

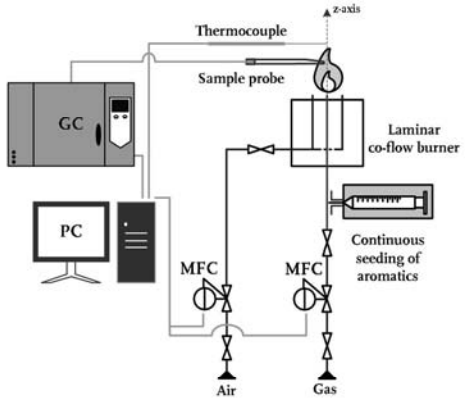
Study the separate effect of:

* Thermodynamics
* Chemical Kinetics
* Molecular transport

Tools

A thermodynamic analysis is performed by executing chemical equilibrium calculations. The chemical kinetics are studied by applying Perfectly Stirred Reactor simulations. Three different reaction mechanisms are assessed. Full 2D simulations give insight in the influence of molecular transport on the process. The 2D model is validated against experimental data (probe & laser diagnostics are applied).

Experimental Setup



Acknowledgements

This project is a collaboration with ECN and financed within the framework of EOS by SenterNovem.

Grate Furnace Combustion: A Submodel for the Solid Fuel Layer

J.M. Burgerscentrum

H.A.J.A. van Kuijk, R.J.M. Bastiaans, J.A. van Oijen, L.P.H. de Goey

Background

- Medium scale biomass combustion: grate furnace (fig. 1)
- Problem: emission limits NO_x
- Main cause: N-precursors (mainly NH_3) released in the solid fuel layer are oxidized in secondary zone
- Solution: adapt operating conditions and furnace design on the basis of simulations with numerical model
- Fuel layer N-release dependent of combustion process parmeters: conversion rate and temperature
- Needed: submodel for combustion process in solid fuel layer

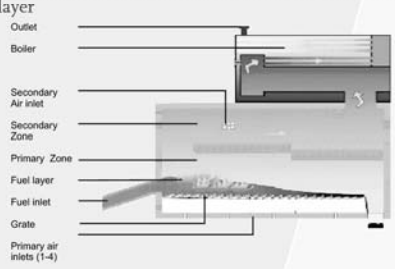


Fig. 1: Grate furnace. (Courtesy: TU Graz).

Fixed bed configuration

- Grate furnace: use reference frame traveling with the grate i.e. replace spatial coordinate s by time t (fig. 2): combustion process silmilar to reverse fixed bed combustion.

Fig.2. Solid fuel layer: grate (left) and fixed bed (right). Reaction front velocity: v_s, gas velocity v_g.

Governing Equations

- Set of equations for porosity ϵ, oxygen mass fraction Y and temperature T :

$$\frac{\partial}{\partial t}\left(\epsilon\rho_g Y\right)+\frac{\partial}{\partial x}\left(\epsilon\rho_g v_g Y\right)-\frac{\partial}{\partial x}\left(\rho_g D\frac{\partial}{\partial x}Y\right)=-\nu R, \quad (1)$$

$$\frac{\partial}{\partial t}\left(\epsilon\rho_g\right)+\frac{\partial}{\partial x}\left(\epsilon\rho_g v_g\right)=R, \quad (2)$$

$$\frac{\partial}{\partial t}\left(\left((1-\epsilon)\rho_s c_{ps}+\epsilon\rho_g c_{pg}\right)T\right)+\frac{\partial}{\partial x}\left(\epsilon\rho_g v_g c_{pg} T\right)-\frac{\partial}{\partial x}\left(\Lambda\frac{\partial T}{\partial x}\right)=-\Delta H_r R. \quad (3)$$

- Assumption: $m_g=\epsilon\rho_g v_g=\text{constant}=m_{gu}$: no continuity equation. The subscript u indicates the unburnt region far upstream; b is used for the burnt region downstream.
- Equations can be solved in reference frame attached to combustion front (not shown here)→ stationary solutions.
- Stationary problem: convenient for fast parametric studies, $m_{su}=(1-\epsilon_u)\rho_{su}v_{su}$ follows directly from transformed equations.
- Mass transfer limitations and kinetics (Arrhenius rate constant; activation energy E_a) are taken into account in source term R. Currently, physical parameters for coal [a] are implemented.

Numerical Results

- Spatial profiles (fig. 3): $T_b\uparrow$ and $\epsilon_b\uparrow$ with $m_{gu}\uparrow$.

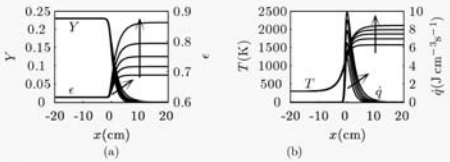


Fig. 3. Spatial flame profiles for varying gas mass flux. Results for Y and ϵ (a) and T and heat release $\dot{q}$ (b). The arrows indicate results obtained with increasing m_{gu} from $m_{gu}=4.9\times10^{-3}$ g cm^{-2}s^{-1} to $m_{gu}=14.6\times10^{-3}$ g cm^{-2}s^{-1} in steps of 2.4×10^{-3} g cm^{-2}s^{-1}.

- Flame parameters as a function of m_{gu} (fig. 4): m_{su} has a maximum, $T_b\uparrow$

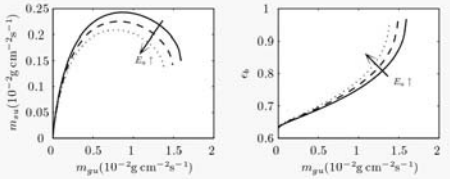


Fig. 4. Flame parameters as a function of gas mass flux for varying activation energy. Results for m_{su} (a) and ϵ_u (b). Solid line: $E_a=150$ kJ mol^{-1}, dashed line: $E_a=160$ kJ mol^{-1}, dotted line: $E_a=170$ kJ mol^{-1}.

Conclusions:

- Main parameters for NO_x-predictions (T, ϵ) result from the model equations
- Use of stationary solution method results in short calculation times: no need to solve the problem analytically as has been done in the past[a]
- Model can be extened with addtional chemistry for a biomass source term

[a] R.Gort, On the propagation of a reaction front in a packed bed, PhD-thesis, University of Twente, 1995

TU/e Technische Universiteit Eindhoven University of Technology

The importance of nucleation on heat transfer

M. H. M. Grooten

Introduction

Research focusses on the mechanism of dropwise condensation from flowing gas with inert components. Drops being formed on a polymer plate grow untill they detach. Heat transfer with dropwise condensation is about 8 to 10 times as high as that of filmwise condensation, but the reasons why are still not fully understood. Based on recent research in our laboratory we expect the initial phase of drop growth to be important. The aim of the project is to determine the importance of the initial phase of drop growth on heat transfer. Applications are the design of condensers that promote drainage of condensate from a plate, and the separation of components in a gas stream.

Figure 1: Compact PVDF heat exchanger.

Measuring strategy

The initial phase of drop condensation, i.e. the nucleation inception, is expected to be relatively most effective in heat transfer, because of the lack of a diffusion limit. The importance of the initial phase would imply that drainage of the condensate from the plates would lead to heat transfer enhancement. A new test rig was therefore designed in which drainage of condensate on the condenser plates can be controlled, in order to validate the principle.

Experimental

The newly designed PVDF heat exchanger is shown in figure 1. The PVDF condenser is a cross flow parallel plate heat exchanger, entirely made of PVDF and with coolant flowing in separate channels as shown in Fig. 2. The first channel uses a separate header to inject drainage water through holes onto the plates, see Fig. 2. The drainage pressure and injection frequency are controlled. A steam/air mixture flows between the condenser plates. Temperature, humidity and flow velocity are controlled. Heterogeneous nucleation of drops will occur on the condenser plates, see Fig. 3. The effects of drainage on dropwise condensation heat transfer enhancement is measured both directly with optics and indirectly via heat transfer rates.

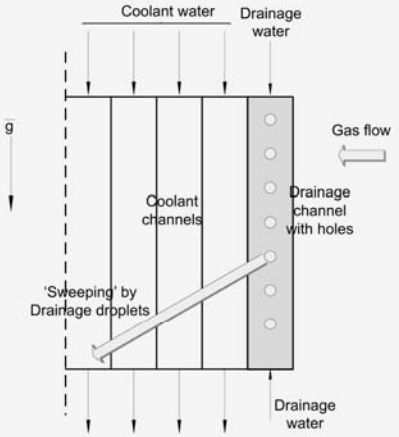


Figure 2: Schematic sideview of an exchanger plate.

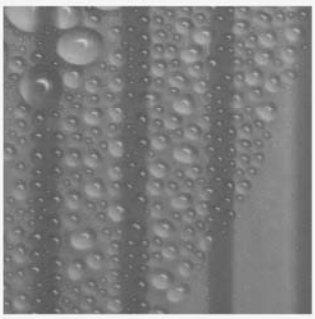


Figure 3: Condensation on an exchanger plate.

Some related previous research:

- F.L.A. Ganzevles, Drainage and condensate heat resistance in dropwise condensation of multicomponent mixtures in a plastic plate heat exchanger, PhD thesis, Technische Universiteit Eindhoven, 2002
- A.S. Lexmond, Drop pinch-off from hydrophobic heat exchanger plates, PhD thesis, Technische Universiteit Eindhoven, 2003
- Various publications in Int. J. of Heat and Mass Transfer and other journals.

Advanced Diagnostics for Thermo-chemical Processing of Biomass

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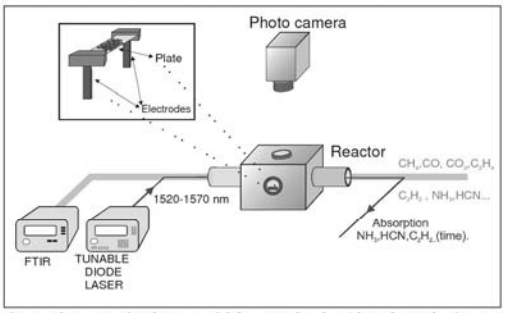
OSPT theme	: Energy Conversion Processes	**Period**	: September 2007 – September 2009

Introduction

The objective of the project is to provide accurate measurements of biomass pyrolysis products (such as CO, CO_2, CH_4, NH_3, and H_2O etc) and their release rates.

Experimental

The measurements are performed in the heated plate reactor. The reactor is capable of heating up the biomass sample with the rate up to 1000 K/s and equipped with windows for optical access. The concentration measurements of biomass products are performed using FTIR (Fourier Transform Infrared Spectrometry) and IR laser absorption techniques. The yields of biomass products are determined



using the equivalent width method (developed in our laboratory). We use the integral absorption (the equivalent width) of a FTIR spectral feature rather than a traditionally employed apparent absorption. Measurements of NH_3, CO, C_2H_2, C_2H_4, CH_4 and NO concentrations performed in a heated gas cell for different pressures, concentrations and FTIR resolutions confirmed the accuracy of the method.

Results

Radiation thermometry technique has been used to determine temperature distribution over the plate.

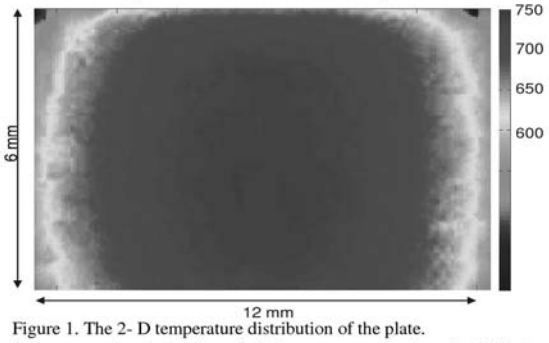


Figure 1. The 2- D temperature distribution of the plate.

Images captured by the digital camera were translated into images of temperature distribution using calibration curve. The curve was determined using the thermocouple attached at the center of the plate.

To test the capability of the TDL absorption technique for measurements of the pyrolysis products and to select transitions appropriate for trace acetylene detection, we performed the direct absorption measurements of C_2H_2 in the sample cell. The results (see, for example, Fig. 2) demonstrate a very good sensitivity of the measurements and confirm the potential of the absorption techniques for kinetic studies.

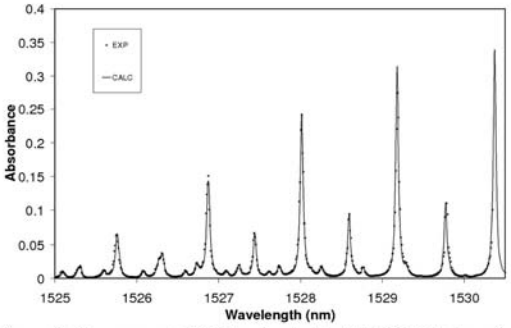


Figure 2. The measured (TDL) and calculated (HITRAN) absorption spectra of C_2H_2 (10000 ppm in N_2). Atmospheric pressure, path length 30 cm.

Figure 3 shows the effect of temperature on the yields of products from rapid pyrolysis of small samples (up to 10 mg) of medium density fiber (MDF) under atmospheric pressure of N_2. The heating rate was approximately 250 K/s and the holding time at constant temperature was 10 s for all experiments.

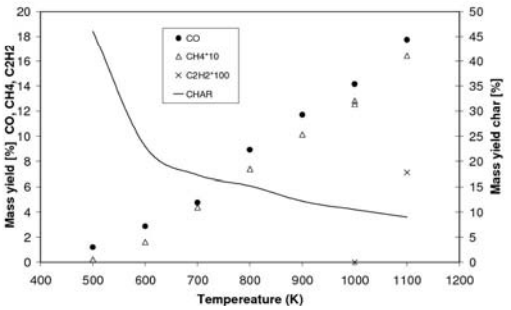


Figure 3. The yields of products from rapid pyrolysis of MDF.

Conclusions

The measured 2-D temperature distribution of the plate show uniform temperature region suitable for the pyrolysis experiments. First TDL absorption measurements of C_2H_2 are shown. The measured and calculated spectra are in good agreement. The concentration measurements of products from rapid pyrolysis of MDF are demonstrated using the equivalent width method.

Technische Universiteit Eindhoven University of Technology

Droplet Size Measurements in Condensing Contaminated Gas

G.Bansal, M.Golombok, J.J.H. Brouwers

Context

- Increasing energy demands and rising natural gas and oil prices.

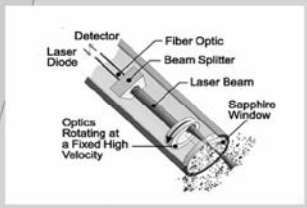
Introduction

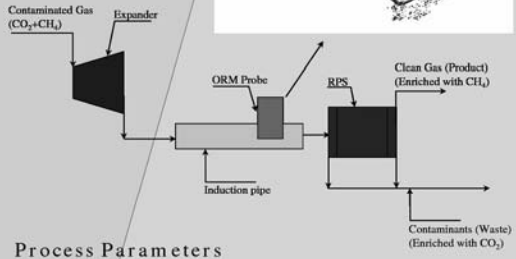
- Nearly 16 percent of currently known natural gas reserves have severe contamination of CO2 and H2S (CO2 > 10 % & H2S > 5 %).
- Approximately energy equivalent to 300 times annual natural gas production of three largest oil and gas companies: Shell Group, Exxon Mobil and BP.
- Condensed contaminant centrifugal separation process using rotational particle separator – An emerging economically viable technology to explore contaminated gas.
- Droplet size of condensing contaminants - A key parameter.

Objectives

- Drop size measurements in condensing contaminated gas.
- Insight of phenomena of growth and droplet formation in lieu of efficient separator and process design.
- Fundamental understanding of the binary mixture condensation process.

Experiments

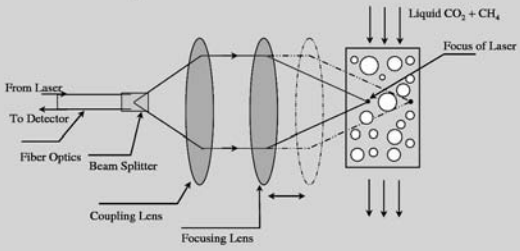




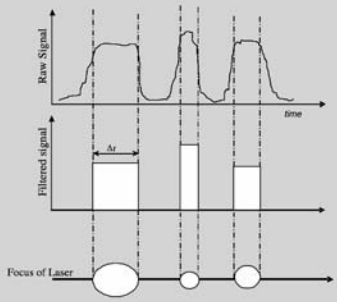
Process Parameters

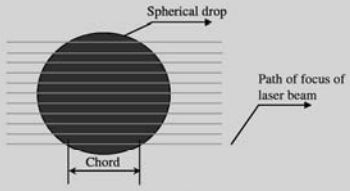
- Composition (CO2 – CH4 mixture).
- Pressure (before and after the expander).
- Temperature (before and after the expander).
- Residence time (time between expander and separator).

Basic Principle of ORM Probe



Measurement of Droplet Diameter





$D \sim \text{scanning velocity} \times \Delta t$

Present status

- Principle of ORM probe has been proved.
- Droplet sizes, which contribute to maximum of liquid volume fraction, are between 1 and 20 micrometers as per very first measurements.

Future outlook

- Controlled and systematic measurements needed to have insight of phenomena.

References

1 J.J.H. Brouwers, R. Wissen, M. Golombok, Novel centrifugal process removes gas contamination, Oil and Gas Journal, 104 (42), 37, 2006.

2. Ralph Van Wissen, Centrifugal separation for cleaning the well gas streams: from concept to prototype, PhD Thesis TU/e Eindhoven, 2006.

Design of the VELO Thermal Control System for the LHCb Vertex Locator

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Period : 2004 – 2008

Introduction

Silicon detectors for the use in high energy particle accelerators such as the Large Hadron Collider (LHC) at CERN, need to be thermal controlled to temperatures below 0°C to avoid the outcome of the radiation damage in the silicon wafers. Cooling systems for silicon detectors must be of low mass in the detector acceptance and the fluid and system hardware must be radiation hard.

Fig.1 The VELO detector with cooling

One of the silicon trackers being built for the LHC program is the Vertex Locator of the LHCb experiment. The cooling system for this detector, the VELO Thermal Control System (VTCS) is being developed at NIKHEF. The VTCS is a two-phase mechanical pumped carbon dioxide loop, which is cooled by an external chilling system.

2PACL system

The principle of the CO_2 loop of the VTCS is a novel design, with new technologies originating from satellite thermal control. The VTCS-loop is a so-called 2-phase accumulator controlled loop (2PACL), and uses a stationary 2-phase accumulator for both evaporator and condenser pressure control.

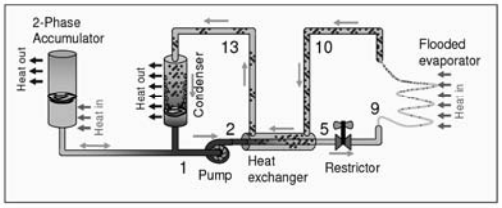

Figure 2: Simplified scheme of the VTCS-2PACL.

The advantages of the 2PACL system is a very accurate remote control of the evaporator section. The evaporator has a very wide operational temperature range from +10°C to -30°C and is very stable over time (<0.05°C).

The 2PACL has a fixed flow and need to reject the heat to a cold source. The temperature of the cold source doesn't have to be stable as long as it is colder than the 2PACL saturation temperature. This makes the accumulator the only accurate controlled item in the system. Figure 3 show the simple control algorithm of the 2PACL accumulator.

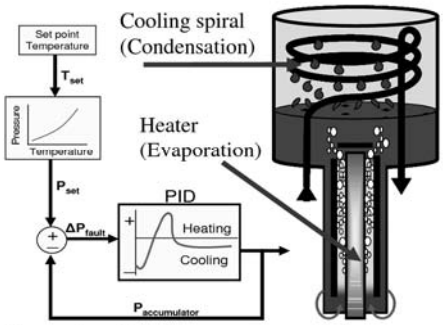

Figure 3: 2PACL pressure control

Commissioning

The VTCS is installed in LHCb in fall 2007. It underwent a commissioning period in 2008 in which both the cooling system and the detector are successfully checked out. Figure 4 show an example of the detector cool down during commissioning in June 2008.

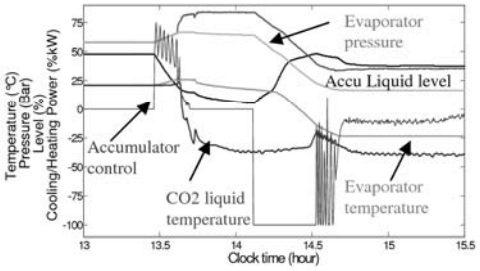

Figure 4: Start-up of the VTCS from room to -25ºC evaporator temperature

Faculty of Chemical Engineering and Chemistry

Process Systems Engineering

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Research Activities

The research activities of the Process Systems Engineering group focus on the systematic design and development of affinity separation process systems. Affinity separation based processes have a tremendous potential to improve the sustainability and economic viability of chemical and biochemical processes throughout the whole process industry. Important examples can be found in the development of processes for high added value products (fine chemicals, pharmaceuticals, food ingredients) and products from complex mixtures, where efficient molecule specific separation for products from complex mixtures determine to a large extend the economic viability. Our goal is to establish a paradigm shift in affinity separation process systems engineering by integrating the development of affinity separation agents (solvents, solids) with the development of process equipment and process systems. Research projects are carried out in three main areas:

Affinity Solvent Separation Systems focuses on the integrated design of affinity solvents with the establishment of design methodologies for process equipment and process systems. Within this field reversible complexing solvents, ionic liquids, supramolecular extractants, functionalized oligomers offer a tremendous potential for the design and development of new affinity solvent systems. To assess process (macro) scale performance, methodologies are being developed for the design, optimization, evaluation and integration of affinity solvents in separation process systems.

Affinity Solid Separation Systems focuses on the integrated design of affinity solids with the establishment of design methodologies for process equipment and process systems. Within this field our focus is on the design and development of new affinity solid separation systems utilizing low-cost high capacity affinity adsorbents, solvent/extractant impregnated resins, affinity textiles and affinity membranes. To assess macro scale performance methodologies are being developed for the design, optimization, evaluation and integration of affinity solids in separation process systems

System Integration and Equipment Intensification focuses on the establishment of methodologies for affinity separation system integration and process/equipment intensification. Main objective of the research activities is eliminating the knowledge hurdles for successful introduction of affinity based separation technologies in an industrial environment.

Designer Solvent Systems for Water Removal

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OSPT theme	: Separation Technology		Research School	: OSPT
Supported by	: DSTI		Period	: 04/08-04/12

Introduction:

Water removal is one of the most costly and energy intensive separation processes because the high heat of evaporation of water. The current state of art for water removal from chemicals streams is based on: Evaporation, Distillation, Extractive Distillation, Azeotropic Distillation, Absorption, Adsorption and Membrane Technology.

Solvent Extraction can also be an attractive alternative to recover water from process streams. The key to have an effective and successful (economical) extraction process is the development or design of a suitable solvent.

Recently, some researchers have started to use specially tailored solvents known as DSS, which due to their unique structures and properties, are promising components for a wide variety of separation processes.

Goal:

Establishment of a new breakthrough technology (Figure 1) for bulk separation of water from chemical streams using Designer Solvent System (DSS).

The main challenges are: reduction of 75% energy consumption and 50% of capital expenditure.

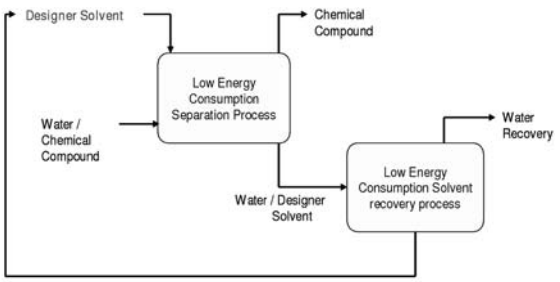

Fig. 1. Breakthrough technology for water removal.

Research:

1st Stage- Concept Generation

- Literature review: Current process separation technologies and DSS options.
- Evaluate current technologies and potential of several DSS.
- Establish a methodology for DSS selection.
- Initial proof of principle experiments for promising DSS.

Acknowledgement:

This is a DSTI project.

Keywords: Designer Solvent System, Water Removal, Energy Consumption.

Trace removal using ion exchange/adsorption

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OSPT theme	:	Separation Technology	Research School	:	OSPT
Supported by	:	DSTI	Period	:	09/08-09/12

Introduction

The term "trace removal" represents the removal of compounds present in concentrations of < 500 ppm from various bulk streams. This project is focused on the trace removal of various species from both organic and aqueous streams. Typically, byproducts that have chemical structures very much alike the main products should be removed from a product stream. Due to the large similarity between the structures, also the physical properties of the byproduct(s) are similar to the product. This leads to difficult separations and very high energy demanding traditional processes. Therefore the use of alternative separation techniques, such as ion exchange/adsorption is being investigated for these trace removal separations.

Six companies are involved with six cases. Five PhD's from three universities are working on these cases applying different separation techniques to tackle the cases.
Based on preliminary results, the best technology for each of the cases is selected for thorough investigation.

Goal

The aim of the study is to reduce the energy consumption of the current processes with a factor 3 to 4, while allowing concentrations of max 10 ppm. Hereto, application of adsorption using ion exchange resins as a carrier for functional groups is investigated.

Approach

A literature study yielded a matrix in which the functional groups of the traces are coupled to promising functional groups of the adsorbers.

	Type of exchangers			
Traces	Anion	Cation	Transition metals	Zeolite
Carboxylic acids	X			
Amine		X		
Aromates			X	X
Nitrile			X	X
Olefins			X	X
Pyridine		X	X	X
Phenol	X		X	
Carbonyl			X	
Sulfide			X	
Ether				X
Halogen			X	

Using model components reflecting the real cases, the type of resin and functional group is selected systematically.
For the trace-adsorber systems in the table, the selectivity and capacity is investigated.

Acknowledgment

This is a DSTI project

Trace component removal by affinity solvent based technologies

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OSPT theme	: Separation Technology	Research School	: OSPT
Supported by	: DSTI	Period	: 03/08-03/12

Introduction

This project aims to offer a solution of the main need of industry regarding removal of compounds present in ppm concentrations (100-1000 ppm) in organic bulk chemical streams and aqueous streams. These solutions should ensure a significant energy consumption reduction, a high product quality and a high competitive advantage. This project is part of a larger DSTI project which is realized by a project team in which, apart from TU/e, two universities, one GTI and six main chemical industries participate. The chemical industries have brought in typical cases which reflect many more similar cases encountered in industry. In all cases the impurities or byproducts which have to be removed are quite similar to the main bulk product.

Objective

The main objective of this project is the development of new breakthrough technology concepts based on separation technology using affinity solvents for selective trace removal of impurities on various applications

Main challenge

Identification of suitable solvents.

Typical directions:

- ✓ Complex forming agents;
- ✓ Ionic liquids.

Technologies:

- ✓ Reactive extraction;
- ✓ Extractive distillation;
- ✓ Complex extractive distillation.

Next to removing the trace components, back integration into the production process will also be explored to achieve process intensification.

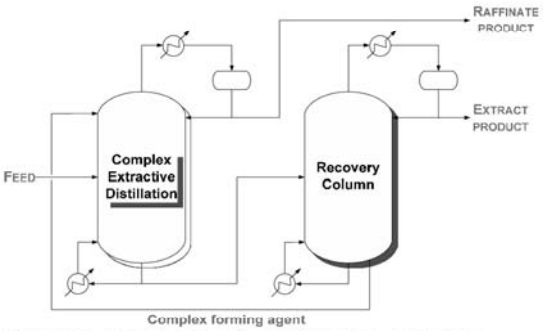

Figure 1. Possible configuration of a complex extractive distillation process.

Acknowledgements

This is a DSTI project.

Keywords: Trace Removal, Ionic Liquids, Complex forming agents.

Multifunctional Extractants for Acids and Bases

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Research Group	:	SPS			
OSPT theme	:	Separation Technology	Research School	:	OSPT
Supported by	:	DSTI	Period	:	03/08-03/12

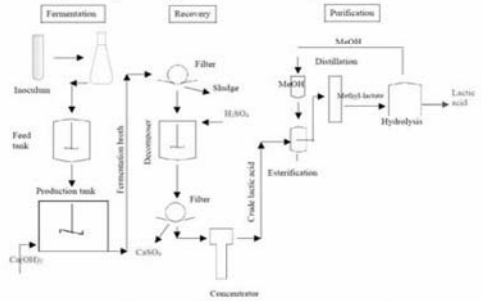
Introduction:

The last centuries brought a dramatic increase in the consumption of fossil fuels. It resulted in the perspective of soon depletion of natural resources and a subsequent sharp increase in petroleum prices. It became clear that most of the traditional processes employed in the syntheses of various chemicals need to be replaced with more environmentally favorable equivalents.

State of art

Lactic acid

Production of lactic acid by fermentation is limited by the high costs of product recovery and by the so-called "inhibition by product" mechanism. A too high concentration of lactic acid in fermentation broth leads to lowered productivity and in later stages to the death of micro organisms. Traditionally, in order to prevent lowering of pH, Ca(OH)2 is added, which results in production of calcium lactate. Calcium lactate is later acidified with H2SO4 giving lactic acid and calcium sulfate. Further purification steps including esterification and hydrolysis by H2O are required.



1,4-diaminobutane (DAB)

Unlike lactic acid, which was in fact discovered in first instance due to its accidental industrial application (bleaching of textile, Scheele, 1780), 1,4-diaminobutane has been known mainly to the biologists. Its application in the production of Stanyl® by DSM has focused the attention on the possibilities of employing fermentative processes in production of DAB. It should enable replacing the traditional method, which includes obtaining succinonitrile by addition of hydrogen cyanide to acrylonitrile and further hydrogenation of succinonitrile in order to yield 1,4-diaminobutane.

Strategy

- Literature review, experimental work and economical analysis should provide the criteria for designing highly specific extractants.
- Molecular modeling of possible extractants that meet imposed criteria will be performed at Wageningen University and is expected to bring the breakthrough.
- Once proven useful and effective the selected extractants (and possible solvent) will be adjusted to be used in suitable process configurations (closed-loop system).

Acknowledgements

This is a DSTI project.

Keywords: Liquid-liquid extraction, Fermentation, Specialty chemicals, Lactic acid, Diaminobutane

Reactive Distillation for Multi-Product Continuous Plant

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Supervisor	: Edwin Zondervan		E-mail	: m.shah@tue.nl
Research Group	: SPS		http://w3.chem.tue.nl/	
OSPT theme	: Separation Technology		Research School	: OSPT
Supported by	: DSTI		Period	: 12/07-12/11

Introduction:

Reactive distillation is a well-known technology for reactive-separation systems close to equilibrium. The integrated reaction and separation holds for many systems clear advantages in comparison with subsequent reaction and separation. The removal of reaction water in condensation/esterification systems is a good example of such a system and has already been extensively studied. However, the current scientific and industrial research is often limited to the optimization of reactive distillation columns for a single product type and/or for relatively large capacities. This makes the application of the outcome of these studies not useful for applying reactive distillation in a multi-product environment with relatively small capacities (such as polycondensations). In order to be able to apply reactive distillation technology in multi-product environments, new concepts need to be developed which allow the combination of significant increase in volumetric productivity with sharp product transitions while new raw materials and catalysts systems are fed to the reactor and process settings like temperature, residence time and column loading are being adapted.

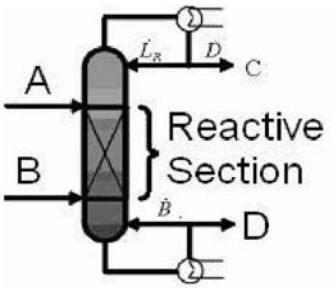

Fig. 1 Reactive Distillation Column

Goal:

The goal of this work is to develop a concept to transfer technology from batch to continuous reactive distillation process for specialty chemicals.

Research:

- Concept generation from Batch to Reactive Distillation
- Conceptual process design
- Model development in Aspen Custom Modular (ACM)
- Model parameter estimation
- Model validation

Acknowledgement:

This is a DSTI project.

Keywords: Reactive distillation, Continuous process, Specialty chemicals, Unsaturated Polyester

Separation of Aromatic and Aliphatic Hydrocarbons by means of Ionic Liquids

TU/e

SPS

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Research group	: ST/SPS	URL	: http://w3.chem.tue.nl/en/the_department/research_groups/process_systems_engineering/
OSPT theme	: Separation Technology	Research school	: OSPT
Supported by	: BP	Period	: August 2005 – July 2009

Introduction

The aim of this project is the separation of aromatic and aliphatic hydrocarbons by means of ionic liquids in order to develop a novel solvent superior to conventional methods. Conventional solvents are polar, organic compounds like Sulfolane®.

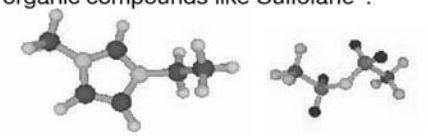

Fig. 1: Example of an ionic liquid

Ionic liquids are liquid salts consisting of large, mostly organic, cations and a great variety of anions (Figure 1). Their positive properties are a wide liquid temperature range (~300 K), low vapour pressure and the ability of tailoring. The latter provides the possibility to design a special solvent for a specific application, e.g. separation of aromatic and aliphatic hydrocarbons.

Approach:

Suitable ionic liquids must be superior to conventional solvents whereas sulfolane is taken as benchmark. In order to show higher performance suitable ionic liquids should have a significant higher extraction capacity, i.e. higher distribution coefficient, and selectivity than sulfolane. Potential ionic liquids have been selected with support of COSMO-RS in order to design an optimal solvent. The results have been validated with an experimental screening method.

Methods:

Screening experiments for ionic liquids are done with liquid-liquid equilibrium measurements; whereas an ionic liquid and a model feed consisting of a representative aromatic/aliphatic component mixture have been mixed and stirred well.

Results:

The ionic liquid [3-methyl-N-butyl pydridinium][dicyanamide] has been found to be the most suitable one. Suitable ionic liquids have a significantly higher capacity than sulfolane; however, the selectivity can be lower. LLE experiments confirmed the simulation results of the COSMO-RS shortcut method.

Conclusions:

COSMO-RS can qualitatively predict the performance of different ionic liquids. Ionic liquids are a good alternative for the extraction of aromatics and can provide significant higher results than conventional solvents.

Acknowledgement:

This research project is carried out with funding through BP International Limited, Sunbury-upon-Thames.

Entrainer-based Reactive Distillation for the Synthesis of Fatty Acid Esters

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	E. Zondervan	Period	: January 2005-September 2009
Research group	: SPS		
OSPT Theme	: Separation Technology	Keywords	: Reactive distillation, Entrainer, Fatty acid esters
Supported by	: STW		

Introduction

Fatty acid esters are natural-based chemicals used in cosmetics, plastics and surfactants among other things. Nowadays the fatty esters are produced in batch processes with use of strong acids like sulphuric acid. Their production processes involve costly separations, large energy consumption and polluting by-products. Because of equilibrium limitations high conversions can be only obtained by using a large alcohol excess.
For a more competitive process it is preferable to produce fatty esters in a continuous way, at higher yields, in multi-product equipment, using a heterogeneous catalyst.
Entrainer-based Reactive Distillation is thought a suitable technique for such a process.
In Entrainer-based Reactive Distillation in situ separation is used to improve the yield of reaction whereas an entrainer feed is added to make the separation feasible by selectively increasing the relative volatility of one of the products.

Objectives

Development of a continuous multi-product process for the synthesis of fatty acid esters, using Entrainer-based Reactive Distillation.

Strategy

Entrainer-based Reactive Distillation promises to be advantageous for the synthesis of fatty acid esters. The entrainer increases the relative volatility of water (by-product) compared to the alcohol (reactant), such that during the reaction the water can be continuously removed by distillation. In this way the chemical equilibrium is shifted such that higher conversions can be obtained.

A suitable entrainer will result in a in a significantly smaller reactive section compared to conventional Reactive Distillation and a pure product will be obtained which makes further purification unnessary. Therefore Entrainer-based Reactive Distillation could become an economically interesting alternative process for the production of fatty acid esters.

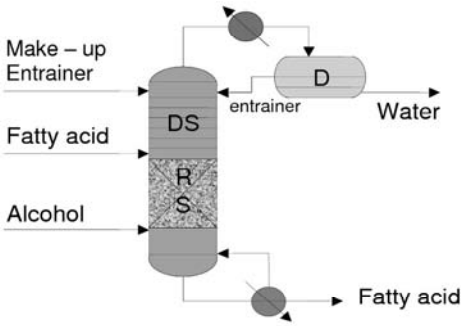

Fig. 1 Entrainer-based Reactive Distillation

Research

- Entrainer selection (theoretical and experimental).
- Experimental determination of reaction kinetics
- Modelling entrainer-based reactive distillation process.
- Establishment of model parameters.
- Pilot scale experimental validation
- Conceptual process design.

Acknowledgement

This project is sponsored by STW, which is kindly acknowledged.

Rate-Based Analysis of Ionic Liquids Performance in Extractive Distillation Column

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Research Group	:	SPS	http://w3.chem.tue.nl/		
OSPT theme	:	Separation Technology	Research School	:	OSPT
Supported by	:	SenterNovem	Period	:	2009 - 2013

Introduction:

Extractive distillation is an important unit operation that allows separating complex mixtures that in ordinary fractional distillation are difficult and expensive to separate.

Chemical engineers have been solving distillation problems by an equilibrium stage model. However, with the EQ models, the capacity and mass transfer performance of the column cannot be solved. In recent years, it has becomes common to simulate it with rated-based or mass transfer model (Fig. 1).

Common organic solvents are used currently in extractive distillation. However, they are used in huge amounts and usually they are volatile liquids that are difficult to contain.

The use of ionic liquids in extractive distillation processes has attracted considerable attention due to their high solvent capacity, easy handling and reduced energy consumption. They also have been called "green solvents".

Goal:

The objective of the project is to simulate the extractive distillation process with ionic liquids using the rate-based model.

Ionic liquids show a higher viscosity than common organic solvents. For this reason, it is very interesting to perform a mass transfer modeling study. Also, it is important to compare the extractive distillation performance with common organic solvents and ionic liquids in terms of efficiency, capacity and operational costs.

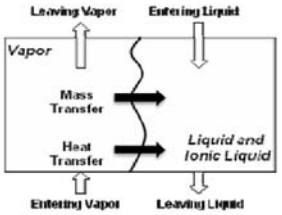

Fig. 1.Nonequilibrium Stage

$$N_i^V = c_i^V k_i^V (y_i^V - y_i^I)$$

$$N_i^L = c_i^L k_i^L (x_i^L - x_i^I)$$

Research:

- Literature review: Current process separation technologies, State-of-Art of the ionic liquids.
- Performance of current organic solvents in extractive distillation.
- Performance of ionic liquids as solvent in this process.
- Carry out experiments for validation of the numerical results.

Acknowledgement:

This is a SenterNovem Project.

Keywords: Rate-Based model, Extractive Distillation, Ionic Liquids.

Aromatics Extraction: Comparison of RDC Performance between [4-Mebupy]BF_4, [3-Mebupy]DCA and Sulfolane as Solvent

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Objective and Approach

- Ionic Liquids (ILs):

  promising solvents extraction aromatic hydrocarbons[1].
- This research:

  hydrodynamic and mass transfer characteristics RDC
- Solvents:

  [4-mebupy]BF_4, [3-mebupy]DCA vs. Sulfolane[2]
- Model system:

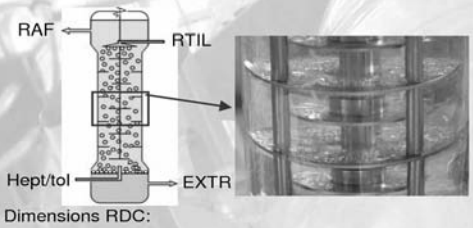
  mixtures toluene/n-heptane (toluene ~ 10/50 wt%)

Equipment

Pilot plant:

- Rotating Disc Contactor (fig. 1)

  → most commonly used in petrochemical processing



Dimensions RDC:

- Total height 2.5 m and 6 m*
- 5 and 9* glass segments 0.36 m
- Inner diameter 0.06 m
- Stator diameter 22 mm
- Rotor diameter 40 mm
- Compartment 32 mm

Ionic Liquids

- 4-methyl-N-butylpyridinium tetrafluoroborate (100 kg)
- 3-methyl-N-butylpyridinium dicyanamide (100 kg)

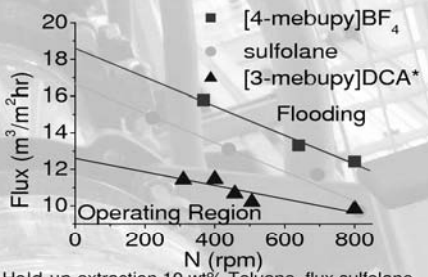
Property	Unit	[3-Mebupy]DCA	[4-Mebupy]BF_4	Sulfolane
Molar Mass	g/mol	216	237	120
Density	Kg/m^3	1043	1184	1261
Viscosity	Pa s	0.023	0.293	0.010
Melting point	K	289	NA	299

[1] G.W. Meindersma, A. Podt, M.B. Klaren, A.B. de Haan, Chem. Eng. Com. 193, 1384 – 1396 (2006)

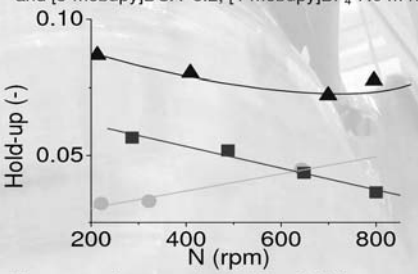
[2] http://www.uop.com/objects/55%20Sulfolane.pdf

Results

Operational region extraction 10 wt% Toluene



Hold-up extraction 10 wt% Toluene, flux sulfolane and [3-mebupy]DCA* 8.2, [4-mebupy]BF_4 7.0 m^3/m^2hr



Mass transfer extraction 10/50 wt% Toluene

Toluene wt%	Solvent	N_s calc	N_s graph	H_{ets} (m)
10	Sulfolane*	3	2.5	1.4
	[4-mebupy]BF_4*	1.3	1.2	2.8
	[3-mebupy]DCA*	2.3	2.5	1.4
50	[4-mebupy]BF_4	NA	1.5	1.3
	[3-mebupy]DCA*	NA	2.9	1.1

* Experiments in pilot plant of 6 m

Conclusions

1. Operational area [4-mebupy]BF_4 > sulfolane > [3-mebupy]DCA* (high density/viscosity [4-mebupy]BF_4)
2. Hold-up [3-mebupy]DCA > [4-mebupy]BF_4 > sulfolane
3. Mass transfer 10 wt % Toluene Sulfolane ~ [3-mebupy]DCA
4. M.T. 50 wt % Toluene [3-mebupy]DCA smallest H_{ets} (smaller droplets due to low viscosity/density)

Supported by: BASF, The Chemical Company

Extractive Distillation with Ionic Liquids

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Research Group	: SPS			http://w3.chem.tue.nl/
OSPT theme	: Separation Technology		Research School	: OSPT
Supported by	: SenterNovem		Period	: 02/2008-02/2012

Introduction:

Distillation is the principal separation technology in petrochemical and chemical industries. However, the operating costs and the energy consumption are high, especially for the separation of close boiling or azeotropic mixtures.

Extractive distillation offers less energy consumption and a higher degree of separation due to the solvent added (Fig 1).

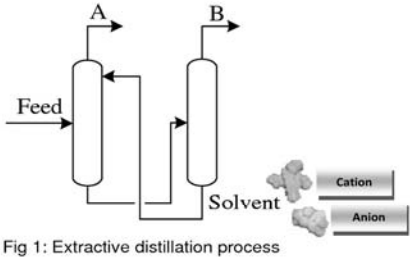

Fig 1: Extractive distillation process

Ionic liquids (IL) offer several advantages over conventional solvents: high selectivity and negligible vapor pressure. They are organic salts which are liquid at T below 100°C.

Goal:

Screening and design of suitable ILs for the separation of close boiling or azeotropic mixtures. Selection of the solvent recovery technology and comparison with the conventional process used in industry. The main challenge is the reduction of >35% in energy consumption.

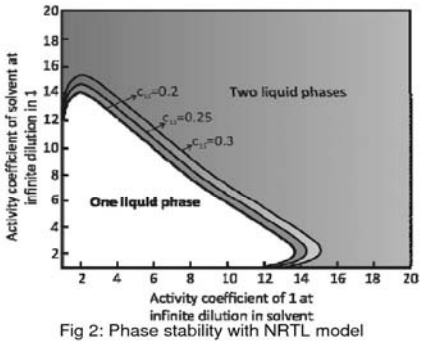

Fig 2: Phase stability with NRTL model

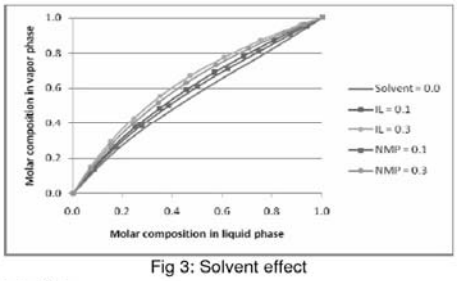

Fig 3: Solvent effect

Results:

In the selection of the suitable ionic liquid for extractive distillation, several variables should be taken into account. Improvements in the selectivity can be achieved by using ILs as solvents.

Acknowledgement:

The support by SenterNovem to this project is kindly acknowledged.

Keywords: Extractive distillation, Ionic liquids, Energy consumption, Separation processes.

Rate-Based Analysis of Ionic Liquids Performance in Extractive Distillation Column

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Supervisor	: Wytze Meindersma	E-mail	: e.quijada@tue.nl
Research Group	: SPS	http://w3.chem.tue.nl/	
OSPT theme	: Separation Technology	Research School	: OSPT
Supported by	: SenterNovem	Period	: 2009 - 2013

Introduction:

Extractive distillation is an important unit operation that allows separating complex mixtures that in ordinary fractional distillation are difficult and expensive to separate.

Chemical engineers have been solving distillation problems by an equilibrium stage model. However, with the EQ models, the capacity and mass transfer performance of the column cannot be solved. In recent years, it has becomes common to simulate it with rated-based or mass transfer model (Fig. 1).

Common organic solvents are used currently in extractive distillation. However, they are used in huge amounts and usually they are volatile liquids that are difficult to contain.

The use of ionic liquids in extractive distillation processes has attracted considerable attention due to their high solvent capacity, easy handling and reduced energy consumption. They also have been called "green solvents".

Goal:

The objective of the project is to simulate the extractive distillation process with ionic liquids using the rate-based model.

Ionic liquids show a higher viscosity than common organic solvents. For this reason, it is very interesting to perform a mass transfer modeling study. Also, it is important to compare the extractive distillation performance with common organic solvents and ionic liquids in terms of efficiency, capacity and operational costs.

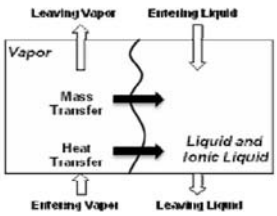

Fig. 1.Nonequilibrium Stage

$$N_i^V = c_i^V k_i^V (y_i^V - y_i^I)$$

$$N_i^L = c_i^L k_i^L (x_i^L - x_i^I)$$

Research:

- Literature review: Current process separation technologies, State-of-Art of the ionic liquids.
- Performance of current organic solvents in extractive distillation.
- Performance of ionic liquids as solvent in this process.
- Carry out experiments for validation of the numerical results.

Acknowledgement:

This is a SenterNovem Project.

Keywords: Rate-Based model, Extractive Distillation, Ionic Liquids.

Renewable carbonyl compounds from biomass

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Research group	:	SPS	**URL**	:	http://w3.chem.tue.nl/
OSPT theme	:	Separation Technology	**Research school**	:	OSPT
Supported by	:	EU - BIOCOUP project	**Period**	:	May 2008 – April 2012

Introduction

Biomass is a potential renewable source of chemicals. In fast pyrolysis, biomass is decomposed into liquid, solid char and non-condensable gases. Pyrolysis liquid (bio-oil) is dark brown liquid with strong smoky odour, which contains more than 300 compounds, including aldehydes, ketones, carboxylic acids, phenols, sugars and lignins. Considering high aldehyde and ketone (carbonyl) contents in bio-oil, the isolation of carbonyl compounds seems promising.

Objective

Investigation of a feasible separation route to isolate carbonyl compounds from bio-oil, especially glycolaldehyde, furfural, acetol and furanone.

Approaches

Carbonyl compounds could be recovered from bio-oil via the route shown in Figure 1. In general, it involves reactive extraction, carbonyls recovery, solvent regeneration and fractionation distillation.

Several researches have been done in the reactive extraction of single carbonyl compounds from both organic and aqueous phases. However, the reactive extraction of a carbonyls mixture may behave differently considering the interaction among solute molecules.

Carbonyls recovery is still an obstacle. The carbonyl adducts formed in the reactive extraction have to be broken in order to obtain a mixture of free carbonyl compounds. Back-extraction and distillation will be investigated to find a more selective method with higher yield.

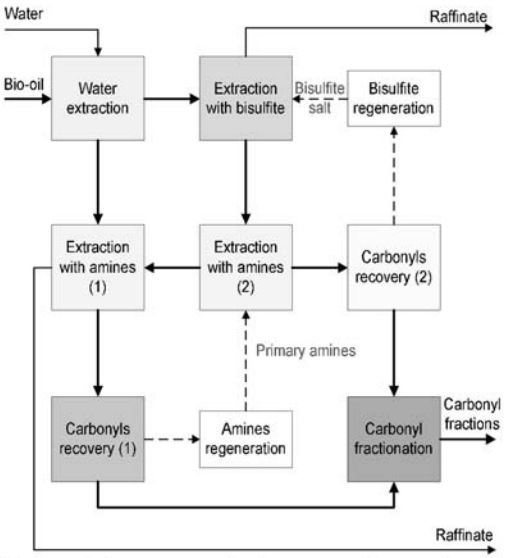

Figure 1 A proposed diagram of a carbonyls isolation process from bio-oil

Project scope

- Water extraction of bio-oil
- Reactive extraction of carbonyl compounds from bio-oil with several types primary amines and diluents
- Carbonyls recovery from a mixture of carbonyl-amine adducts
- Fractionation of carbonyls mixture
- Conceptual process design

Acknowledgement

The financial support from the EU through BIOCOUP Project (Contract Number: 518312) is gratefully acknowledged.

Keywords: bio-oil, carbonyl, reactive extraction

Extraction Intensification

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Research Group	: SPS	http://w3.chem.tue.nl/	
OSPT theme	: Separation Technology	Research School	: OSPT
Supported by	: DSTI	Period	: 11/08-11/12

Introduction:

Extraction is an important separation process in chemical and pharmaceutical industries. Intensification of this process step is a challenging task due to hydrodynamic interaction and mass transfer limitations.

Goal:

The goal of this project is to intensify liquid-liquid extraction operations through improved control of hydrodynamic condition (flooding) and enhanced separation of dispersed phase by promoting coalescence.

Key objective of this research is to increase the capacity of existing extraction columns by stable operation in the proximity of flooding regime. This involves change of operating point from the design capacity (usually 70% flooding capacity (point A)) towards and above the flooding point (point B). For this, a model-based controller will be developed and implemented in a pilot scale rotating disc contactor (RDC).

The secondary objective is to enhance the coalescence and separation of emulsified systems resulting from industrial extraction operation so that the given separation requires less residence time and smaller size equipment.

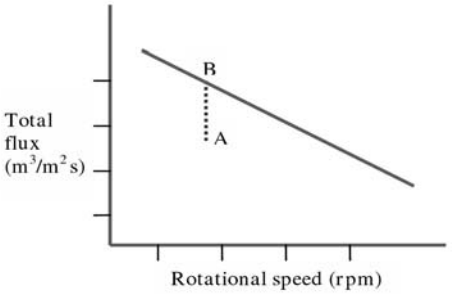

Figure 1: Limiting throughput(flux) at flooding point versus rotational speed for RDC

Research:

- 1st Stage- Flooding control
- Literature review of the different approaches used in flooding control
- Identification of the plant dynamic model describing the flooding behavior from pilot experiment
- Design of a controller based on identified model
- Implementation of the controller in the pilot column

Acknowledgement:

This is a DSTI project.

Keywords: Coalescence, Flooding, Model–based controller.

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Research Group

Green Chemical Reaction Engineering

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Activities of the Green Chemical Engineering Group
The research performed in the OSPT context is organised along three lines:

- ***Catalytic conversions and technology development for biomass conversions***
In this theme, novel catalytic conversions as well as activities to improve the performance of existing catalytic processes for biomass conversions are explored. The emphasis is on low-medium temperature (< 400 °C), liquid phase catalytic systems using both homogeneous and heterogeneous catalysts. Three types of biomass and derived products have our special attention: fast-pyrolyis oil, vegetable- and animal oils and fats and glycerol.

- Applications of highly intensified reactors for chemical conversions
In this theme, highly intensified mixer- settler equipment (CINC), commonly used for extractions, is explored to perform biphasic liquid-liquid chemical reactions and reactive extractions. The overall objectives are to demonstrate its potential for the continuous manufacture of (chiral) fine chemicals and pharmaceuticals, to provide the proof of principle for using a cascade of CINC's for integrated bio-and chemo catalysis and to improve the overall conversion rates of fast biphasic liquid-liquid catalytic reactions by intensive mixing.

- Starch modifications to high added value green products
In this theme, novel conversion technology for various types of starches are explored. Examples of projects are starch modifications in green solvents and the development of efficient chemical conversions for biodegradable polymers on the basis of starch and polycaprolactone.

Liquid Transportation Fuels from Pyrolysis-oil

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OSPT theme:	Energy Conversion Technology	Period:	March 2005 – March 2009
Supported by:	SenterNovem		

Introduction

Environmental concerns and possible future shortages have boosted research on alternatives for fossil derived liquid transportation fuels. Biomass is considered a promising alternative and various products from different sources have been proposed. A potentially very interesting, second generation, green liquid transportation fuel is modified pyrolysis oil.
Pyrolysis oil may be obtained from biomass by flash-pyrolysis in yields up to 70%-wt. As such, the oil is not suitable for applications in instationary internal combustion engines and upgrading is required.

Objectives

To develop technology for upgrading flash pyrolysis oil to a liquid transportation fuel. A possible upgrading technology is hydro-deoxygenation (HDO), the removal of oxygen by the action of hydrogen under the formation of water. Typically, catalysts and harsh conditions are required to obtain high volumetric production rates.

Research activities

Catalysts selection
A wide variety of catalysts will be tested for activity, selectivity and stability. Criteria will be developed for determination of the preferred catalyst.

Catalyst and process optimization
Kinetic studies will be performed with the catalyst of choice to quantify activity and stability for a broad range of process conditions

Determination of process-product relations
Process-product relationships will be established and optimum process conditions will be determined to obtain products with the desired product properties.

The results of the studies conducted in the phases described above will be used as input for the design of a continuous pilot scale unit.

Results

Catalyst selection
Several catalysts have been tested in a dedicated laboratory batch set-up. A ruthenium based heterogeneous catalyst shows good potential and reduction in the oxygen content from 40%-wt to 10%-wt were realized at short reaction times.

Product-process relations:
To gain insights in the HDO process on a molecular level, 2D-GC has been applied to characterize the oil before and after hydrodeoxygenation reaction. Promising results were obtained, suggesting that 2D-GC may be a useful analytical tool to characterize pyrolysis oil and its derivatives.

Acknowledgments

Biomass Technology Group for supplying the raw material and for their helpful discussions. This research project is carried out with support from SenterNovem.

university of groningen

Chemicals from Biomass: Levulinic Acid Production from Giant Grass (Miscanthus x giganteus)

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Introduction

Biomass is identified as a very promising renewable resource for the generation of energy and (bulk)-chemicals. Particularly, the C5- and C6-sugars are interesting precursors for a broad range of interesting chemicals. Recently, levulinic acid (LA) has been proposed as a very attractive green platform chemical from biomass. It is easily accessible by the acid catalyzed hydrolysis of the C6-sugars of biomass at relatively mild conditions (150-240°C). Giant grass is a particularly interesting source of biomass as it is fast growing. The use of giant grass as a raw material for the synthesis of LA has being explored and the result are provided.

Results and Discussion

The sugar distribution in giant grass was determined using NREL laboratory analytical procedures (Figure 1).

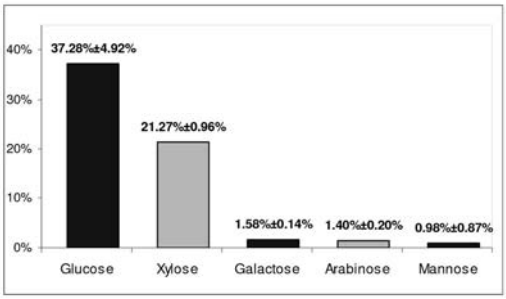

Figure 1 Sugar Distribution in giant grass (wt% oven dry basis)

The acid-catalyzed hydrolysis of giant grass was performed by high throughput experimentation in glass batch reactors. The effects of process conditions like reaction time, reaction temperature (150-200 °C), sulfuric acid concentration (0.01-1M), and giant grass loading (5%-10%) on the yield of LA were examined and the results are given in Figure 2.

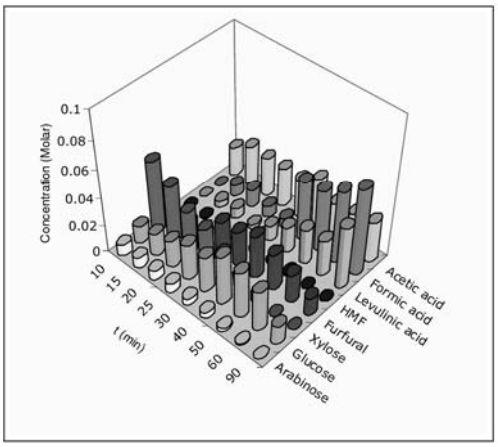

Figure 2 Concentration profile of acid-catalyzed hydrolysis of giant grass with 0.1 M H_2SO_4 as catalyst at 175°C.

Besides LA, a variety of other sugar derived products like furfural, xylose and hydroxymethylfurfural were observed in the course of the reaction. The highest LA yield based on dry-weight of giant grass was 18%-wt obtained at a low biomass loading, high acid concentration and high temperature.

A kinetic model has been developed based on the reaction scheme provided in Figure 3.

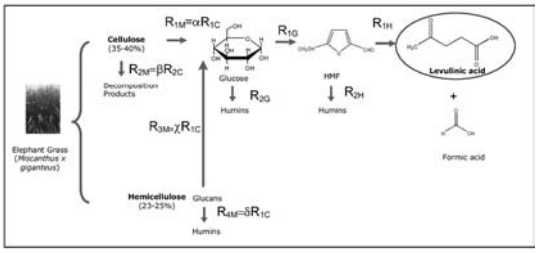

Figure 3 Reaction scheme for the acid-catalyzed hydrolysis of giant grass

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Methanol synthesis from crude glycerine-derived syngas

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Introduction

Crude glycerine is a major by-product of bio-diesel production by trans-esterification of a vegetable oil with methanol. Due to increased bio-diesel production levels, large amounts of crude glycerine are produced for which alternative outlets are sought. The conversion of crude glycerine to methanol is a very attractive option as it allows re-use of a by-product and leads to green methanol [1].

An attractive process option to convert glycerol to methanol consists of reforming crude glycerine in supercritical water to syngas, followed by methanol synthesis. This concept is explored in detail in the EU-FP7 'Supermethanol' project [2]. Both the pressure and the composition of the syngas produced by supercritical water gasification differ considerably from that used in conventional low pressure methanol synthesis processes.

Approach

In this project we will perform in-depth reactor engineering studies and investigate important parameters on the methanol yield like the composition of the syngas, the syngas pressure, temperature, catalyst type and reactor geometry. In addition, equilibrium calculation will be performed and validated with experiments. With this information available, the optimum reactor configuration for methanol synthesis from syngas obtained from glycerine gasification in super critical water will be determined and modeled.

Current Results

Three equilibrium reactions are involved in the synthesis of methanol from syngas:

$$CO + 2\,H_2 \rightleftharpoons CH_3OH \quad (1)$$
$$CO_2 + 3\,H_2 \rightleftharpoons CH_3OH + H_2O \quad (2)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3)$$

Methanol is produced in reactions 1 and 2. Reaction 3 is the water-gas shift reaction. All reactions are exothermic.

To gain insights in the methanol equilibrium yields as a function of process conditions, the Soave-Redlich-Kwong equation of state was applied. Figure 1 shows the pressure-temperature dependency of the conversion of H_2. Validation with experimental data is in progress. If necessary the model will be modified/extended to give a better description of the equilibrium conversion for the process under study.

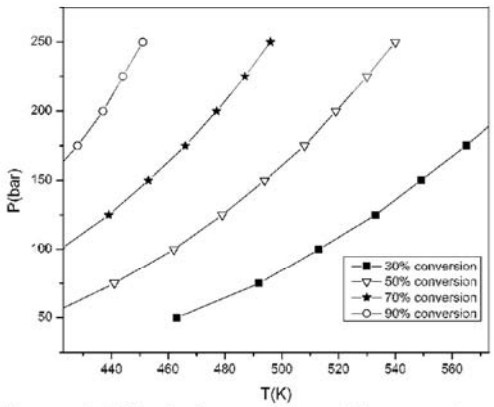

Figure 1. Effect of pressure and temperature on the hydrogen equilibrium conversion for methanol synthesis

References

[1] D. Goetsch, I.S. Machay, L.R. White, United States Patent 7388034, 2008
[2] www.supermethanol.eu

Power generation by Reverse Electro Dialysis: System Design

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OSPT theme	: Sustainable Energy	**Period**	: January 2005 – August 2009
Supported by	: Wetsus, SenterNovem, NHL	**Key word**	: reverse electrodialysis, design

Introduction

Reverse Electro Dialysis (RED) is a promising technique for extracting energy from the salt difference between sea- and river water. This method is potentially sustainable and clean. In theory the Rhine can deliver 5.6 Gigawatt energy on mixing with the North Sea. (present average electricity consumption is 13.5 GW in the Netherlands). Assuming an ideal process, there is no overall energy effect and the process is balanced by cooling the effluent 0.1 degrees or so. Extraction of a part of this 5.6 GWatt is an exciting idea.

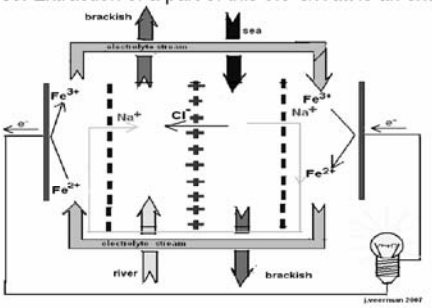

Fig.1 *A Reverse Electro Dialysis stack with one cell.*

The RED-method uses permselective membranes of two types: cation-exchange (CEM) and anion-exchange membranes (AEM) (Figure1). By using a membrane stack with alternating 50 CEM and 50 AEM with spacers for the delivery of sea-water and Rhine water, an electrical potential 8.6 Volt can be obtained. A commercial installation uses many of such modules.

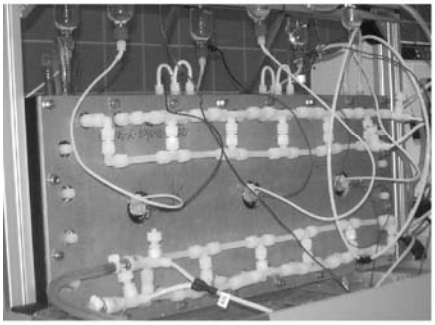

Fig.2 *A working model delivering 20 Watt.*

The technological challenge is to scale up the apparatus from 20 W to 200 MW.

Aspects of further investigations:

- spacer design
- hydrodynamics
- pressure drop
- module design
- prevention of leaking currents
- minimization of electrical resistance
- fuel efficiency
- power density

State of the art

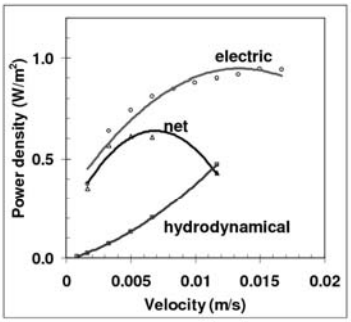

Fig. 3 shows the results of a typical flow experiment. The maximal obtained power and the optimal velocity of the feed water is strongly dependent on the used spacers.

Fig. 3. *Power balance of a small test stack.*

Literature

- J.W.Post et al. *Salinity-gradient power: Evaluation of pressure-retarded osmosis and RED*, J.Membr.Sc. 288 (2007), 218-230.
- J.Veerman et al. *Reducing power losses caused by ionic shortcut currents in RED stacksl*, J.Membr.Sc. (310) (2008), 418-430.
- J. Veerman et al. RED: *Performance of a stack with 50 cells*, J. Membr.Sc. 327 (2009),136-144

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Fundamentals of Chemical Reaction Engineering

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The activities of the Fundamentals of Chemical Reaction Engineering (FCRE) group

The research group FCRE participates amongst others in the OSPT and the J.M. Burgerscentrum for fluid mechanics and focuses on fundamentals of the discipline of chemical reaction engineering. Our main area of interest is the quantitative description of transport phenomena (including fluid flow) and the interplay with chemical transformations in multiphase chemical reactors. The generation of new knowledge and the development of new reactor models with improved predictive capability for this industrially important class of chemical reactors constitute important goals of our research activities. Through the intended co-operation with other (application oriented) research groups both fundamental aspects and those closely related to applications will be studied through concerted action. The main research topics of the new group FCRE can be divided into the following three areas:

1. Multiphase Reactors
2. Advanced Experimental Techniques
3. Novel Reactors which will be discussed below in more detail.

Multiphase Reactors

An important area of attention is the development of advanced reactor models for multiphase reactors with industrial relevance. At present our research focuses on the hydrodynamics in these reactors because it is generally recognized that the lack of understanding of the flow phenomena is one of the central difficulties in the design and scale-up of multiphase reactors. In the near future the interplay of flow phenomena with chemical reactions will be studied in great detail.

We use various types of CFD models (both commercial codes but mostly “in house” made codes) to study the relevant hydrodynamic phenomena at all relevant length and time scales (i.e. at the microscopic, mesoscopic and macroscopic scale). In our group both multi-fluid models are being developed and models which treat the dispersed phase (particles, bubbles or droplets) in a discrete manner accounting for possible encounters between the dispersed elements. Furthermore we develop various DNS models that account for the interfacial interaction without any prior assumptions. The latter can be used to provide closure information for the multi-fluid or discrete models.

Advanced Experimental Techniques

The second important area of our research deals with the development of advanced experimental techniques to measure key quantities (i.e. local volume fractions and velocities of the dispersed and continuous phase). As an example we can mention the development of the digital particle image velocimetry technique to measure in a non-intrusive manner the velocity map of both the liquid phase and dispersed gas bubbles in (dense) gas-liquid dispersions. This type of flow very often arises in a variety of gas-liquid contactors/reactors. In this area we co-operate with specialists within the J.M. Burgerscentrum for fluid mechanics. Of course this research activity is intimately connected to the first research topic.

Novel Reactors

Our third important area of research deals with the development of novel (multiphase) reactors with emphasis on integration and intensification of relevant process steps. As an example we can mention here the Rapid Reaction Cycling Reverse Flow (RRCRF) which integrates (in a thermal sense) endothermic and exothermic heterogeneously catalyzed chemical reactions where the endothermic reaction causes rapid (reversible) catalyst deactivation. These types of chemical reaction systems often arise in practice for instance in the production of lower alkenes form the corresponding alkanes via heterogeneously catalyzed dehydrogenation. Other examples include membrane-assisted packed bed and gas-fluidized bed reactors. The knowledge and tools developed within the other two areas of attention provide a sound basis to place this research activity on a firm footing.

The activities for Process Plant Design

Process Plant Design deliverables are process design reports and publications. Process synthesis is applied and further developed. Subjects for process design originate from industrial partners and from PhD studies in the department. In this way process design activities form links with other groups in the department. In many of the more than 160 process designs prepared, the focus is on new raw materials, new reactor and separation technologies leading to more sustainable processes.

Fluid-particle slurry flows through constricted channels

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: IMPACT	**Period**	: 02/08 – 02/10

Introduction

We propose to study shallow fluid-particle flows or slurries in channels with complex geometries in general, and channels with constrictions in particular. Slurry flows are multiphase flows, common in industry and nature. The dense-conveying of molten metals and iron ore, mud flows in the building industry, and ice flows in rivers are typical examples.

Methodology

We are preparing to perform laboratory experiments on slurry flows through a channel with a constriction to obtain a dataset for comparison against analytical predictions and 3D simulations. An experimental set-up is designed for slurry flows consisting of water as a carrier fluid and solid particles of similar density (high density polyethylene). Subsequently, slurry flows through channels with constrictions will be studied experimentally, following and extending Akers (2005; experiments with water and some trials with polystyrene beads) and Vreman et al. (2007; experiments with dry granular matter).

The shallow nature of the flow facilitates the construction of analytical, hydraulic theories based on depth- and cross-averaged approximations. Such an analysis builds on the analysis in Vreman et al. (2007) but concerns much more complex multiphase flow. The shallowness or anisotropy of the flow implies the quasi-2D character of the 3D flows, which allows saving computation time (in the depth-averaged models).

In the mean time, we are developing a 3D simulation code for the problem (liquid-solid flow in an inclined chute with a linear contraction in the middle of the channel) using a Discrete Particle Model (DPM). The description of the original code can be found in Patil et al. (2005). In parallel discontinuous Galerkin finite element models are built in NACM group for dispersed fluid-solid flows (Rhebergen et al. 2008).

Modifications for the DPM code are taking place to allow us treating shallow liquid-solid inclined flows, especially by taking into account the free surface effect. Comparison with the experimental results will aim mainly to improve the modeling of the constitutive relations and frictional parameterizations used in the depth-averaged models.

Understanding, prediction, and analysis of multiphase fluid-particle flows are core research activities at IMPACT. The multidisciplinary team brings all these aspects together in one project rather than in fragmented numerical, analytical and experimental work. This synergy of research efforts aims to assist in identifying and controlling bottlenecks in industrial production lines involving fluid-particle flows.

Mid Term Perspective

We aim to reach firm results within a year such as to write a corresponding (STW/FOM) proposal in collaboration with industrial partners in the metal and oil industry.

References

B. Akers 2005: Shallow water flow through a contraction. Report GFD Fellowship Program, Woods Hole Oceanographic Institution. Supervised by Bokhove. http://gfd.whoi.edu/proceedings.html

D.J. Patil, M. van Sint Annaland & J.A.M. Kuipers 2005: Critical comparison of hydrodynamic models for gas–solid fluidized beds—Part I: bubbling gas–solid fluidized beds operated with a jet. *Chemical Eng. Sciences* **60**, 57-72.

S. Rhebergen, O. Bokhove & J.J.W. van der Vegt, 2008: "Discontinuous Galerkin methods for multiphase fluids with nonconservative products" *J. Computational Physics*, **227**, 1887-1922

A.W. Vreman, M. Al-Tarazi, J.A.M. Kuipers, M. van Sint Annaland & O. Bokhove 2007: "Reservoir formation in shallow granular flows through a contraction", *J. Fluid Mech.*, **578**, 233-269.

Dispersed two - phase flows

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OSPT theme	: Multiphase reactors		
Supported by	: IMPACT	**Period**	: May 2006 - May 2010

Introduction

Bubble column reactors are used in a large variety of industrial processes. Despite their great significance, the fundamentals of dispersed two phase flows are presently poorly understood, which for a large extent can be attributed to the complex flow structure prevailing at the macroscopic scale. This has significant consequences for the scale-up of industrial processes and additionally the process operation is often far from optimal. Therefore, a better understanding of the essential physical mechanisms controlling complex two phase flows is severely necessary. Thus, accurate physical models and computational techniques to simulate complex two phase flows will become possible.

Objective

Bubble columns typically operate in the so-called heterogeneous flow regime where simultaneously "small" (bubble diameter typically equals a few mm) and "large" (bubble diameter typically equals a few cm) bubbles rise through a liquid in which a turbulent flow structure exists.

The objective of the project will mainly focus on several aspects as follows:

- The effect of important (design) variables (physical properties of liquid phase, superficial gas velocity) on the flow structure (gas hold up and large scale circulation patterns),
- The understanding of the coalescence and breakup of bubbles,
- The effect of turbulent fluid motion and the effect of neighbouring bubbles (swarm effects) on drag, lift and virtual mass,

Approach

Both experimental techniques and numerical simulations are used in present work. Optical fibre probes have the advantage of simplicity of setup, easy interpretation of results and can provide estimates for local void fraction and dispersed phase velocity.

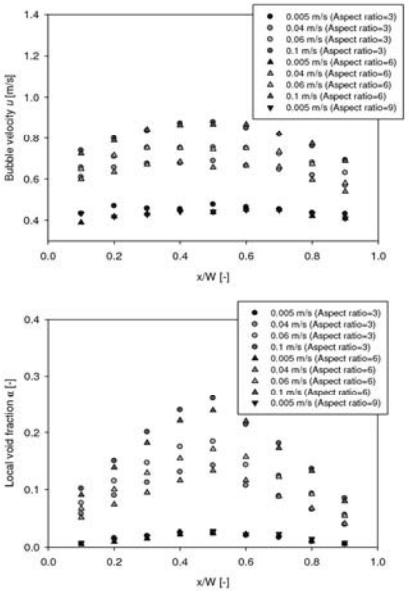

Figure 1 Distributions of bubble velocity (upper panel) and void fraction (lower panel) at z/H=0.75 with different superficial gas velocities and column heights

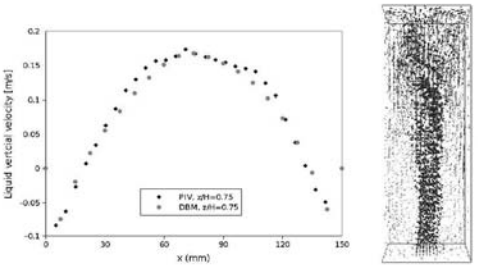

Figure 2 Comparison between PIV measurements and DBM results at z/H=0.75 (left panel) and snapshot of velocity filed and bubbles (right panel)

Acknowledgements

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Fundamentals of fluidized bed granulation processes

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OSPT theme	: Comp. & Exp. Chem. Eng.		
Supported by	: FOM/STW/Yara Sluiskil	**Period**	: September 2006 – September 2010

Introduction

Granulation processes are widely applied in spout fluidized beds for the production of detergents, pharmaceuticals, food and fertilizers. In spout fluidized beds, contact between large particles, droplets and gas are of great importance. However, detailed understanding of the complex behavior of these systems is lacking.

Objectives

The objective of this research is to study the effect of the inter-particle interaction on the bed dynamics, by investigating the bed height, pressure drop and vertical particle velocity as function of the restitution coefficient.

Strategy

Simulations are conducted with the discrete element model (DEM), which describes the dynamics of the continuous gas-phase and the discrete elements. The DEM has been further developed by changing the restitution coefficient into a moisture dependent variable, to define the effect of the droplets on the inter-particle interaction. Additionally, evaporation of moisture from the particles has been taken into account. (see van Buijtenen et al. [1] for further details).

Conclusions

Decrease of the restitution coefficient causes instability of the overall bed dynamics, due to the presence of more bubbles. This effect is enhanced when the restitution coefficient changes in time and space.

References

[1] Buijtenen, M.S. van, Deen, N.G., Heinrich, S., Antonyuk, S., Kuipers, J.A.M., "A Discrete Element Study of Wet Particle–Particle Interaction During Granulation in a Spout Fluidized Bed", CJChE **87,** 308-317 (2009)

Acknowledgement

Financial support from FOM, STW and Yara Sluiskil, The Netherlands, is gratefully acknowledged.

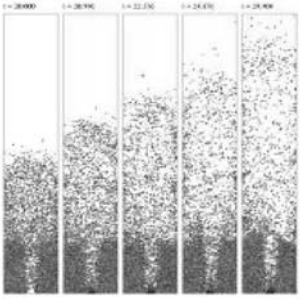

Fig. 1: Simulated instantaneous particle positions at different wetting process stages.

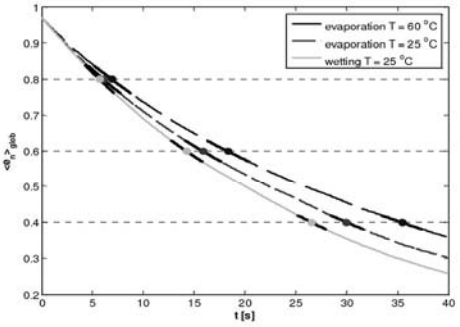

Fig. 2: Overall averaged restitution coefficient versus wetting time, for i) wetting, ii) wetting and evaporation, and iii) wetting and extended evaporation.

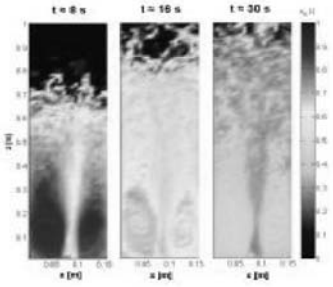

Fig. 3: Spatial distribution of the locally time-averaged restitution coefficient.

Comparison of packed bed and fluidized bed membrane reactors for methane reforming

FCRE

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Supported by : SenterNovem (EOS-LT)

Period : Aug. 2007 – Aug. 2009

Introduction

In this work the performance of different membrane reactor concepts, both fluidized bed and packed bed membrane reactors, have been compared for ultra-pure hydrogen production via methane reforming. Using detailed theoretical models, the required membrane area to reach a given conversion and the prevailing temperature profiles have been compared. The extent of mass and heat transfer limitations in the different reactors have been evaluated, and strategies to decrease (or avoid) these limitations have been proposed.

Fluidized bed membrane reactor concept

A schematic representation of the considered fluidized bed membrane reactor configuration is reported in Fig. 1.

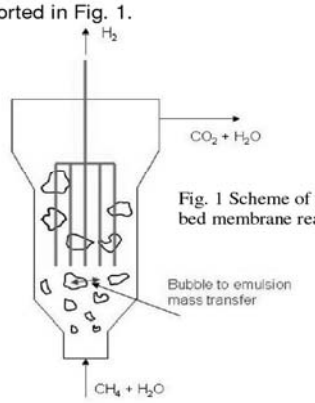

Fig. 1 Scheme of the fluidized bed membrane reactor

Pure hydrogen is recovered via Pd-based membranes inserted into the fluidized bed. With the fluidized bed membrane reactor a virtually isothermal condition can be achieved and bed-to-membrane mass transfer limitations are largely avoided. On the other hand, bubble-to-emulsion phase mass transfer limitations and the extent of gas back-mixing could deteriorate its performance. In particular, the use of membranes inside the reactor could decrease the extent of back-mixing and can also help decreasing the bubble diameter, enhancing the bubble-to-emulsion phase mass transfer. With the help of a two-phase phenomenological model, the effect of bubble-to-emulsion phase mass transfer limitations and gas back-mixing have been quantified.

Packed bed membrane reactor concept

The typical tube-in-tube packed bed membrane reactor configuration was considered (see Fig. 2).

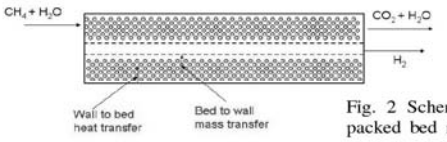

Fig. 2 Scheme of the packed bed membrane reactor

The reactor has been studied with both a 1D model and a detailed 2D model in order to identify the extent of wall-to-bed heat transfer limitations and the bed-to-membrane mass transfer limitations (concentration polarization) and their effect on the temperature profiles and reactor performance. The influence of the reactor and particle dimensions has been investigated.

Simulations have shown that the packed bed membrane reactor is always plagued with a temperature decrease at the reactor inlet (see Fig. 3) which results in a typically 25% higher required membrane area in comparison with isothermal conditions. Also the effect of concentration polarization on the required membrane area has been quantified.

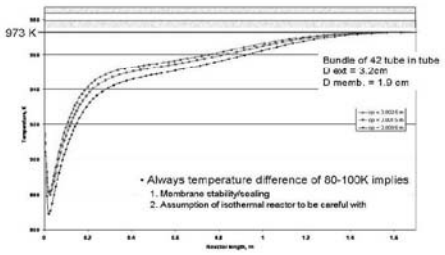

Fig. 3 Temperature profile for a packed bed membrane reactor

Experimental and computational study of high pressure fluidization of polymeric materials

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Period : June 2005 – May 2009

Introduction

Fluidised-bed solid catalysed olefin polymerisation has long been recognised as one of the main roads for producing polyolefins.

Objective

The main objective of this research is to develop detailed understanding and quantitative descriptive tools for the pressure effect on the fluidisation behaviour of polymeric (i.e., polypropylene) materials. The impact of operating conditions such as superficial gas velocity, operating pressure (from atmospheric pressure up to 20 bar) and polymer properties on the fluidisation characteristics will be quantified on basis of a detailed experimental study utilising a dense gas-fluidised bed of sufficiently large diameter (0.3 m) to exclude pronounced scale effects. The results of the experiments will be used to further develop and validate advanced in-house developed CFD models which can subsequently be used as a tool to support the design and optimisation of engineering scale gas-phase polymerisation reactors with confidence.

Experimental

Electrical Capacitance Tomography (ECT) is a powerful non-invasive measuring technique and will be used in this project to obtain high-resolution instantaneous and time-averaged voidage maps in a 0.3 m diameter gas-fluidised bed operated up to 20 bar. With ECT information on the gas bubble behaviour (size and frequency information) can be obtained offering considerable advantages over (conventional) probe techniques which suffer from i) disturbance of the bed behaviour ii) problems with interpretation of the probe signals. In addition we will make use of dynamic pressure measurements to characterize the gas bubble behaviour. Measured porosity distributions correspond very well with computational results.

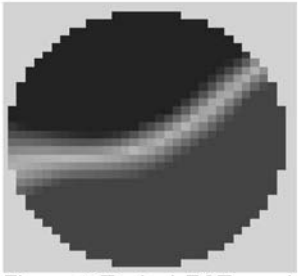

Figure 1: Typical ECT result of a horizontal plane in a small scale fluidized bed.

Computational

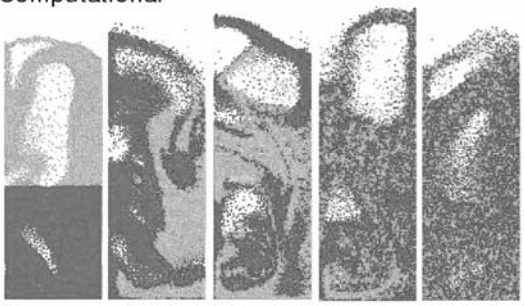

Figure 2: Solids mixing at 0, 0.25, 0.5, 0.75 and 1 seconds after the initial colouring.

Full three dimensional discrete particle simulations results and two fluid simulations results are analysed with sophisticated algorithms for bubble detection and solids mixing. We found that with increasing pressure the bubble-emulsion structure is less distinct and more homogeneous. Furthermore, the bubble size decreases and solids mixing improves. An example of a solids mixing simulation is shown in figure 2.

Acknowledgement

This work is part of the Research Programme of the Dutch Polymer Institute (DPI) as project number #547.

Autothermal membrane reactor for production of pure hydrogen with CO_2 capture

Introduction

With carbon capture and a future hydrogen economy high on the political agenda, a process for clean conversion of methane to pure hydrogen and concentrated CO_2 is needed. A very promising novel reactor concept using membrane assisted fluidized beds has been proposed and patented by Shell.
The aim of this project is to fundamentally research fluidized bed membrane reactors and to validate a model with experimental results.

Reactor Concept

In the bottom section of the reactor perovskite membranes submerged in a fluidized bed provide pure oxygen for the partial oxidation of methane. The generated heat is used for the steam reforming of methane in the top section of the reactor. Palladium coated membranes within a fluidized bed extract the hydrogen, overcoming thermodynamic equilibrium limitations. A stream of CO_2 and steam leaves the reactor.

Research

Fundamental research will be carried out focusing on how the thermodynamics of a fluidized bed is affected by the presence of and permeation through membranes. CFD results from an advanced 3D discrete particle model and continuum modeling will be compared with experimental results.
A labscale reactor will be constructed to demonstrate the reactor concept and to validate the simulation results.

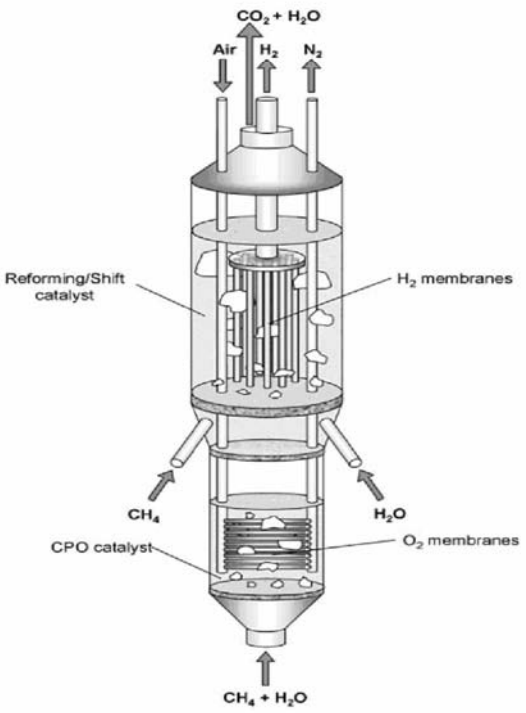

Fig.1: schematical drawing of the novel reactor concept for autothermal steam reforming of methane with integrated CO_2 capture

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Experimental and computational study of dense gas-fluidized beds with liquid injection

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Supported by	: Dutch Polymer Institute (DPI)	**Period**	: Feb. 2008 – Feb. 2012

Introduction

Liquid injection into dense gas-fluidized beds has widespread industrial application such as in gas phase polymerization, fluidized bed granulation and partial oxidation involving liquid hydrocarbons. However, systematic study of such systems has so far received limited attention from the academic research community.

Objectives

The main objective of this research project is to develop detailed understanding and quantitative descriptive tools for dense fluidized gas-solid suspensions, in which one of the reactants is injected into the bed as a liquid (through bottom or top spraying/atomization), taking into account the associated heat effects. The impact of operating conditions on the fluidization behavior will be quantified experimentally. The results will be used in further development and validation of advanced in-house developed CFD models. These can subsequently be used to support the design and optimization of engineering-scale gas-phase polymerization reactors with special emphasis on the thermal aspects of the operation.

Scientific and technological approach

A combined computational and experimental approach is applied.

Existing in-house developed CFD models will be extended with additional mass and thermal energy equations. A multi-level modelling approach is adopted.

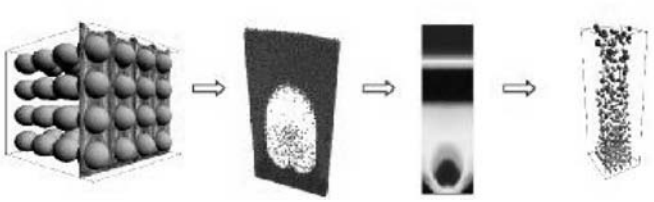
For validation of the numerical models experiments are planned for liquid injection into dense fluidized beds. Both thermal and dynamic aspects will be quantified.

Technological impact

Validated CFD models to be obtained from this project can support the design of engineering scale gas-phase polymerization reactors with confidence. Careful design of liquid injection devices directly affects reactor throughput and thus has a direct impact on the economical viability of these processes.

Acknowledgement

This work is part of the research program of the Dutch Polymer Institute (DPI) under project number #632.



FCRE The study of gas-solid interactions in polydisperse suspensions of spheres

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OSPT theme	: Comp. & Exp. Chem. Eng.		
Supported by	: NWO	**Period**	: Jul. 2006 – Jul. 2010

Introduction

The CFD models that are currently used in simulations of fluidized bed reactors require a closure to account for the effective momentum exchange between fluid and solid (drag force). It is found that the results can be strongly influenced by the drag force relation that is used.

Numerous drag force correlations are available in literature, most of them based on the simulation results for static arrays of particles (DNS) or pressure drop experiments on packed beds. In both cases the average drag force is obtained for relatively homogeneous systems.

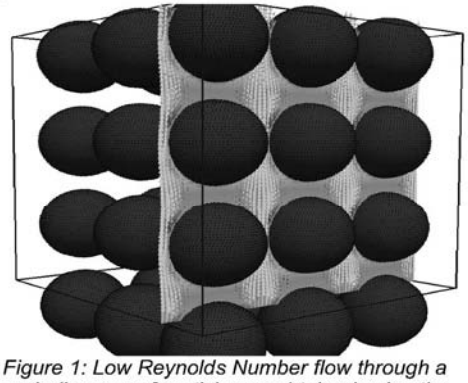

Figure 1: Low Reynolds Number flow through a periodic array of particles as obtained using the immersed boundary method

In fluidized beds on the other hand the particles are constantly moving with respect to each other (granular temperature) and pronounced heterogeneity, such as bubbles, are likely to occur.

Objectives

The goal of the project is to improve existing or to derive new closures for the drag in fluidized beds in order to account for effects such as heterogeneity and particle mobility (granular temperature) which are currently not included when modelling drag in larger scale models such as Discrete Particle Model and Two Fluid Model.

Computational

Direct Numerical Simulation will be done to study the flow in small model systems.

To this end a lattice-Boltzmann (LBM) code by Anthony Ladd, which has already extensively been validated, will be used. Further an Immersed Boundary Method (IBM) has been implemented in an in-house CFD code and is currently tested.

A comparison of results obtained with both very different methods will give an indication on their reliability.

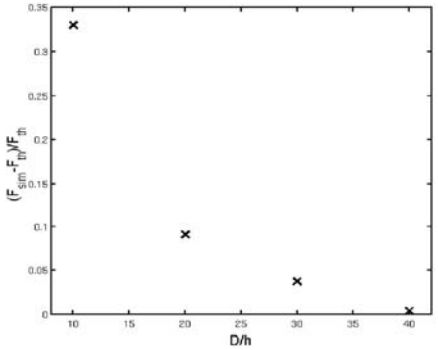

Figure 2: Deviation of the drag force obtained from IBM simulation from exact results for different particle diameter to grid size ratios

Results

Simulations of low Reynolds-Number flow through a periodic array of particles, as shown in figure 1, were done. The results for the drag force compared to exact solutions available in literature and the influence off numerical parameters, such as diameter to grid size ratio, on the results were studied.

Acknowledgement

This project is funded by CW-NWO.

Anthony Ladd is greatly acknowledged for sharing his Lattice Boltzmann Code.

Development of Simulation Models for Fluidized Bed Reactors with Polydisperse particles

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OSPT theme	: Multiphase Reactors	**Research school**	: OSPT
Supported by	: NWO	**Period**	: Sep 2008 – Aug 2012

Introduction

Numerical models of gas-fluidized beds have become an indispensable tool in the design and scale-up of gas-solid chemical reactors. Due to the wide range of scales present in life-size fluidized beds, a multi-level modeling strategy has to be adopted, where dense gas-solid flows is considered via three distinct levels of modeling namely, Direct Numerical Simulation (DNS) models, Discrete Element Models (DEM) and the continuum model based on the kinetic theory of granular flow (KTGF).

Project Aim

This project is concerned with the modeling at the largest scale, using the KTGF, with a focus on the effects of polydispersity. For this, novel closures for the solid phase viscosity and gas-solid momentum exchange have to be developed and/or implemented.

Modelling Approach

The existing two-fluid code for bidisperse systems will be tested extensively by making a detailed comparison with corresponding simulations using the DEM code. This also includes testing the assumptions underlying the KTGF, such as the Maxwellian distribution of velocities. In order to make a clean comparison, friction will not be included in the DEM simulations, since this is also not included in the KTGF. Subsequently, the effect of including friction in the DEM model on the flow phenomena will be studied in detail, on the basis of which conclusions will be drawn on the range of validity of the current class of KTGF models. Subsequently, the effect of new, polydisperse drag force correlations, again both at the two-fluid level of modeling and in the discrete particle model, will be investigated.
On the basis of the insights obtained from the activities described above, possible improvements of the KTGF will be considered; also the latest developments of further improving the KTGF for monodisperse systems (which is part of a parallel project) will be included.

Experiments

The novel closures will also be validated with real-life experiments, using non-invasive methods, by comparing bubbling velocities, bed expansion and segregation rates.

Outlook

The main projection for subsequent years is the move to general polydisperse systems by developing a general multi-fluid code. All the steps which are taken in the first year for binary systems will be repeated for polydisperse systems.

Acknowledgement

This project is financially supported by the Netherlands Organisation for Scientific Research

Fundamentals of heterogeneous bubbly flow: Mass- and heat transfer and chemical reaction in bubbly flow

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Supported by	: IPP-FOM	**Period**	: Aug. 2007 – Aug. 2011

Introduction

Gas-liquid contactors are frequently employed in (bio)chemical, metallurgical and physical processes. Recent developments in the understanding of dispersed gas-liquid flow systems are mainly focussed on low gas volume fractions in the homogeneous regime. Closures for the hydrodynamics (drag, virtual mass) are derived using simulations and experiments, mainly with single, isolated bubbles. However, most industrial processes operate at high gas fractions in the heterogeneous regime, in which the interaction between neighbouring bubbles is of crucial importance. The interaction does not only have a high impact on the hydrodynamics, but also on the mass- and heat transfer rates throughout the system. Closures for these phenomena are essential for models describing industrial scale contacting devices.

Project Objectives

- Derivation of hydrodynamics- and mass- and heat transfer closures at high gas fractions
- Extension of the Front Tracking model with adaptive mesh refinement
- Study swarm effects on the mass, momentum and heat transfer rates

Modeling and Numerical Simulations

A previously developed 3D Front Tracking (FT) model is used to track the interfaces of multiple bubbles (see Fig. 1). The FT model is capable of simulating swarms with high gas phase fractions (up to 42% was already achieved). Because mass transport phenomena take place at very small scales, the model will be extended with Adaptive Mesh Refinement (AMR) to incorporate mass and heat transport. As a result, a refined grid can be used where large gradients in mass and heat fluxes prevail, while a coarser grid is used in regions with smaller gradients. Besides the AMR, mass- and heat transport phenomena as well as chemical reactions will be included.

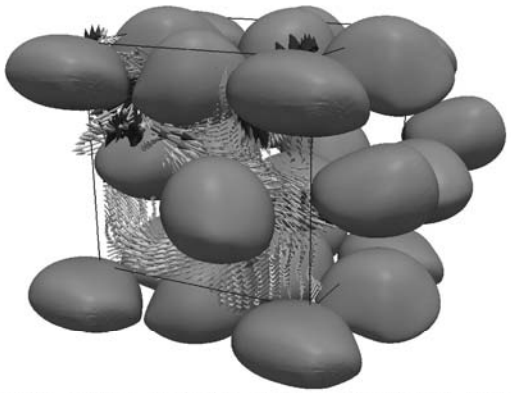

Fig.1: Rising bubble cluster simulated with periodic boundary conditions.

Experiments

An experimental setup is constructed which is capable of injecting bubbles with a predefined size at a predefined location, so that we can position the bubbles for each experiment. PIV and DIA experiments will be used to obtain experimental data to compare with our simulations.

Outlook

The closures derived from high-detail, small scale models (such as the FT model), and to use these closures in larger-scale models. The ultimate goal is to be able to simulate industrial processes on a real-life scale.

Acknowledgement

This project is part of the Industrial Partnership Programme number I13 of the 'Stichting voor Fundamenteel Onderzoek der Materie (FOM)', which is financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO)'.

Cryogenic CO_2 capture from flue gases

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OSPT theme	: Separation Processes		
Supported by	: Shell	**Period**	: May 2007 – May 2011

Introduction

Due to increasing concerns about green house gas emissions, several CO_2 capture processes have been developed, such as pressure swing adsorption (PSA), amine scrubbing and membrane processes. A promising novel option is to freeze out CO_2 from flue gasses onto cryogenically cooled solid surfaces.
Due to the atmospheric operation, expensive flue gas compression can be avoided. The required cold can be obtained during the re-gasification of LNG (liquefied natural gas). Due to the increasing demand in LNG, an economically attractive operation is ensured.

Project aim

- Development and construction of a pilot plant for capturing CO_2 based on de-sublimation.
- Development of a suitable model to describe the process, necessary for scale-up.
- Fundamental understanding of the CO_2 (de)sublimation process.

Results

A novel cryogenic CO_2 capture process has been proposed and developed. The concept is based on cryogenic CO_2 freeze-out in dynamically operated packed beds. When feeding a flue gas containing CO_2, H_2O and inert gases to a previously refrigerated packed bed, an effective separation between CO_2, H_2O and the permanent gases can be achieved on the basis of differences in dew and sublimation points. Temperature and concentration fronts will develop, which move through the bed with different velocities. H_2O and CO_2 will condensate and desublimate respectively (Fig. 1), extracting the cold energy stored in the packing and therefore avoiding unacceptable pressure drop or plugging. Great advantage is that both water and CO_2 can be separated from a flue gas simultaneously, circumventing costly pre treatment steps. Furthermore, no chemical absorbent or elevated pressures are required.

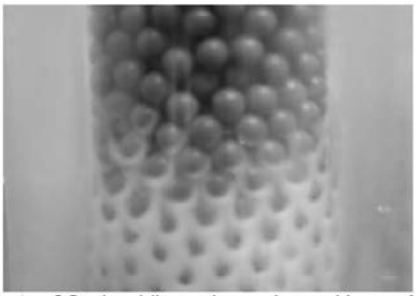

Fig. 1 – CO_2 desublimated onto the packing surface

Experiments have been carried out and demonstrated that CO_2 can be well separated from N_2. The process is described by a pseudo homogeneous 1D model. The resulting simulations show good resemblance with experiments as shown if Fig. 2 below.

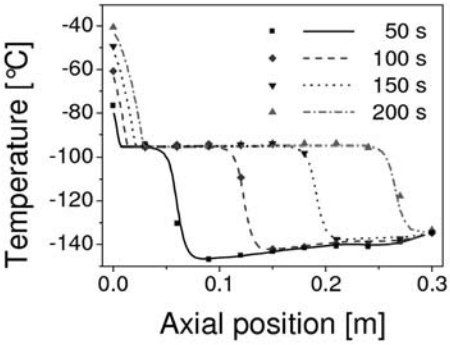

Fig. 2 – Experimental (markers) and simulated (lines) evolution of axial temperature profiles

Acknowledgement

Shell Global Solutions International is kindly acknowledged for their financial support.

Why the two-fluid model fails to predict the hydrodynamics of Geldart A particles in gas-fluidized beds

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Period : Feb 2008-Feb 2010

Introduction

Although great progress has been made in modeling the fluidization of Geldart B and D particles and dilute gas-solid flow in gas-fluidized beds by standard two-fluid model, researchers have shown that such method fails to reproduce the hydrodynamic characteristics of Geldart A particles in gas-fluidized beds. However, the question remain is why the standard two-fluid model fails.

Project aim

The objectives of this research are to explore the underlying mechanics of the failure of standard Eulerian model in simulation of Geldart A particles in gas-fluidized beds.

Results

We found that lack of scale resolution is the main origin of the previously reported failure of two-fluid modeling of Geldart A particles. The bed expansion characteristics (Fig.1) as well as the effect of gas and particle properties on the minimum bubbling velocity (Fig.2) can be reasonably predicted, provided that a sufficiently fine grid size and small time step is used.

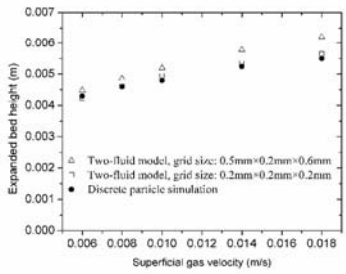
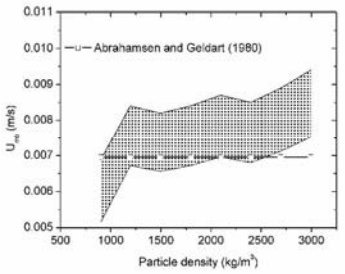
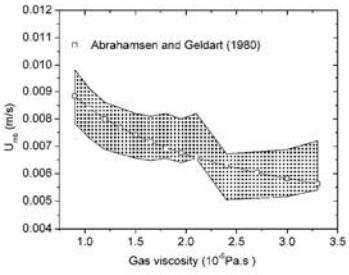


Figure.1. Comparison between the expanded bed height simulated by two-fluid and discrete particle models at various superficial gas velocities and two different grid sizes. Size of the fluidized bed: 3.0mm×1.2mm×12mm; Time step: 1.0×10^{-6}s; d_p=75μm; ρ_s=1290kg/m^3



(a)



(b)

Fig.2. The effect of particle density (a) and gas viscosity (b) on the minimum bubbling velocity of Geldart A particles in gas fluidized beds. d_p=75μm; Domain size: 20mm×40mm, Grid size: 0.2mm×0.2mm; time step: 1.0×10^{-6}s. (a) $\mu_g=1.8\times10^{-5}$Pa.s; (b) ρ_s=1495kg/m^3

Acknowledgement

This research project is financially supported by NWO.

Fundamentals of heterogeneous bubbly flow: Coalescence, breakup & scale effects

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Research group	: TNW / FCRE	**Research school**	: JMBC
Supported by	: IPP-FOM	**Period**	: August 2008 – July 2012

Introduction

Even though industrial bubble columns are operated under heterogeneous conditions, most numerical studies have been limited to bubbly flow in the homogeneous regime. Recently within the FCRE group [1], a first attempt has been made to study heterogeneous bubbly flow with the aid of a Euler-Lagrange model or a so-called discrete bubble model (DBM). This model has the advantage that a bubble distribution can be incorporated in a straightforward manner. However, the used closure relations (drag, lift and virtual-mass coefficients) are derived for the homogeneous regime. Building on this knowledge, the DBM will be further improved. The main aim of this project is to provide a validated DBM, which is capable to simulate heterogeneous bubbly flow of large scale systems.

Project objectives

- Use new developed or improved closure relations from present literature studies
- Incorporations of coalescence and breakup models
- Study of reactive bubbly flows at different scales

Numerical modeling

Simulations are performed with the DBM, which consists of two coupled parts: a Lagrangian part, where each individual bubble is tracked, and an Eulerian part, where the liquid phase motion is described (Fig. 1). The bubbles are tracked by solving the second law of Newton for each individual bubble. The liquid phase contributions are taken into account by the net force, experienced by each individual bubble. For an incompressible bubble:

$$\rho_b V_b \frac{d\vec{v}}{dt} = \vec{F}_p + \vec{F}_g + \vec{F}_d + \vec{F}_l + \vec{F}_{vm}$$

The liquid phase is represented by the volume-averaged Navier-Stokes equations.

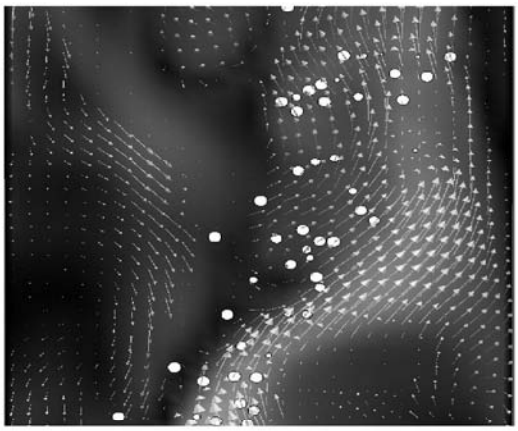

Fig. 1: Illustration of Lagrangian tracking of bubbles in an Eulerian fluid in a two dimensional plane.

The presence of the bubbles is reflected by a volume fraction and an extra term in the momentum equations. Turbulence is modeled for the liquid with a subgrid scale model.

Experimental modeling

To acquire data for validation of the numerical results, an experimental setup containing a flat column will be developed. Shadowgraphy will be employed for the measurements of the bubble data and PIV for the liquid data.

Acknowledgment

This project is part of the Industrial Partnership Programme number I13 of FOM, which is financially supported by NWO.

References

[1] Darmana, D. *On the multiscale modeling of hydrodynamics, mass transfer and chemical reactions in bubble columns*. PhD Thesis, University of Twente, the Netherlands, 2006.

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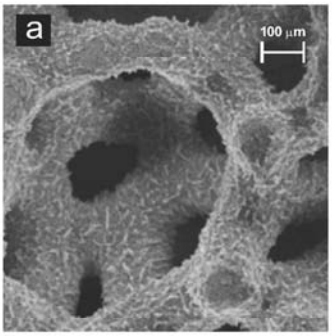
CPM applies fundamental knowledge on molecular diffusion and reactions in/on heterogeneous catalysts for exploration of new catalytic materials, catalytic devices and processes of relevance for industry and society. The drive towards processes is reflected in CPM's membership in the local research institute IMPACT, while preparation and design of micro and nano-structured catalytic materials and devices, e.g. carbon-nano-fiber supports and microreactors, is reflected in the participation in MESA+.

Selective oxidation is a typical example of the need for high-precision catalysis, because usually oxidations have low yields caused by consecutive conversion to undesired side-products. CPM focuses on unconventional methods to achieve selectivity. An example is partial oxidation of methane to synthesis gas over yttrium-stabilized zirconia at high temperature, which proceeds via a surface-redox mechanism in which reduction and oxidation of the catalyst is confined to the surface layer of the oxide. Detailed insight in the properties of the zirconia surface is now used for industrially relevant processes like dehydrogenation of ethylbenzene to styrene, using CO_2 as a soft oxidant. Soft oxidants like CO_2 and H_2O are studied in a number of projects, and in future also in the liquid phase.

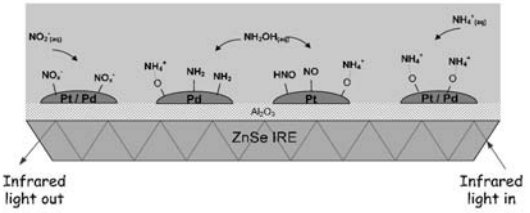
Very promising is the oxidative cracking of alkanes to olefins over Li-MgO catalysts. Here, a surface-initiated radical chain mechanism is active in the gas phase. The initial activation of C-H bonds occurs at the O-radical ions present in Li+O- ion-pairs. Catalyst activity was improved by creating a larger surface area via sol-gel procedures. Micro-plasma reactors were developed, allowing for the first time to monitor radical reactions on the catalyst surface.

Concentration management in liquid phase heterogeneous catalysis is motivated by the idea that mass transfer in liquids is slow, which affects reaction rates and selectivity.



SEM micrograph of CNFs-Ni foam

Innovative highly-porous micro-structured supports, based on carbon-nano-fibers (CNF) attached to monoliths, metal foams (see figure) and microchannels are a solution to this problem. Analysis tools like Attenuated Total Reflection (ATR) IR were developed to study the interaction of reactants, intermediates and products with catalyst surfaces in liquids (see figure). A key step in this research was the



development of stable thin catalyst layers on the ATR crystals. In addition, a transient reactor for pulse and step-change experiments in liquid phase was developed, allowing detection of multiple components during operation.

Another topic is catalysis for sustainable processes for fuels and chemicals from renewable feedstocks. This involves catalytic routes to syngas or H_2, or direct conversion of solid biomass to liquid fuel precursors via so called Catalytic Flash Pyrolysis. It was found that on Pt acetic acid, a key constituent in flash-pyrolysis oil, decomposes to H_2, CO, CO_2 and a carbonaceous residue which deactivates the Pt surface. This residue can be gasified with water to form additional H_2 and CO_2 and re-activate the Pt. In the conversion of biomass to a liquid bio-oil, the main challenges for applications relate to the energy density of the bio-oil, its acidity and its stability. Use of a catalyst during pyrolysis overcomes these problems. This is a rather new area of significant societal relevance and CPM has been in the forefront of developments.

BIOeCON

Catalytic pyrolysis of solid biomass to bio-oil

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Introduction:

The role of biomass resources as an energy source is expected to increase gradually because of their worldwide availability, zero net CO_2 emission, and low price. Solid biomass conversion to bio-liquid fuel is a promising process to overcome logistic problems associated with the distances between locations where biomass is available and sites where fuel is needed. It makes transportation, storage and further processing easier. Thermal cracking of biomass (pyrolysis) is a well-known process to produce bio-liquid under relative mild conditions (atmospheric pressure and 450 - 550 °C), but the quality of the oil produced is far too poor for direct use as transportation fuel or even for upgrading in oil refineries. In the presence of catalysts pyrolysis process can result in more selective conversion of solid biomass under milder thermal conditions. Lowering the temperature is crucial for improved product quality. One of the main problems in catalytic pyrolysis of solid biomass is to provide efficient contact between the solid catalyst and solid biomass.

Objective:

The aim of this project is to develop approaches for biomass pre-treatment to enhance contact between solid catalyst and solid biomass (biomass pre-activation).

Project approach and results:

Effectiveness of catalyst and pre-activation approach will be estimated from TGA data with MS analysis of the gaseous products formed. Thermal conversion of model compounds, mimicking biomass composition (cellulose, xylan (hemicellulose) and lignin), as well as different types of lignocelluosic biomass (wood, sugar cane) in presence of catalysts will be studied. Pyrolysis experiments, resulting in bio-oil samples, will be performed in a flash pyrolysis reactor. Bio-oil obtained from classical and catalytic pyrolysis runs will be characterized regarding pH value, CHO-content and heat of combustion value. Detailed composition of produced oil will be determined with GC-MS.

Acknowledgement:

This project is financially supported by BIOeCON, KiOR.

KiOR

Oxi-cracking as a route to olefins - Efficient conversion of alkanes to olefins over nanometer range clusters of non-redox alkaline earth oxide catalysts

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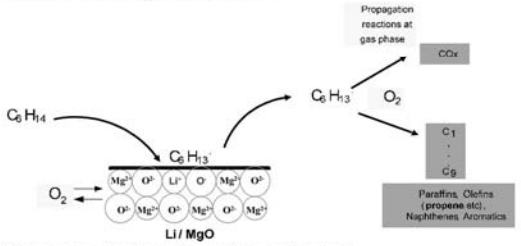
Introduction

The world production capacity of ethylene and propylene is around 90 and 42 million metric tones per year, respectively, and a growth rate of 4% is predicted for coming years. Steam cracking is currently the major route for the production of olefins. Catalytic oxidative cracking (COC) is conceptually a promising alternative to steam cracking for the production of olefins because the reaction is exothermic and therefore the energy required for cracking can be generated internally.

Objectives

Aim of the project is to develop nanoscopic mixed oxide catalysts for efficient oxygen assisted cracking of naphtha range alkanes (hexane) to light olefins. Our target is to: (1) produce higher yields of light olefins at milder conditions than that of steam cracking, (2) Increase selectivity to propylene and (3) Minimize CO_x formation.



Schematic diagram of reaction mechanism

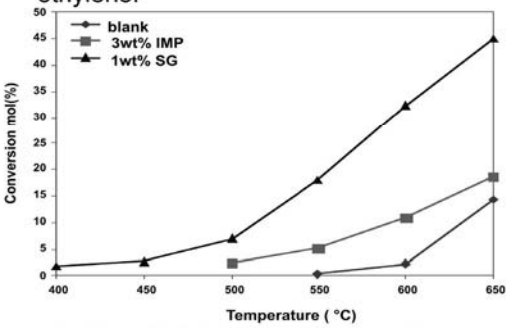
Project Background

In catalytic oxidative cracking of propane Li promoted magnesia had shown very promising results. [Li^+O^-] defect site is responsible for catalytic activity. Li/MgO prepared via the sol-gel method introduced significant improvements in activity and selectivity to olefins. [1] Advantages of the sol-gel catalyst are: (1) Higher surface areas, (2) Higher concentration of active sites, thus higher activity and selectivity towards olefins. This catalyst will be applied in catalytic cracking of hexane.

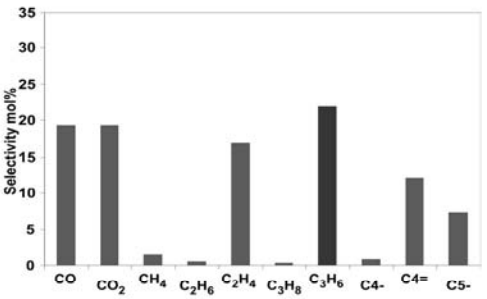
Results of Current work

Catalytic oxidative cracking of hexane was performed over both sol-gel and impregnated Li/MgO catalyst.

(1) Sol-prepared catalyst showed higher conversions of hexane.
(2) Selectivity to propylene is higher than to ethylene.



Conditions: 100ml/min, 10% hexane, 8% oxygen, 100mg



Conditions: 100ml/min, 10% hexane, 8% oxygen, 100mg sol-gel 1wt%Li/MgO catalyst. Conversion = 18%

References

[1] Formation of high surface area Li/MgO-Efficient catalyst for the oxidative dehydrogenation/cracking of propane C.Trionfetti,I.V.Babich,K.Seshan,L.Lefferts. **Applied Catalysis A: General 310 (2006) 105-113**

Acknowledgement:

This project is financially supported by ASPECT, project number: 053.62.011

Hairy Foam Catalysts - Towards control at the catalytic site

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Typical problems encountered in three phase fixed bed catalytic reactors are heat/mass transfer limitations and pressure drop. One of the ways to overcome these problems is to use structured materials, *i.e.,* to deposit catalyst on a rigid, ordered, porous support body, for e.g., metal or ceramic foams. Solid foam packing has been demonstrated to be able to increase gas-liquid mass transfer and optimize hydrodynamics [1].

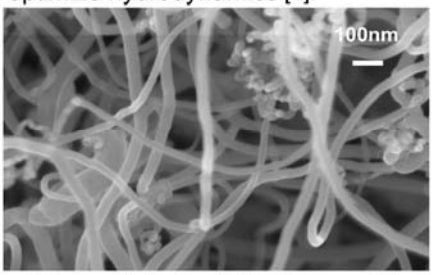

Figure 1 Entangled CNFs on Ni

In order to meet the demands of catalysis, enhancement of surface area and porosity of the foam is essential. This can be achieved by preparing carbon Nanofiber (CNF) layer (e.g. Fig 1) on the metal foam (Fig 2), designated as 'Hairy foam' [2]. Such a layer allows for manipulating catalytic properties by anchoring well dispersed (improved activity) uniform (selectivity) catalyst particles. Maximizing the porosity and minimizing the tortuosity in the catalyst particle will reduce the internal mass transfer limitations.

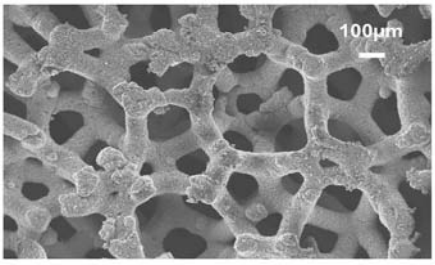

Figure 2 - Ni foam covered with CNFs [3].

CNF growth on Ni foam was carefully optimized. The surface area of the CNFs formed was 90m^2/g and the total surface area of the structured composite was increased to 30m^2/g. The CNF layer formed is well attached to the Ni surface *via* a microporous carbon layer, which is formed between Ni surface and

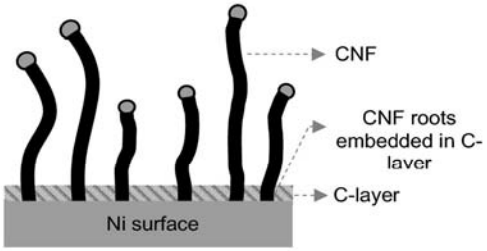

Figure 3 - Scheme showing attachment of CNFs to Ni surface *via* C-layer.

The aim of the project is to test the suitability of hairy foam catalysts (Pd-CNF-Foam) for a liquid phase catalytic reaction in a fixed bed reactor and to compare with the conventional porous catalysts. Experimental work is under progress to investigate the performance of Hairy foam catalysts considering a fast reaction such as nitrite reduction to N_2 where large effects of concentration gradients are expected along the catalyst particle.

References

1. C. P. Stemmet, Ph. D. Thesis, Technical University of Eindhoven, 2008.
2. N. Jarrah, F. Li, J. G. van Ommen and L. Lefferts, *J. Mater. Chem.,* 2005, *15*, 1946.
3. J. K. Chinthaginjala, D. B. Thakur, K. Seshan, L. Lefferts, *Carbon*, 2008, 46, 1638.

Acknowledgement

This project is financially supported by STW-EPC, Project number 6601.

Alkane oxygenation using oxide ion conducting membranes

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Introduction

Selective oxidation of alkanes to oxygenates and olefins is still one of the holy grails in catalysis, because the yields that can be obtained are, in most cases, far too low to arrive at practical application. Typical catalysts for selective oxidation of alkanes are metal oxides in which the valency of the metal ion as well as its oxygen content can easily change.

Research in this project focuses on the oxidation of small alkanes to olefins and oxygenates by dense ion conductor membranes with suitable catalytic properties in a Catalytic Membrane Reactor (CMR). The key idea is that oxygen species are delivered at the surface in contact with the alkane via solid-state diffusion exclusively, which results in the sole formation of lattice-oxygen (Mars-Van Krevelen mechanism), avoiding direct contact between alkane and oxygen gas (deep oxidation) (fig.1).

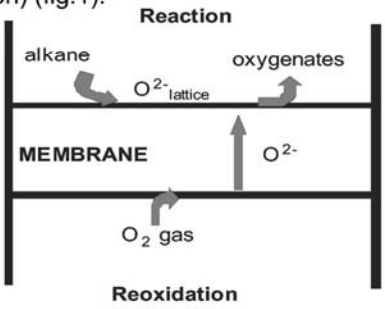

Figure 1: Scheme of the CMR using ion-oxide conductor

Objectives and strategy

The overall aim of the project is exploring the new opportunities for selective oxidation of light alkanes. Employing propane pulses on powdered materials, catalyst surface is titrated and products distribution at different catalyst oxidation degree is investigated.

Results

Fig. 2 shows the variation of oxidation degree in terms of amount of over-stoichiometric oxygen (delta, δ) and the appearance selectivity (Mass Spectrometer signals are used instead of concentrations) during pulse test of propane on $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$.

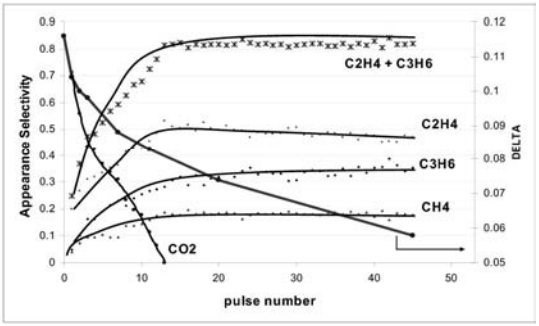

Figure 2: Appearance selectivity during titration test on $La_2Ni_{0.9}V_{0.1}O_{4+\delta}$ and relative catalyst oxidation degree

Observations and conclusions

- Not selective catalyst at high oxidation degree ($0.12<\delta<0.08$; CO_2 is the major product)
- $\delta<0.08$ showed promising selectivity (CO_2 production is below the MS threshold; only olefins and methane are constantly produced)
- H_2O formation throughout the entire experiment (not shown in the figure) testify the catalyst activity providing oxygen species

Acknowledgement:
This project is financially supported by ACTS, project number 053.62.004

*TRANS*verse rein*FORCE*ment of carbon fiber composites with carbon nano fibers

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Introduction

The increasing application of lightweight structures, for example, in aerospace, automotive and wind energy, requires advanced composite materials. Continuous carbon fiber reinforced polymers (CFRPs) are characterized by high strength and stiffness at low weight[1]. The high stiffness and strength are predominantly obtained in the direction of the carbon fiber reinforcement. The mechanical strength in the direction perpendicular to the fiber (so called transverse properties) is generally an order of magnitude lower than the strength in the fiber direction.

The surface modification of carbon fibers by the growth of carbon nanofibers by catalytic decomposition of hydrocarbon gas over metal particles is a most promising technique for the improvement of the transverse properties[2].

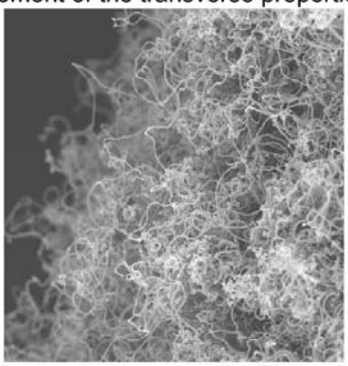

Figure 1: Close-up of a CNF layer

Objective

Although much insight has been gained over the last years, a clear picture on how surface area, pore-volume, and shape of the fibers can be manipulated is not yet available.

Therefore, the main goals of this project are:

1. the development of the optimized methods for preparation of carbon nanofibers on carbon micro fibers (control of the growth of CNFs onto CMFs with respect to CNF length, diameter, density and distribution) and
2. scale up of the process from laboratory level to demonstration level.

Obtained larger pieces of CNFs immobilized on carbon microfibers will be further applied in CFRPs.

General approach

To achieve the objectives mentioned, an extensive research on catalytic growth of CNFs over metal particles will be performed. The experiments will reveal how the primary structure of the CNFs (several orientations possible), diameter and length of the fibers, their shape, as well as their density and distribution over the CMF surface can be controlled.

The construction of a reactor for the larger samples of $0.3 \times 0.3 m^2$ will also be done, which will allow production of CNFs on CMFs for the actual sized demonstrator. The optimal configurations in terms of materials and procedures will be defined, followed by static and dynamic testing of the mechanical properties of the composite materials.

References

[1] W.B. Downs and R.T.K. Baker, *Journal of Materials Research*, **10** (3) 625–633, 1995.

[2] S.W. Hudnut and D.D.L. Chung, *Carbon*, **33** (11), 1627–1631, 1995.

Acknowledgement

Financial support from STW (project № 10091) is gratefully acknowledged.

Oxidative dehydrogenation with CO_2 as a soft oxidant

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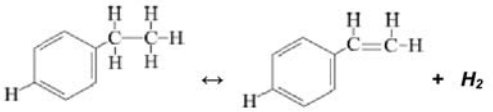
Introduction

Current technology solution for styrene (STY) production from ethylbenzene (EB) requires the presence of super heated steam, i.e. it is extremely energy intensive process.



As recognised by many researchers, an alternative reaction pathway is based on the fact that in principle CO_2 could replace steam, as long as the catalyst (Fe, V, Cr or Ce oxides) is able to activate CO_2. Namely, CO_2 could play a role in:

- gasification of carbon deposits (prevention of catalyst deactivation)
- control of the oxidation state of the catalyst
- effective heat transfer

as steam does as well; besides, it might bring an additional advantage:

- an increase in EB conversion level, i.e. the reverse water gas shift (RWGS) reaction takes place:

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$

Actually, the process would turn into a mild oxidative dehydrogenation, formally described as:

$$EB + CO_2 \leftrightarrow STY + CO + H_2O$$

As an additional benefit, CO_2 can be separated easily from the oil, in contrast to steam and needs only heating before reuse. The overall process is thus much less energy demanding.

Objective and Strategy

Apparently, zirconia is able to activate CO_2 and provides significant activity for this reaction [1]. However, details on the reaction mechanism are lacking so far. Interestingly, recent work in our group [2] has revealed that oxygen-coordinatively unsaturated Zr sites are attributed with pronounced affinity towards N_2O activation.

Remarkable differences between low-index planes vs. steps and edges in terms of activation of N_2O have been observed. Our working hypothesis is that the same type of active site is involved in CO_2 activation as well. Objective of this research is the preparation of materials with distinct and tunable morphology and controllable surface defects concentration; i.e.:

- bulk nano zirconia clusters
- zirconia clusters deposited on inert support.

Based on recent progress in the Inorganic Membranes group the influence of modifying ligands on the sol-gel chemistry of metal alkoxides and the effect of these ligands morphology of the derived materials will also be considered [3]. Catalysts will be characterized with several techniques, i.e.: TGA, FT-IR, XRD-LB, $^{18}O_2$ exchange, TPR/TPD/TPO/TPReaction, etc. to get insight into the nature of active sites in differently prepared fresh/used zirconia samples. Together with test reaction results (in steady state as well as in transient mode) it would contribute to understanding of structure-performance relationship of the target reaction and will govern our research in finding the most effective (long term stable, but selective) zirconia based catalyst for oxidative dehydrogenation of EB.

References

1. J.-N. Park, J. Noh, J.-S. Chang and S.-E. Park. Catal. Lett., **65** (2000) 815.
2. J.Zhu, Thesis, Catalytic partial oxidation of methane over zirconia based defective oxides, UT, 2005.
3. G.I.Spijksma, Thesis, Modification of zirconium and hafnium alkoxides, UT, 2006.

Acknowledgement

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Sustainable hydrogen *via* catalytic steam reforming of model oxygenate compounds present in bio-oil

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Introduction:

Currently, there is tremendous interest in the use of hydrogen as a clean fuel, especially for power generation with fuel cells. Sustainable sources, *e.g,* biomass, is key for a CO_2 neutral energy supply. Recent developments in fast pyrolysis technologies make it possible to convert lignocellulosic biomass efficiently to a bio-oil, which is easier for handling and transport [1]. The bio-oil contains a variety of aliphatic and aromatic oxygenates (aldehydes, ketones, acids, alcohols).

The most promising catalytic option to generate hydrogen from bio-oil is *via* catalytic steam reforming followed by water-gas shift reaction, since these reaction steps maximize the hydrogen yield.

Steam reforming of oxygenates

$$C_nH_mO_k + (n-k)H_2O \rightarrow nCO + \left(n + \frac{m}{2} - k\right)H_2$$

Water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

Design of a stable catalyst for the generation of hydrogen from biomass has enormous interest currently.

Objective:

The main purpose of this study is to elucidate the reaction and deactivation mechanisms in order to help in the design of active and stable catalysts for steam reforming of oxygenates. Since the bio-oil is a very complex mixture of oxygenate components ($C_xH_yO_z$), a selection of the major oxygenates that are part of the bio-oil is required in order to establish structure, activity and mechanism correlations. Acetic acid has been chosen as a light oxygenate model molecule as it is one of the major compounds in bio-oil.

Earlier studies [2] on the steam reforming of acetic acid have shown excellent activity over Pt/ZrO_2. However, the catalyst deactivated rapidly due to coke accumulation. In this investigation, we explored the influence of small amounts of oxygen in the reforming feed as well as the use of a catalyst support with red-ox properties as approach to minimize coke accumulation and thus catalyst deactivation. Oxygen availability for gasification of coke deposited on the support can be enhanced by using reducible supports such as CeO_2. Ability of these metal oxides to store and release oxygen, the so called "oxygen storage capacity (OSC), may help to minimize/prevent coke accumulation and result in more stable catalysts.

For this purpose, we compared the catalytic performance of Pt/ZrO_2 and Pt/CeO_2 in the presence and absence of oxygen. Additonally, an insight in the mechanism of coke formation or in the relationship between coke properties and deactivation is reported.

References

1. Bridgewater, A.V., Catal. Today, 29, 285 (1996)
2. Seshan, K., Mercera, P.D.L., Xue, E. and Ross, J.R.H., US Patent 537791,

Acknowledgement:

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MESA+
Institute for Nanotechnology

Slip Behaviour on Nanostructured Surfaces in Microfluidic Structures

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Introduction

A generally accepted notion is that wetting (Hydrophilic) surfaces obey the no-slip boundary condition (Wenzel State). Clean non-wetting (Hydrophobic) surfaces exhibit apparent slips (Cassie-Baxter State) often to a surprisingly large extend. The effect becomes more important and dominates fluid flow in Microfluidic and Nanofluidic systems, which are distinguished by a large surface-to-volume ratio and flow at small Reynolds, capillary, and Bond numbers.

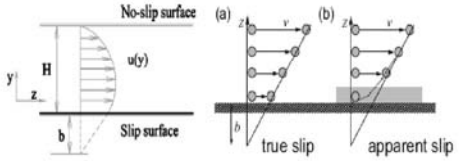

Fig.1: Slip behavior of fluids on boundaries [1, 2]

The slip length is the distance beyond the liquid/solid interface at which the liquid velocity extrapolates to zero. True slip occurs at the liquid- solid interface whereas apparent slip occurs at the liquid-gas interface [2]. Of special interest is the corresponding reduction in drag, which can be achieved by partial substitution of liquid-solid contact area (no-slip) with liquid-gas contact area (no shear, infinite slip). Practical means to reduce drag is of importance for biomedical and chemical engineering applications, e.g. in flow in pipelines of chemical production units, where pressure losses become substantial particularly if dimensions become smaller (Microchannels, Microfilters etc).

Objective

To achieve a controllable and reproducible growth of superhydrophobic carbon nanofiber (CNF) jungle (CVD/PECVD) on the microchannel walls and to study the influence of the structure of the walls of microchannels on slip length (Flow Profile Measurements via micro-Particle Image Velocimetry (μ-PIV) and drag (Flow-Pressure Measurements).

Experimental Approaches

1. Preparation of CNF jungles on microchannel walls: CNFs are graphitic materials that can be catalytically produced by the decomposition of hydrocarbons (C_mH_n) or carbon monoxide (CO) over preshaped transition metal surface such as nickel (Ni), iron (Fe), cobalt (Co) and/or their alloys. CNFs comprise the advantages of being intrinsically hydrophobic, having high porosity as well as extremely high surface roughness. We could grow a homogenous and stable CNF layer inside microchannel. At present, we are tuning the morphology of the CNF layer (surface roughness, density, pore size, hydrophobicity, thickness and diameter of CNFs) by varying the pretreatment, reaction mixture, time, temperature.

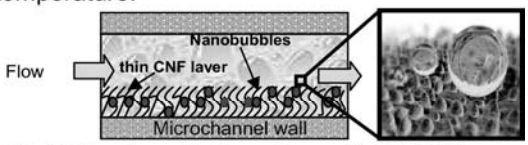

Fig.2: Microchannel with gas trapped inside CNF layer

2. Slip Length and Drag measurements: A μ-PIV technique is used to study the behaviour of fluids inside Organosilane [FOTS] coated patterned microchannel. The channel wall is made hydrophobic at the bottom and hydrophilic at the top to study the slip and no-slip behaviour. The main factors that influence the occurrence and magnitude of slip are surface wettability, surface roughness and the presence of nanobubbles or gaseous films.

References

[1] J.Ou et.al, Physics of Fluids, 16 (2004) 4635
[2] Chiaro Neto et.al, Rep.Prog.Phys.68 (2005) 2859

Acknowledgement:

This project is financed by University of Twente, MESA+.

Production of a green refinery feed via catalytic pyrolysis of biomass

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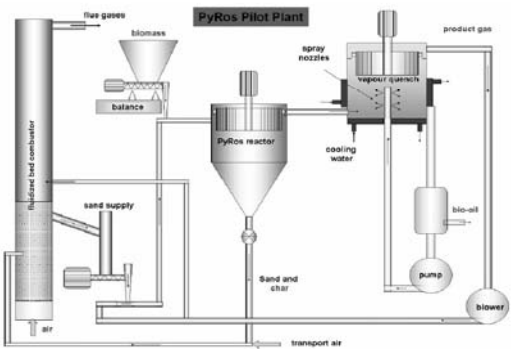
Aim of the Project

The central theme of this project is to establish ways to improve the quality of pyrolysis oil by developing: (i) a catalyst for selective deoxygenation of biomass and (ii) a cyclonic pyrolysis reactor with an integrated high-efficient rotating particle filter and a catalyst regenerator.

Introduction:

Among biomass to energy conversion technologies, pyrolysis of biomass is a promising route since the liquid products of this process (aka pyrolysis oil) (i) has (3-5 times) higher energy density, (ii) can be easily stored and transported and (iii) is cleaner and more homogeneous than the parent biomass.
However, the challenge here, from a fuel utilization point of view, is the high oxygen content of the pyrolysis oil. This high content (i) imparts acidity and corrosive properties to the oil, (ii) makes it immiscible to fossil hydrocarbons, (iii) makes it susceptible to gum formation on storage, and (iv) lowers its heating value. Therefore, selective removal of oxygen (deoxygenation) is necessary to make pyrolysis oil applicable as a fuel.



Approach

To overcome the challenge, a combination of flash pyrolysis and catalytic deoxygention is employed.

This approach is divided into four work packages:

i. Design and development of a selective and efficient deoxygenation catalyst.
ii. Testing and optimizing the catalyst under real pyrolysis conditions.
iii. Pyrolysis oil characterization and optimization.
iv. Design and development of a cyclonic reactor system for catalytic pyrolysis.

Planning

i. Catalyst screening: several catalysts will be mixed together with biomass and pyrolysed in the IR furnace, which mimics the real pyrolser.
ii. Promising catalysts will be then tested in the PyRos reactor. This part is carried out in collaboration with Thermal Engineering group, University of Twente.

Acknowledgement

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Carbon nanofiber jungles: towards a switchable super-hydrophobic surface

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Period : Feb. 2007 – Feb. 2011

Introduction

The study of super-hydrophobic surfaces (contact angle higher than 150°) is currently a hot topic in material and surface science. It is inspired by the remarkable properties of the Lotus leaves, on which surface droplets of water move freely and pick up dirt (self-cleaning effect). Super-hydrophobic surfaces have various applications in industry, e.g. self-cleaning paints, glass windows and textile.

Carbon nanofibers (CNFs) combine the advantage of being intrinsically hydrophobic with having high porosity as well as extreme high surface roughness. These three factors can induce strong super-hydrophobicity (Fig.1). CNFs are deposited on metal foils via the catalytic decomposition of ethylene by the thermal chemical vapor deposition (TCVD).

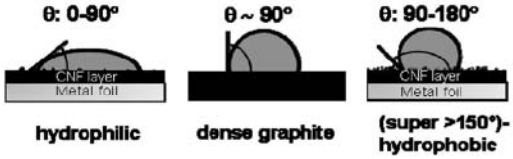

Fig.1: different states of wettability depending on the contact angle (θ) that the drop forms with the surface

Objective

To control the wettability of the carbon layers by changing the CNF growth conditions, such as hydrogen concentration, time of growth and type of pre-treatment.

Experimental approaches

The morphology of surfaces is analyzed by SEM (top view and cross section). The surface roughness and porosity is characterized by 3D reconstruction of the surface from SEM tilted images.

Results

The control of the multi-scale roughness leads to an enhancement of hydrophobicity, allowing us to create super-hydrophobic surfaces with contact angles higher than 150°. The higher the 3D surface roughness and void volume on the surface, the higher the contact angle (Fig. 2).

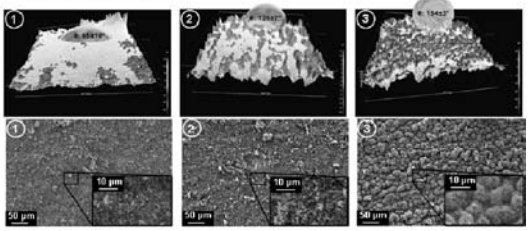

Fig.2: 3D reconstructions of 3 CNF layers (~ 300 x 450 µm) from 3 tilted SEM images (MeX software) and top view SEM pictures

The addition of H_2 increases the thickness of the carbon layer. It seems there is an optimum value for the total thickness of the CNF layer and higher contact angle (Fig. 3).

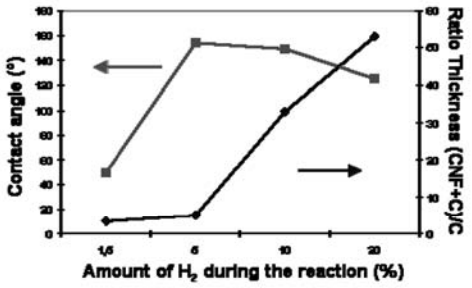

Fig. 3: effect of the amount of H_2 added during the reaction on the thickness of the layer (dense carbon + CNFs) and the contact angle

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Smart Microreactors

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Introduction:

Currently, there is a great interest in the field of micro structured gas-liquid contactors comprising specially modified catalytic coatings on microstructural internals.

The most recent trend in the design of three-phase catalytic microreactors focuses on the use of structured catalyst supports, i.e. the catalyst is deposited on a rigid, orderly arranged support body. The catalytic support layer based on Carbon nanofibers (CNFs), which can be produced via catalytic decomposition of a carbon containing gas over transition metal catalyst (e.g. nickel), poses as a novel option to facilitate this task. With their inherent high surface area-to-volume ratio CNFs provide more catalytic surface area, obtaining sufficient activity per unit of volume of catalyst. Additionally the density, diameter and length of the fibers can be manipulated to achieve high porosity (macroporous structure) with minimized tortuosity in order to optimize the accessibility of the active phase deposited on the CNFs. This also eliminates the internal diffusion limitations by preventing any concentration gradients inside the CNF layer.

Objective:

To develop a gas-liquid 'micro' contactor (microreactor) module with CNFs incorporated into microchannles as a structured catalyst support for depositing active catalytic phase.

Experimental approach:

a) Preparation of CNFs in microreactor channels: Entangled jungle of CNFs can be synthesized on flat substrates using thin film catalyst. Initial efforts of growing CNFs on fused silica substrate with thin Ni film (100 nm thick) produced promising results in terms of CNF morphology and their attachment to substrate (Fig.1).

*b) Catalytic active phase preparation: S*pecific procedures will be developed to achieve a good control over the deposition of the active phase (e.g. Ru or Pd) on the CNF support layer throughout the reactor.

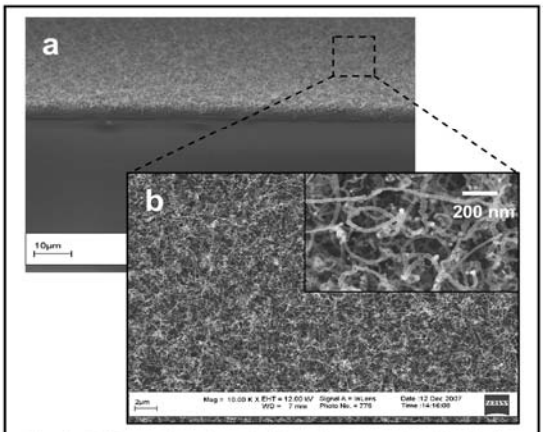

Fig. 1: CNF growth on fused silica substrate using Ni thin film
a. Cross sectional view of stable and uniform CNF layer on F. silica substrate;
b. Entangled jungle of CNFs (top-side view)

c) Testing CNF integrated microreactor module: The microreactor performance will be tested in the hydrogenation or oxidation reactions.

Additionally, special features (porous columns) will be designed inside microchannels to introduce gas into liquid phase.

Expected results:

In general, using microstructured multiphase reactors should enhance activity and selectivity thus facilitating significant size reduction of equipments and obtain reduced loss of waste products, achieving profitability for the fine chemicals and pharmaceutical industry in addition to the environmental benefits.

Acknowledgement:

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Hydrodynamics and heat exchange of Carbon Nano Fibers

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Period : Oct 2008 – Oct 2009

Introduction

In these work we intend to investigate the feasibility of carbon nano fibers CNFs. In two types of MEMS applications.The first is to increase the heat exchange between a fluid and a solid wall, and the second is to create relatively long beams to be used in gas-flow detectors.

In heat exchangers, usually, there is a conflict between heat exchange (requiring large contact area and narrow channels) and viscous losses or pressure drops (requiring small contact area and wide channels). The idea is to have CNFs on the channel walls to increase the heat exchange without significantly increasing the fluidic losses [1]. This problem is relevant in the development of microcoolers in the group of Ter Brake.

Sensors for gas-flow velocity fields, inspired by mechano-sensors present in crickets are developed by Kriijnen [2]. Basically, a long beam is used in a flow that generates a drag torque inducing a rotation which is sensed by capacitive read-out. To stick through the viscous boundary layer, the beams have to be relatively long (0.5-1 mm). In order to realize high sensitivity and high bandwidth the suspension should be very flexible and the beam should have a very small inertial moment. Using bundles of CNF's, having low average specific weight (400 kg/m^3 vs. 1200 kg/m^3 for e.g. SU-8) but so close together that they are "hydrodynamically dense", large sensitivity improvements of sensors can be obtained.

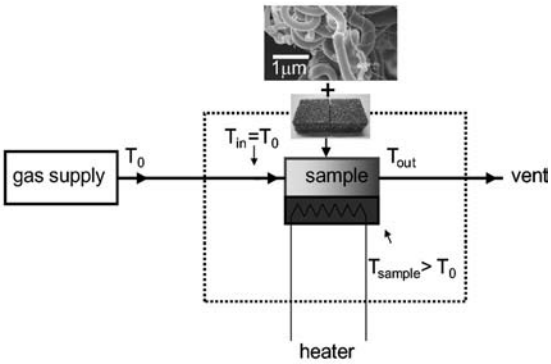

Fig. 1. *Schematic arrangement for heat exchange measuring.*

General plan of work

- Fabrication of Ni, Fe, Co templates with different morphologies.
- CNF and CNT growth on these template areas and their mechanical stability evaluation. CNF bundles of a total diameter of 10-50 □m are required for the flow sensor.and a length of about 1 mm x 1 mm with a fibre height up to 0.1 mm. A large part of the research will be devoted to investigation of growth conditions and Ni, Fe, Co template morpfologies producing the required structures.
- Evaluation of morphology, flow resistance and heat exchange (Fig. 1).
- Experiments on CNF bundles in flow velocity fields.

References

[1]. Fahong Li, Leon Lefferts,Theo H. van der Meer, 6th World Conference on Experimental Heat Transfer, Fluid Mechanics, and Thermodynamics April 17-21, 2005, Matsushima, Miyagi, Japan.

[2]. M. Dijkstra, J.J. van Baar, R.J. Wiegerink, T.S.J. Lammerink, J.H. de Boer, G.J.M. Krijnen, *J. Micromech. Microeng.*, 15, pp. S132-S138, 2005.

Catalytic hydrothermal generation of hydrogen from aqueous biomass: integration with a crude oil refinery

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Aim of the Project

The general aim of this project is to generate hydrogen from aqueous waste streams containing organic compounds. A very interesting application could be hydrogen production from the aqueous fraction of the pyrolysis product. This hydrogen can be further used to upgrade the bio-fuel made from the pyrolysis oil.

Introduction:

1) oxygenate + $H_2O \rightarrow CO + H_2$

2) $CO + H_2O \rightarrow CO_2 + H_2$

3) $CO + 3H_2 \rightarrow CH_4 + H_2O$

In this study, catalysts will be developed and optimised for aqueous phase reforming of sugar (model compound) to hydrogen. Operating conditions for aqueous phase reforming are determind to be 175-250°C at elevated pressures (up to 50 bar).

Sugar can be converted under these conditions to carbon monoxide and hydrogen (1). Hydrogen yields can be further optimised by the water gas shift reaction (2). Methane formation is also favored under these condition and should be surpressed to optimise hydrogen yields (3).

Preliminary approach:

Catalysts for aqueous phase reforming should posses the following characteristics.

- Active for C-C bond Breaking
- Active for C-H bond Breaking
- C-O bond breaking should be avoided
- WGS active
- Stable under operating conditions
- Cheap

Platinum and other noble metals are known for their activity in hydrogen production from reforming organic compounds. Noble metals are however expensive and should therefore be avoided.

Nickel and Ruthenium are also known to be active for reforming of organic compounds, although less selective towards hydrogen compared to noble metals. The water gas shift reaction is thought to be the rate determining step on Ni an Ru based catalyst in aqueous phase reforming reactions. Deposition of Ru and Ni on a reducible (wgs active) support might increase the overall reforming activity. Also addition of water gas shift active metals (Cu) might be an interesting investigation.

The following catalysts will be tested first (based on the argumentation above) and compared to the benchmark catalyst $3\%Pt/Al_2O_3$:

- $3\%Ru/TiO_2$
- $3\%Ru\text{-}1\%Cu/TiO_2$
- $3\%Ru/Al_2O_3$
- $3\%Ru\text{-}1\%Cu/Al_2O_3$
- $3\%Ni/TiO_2$
- $3\%Ni\text{-}1\%Cu/TiO_2$
- $3\%Ni\text{-}1\%Cu/Al2O_3$

Acknowledgement:
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XRF in catalysis

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OSPT theme : Process Intensification

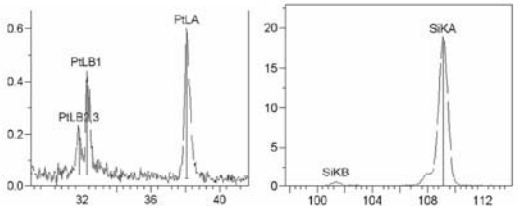
XRF is a powerful technique to investigate the composition of an unknown sample. This can

be done qualitatively as well as quantitatively. All elements heavier than Neon can be detected.
A qualitative spectrum is measured in about half an hour. Of course the total time of the analysis also depends on the sample preparation. Most samples do not need such a time-consuming preparation. Which means that very quickly one can have an idea about the elements present in a certain sample. Samples can be powdered, liquid or solid.

Quantitative measurements are based on measuring standards of known composition together with the unknown. A lot of different standards are available which makes it possible to measure all kinds of samples. The accuracy depends highly on the sample-preparation, the amount of sample and the concentration of the elements to be measured.

If a sufficient amount of sample is available and a full calibration is carried out a relative error in the analysis of 1 % can be obtained. For low concentrations and small amounts of sample this error will be larger.
With XRF it is also possible to investigate the thickness of thin films and its composition. Also multi-layers can be analysed.

In catalysis XRF is often used to analyse the concentration of noble elements. The concentration mostly is low, ca. 0.1 – 0.5 wt %. Calculations are based on the fundamental parameter (FP) method. This software allows the use of standards that are far from the



Pt in SiO_2, 146 mg pellet 13 mm. Result: 0.44 % Pt (CSE 0.2 %)

concentration of the unknown. In this example it means that pure Pt metal can be used as a standard. Such an analysis can be done in a very short time.

Constrains, iteration schemes and convergence criteria for concentrations in X-ray fluorescence spectrometry with the use of fundamental parameter methods;
M. Bos, J.A.M. Vrielink.
Analytica Chimica Acta 373 (1998) 291-302.

Non-destructive analysis of small irregularly shaped homogeneous samples by X-ray fluorescence spectrometry;
M. Bos, J.A.M. Vrielink, W.E. van der Linden.
Analytica Chimica Acta 412 (2000) 203-211.

Determination of diffusion profiles of silver ions in soda-lime-silica glass by X-ray fluorescence spectrometry;
M. Bos, B.A. Boukamp, J.A.M. Vrielink.
Analytica Chimica Acta 459 (2002) 305-311.

The influence of scattering processes in quantitative X-ray fluorescence analysis;
M. Bos, J.A.M. Vrielink.
Analytica Chimica Acta 545 (2005) 92-98.

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Thermo-Chemical Conversion of Biomass

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General introduction

Development of fundamental knowledge with respect to novel biomass conversion and CO_2 removal processes and the processing / upgrading of primary biomass derived products to commercial end products like transportation fuels, chemicals and power. The theoretical and experimental activities are based on the integrated utilization of process engineering, separation technology, thermodynamics and catalysis. A strong interaction with the business community and the government on basis of a global drive towards sustainable technology gives direction to all activities.

Fast pyrolysis of biomass
Hot gas vapor filtration

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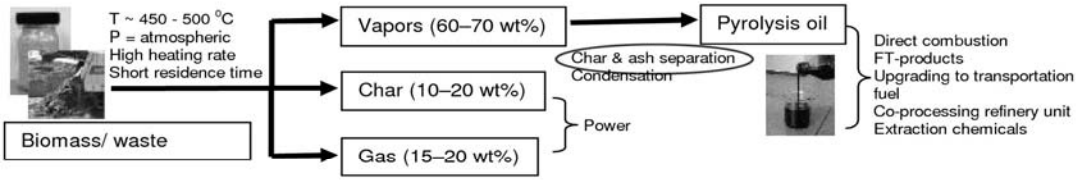
OSPT theme	: Energy conversion processes		
Supported by	: EU	**Period**	: Sept. 2006 – Sept. 2010



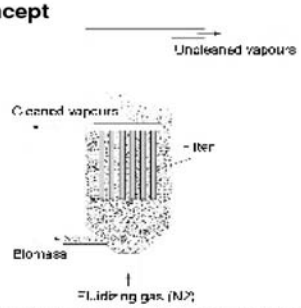
Introduction

Fast pyrolysis is a technology for the conversion of a bulky solid biomass into a liquid with an energy density half of that of fossil oil.

Why char and ash separation?

- It makes pyrolysis oil unsuitable for direct combustion in oil/gas turbine operations.
- It catalyzes secondary cracking in the vapor phase thereby lowering the pyrolysis oil yield.
- The instability of oil during storage can be positively related to the content.
- The requirements on the catalysts used for upgrading pyrolysis oil with respect to poisoning and de-activation will be less severe.

Novel concept

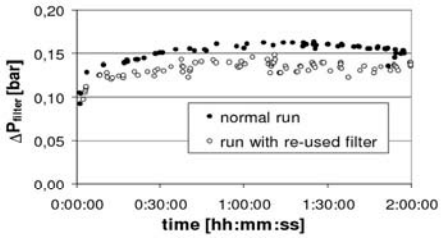


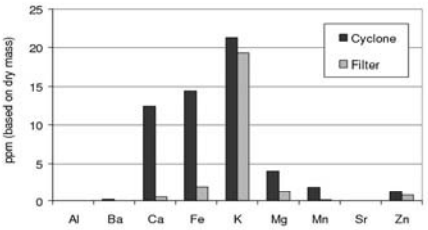
- Char is filtered from the vapors before condensation
- The filters are cleaned due to the sourcing action of the bed preventing an increase in pressure drop across the filter
- Short vapor residence time resulting in higher oil yields by preventing secondary cracking reactions

Set-up

A 1 kg/hr continuous fast pyrolysis pilot plant is designed and constructed.

Results





Conclusion

Operability

- Good performance during operation time

Pyrolysis oil yield and properties

- Lower alkali/alkaline metal, ash and char content for filtered oil
- In situ filtering does not decrease oil yield
- Lower molecular weight for filtered oil
- Even ash/char free pyrolysis oil is not stable during storage

Acknowledgement

This research is part of the BIOCOUP project (Co-processing of upgraded bio-liquids in standard refinery units) within the 6th Framework Program of the European Union. (Contract Number: 518312)

SUPERCRITICAL WATER GASIFICATION OF BIOMASS

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OSPT theme	:	**Research school**	: (OSPT)
Supported by	: TNO,SenterNovem	**Period**	: Nov 2007 – Nov 2011

Introduction

In supercritical water (SCW; T>374°C, P>220 bar) biomass gets rapidly decomposed by hydrolysis and cleavage and produces high energy value product gases. The main product gases of SCW gasification of biomass are H_2, CO and CH_4 and CO_2. The selectivity towards these can be attained by optimizing the operating conditions (T, P, τ, Conc.) and by the usage of proper catalysts. The technological challenges for large scale implementation are related to the introduction of biomass at high pressure, materials of construction, fouling due to coke/tar formation and precipitation of salts/ash present in the biomass.

Objectives

- To study the chemistry aspects (like reaction pathways, kinetics, gasification yields) for SCW gasification of biomass model compounds and *real* biomass
- To investigate the catalytic and non-catalytic SCWG of biomass (to reduce temperature of process and to reduce char formation)

Experimental

Continuous flow tubular reactor:

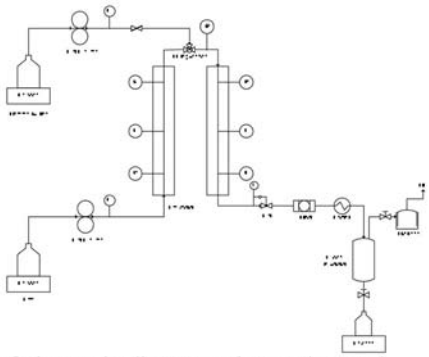

Fig.1: Schematic diagram of experimental set-up

Results

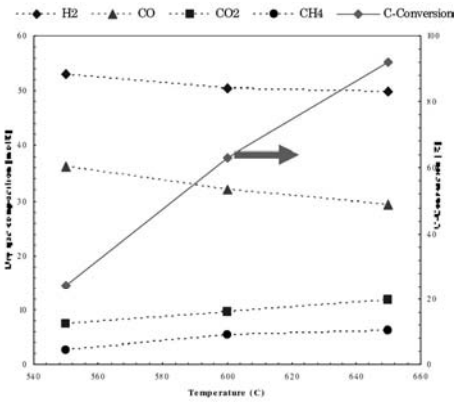

Fig.2: Effect of temperature on glycerol (10 wt %) gasification in hot compressed water.

Increased conversions at higher temperatures

Key words: Supercritical water, gasification, biomass model compounds

Amino acid salts as potential solvents for CO_2 capture

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Supported by	: CATO	**Period**	: March 2005 - March 2010

Introduction

To solve the problem of chemical absorption into a suspension is important for the development of processes such as the removal of H_2S and NO_x. Recently, the reactive crystallization for the removal of CO_2 from flue gases has drawn attention. This novel gas separation technology combines the use of aqueous amino acid salt solutions with benefits of the solid formation in the absorption systems.
Due to the novel character of these three-phase CO_2 absorption systems, much is still unclear on for example the character of the precipitate itself, on window of operation for both precipitating and non-precipitating systems or absorption capacities.

State of affairs

First, chemical compositions of precipitating solids were investigated, which is important for example form the slurry handling point of view as well as for mechanistic considerations.
The precipitates formed upon a reactive absorption of CO_2 into aqueous solutions of the potassium, sodium and lithium salts of a series of amino acids were identified using CHN analysis, AAS, XRD, ^{13}C and ^{1}H NMR. The precipitating solid was found to be *an amino acid (salt)*, a *bicarbonate* or *a mixture of these compounds*. Simple qualitative correlations between chemical composition of the solvent and the solids formed were derived.

Second, a window of operation for the precipitating and non-precipitating CO_2 absorption systems has been investigated using specially design screening set-up. The operational window is determined by varying the operating conditions of the absorption process, like absorption temperature, CO_2 partial pressure, the composition and concentration of the amino acid salt. Experimental investigation is done for absorption temperatures in the range of 20-60°C and CO_2 partial pressures relevant to the flue gases conditions.

Further studies

Absorption characteristics of a few selected amino acid salts will be investigated using the continuously operated stirred cell (Figure 1). Of a primary interest will be to determine equilibrium solubilities of CO_2 in amino acid salts and determine how the precipitate formation influences absorption capacities of these novel chemical solvents.

Figure 1: The equilibrium cell for CO_2 solubilities and induction periods determination: thermostated glass reactor, IR CO_2 gas detector, pH electrode, conductivity probe, temperature and pressure indicators, mass flow controllers.

Acknowledgement

This research is carried out within the framework of the CATO programme. It is financially supported by the Dutch Ministry of Economic Affairs (EZ) and the consortium partners. (www.co2-cato.nl)

Fuels from Algae

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Introduction

Photosynthetic organisms include plants, algae and some photosynthetic bacteria.
Photosynthesis is an important biochemical process in which the above listed organisms convert the energy of sunlight to chemical energy. This research is focused on photosynthetic organisms that grow in aquatic media such as microalgae as a potential alternative for fuel applications.
Algae can be considered as a suitable candidate for biological carbon dioxide fixation (via photosynthesis) and liquid fuel producer as well as other remarkable advantages such as its high production rate. Algal biomass contains three main components: carbohydrates, protein and lipids such as triglycerides which are considered a suitable source of renewable diesel.

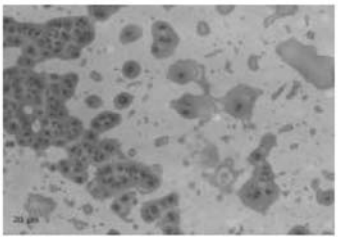

Figure 1. Optical Microscope image of algae feesdstock

For all of these reasons algae can be considered as second generation biomass feedstock with a highly outlook in terms of energy requirements.

Algae Biorefinery concept

The proposed algae biorefinery concept has the main purpose of the possibility of producing biofuels at large scale from industrially grown algae.

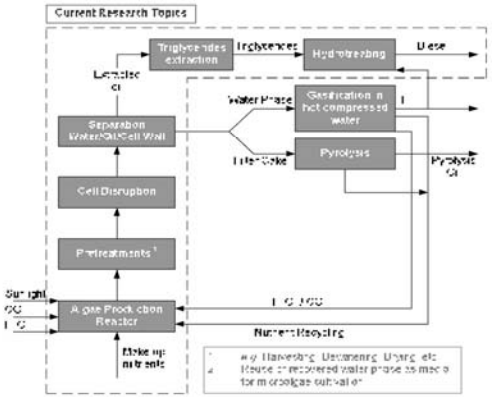

Figure 2. Proposed Algae biorefinery scheme

Research topics

Currently, microalgae culture for the production of lipids has become a popular topic in view of the multiple secondary uses of this group of naturally occurring organic compounds (e.g. the use of fatty acids in the human nutrition, the treatment of triglycerides to obtain biodiesel, etc.). A potential way to recover these functional lipid components consist of an oil (which contains these compounds) extraction from algae feedstock. Therefore, the starting point of this research has been to study of a separation/extraction method of water/oil/cell wall. Other topics of this research are:

- Design of a suitable reactor concept for algae production at laboratory scale
- Separation/extraction of water/oil/cell wall
- Use of standard techniques for the analysis of the obtained oil
- Recovering/treatment of the algae triglycerides to produce "green diesel"

Acknowledgement
This project is financially supported by IMPACT

Pyrolysis oil Upgrading

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Period : May 2006 – May 2010

Introduction

The European roadmap for sustainability states that in 2020, 20% of the energy produced in the European Union will have to come from renewable sources and 10% of the transportation fuel should come from bio-fuels. One of the options to introduce second generation bio-fuels in the market is the co-processing of pyrolysis oil, or products derived from it, in existing refinery units. However, the direct introduction of pyrolysis oil in standard refineries is not possible due to its high water (20-35 wt.%) and oxygen (approx. 50 wt.% in wet basis) content, which also results in a low energy density. An upgrading step is necessary.

Objective

The aim of this project is to study the upgrading of pyrolysis oil in order to produce an oil that can be co-processed in conventional petroleum refineries.

High Pressure Thermal Treatment

One of the possible upgrading routes is the high pressure thermal treatment (HPTT) of pyrolysis oil. It is a cheap process (neither hydrogen nor catalyst are required) compared to hydrodeoxygenation or catalytic cracking.

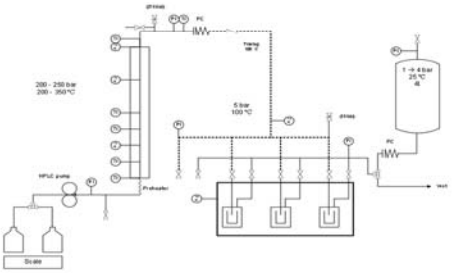

Figure 1: Experimental set-up for the HPTT process

Experimental set-up and results

A continuous set-up (Figure 1) was built with aim of studying the HPTT of pyrolysis oil with a fully controllable temperature profile along the reactor ($T_{reaction}$ +/- 5 ºC) and to obtain good mass balance closure (for all reported experiments: 96-101 wt.%).

During the process and due to the reduction in oxygen and water content, the energy content (higher heating value, HHV) of the product oil increased after HPTT (Figure 2). However, an increase in molecular weight and viscosity was also observed (Figure 3).

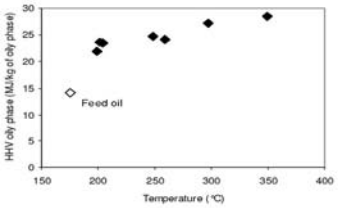

Figure 2. Higher heating value of HPTT oils processed at different temperatures (P = 200 bar, τ = 3.2 min).

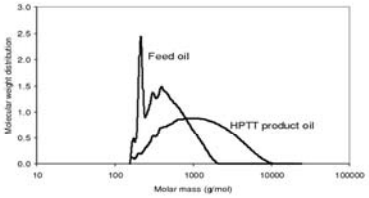

Figure 3. Molecular weight distribution of feed pyrolysis oil and HPTT oil at 300 ºC (P = 200 bar, τ = 3.2 min).

Acknowledgement

This research is part of the BIOCOUP project (Co-processing of upgraded bio-liquids in standard refinery units) within the 6th Framework Program of the European Union (Contract Number: 518312) and the CORAF project of SenterNovem.

Development of Novel Solvents for CO_2 Absorption

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OSPT Theme	: Separation Processes	**Research School**	: OSPT
Supported by	: CATO; www.co2-cato.nl	**Period**	: March 2005 – March 2010

Introduction

CO_2 separation by absorption in solvents such as MEA (monoethanolamine) is technologically viable option for capturing CO_2 from flue gases. A major operational cost of this process is the solvent regeneration. Additional problems, such as degradation, precipitation, corrosion, foaming, etc have to be taken into account. Therefore, new solvent have to be developed, for which amine based solvents were chosen as starting point. CO_2 reacts with amines according to:

$$2RNH_2 + CO_2 \rightleftarrows \underset{Carbamate}{RNHCOO^-} + NH_2$$

$$RNHCOO^- + H_2O \rightleftarrows RNH_2 + \underset{Bicarbonate}{HCO_3^-}$$

$$HCO_3^- \rightleftarrows \underset{Carbonate}{CO_3^{2-}} + H^+$$

$$RNH_3^+ \rightleftarrows RNH_2 + H^+$$

$$H_2O \rightleftarrows H^+ + OH^-$$

Project Scope

In this PhD project novel solvents for the absorption of CO_2, which have the following key properties, will be developed.

- High CO_2 capacity
- Lower regeneration energy
- Less solvent degradation
- Less corrosive

Strategy

For the development of novel absorbent following approach will be used.

- Determine the relationship between molecular structure-solvent properties
- Synthesis and characterization of new solvent
- Determine CO_2 absorption properties

Results

The structure and activity relationships for various amine based absorbents were investigated by performing screening experiments for absorption and desorption of CO_2. Results have shown the clear effect of structural changes in the performance of absorbents for CO_2 absorption and desorption. Many absorbents have shown high desorption capacity at lower temperature (80 °C). That leads to an effective decrease in the energy consumption for the regeneration unit in CO_2 capture process. Absorbents have also shown the high initial desorption rate in desorption screening experiments. Hence, lower solvent circulation rate can be achieved with many absorbents that will reduce the cost of solvent consumption in CO_2 capture process.

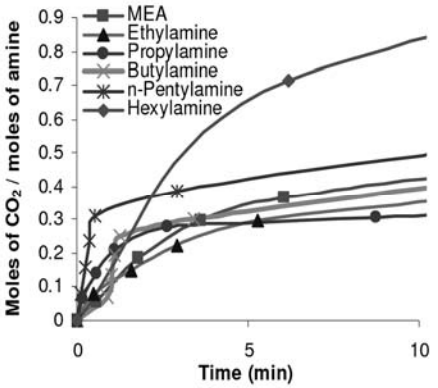


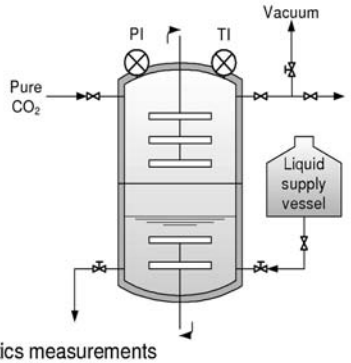
Figure 1, Influence of the chain length in alkylamine for the absorption of CO_2 in aq. absorbents.

Results from absorption screening showed that an increase in the chain length in alkylamines results in a decrease in the initial absorption rate, whereas the absorption capacity increased in most alkylamine see Figure 1.

Future Work

The sorption characteristics of the newly developed solvents will be determined in more detail:

Solubility of the selected absorbents will be determined over the CO_2 partial pressure in following experiment set-up.



Kinetics measurements
Degradation tests
Corrosion tests

Acknowledgement

This work is a part of research programme CATO (CO_2 Capture Transport and Storage in The Netherlands) project.

Fast pyrolysis of biomass

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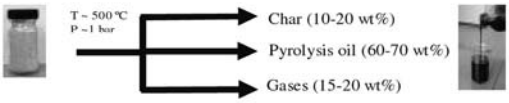
OSPT theme	: Energy Conversion Processes	**Research school**	: OSPT
		Period	: 2007-2009

Introduction:

To replace fossil fuels in the production of power, heat, transportation fuels, and chemicals, various biomass conversion routes are possible. One of the biomass conversion technologies is fast pyrolysis. The process offers the advantage of a liquid product that can be easily stored and transported

Fast pyrolysis is a conversion technique in which biomass is transformed to liquid (main product), char, and gasses. Essential in this method is a rapid heating of the biomass particles to around 500 °C in the absence of oxygen and a short (<2 sec.) residence time of the vapors.



Next to the quantity of pyrolysis oil also the quality is a very important parameter. Probably all applications require different specifications with respect to the pyrolysis oil quality. Water is the most abundant compound in pyrolysis oil. Generally, less water is beneficial for the energy density, transportation cost, stability and acidity.

Pyrolysis experiments are performed in a continuous bench scale pyrolysis plant (intake = 1 kilogram of biomass per our) equipped with a fluidized bed reactor.

Objective:

Evaluate several options, available within the fast pyrolysis process, to improve the quality of fast pyrolysis oil.

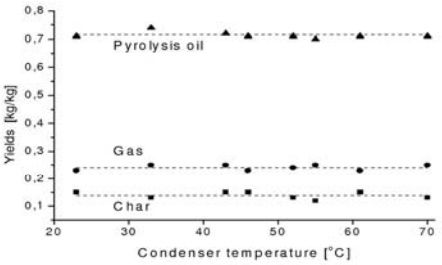


Figure 1: *Yields of char, gas and pyrolysis oil of 9 identical experiments with respect to the reactor conditions, but different temperatures of the condenser. Conditions: $T_{reactor}$ = 480 °C, $T_{cyclones}$ = 500 °C, t_{hot} = 1.32 s, $t_{reactor}$ = 0.78 s, moisture content feed = 12 wt%. The dashed lines represent the average value of the 9 experiments.*

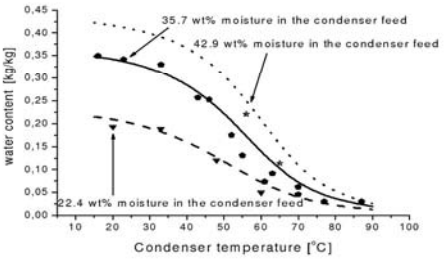


Figure 2: *Water content of the pyrolysis oil product as function of the condenser temperature. Experimental results (presented by points) are compared with flash condensation model predictions (presented by lines). Conditions: $T_{reactor}$ = 480 °C, $T_{cyclones}$ = 500 °C. Condenser temperature varied between 15-90 °C.*

Research topics:

Improving the pyrolysis oil quality within the pyrolysis process by varying process parameters:

- Reactor and vapour phase; char hold-up, temperature, vapor residence time.
- Biomass particle size
- Condensation temperatures

Research on fluidized bed reactor scale-up

Self-Gasification of Biomass to SNG

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OSPT theme	: Energy Conversion Processes	**Research school**	: OSPT
Supported by	: Senter Novem	**Period**	: Sept 2007 – Sept 2011

Introduction

Self-gasification of biomass offers an alternative and energy-efficient process for bio-methane production. *Self-gasification* is:

Autothermal, because of the coupling of the gasification reaction and the methanation reaction in a *single* reactor. No O_2 addition is needed.

Autocatalytic, because the ash/salts within the biomass can act as catalysts for the aforementioned reactions.

Experimental Technique

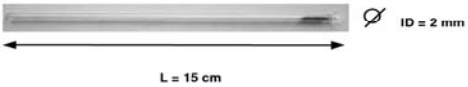

Figure 1: Capillary micro-reactor.

Experiments are realized with the help of batch capillary micro-reactors made of quartz (V_r=0,5 ml). The technique is fast, cheap and safe. The reaction can be inspected visually and the quartz material provides a catalytically neutral reaction environment. It can withstand up to 600 bar and 900 °C.

Results

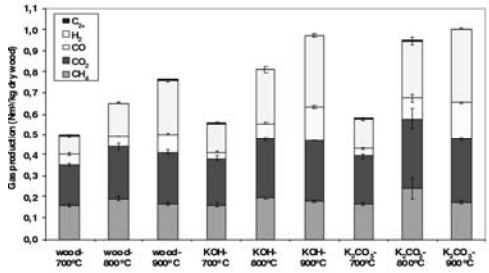

Figure 2: Gas production vs. temperature and catalyst type. S/C (mol) = 1.5, Reaction time= 15 min, catalyst loading =10.9 wt% on dry wood, P=121 bar.

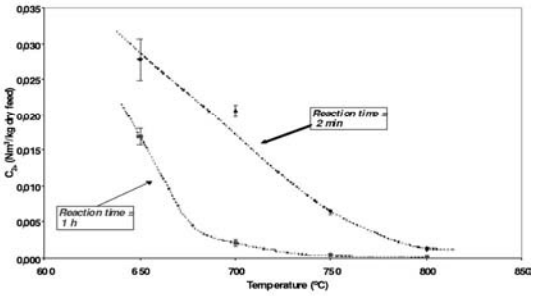

Figure 3: Production of C_{2+} hydrocarbons vs. temperature and reaction time. S/C (mol) = 1.5, P=60 bar. Wood sample.

Gas production increases with temperature. C_{2+} hydrocarbons decrease with temperature and reaction time. The impregnated KOH and K_2CO_3 increase gas production for T>700 °C.

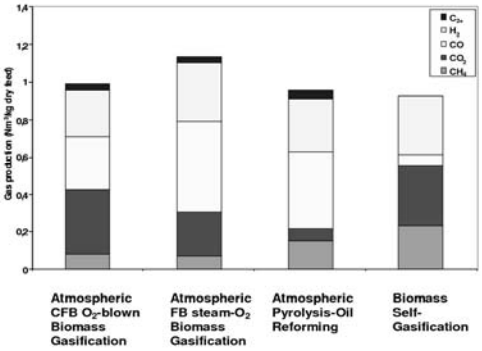

Figure 4: Comparison of self-gasification with conventional gasification technologies.

Self-Gasification of biomass produces higher amount of CH_4 and no C_{2+} compared to conventional gasification technologies and shows very good potential for future CH_4 applications.

SenterNovem
Agentschap voor duurzaamheid en innovatie

CATALYTIC REFORMING OF PYROLYSIS OIL

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OSPT theme	: Process technology	**Research school**	: OSPT
Supported by	: SenterNovem	**Period**	: Jan 2008 – Jan 2011

Introduction

Pyrolysis oil is obtained by flash pyrolysis of biomass around 500 ºC, where tar vapors are condensed to liquid (~ 70 wt% of original biomass). By gasifying the bio-oil with steam, syn-gas ($CO+H_2$) is produced. A two bed concept (1st step = atomization, 2nd step = catalytic reforming of vapors/gases), has resulted in methane free syn-gas[1]. In this PhD project the atomization step is studied in detail and operation under pressure is investigated.

Pyrolysis oil atomization

The objective is to study the effects of droplet size, temperature, residence time, etc., on the product distribution of pyrolysis oil atomization. This is investigated in the set up shown in the figure 1. Products are lumped into the classes: char, vapors and gases.

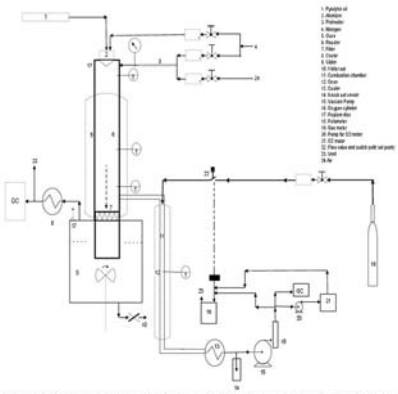

Figure 1 Schematic diagram of set up for bio-oil atomization/vapourisation

Keywords : Pyrolysis oill, atomization, syn-gas

Results

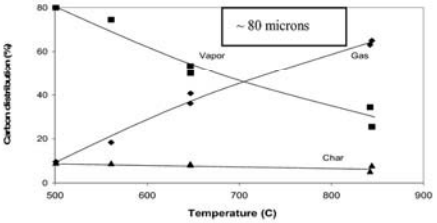

Figure 2 Product yields of pyrolysis oi atomization

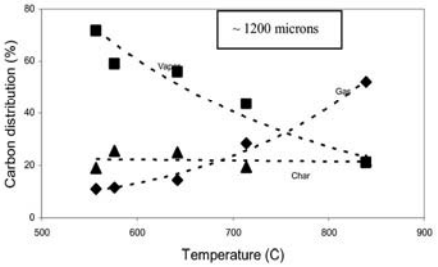

Figure 3 Product yields of pyrolysis oi atomization

Conclusions

- Bigger droplets give more char.
- Amount of char formed is not/slightly depend on the temperature.
- Cracking of vapors to gases is very sensitive to the temperature.

Reference

1. Catalytic and Non catalytic Gasification of pyrolysis oil, *Guus van Rossum, S.R.A.Kersten & W.P.M. van Swaaij. Ind. Eng. Chem. Res. 2007, 46*

Faculty of Engineering Technology

Research Group Engineering of Fibrous Smart Materials

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The research group Engineering of Fibrous Smart Materials

General
The main activities of the research group Engineering Fibrous Smart Materials are education and research in the area of functionalized fibrous materials. Education is not only given via courses for regular students at the University of Twente, but the research group also participates in the European Masters program E-TEAM (European Textile Engineering Advanced Masters). Various possibilities and research projects are offered for M.Sc. and Ph.D.-students.

The group is financially supported by the Dutch textile and related industries organized in the foundation for EFSM. Therefore the research program is directed towards the long time requirements and expectations of that industry. The close collaboration with the industry and TNO Industry resulted in a strategic alliance, according to the principles of 3rd generation R&D. This partnership allows the successful introduction of new and innovative technologies into industries. The scientific program acts as a stimulant for the industry and can improve existing and introduce new more efficient and environmentally fully acceptable processes and advanced materials with special properties and functionalities. The research group participates in the OSPT, IMPACT and the AUTEX (Association of Universities in Textiles in Europe).

Research
The group stands for product driven fibre surface engineering and the research projects are related to this overall mission. The following projects are currently running:

-functionalization of fibres by responsive hydrogels
-functionalization of fibres by slow release systems using ink jet technology
-the development of a sustainable pre-treatment process for grey cotton
-locally functionalized fibrous materials by ink jet technology
-the development of a low temperature laundry process using bleach catalysts
-the application of ultrasound in the dry cleaning process using dense carbon dioxide

The group has advanced research facilities such as: a climatic chamber, an auto-porosimeter, a HPLC with PDA and RI detector, a tensile strength tester, equipment to measure the dynamic surface tension and high resolution ADSA equipment to measure the dynamic wetting characteristics apart from an inverted optical microscope, UV spectrophotometer, X-rite spectra eye, and ultrasound equipment.

Incorporation of thermo and pH-sensitive microgel onto nitrogen plasma activated cotton surface

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OSPT theme : Products and Processes
Supported by : EU (6th FP)

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Research school
Period : Sept. 2007 – Sept. 2009

Introduction:
The topics of Marie Curie Excellence Grant project ADVANBIOTEX are textile materials with new **advanced functionalities** and **environmental responsiveness**. The project explores the potential to modify the surface of textile fibres by coating existing textile materials (mostly cellulose based) with a thin layer of **thermo and pH-sensitive** microgel based on **biocompatible polymers**.

Scope of the project:
The focus of the project is on preparation of poly(N-isopropylacrylamide)/chitosan microgel (PN/CS) and integrating it onto nitrogen plasma activated cotton fabric with sufficient durability, while still retaining the effectiveness of the surface modifying system.

Results:

(1) PN/CS microgel responsiveness
Chitosan is a typical pH-sensitive polymer which responds to changes in the pH of the surrounding medium by protonation /deprotonation that imparts charges on its amino groups. The pH-induced phase transition results in varying dimensions (swelling and deswelling) of the hydrogel (Fig.1).

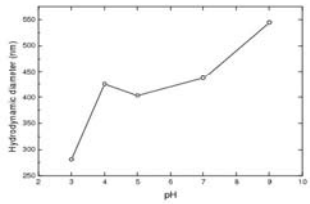

Fig.1: Hydrodynamic diameter of PN/CS microparticles in aqueous suspension (1.1 10^{-1} g/L) at 25°C as a function of pH.

Poly(N-isopropylacrylamide) is synthetic polymer, which creates thermosensitive gel when crosslinked. When heated above 34 °C the gel shrinks (Fig.2).

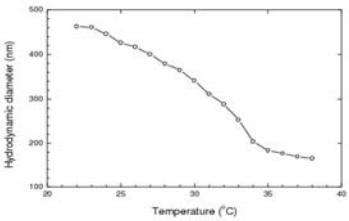

Fig.1: Hydrodynamic diameter of PN/CS microgel in aqueous suspension ($2.3 \cdot 10^{-1}$ g/L, NaCl 1 mM, pH 7.3) as a function of temperature.

(2) Incorporation of PN/CS microgel to plasma activated textile material
Plasma treatment produces chemically active species such as radicals, free electrons and ions, which generate free radicals on the cotton fabric surface. After plasma treatment, activated cotton was immersed into a microgel suspension. PN/CS particles are clearly visible at the cotton surface (Fig.3). This result shows that this method is an efficient and environmentally acceptable pretreatment for biopolymer cotton surface incorporation.

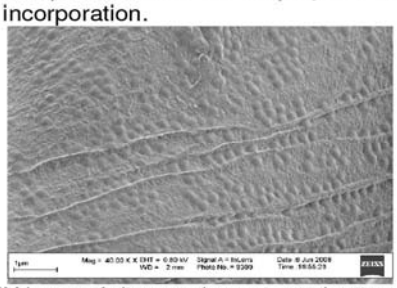

Fig.3: SEM image of nitrogen plasma treated cotton surface with incorporated PN/CS microgel.

Acknowledgement
Financial support for this work was provided by Marie Curie Excellence Grant (EXT) project ADVANBIOTEX (MEXT-CT-2006-042641) (FP6).

Fast-responding microgels from Chitosan/NIPAAm/Acrylic acid

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Period : June 2007 – June 2011

Introduction

Aqueous microgels are extensively used in production technologies to modify the rheological properties of the materials and to facilitate end uses such as substance encapsulation. Stimuli-responsive microgels are drawing even more attention because of their ability to tune their properties according to the physico-chemical conditions (e.g. temperature, pH) of their environment. The preparation of responsive microgels based on chitosan (CS), a natural polysaccharide, N-isopropylacrylamide (NIPAAm) and acrylic acid (AA) is reported here.

Scope

This work aims to the preparation of a fast-responding microgel based on the pH-sensitive CS and the temperature-sensitive copolymer P(NIPAAm-AA). The microgel's development is the first step for the surface modification of polyamide fabric for sportswear applications. It is expected that via fast swelling/deswelling cycles of the microgel (owing to temperature and pH changes when in contact with the skin and sweat), the modified fabric will exhibit better moisture management properties compared to the reference polyamide.

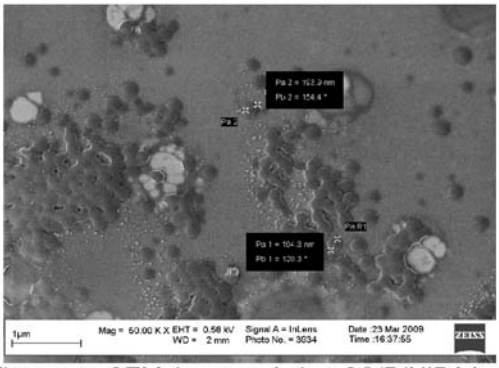

Figure 1: SEM image of the CS/P(NIPAAm-AA) microparticles air-dried on a silicon wafer.

Results

Scanning Electron Microscopy (SEM) was used for the structural characterization of the microgel. As seen in Figure 1, the produced micro-particles are of uniform shape and size and about 200 nm in dry state.

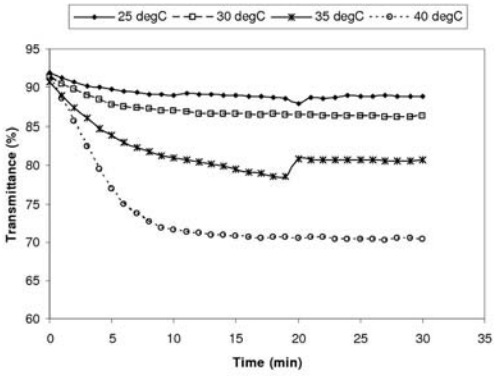

Figure 2: Kinetics of the transmittance changes of the CS/P(NIPAAm-AA) microgel at different temperatures.

To test their thermo-responsiveness – for using it later at certain body temperatures observed during athletic activitites – microgel samples were monitored at 480 nm and at various temperatures. Figure 2 shows that above 30°C the transmittance values (T%) drop significantly with time due to PNIPAAm's phase transition around 32°C, which renders the micro-particles more hydrophobic and opaque. At 35°C, T% stabilizes after 20 min whereas at 40°C half the time (i.e. 10 min) is needed for stabilization. This data confirms the fast response rate of the prepared microgel.

Acknowledgement

Financial support is provided by the project ADVANBIOTEX, a Marie Curie Excellence Grant (MEXT-CT-2006-042641) of the EU 6th Framework Programme.

Upgrading from lab scale experiment to industrial pretreatment of cotton via pilot scale experiments: a matter of shear.

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Supported by	: EFSM/Saxion/Tanatex	**Period**	: 2006 – August 2010

Introduction

We have developed a catalyst based pretreatment process for cotton on lab scale. The new process is expected to reduce water and energy consumption with 20% and reduce waste water production with 40%. The basis of the new process is the substitution of high concentration of harsh and non specific chemicals by enzymes for scouring and the use of MnTACN as catalyst for peroxide bleaching.

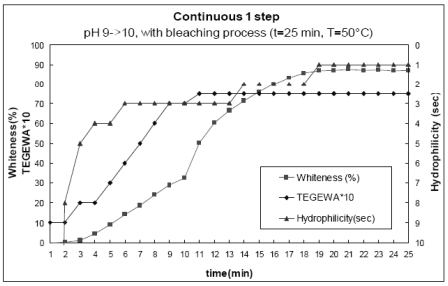

Fig. 1 One bath, continuous pretreatment, performance; 15 min, 50°C., lab scale

To upgrade from lab scale experiments to pilot scale or even industrial scale processing, it is necessary to research the chemical reaction and the process velocity due to mass transfer.

Process intensification with mechanical shear

Textiles consist of two different zones, one zone with small pores between the fibers (intra-yarn) and the other zone with larger pores between the yarns (inter-yarn). Based on this pore distribution in textiles we distinguish a stagnant core where the driving factor for mass transfer is molecular diffusion and the convective shell where convection is the driving force.

To evaluate the difference between lab, pilot and industrial scale, we study mass transfer of model dyed fabric. The release of Procion Rot PX-8Bfl33 from the fabric into the bulk as a function of stirring, squeezing, stretching and compressing was studied.

The release of colorant as a function of different mechanical shear from the dyed fabric to the bulk will be measured with the continuous flow cell UV-Vis photo-spectrometer and result can be modeled. The combination of chemical reaction and mass transfer velocity provides know how to predict the performance of the new industrial process with enzymes and MnTACN.

Challenges on the development path

The proven principle on lab scale will be upgraded to industrial scale via pilot scale. Harsh chemical pretreatment process will be replaced by ambient enzymatic continuous process based on mass transfer as a result of mechanical shear and exhaustion.

Collaboration with industry

Lab research has to lead to a new process developed and tested on industrial scale. Implementation of the new process is not only dependant on process conditions and output, but also on common interest in realization of the partner's goals.

Acknowledgement

This work is financially supported by Stichting EFSM, Saxion and Tanatex Chemicals.

Faculty of Science and Technology

Research Group

Membrane Science and Technology

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Activities of the group Membrane Science and Technology

The strategy of the membrane technology is the application of multiple disciplines to challenging fields of separation processes and mass transport control. These disciplines are:

Interface science
Focuses on modification and tailoring of surfaces and interfaces, concerning the chemical composition and morphological structure. Ongoing research spans from chemical modification to control protein adsorption to microstructuring of membranes.

Material science
The largest topic of research activities and traditionally the core of the research program. The scientific activities span from polymer synthesis and modification to polymer and membrane characterization methods.

Material processing
Covers techniques to shape membrane morphologies: casting flat-sheet membranes, spinning of hollow fibers, coating techniques for the formation of laminate composite membranes and mixed matrix membranes hosting specific separation functionality (by incorporation of particles such as zeolites, ion exchange and adsorptive particles).

Mass transport
Covers the analytical description of mass transport through membranes as well as permeate and feed side diffusional boundary layers in a variety of applications. Input to these modeling efforts stem from experimental equipment designed and constructed in-house.

Equipment design
Aims to produce small-scale and bench-scale membrane modules from the membranes designed in the previous disciplines. The modules can be applied for wide range of separation processes.

Process technology
Covers the investigation of how the newly developed membranes or commercially existing membranes can be used to perform reliably a desired separation task under realistic conditions. It concludes the research and development process with process flow sheet simulations and technical-economical evaluations.

The research program distinguishes four clusters based on membrane functionality:
•**Dense membranes** (gas separation and pervaporation).
•**Porous membranes** (microfiltration, ultrafiltration, nanofiltration and reverse osmosis).
•**Affinity membranes** (with specific separation function based on chemical recognition).
•**Ion exchanged based membranes** (electrodialysis, diffusion dialysis and energy conversion i.e. fuel cells)

Porous Ceramic Membrane Microreactors

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OSPT theme : Multiphase Reactors
Supported by : STW

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Period : May 2007 – May 2011

INTRODUCTION

Microreactors are suitable for exploring and performing highly exothermic and fast reactions. Due to the reduced length scales, enhanced mass and heat transfer is obtained. Use of ceramics as microreactor material provides optimal stability at high temperatures, pressures, and aggressive media.
We aim to integrate membrane functionality into microfluidic devices, economically fabricate new ceramic microreactors and explore new concepts for gas-liquid(-solid) reactions inside these reactors. The gas- liquid contacting for reaction purposes is achieved using membrane technology by permeating the gas reactant through a porous ceramic membrane, reaching the liquid reactant flowing in the microchannels (Figure 1). This would reduce the mass transfer limitations in the gas-liquid-solid reaction processes.

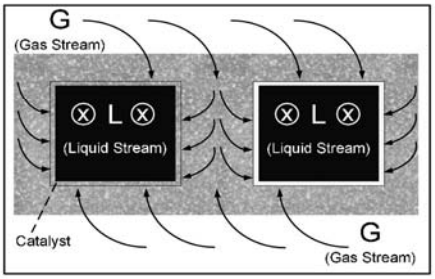

Figure 1: Novel gas / liquid contacting concept inside microreactors

DESCRIPTION

Microstructuring and fabrication of the ceramic microreactors are realized via simple replication and sintering processes. Also commercial ceramic hollow fibers are used as microreactor channels.
The channel surfaces are hydrophobized with a surface modification step. According to the final application also catalyst is immobilized on the microchannel walls.

RESULTS

Using the above described fabrication techniques we have fabricated multichannel and multilayer ceramic microfluidic devices and new geometries with good mechanical properties together with high porosity. Commercial ceramic hollow fibers with initially low catalytic surface area were coated with γ-Alumina as catalyst support (Figure 2). With the surface modification step we could prevent wetting of the originally hydrophilic porous membrane material by the liquid stream in order to achieve a stabilized gas-liquid interface.

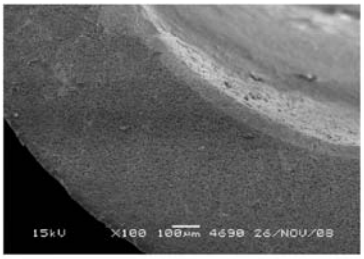

Figure 2: Inner surface of commercial hollow fiber, coated with γ-Alumina as catalyst support

Two model reaction systems for the proof of the new principle inside our ceramic membrane microreactors have been chosen: reactive absorption of carbon dioxide in water, hydrogenation of nitrite in water. Using the first system we have achieved a stabilized gas-liquid interface inside microchannels and proved our new contacting principle by mass transport characterization experiments. We have demonstrated good agreement between our finite element simulations and experimental data. With the latter reaction system we verified our catalyst immobilization techniques and in the preliminary experiments we have observed promising catalytic conversion.

ACKNOWLEDGEMENT

This project is financially supported by STW.

Dissolution of entrapped gases in polymer solutions

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Period : Oct 2005 – Oct 2009

INTRODUCTION

The main research focuses on exploring the potentials of Phase Separation Micro Fabrication (PSμF). This process entails the precipitation of a polymer from a solution that is in contact with a microstructured mold. When a mold consists of an array of wells, the replication of the features can be hindered due to entrapment of bubbles during casting (Figure 1)

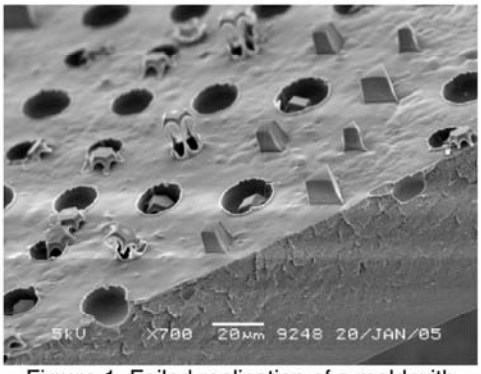

Figure 1. Failed replication of a mold with polygonal wells. The bubbles entrapped during casting are clearly seen after solidification.

DESCRIPTION

To study the evolution of the bubbles in time, a chip has been designed for inspection by means of optical microscopy (Figure 2). This chip possesses channels and a glass lid, so that the process can be followed in time. Including a modeling step, the shape and volume of the confined bubble could be calculated.
This system is being in use for studying the effect of channel shape, chosen gas and solution composition on the dissolution rate of the bubbles.

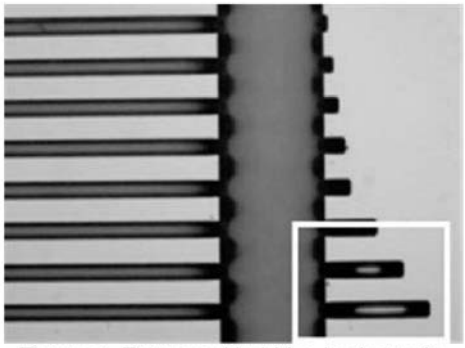

Figure 2. Entrapped bubbles in channels. The width of the horizontal channels is 15 μm.

RESULTS

This system has allowed us to quantify the dissolution process and study the effects of a number of variables. It has been seen that the addition of poly (methyl methachrylate) to the solvent (N-methylpyrrolidone) increases the dissolution rate for nitrogen. This effect was seen for different molecular weights of the polymer and increases with higher concentrations of polymer.
Different gases present different dissolution rates. Carbon dioxide proceeds about 800 times faster than nitrogen or oxygen, which are close to one another.
Channel dimensions can affect in varying ways as the interfacial area can increase or decrease while the internal pressure of the bubble can vary in the opposite way. The final effect is a matter of balance between these variables.

ACKNOWLEDGEMENT

This project is financially supported by MicroNed.

Gas-liquid membrane contactors for CO_2 separation

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Period : March 2006 – March 2010

Introduction

CO_2 is one of the major contributors to the greenhouse effect and capture and separation of CO_2 is necessary to reduce its emission. A membrane contactor (Figure 1) combines absorption and membrane technology.

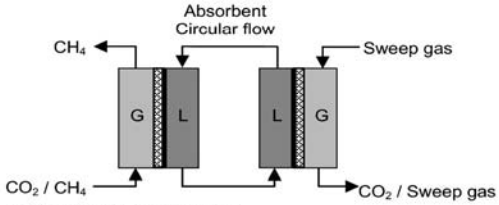

Figure 1: Membrane contactor.

A gas feed and an absorption liquid are brought into contact through a membrane and one of the feed components (CO_2) is selectively absorbed by the absorption liquid. The loaded liquid is circulated from the absorber to the desorber, in which desorption of CO_2 occurs.

Mono ethanol amine the traditional absorption liquid for CO_2 removal has high product yields and purities, but the disadvantage of this solution is its high liquid loss due to evaporation of the solvent. Amino acids have, next to high CO_2 capacity, the advantage that they can be made non-volatile by using their salt form (Figure 2), which makes them promising for CO_2 removal.

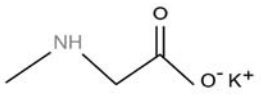

Figure 2: Potassium salt of sarcosine.

Experimental

A solution of mono ethanol amine (MEA), the traditional absorption liquid for CO_2 removal, and a solution of the potassium salt of sarcosine, a novel and promising amino acid salt solution, were used as absorption liquids in a membrane contactor for the separation of CO_2/CH_4 (20/80 vol.%).

Porous poly propylene (PP) hollow fiber membranes were used as absorber and desorber. The gas feed pressure was 1.2 bar. The effect of the temperature difference between absorption and desorption (ΔT = 0 – 35°C) was investigated, while keeping the absorber temperature constant at 29°C.

Results and Discussion

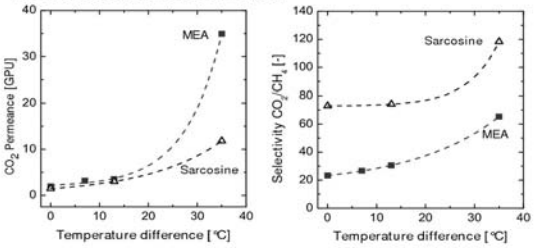

Figure 3: CO_2 Permeance and CO_2/CH_4 selectivity over temperature difference between absorption and desorption (T_{abs}=29°C).

Figure 3 shows the CO_2 permeance and the CO_2/CH_4 selectivity as a function of the temperature difference between absorber and desorber for the two different absorption liquids.

Especially at higher temperature difference MEA gives a higher CO_2 permeance compared to sarcosine, which is most likely caused by the higher CO_2 capacity of MEA compared to sarcosine. At the same time sarcosine has a significantly higher CO_2/CH_4 selectivity than MEA, due to the lower CH_4 permeance.

Even without a temperature difference between absorber and desorber, a CO_2/CH_4 selectivity of over 70 could be achieved, which makes sarcosine to a very promising solution.

Acknowledgement

This project is financially supported by NWO. This project is a collaboration with the TCCB (Thermo-Chemical Conversion of Biomass) group of the University of Twente.

Nanofiltration at extreme conditions

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Supported by	: Dutch Separation Technology Institute (DSTI)	Period	: August 2007 – August 2011

Introduction

The use of nanofiltration (NF) membranes under extreme conditions, more popularly known as Solvent Resistant Nanofiltration (SRNF), is a relatively new technology, which has recently attracted a lot of interest in the research world. Among other NF membranes, composite membranes offer an advantage of having a very thin selective layer on a porous support, thereby generating a high flux. Further, each layer can be optimized independently to obtain an optimal membrane performance. Cadotte [1] developed the Interfacial polymerization (IP) technique which has become a very popular and useful method for the manufacture of thin film composite (TFC) membranes, which we have decided to use in this project. In this process, a polymerization reaction occurs between two very reactive monomers at the interface of two immiscible solvents, on top of a suitable support (Figure 1).

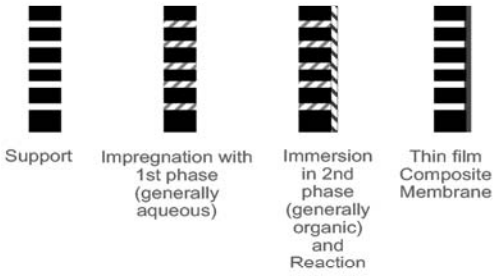

Figure 1: Formation of composite membranes

Aim of the Project

At present most commercial NF membranes are suitable for treatment of aqueous streams at pH levels between 2 and 10. However most potential applications in the chemical industry require separation processes at much more aggressive conditions.

Thus, our research is focused in developing SRNF membranes via IP technique encompassing:

- A Molecular weight cut off below 500 Da
- Stability in aggressive organic solvents
- Stability at high and low pH aq. solutions
- Stability in oxidative environments
- Substantial mechanical stability

Results and Discussion

Figure 2 shows a SEM image of a polyamide IP layer formed by the reaction of diamine with an acyl chloride, developed in our laboratory.

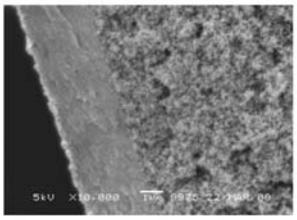

Figure 2:A 3µm IP layer on a solvent resistant support

As a first step, the developed membranes are tested under neutral conditions in order to optimize their molecular weight cut off and flux, by varying the fabrication conditions. In the second step the developed membranes are being analyzed at extreme pH conditions in order to evaluate their stability. The newly developed membranes are also being compared with the state of the art commercial membranes used in the industry today.

Acknowledgement

This is a Dutch Separation Technology Institute (DSTI) project

[1] Cadotte J.E., US patent 4277344 (1981)

Molecularly imprinted membranes for the removal of trace components

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Supported by	: DSTI	**Period**	: March 2008 – March 2012

Introduction

The removal of trace components from bulk streams is an important separation in the chemical industry. Distillation is by far the most frequently used. The relatively high energy consumption, high total costs of the separation and the limited stability of some organic compounds at elevated temperatures are important drivers to develop alternative separation technologies.

This project aims to lower the energy consumption associated with the removal of trace components or to add value to the product by removing trace components from aqueous and/or organic bulk streams using membrane technology.

Background

One of the challenging concepts is the field of molecular imprinted membranes (MIMs). These membranes have recognition functionality for the target molecule(s). Such 'smart' membranes have a molecular selectivity due to the use of templates to create well-defined and selective trans-membrane transport pathways.

MIMs are membranes that have functional groups, but that were processed or polymerized in the presence of a template molecule. By this means the membrane not only contains specific binding sites, but these binding sites are also ordered in a three dimensional structure making the membrane shape selective for the target molecule [1, 2].

The general method to make an imprint in a polymer is by polymerization of functional monomers and crosslinking of these monomers in the presence of the template molecule (the target molecule) (see Figure 1). A template molecule, functional monomer, crosslinker and solvent are mixed (1). During mixing complexes are formed between the template molecule and the functional monomer (2), these are stabilized by crosslinking the polymer (3). Extracting the template from the polymer results in an imprinted polymer with recognition functionality for the molecule (4).

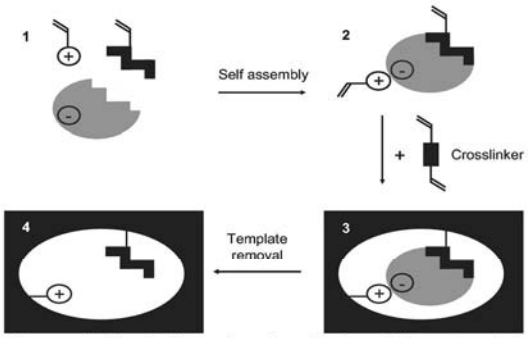

Figure 1: Illustration of molecular imprinting: 1, mixing of template and reactants; 2, self-assembling of template and reactants; 3, stabilization of template molecule; 4, extraction of template molecule.

Outlook

In this study we study the preparation of such MIMs for the specific separations and systematically investigate the relation between MIM properties and performance for trace removal applications.

Acknowledgement

This is a DSTI project.

References

[1] Piletski, S.A. et al. Journal of Membrane Science, 1999. 157 (2): p263-278

[2] Ulbricht, M. Journal of Chromatography B: Analytical Technologies in the Biomedical and Life Sciences, 2004. 804(1): p.113-125.

Porous Ceramic Membrane Microreactors: Principle, Design and Fabrication

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Introduction

Microreactors have submilimeter dimensions that provide high surface to volume ratio and also provide enhanced heat/mass transfer rates for desired reactions. Membrane microreactor suits industrially important chemical processes e.g. gas-liquid hydrogenation and immiscible liquid-liquid nitration. The development of fundamental models describing chemical, physical phenomena in such miniaturized reactors attracts considerable interest in recent years.

Objective

- To explore and examine new concepts for gas-liquid contacting inside porous ceramic membrane
- Economical fabrication of new porous membrane microreactors
- To benchmark gas-liquid contacting strategies for various microreactor designs

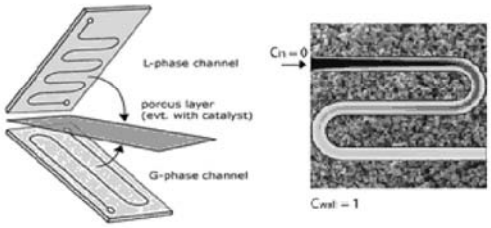

Figure 1: Porous microreactor concept

Experimental and Numerical Methods

Ceramics offer excellent thermal and mechanical stability particularly at extreme conditions i.e. high temperature and pressure. Commercially available alumina was used as a primary membrane material. Homogeneous suspension of ceramic solution was made using dispersant (PA), plasticizer (BBP), solvent (ethanol or butanol) and binder solution (PVB). Two pathways are to follow in fabrication of ceramic membrane microreactor: planer and hollow fiber geometry.

To aid in the design special emphasis will be given to flow behaviour inside porous structure. Hydrodynamics play a very important role in the microreactor design and operation. With known component properties, a good prediction with respect to mixing, reaction and heat generation can be obtained.

Results

The planer and hollow fiber porous membrane has been successfully fabricated using replication and dip coating methods respectively.

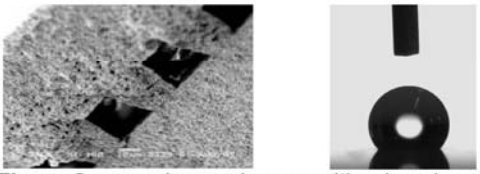

Figure 2: ceramic membranes with microchannel & surface modified membrane

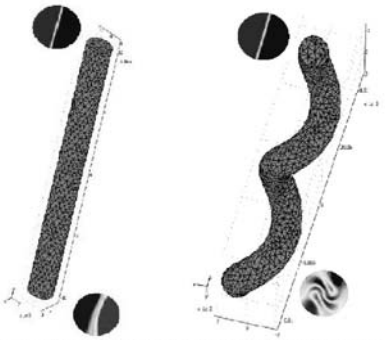

Figure 3: Mixing in straight & helical hollow fiber

The enhancement in mixing and mass transfer of the hollow fiber geometry has been predicted numerically. This phenomenon is observed due to secondary flow induced by curvature. This phenomenon is observed due to secondary flow induced by curvature.

Acknowledgement

This project is financially supported by STW.

Electrodialysis for the production of building blocks for chemicals from protein sources

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Introduction

The depletion of fossil feedstocks, increasing oil prices and ecological problems associated with CO_2 emissions urges the chemical industry to develop novel routes to produce building blocks for chemicals. In this work, we explore the potential of electrodialysis (ED) for the separation of amino acids obtained from cheap feedstocks, e.g., proteins from cereals and oilseeds to produce such building blocks.

Motivation

Conventional route: The conversion of crude oil products towards functionalized building blocks (Figure 1) needs primary products (e.g. ethylene), co-reagents (e.g. ammonia) and various process steps to introduce the required functionalities.

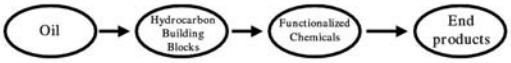
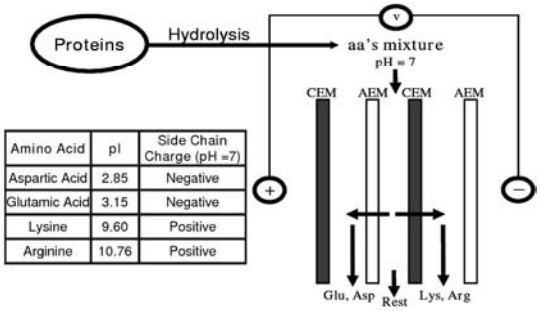


Figure 1: Conventional route for the production of functionalized chemicals.

Novel route: Cheap protein sources are hydrolyzed to a mixture of 20 amino acids, which often already possess the required functionalities. Electrodialysis is applied for the isolation of the different amino acids (Figure 2).

Electrodialysis (ED): Electrodialysis uses an electrical potential difference as driving force for the selective extraction of ions or zwitterions (e.g. amino acids). In principle ED can isolate every single amino acid as long as there exists a difference in isoelectric point (pI, Figure 2). In specific cases, enzymatic amino acid modification is needed to increase the difference in the pI's for further separation (Figure 3).



Amino Acid	pI	Side Chain Charge (pH =7)
Aspartic Acid	2.85	Negative
Glutamic Acid	3.15	Negative
Lysine	9.60	Positive
Arginine	10.76	Positive

Figure 2: Electrodialysis for the separation of amino acids from protein sources

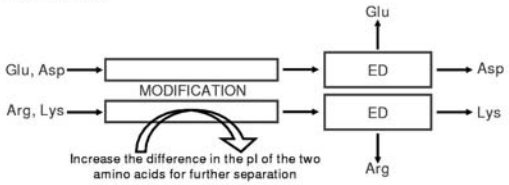


Figure 3: Modification of amino acids for further separation.

Research approach

Proof of principle: Critical design parameters for membrane development, module & process optimization.
Membrane development: New membrane concept for energy efficient ED.
Module and dynamics: Optimized module concept with improved hydrodynamics for the proposed application.
Reaction and separation: Integrated process design for the reaction and the separation.

Acknowledgement

This research is financially supported by the Dutch Technology Foundation STW, applied science division of NWO. The project is performed in close collaboration with Wageningen University.

Nanomembranes against global warming

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OSPT theme	: Separation Technology	Research school	: OSPT
Supported by	: EU / NMP3-CT-2007-026735	Period	: June 2006 – June 2010

Introduction

The ultimate way to reduce CO_2 emissions from fossil fuel fired power stations is by CO_2 capture. Currently existing methods (e.g. adsorption, non selective cooling) are not very cost- and energy effective. The use of gas separation membranes to reduce the emission of CO_2 is currently non-existing in industrial applications, but the potential of this technology is large. The implementation of the technology is currently limited by the availability of suitable and reliable membranes at an acceptable price level.

Aim

To overcome these limitations, the aim of this project is to develop cheap, high flux, polymeric diffusion transport membranes that selectively remove CO_2 or CO_2 and H_2O from flue gases.

Research

To remove both water vapor and carbon dioxide, hydrophilic polyether based block copolymers are of interest. They combine high water vapor permeability with high polar/non-polar gas selectivity. These block copolymers consist of a flexible, soft amorphous phase through which the gas permeates and a rigid, hard crystalline phase which provides mechanical strength and solvent resistance.

In the present work we systematically varied the nature of the hard and soft segment and investigated the effect on the gas permeation properties.

The hard segments studied are a di-amide (short) and a tetra-amide (long). The soft segments studied are poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO).

Results

Figure 1 shows the CO_2 permeability at 35°C for the synthesized membranes.

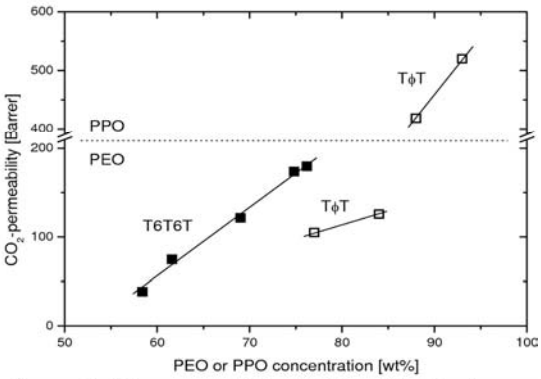

Figure 1: CO_2 permeability at 35°C of the block copolymers (1 Barrer = $2.7*10^{-9}$ $m^3*m/m^2*h*bar$).

The CO_2 permeability can be easily tuned by the type of soft segment. Replacing linear PEO with more bulky PPO gives a significant increase in permeability due to increase in free volume. Use of the longer hard segment reduces the overall concentration of soft phase available for gas permeation, but results in better phase separation. This is advantageous for the gas permeation properties and the thermal and mechanical properties.

Conclusion

The use of block copolymer based membranes for CO_2 removal allows the systematic variation of the gas permeation properties of the membranes.

Faculty of Science and Technology

Research Group

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Membrane Process Technology

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Activities of the group Membrane Process Technology

The group Membrane Process Technology carries out the scientific research in the area of environmental technology, particularly membrane technology. The disciplines are:

Closed water systems
Description and modeling of membrane fouling; description and modeling of quality of permeate in relation to type of membrane and module configuration; system design, 'cross-flow' versus 'dead-end'.

Treatment of membrane concentrates
Membrane technology and biological methods (MBR's) for treatment of membrane concentrates; removal of colour, pesticides, salts, micro-organisms and other solutes.

Water purification
Various membrane processes are studied for water purification.

Membrane bioreactors
Combination of membrane technology and biology (bioreactors) is studied in relation to improvement of process efficiency, water quality; investigation of different concepts (crossflow versus submerged) in relation to membrane fouling, energy consumption, permeate quality and costs; development of MBR's for the removal of specific compounds.

Sustainable energy
Investigation of efficiency and limitation of pressure retarded osmosis (PRO); development of polymer electrolyte membranes (PEM's) for fuel cells.

The influence of the membrane properties on SDI

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Introduction

Production of potable water with RO membranes is limited by fouling problems, which causes a lower productivity of the membranes. The water fouling potential can be measured using the Silt Density Index (SDI ASTM-4189). However, several drawbacks and contradictions are observed in SDI measurements, leading to unreliable results. In this work, the influence of variation of membrane properties within and between batches on the SDI results is studied.

Experimental

Figure 1: ASTM SDI setup.

Three flat sheet membranes from 1 batch (Millipore HVLP pore size 0.45μm) were characterized (pore size and -distribution, porosity, surface roughness and – charge) and SDI was measurements. Feed water permeabilities were measured. From the flow chart (volume vs. time) the SDI was calculated by:

$$SDI = \%P_{30\,psi} / T_t = 100 \times \frac{(1 - \frac{t_1}{t_2})}{t_f}$$

Where t_1, t_2 are the time to collect the first and second sample and t_f is the elapsed time after the permeation started.

Ultrapure water and a solution of α-alumina particles (4 ppm) in ultrapure water were used as model feeds. AFM (AFM Veeco multimode) was used to characterize the structure of the membrane. The porosity was measured by pycnometry (AccuPyc 1330). Furthermore, the pore size distribution is determined by Coulter Porometry.

Results and Discussion

The membrane properties and SDI results are as follows:

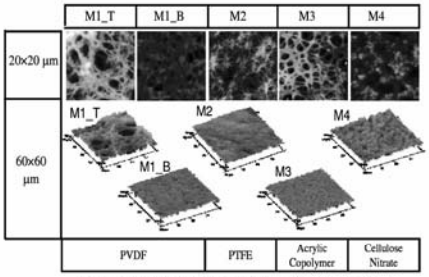

Figure 2: *2D and 3D AFM pictures for the 0.45 mm manufactured membrane M1, M2, M3 and M4*

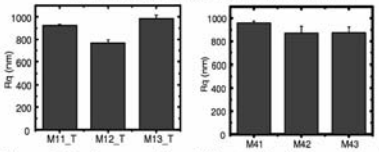

Figure 3: Membrane variation within a batch: Average pore size and surface roughness

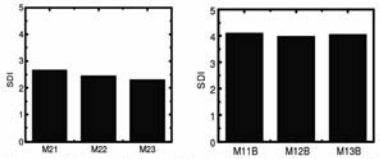

Figure 4: SDI for a 4 ppm α-Alumina particle solution using 3 samples of M2 and M1 Backside

Conclusions

Variations of the membrane within a batch influences the SDI results

Acknowledgement This project is financially supported by Vitens and Norit.

Microfluidic Filtration

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Introduction

Membrane filtration systems are being extensively used in pretreatment, desalination, waste water treatment and even in bioreactors. However, with the acceptance of membrane filtration systems in various applications, comes the problem of fouling and deposition of particles on the membrane surfaces. This causes a large reduction in the fluid flow through the membrane and thus an economic loss to the industries

Aim

The ultimate aim of this work is to monitor the flow of liquids along and through porous structured membranes. Besides, direct observation of the flow profiles in channels with porous walls will be used to understand the fundamentals of fouling in membrane filtration systems.

Research

Phase separation micro molding (PSμM) is used in making membranes with porous channels structures (fig. 1). The polymer solution is cast on a glass plate with glass capillary tubes on the surface to create the structures. This is then phase separated in a non-solvent and sealed to form a transparent chip. The pore size of the membranes is initially targeted in the microfiltration (0.5 to 5 μm) range (fig. 2). As fluid can permeate the wall of such porous channels, the filtration process is mimicked. Particle deposition (6 μm polystyrene particles) has been observed during a filtration experiment showing an initial increase in deposition at the channel exit, with a final homogenous cake layer (fig. 4).

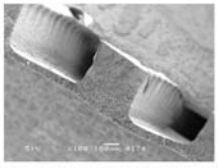

Figure 1 Porous membrane with channels

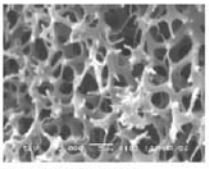

Figure 2 Highly interconnected pores

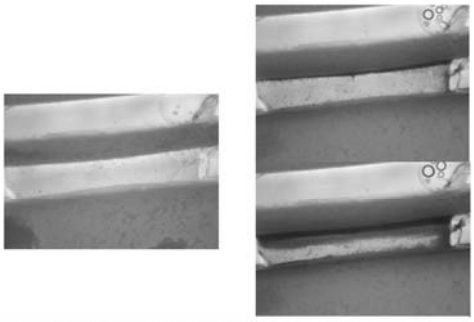

Figure 3 Images of fouling experiment (clockwise; 5 min, 5 hrs and 10 hrs)

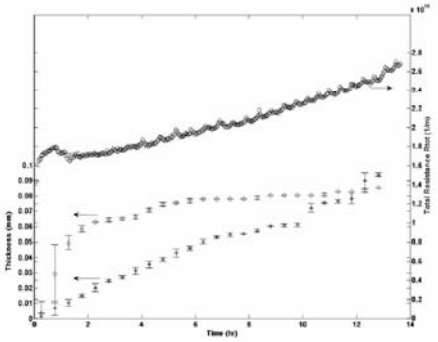

Figure 4 Fouling experiment (o – Rtot (1/m), * - channel inlet, ◊ – channel exit cake thickness (mm))

Conclusions

Results show that we can observe the particle deposition online during filtration. We have also been able to obtain reproducible pillars on the surface of our membranes.

Acknowledgement

This research is financially supported by Vitens.

Influence of operational parameters on biofouling of membranes

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Research group	:	CT/MPT/WETSUS	**Research school**	:	OSPT
OSPT theme	:	Separation Technology	**Period**	:	09-2005 – 09-2009

Introduction

In many water purification installations RO (reverse osmosis) membranes are used. Very often, biofilms, consisting of micro-organisms and their extracellular polymeric substances (EPS), are formed on the surfaces of the membrane.

The stages in the development of the biofilm are shown in figure 1A. When a threshold of interference is exceeded, the biofilm is called "biofouling". At that stage the formed biofilm has a negative effect on the production capacity and quality of the permeate (figure 1B), the energy consumption, and the costs per amount of purified water.

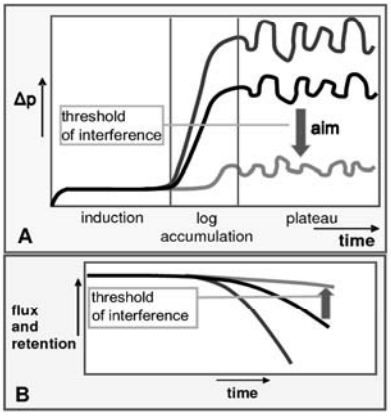

Figure 1. Biofouling development versus time. A. Pressure drop along the flow direction versus time. [Flemming, H.-C., Appl. Microbiol. Biotechnol. 59 (2002) 629-640]. B. Flux and retention by the membrane versus time.

Aim

The aim of this project is to obtain a situation in which the biofilm does not exceed the threshold of interference in neither the pressure drop, flux, nor retention. The process conditions are changed to reach this aim.

Experiments

In a series of experiments, the effect of the applied crossflow velocity on biofouling was determined in a flat sheet test cell. Tap water, to which nutrients were added, was used as feed. The pressure drop and flux were followed in time. In addition, the conductivity of the concentrate and permeate were measured in time. From these values, the retention was calculated. When a plateau in the pressure drop was reached, the experiment was stopped and the biofilm was analyzed with respect to the carbon, nitrogen, calcium, magnesium and sodium content. In addition, the number of colony forming micro-organisms was determined and SEM pictures. In figure 2, a SEM picture of a representative biofilm is shown.

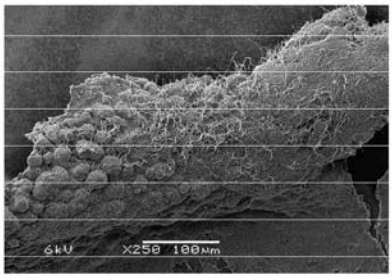

Figure 2. SEM picture of a representative biofilm, various micro-organisms are present. They are embedded in a layer of their extracellular polymer substances.

Faculty of Science and Technology

Research Group

Inorganic Membranes

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Activities of the group Inorganic Membranes

Advanced ceramics processing
The objective is the fabrication of (new) advanced ceramics and to examine its mircrostructure. It concerns preparation, consolidation and microstructural characteristics of (ultra) fine-grained (oxidic) powders, ceramics and coatings.

Solid state ionics
Research within this theme encompasses the study of fast ionic and mixed ionic-electronic transport in condensed phases and associated interfacial/electrode reactions. Main interest is focused to the fundamentals of technological applications, such as dense ceramic membranes and solid oxide fuel cells (SOFC).

Microporous ceramic membranes
Research within this theme encompasses the study of inorganic micro- and mesoporous ceramic membranes for use in energy-efficient gas separation, pervaporation and nanofiltration processes as well as the use of these membranes in membrane reactors.

Surface Modification of Inorganic Membranes

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OSPT theme : Separation Technology
Supported by : DSTI

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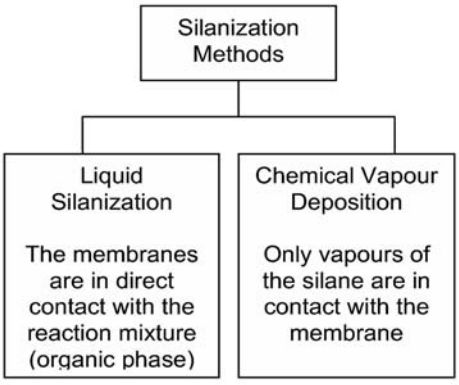
Introduction

In affinity based membrane transport, one of the feed components preferentially permeates based on the greater solubility in the membrane. One of the approaches is by designing organic-inorganic hybrid membranes which can deliver the desired chemistry and free-volume. Functional organosilanes can be used to modify the surface chemistry of an inorganic membrane by grafting the desired chemical moieties which can enhance the interaction of specific feed components.

For the resulting membranes the following specific applications will be investigated:

- Nanofiltration (A.F.M. Pinheiro)
- Gas separation (V.G.P. Sripathi)

Experimental



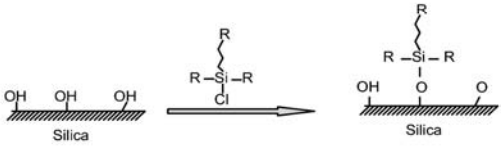


Figure Reaction of alkylchlorosilanes with silicon dioxide surfaces

- Functional organosilanes forms hydrolytically stable Si–O–Si–C bonds with surface hydroxyl groups by hydrolysis and condensation of functional groups (Cl, OR).
- Nature of silanization depends on the number and type of hydrolysable functional groups present on the silane molecule ($R_{(4-n)}$–Si–X_n).
- The reaction conditions (silane concentration, temperature, time, nitrogen atmosphere) and the properties of the support (surface hydroxylation, surface water and pore size) can play an important role in silanization.

Acknowledgement: These are DSTI projects

Fabrication of multi-layer ceramic hollow fibres

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OSPT theme	: Separation Technology	Research school	: OSPT
Supported by	: STW	Period	: January 2007 – January 2011

Introduction

Ceramic membranes show good mechanical, chemical and thermal stability. However, high cost of fabrication, time consuming production as well as low surface area per unit volume (A/V ratio) hamper their industrial application. The A/V ratio of ceramic membranes is highest when they have hollow fibre geometry. Single layer ceramic hollow fibers have been prepared by the wet-spinning technique. The corresponding fibers do not directly display the selectivity required for most industrial applications. Modification of the ceramic hollow fibres via grafting [1] or (sol-gel, polymeric) coating [2, 3, 4] can be an option for achieving the desired selectivity. Another approach could be co-spinning/co-extrusion of multiple layers in a single step, followed by co-sintering [5]. Such a procedure requires a minimum number of steps and allows for very convenient and cost efficient membrane fabrication.

Aim of the project

Fabrication of solvent resistant nanofiltration (SRNF) membranes with a high surface area per unit volume (A/V-ratio).

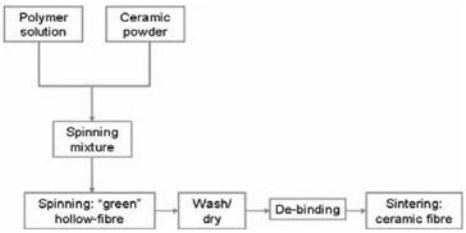
Ceramic hollow fibre membranes

- Fabrication of a multi-layer ceramic hollow fibre support in one single step by wet spinning (phase inversion).
- Identifying critical process steps and process parameters.
- Characterization of microstructure and microstructural changes during the process.

Acknowledgement

This project is financially supported by STW

Process steps are illustrated in this scheme:



We will start with a system containing two α-Al_2O_3/α-Al_2O_3 layers (porosity: ± 40%):

- Outer layer: pore size: ~ 50 nm.
- Inner layer with a pore size of several hundreds of nanometers.

For defect-free hollow fibre supports control of several parameters is necessary; like:

- ratio polymer/ceramic powder
- viscosity of spinning mixture
- adhesion between individual layers
- sintering (temperature, heating rate, etc.)

SEM photographs of sintered double-layer ceramic hollow fibre [5]

[1] S. Koonaphapdeelert, K. Li, J. Membrane Sci. 291 (2007) 70-76
[2] T.A. Peters, J. Fontalvo, M.A.G. Vorstman, N.E. Benes, R.A. van Dam, Z.A.E.P.Vroon, E.L.J. van Soest-Vercammen, J.T.F. Keurentjes, J. Membrane Sci. 248 (2005) 73-80
[3] S. Liu, W.K. Teo, X. Tan, K. Li, Separation and Purification Technology 46 (2005) 110-117
[4] X.L. Pan, N. Stroh, H. Brunner, G.X. Xiong, S.S. Sheng, Separation and Purification Technology 32 (2003) 265-270
[5] J. de Jong N.E. Benes, G.H. Koops, M. Wessling, J. Membrane Sci. 239 (2004) 265-269

Tailored Stable Membranes for Molecular Separation with Continuous Reaction under Supercritical Conditions

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Introduction

In general a major part of the total cost of chemical processes is associated with molecular separation of different components. In particular for applications involving harsh conditions (high temperature, high pressure, extreme pH values, etc.) practical and economical viability is limited by the absence of robust unit operations for molecular separation.

Furthermore, at present there is insufficient knowledge concerning optimal membrane properties, such as pore morphology and internal surface features. A combination of characterization and permeation will be used and developed to obtain insight in physical and chemical phenomena that determine the separation performance as well as the stability of membranes.

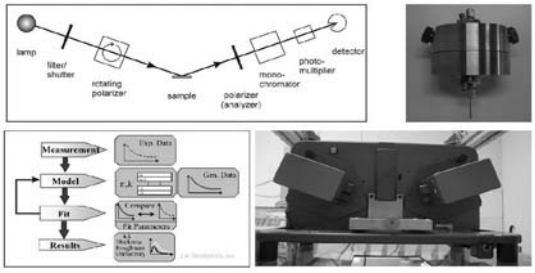

***Figure 1**: Overview of the basics of using ellipsometry (left) and the set-up used (right)*

Aim of the project

The research is aimed at the development, characterization and application of stable membranes with properties tailored for harsh conditions. Special emphasis will be on the development of membrane characterization methods that can be applied under realistic conditions.

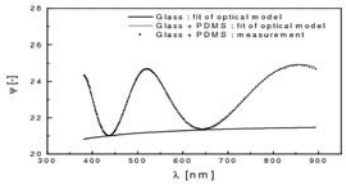

***Figure 2**: Example of an ellipsometry spectrum*

Current status

Preliminary results on a model system of PDMS show that ellipsometry can be used to determine swelling behavior. A systematic study is done on these PDMS films on glass substrates in a n-hexane solution. This study will show the benefits of using ellipsometry as an in-situ characterization technique for better understanding of membrane layer behavior. This includes the effects of cross-linking degree, temperature, and pressure.

Future work

Ellipsometry studies on swelling of polymeric layers in various solvents, including pressurized carbon dioxide, will be continued. Ellipsometry will also be used for analysis of sol-gel derived membranes: focus will be on layer thickness and porosity, <10 bar sorption of water and other vapors, carbon dioxide sorption up to high pressures, i.e. >100 bar). In addition, associated high pressure permeance studies of the sol-gel derived membranes will be conducted.

Acknowledgement

This research is financially supported by the Technology Foundation STW, applied science division of NWO and technology programme of the Ministry of economic Affairs (VIDI EPC.7055).

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Activities of the Thermal Engineering Group

The research is concerned with questions related to industrial applications of thermodynamics, fluid mechanics and heat and mass transport. Using a combined approach of theoretical analysis, numerical calculations and experimental investigations, the group aims to develop new or advanced knowledge in industrial design. Priority is given to the efficient use of energy and the minimisation of environmental pollution.

The research on turbulent combustion is primarily applied to the combustion of natural gas and other gases, like synthesis gas and biogas, in gas turbines. Next to the combustion/turbulence interaction also the generation of sound by a turbulent combustion process and its interaction with the structure of a combustion chamber is studied.

The research on the combustion of solid fuels is primarily related to the combustion of biomass or waste in power plants (co-fring) and in waste incinerators.

Next to the combustion of biomass and waste also the gasification and pyrolysis of biomass and waste is studied. This research is mainly aimed at understanding these thermal conversion processes in order to produce biogas free of tar and bio-oil free of char particles. Gasification in supercritical water of wet biomass streams is studied to produce a hydrogen rich biogas. Flash pyrolysis is studied in a cyclone reactor. Here the emphasis is on the separation of small char particles from the pyrolysis gas and de-oxygenation of the pyrolysis oil in the reactor itself.

Other thermal conversion processes of fuels that are studied are the reforming of natural gas to synthetic gas by partial oxidation in a partial oxidation gas turbine.

Defence Materiel Organisation

Development of a Supercritical Diesel Reformer in a Hybrid Fuel Cell System

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OSPT theme	: Energy Conv. Processes	**Research school**	: OSPT
Supported by	: SenterNovem and Mindef	**Period**	: September 2003 – October 2010

Introduction

In the next decades diesel fuel will remain the preferred logistic fuel for NATO forces. For reasons of logistic support and stealthness of military operations, the use of fuel cells for power generation is an attractive solution. Moreover, in comparison to diesel-generators fuel cells offer higher efficiency and lower emissions of NO_x, PM (particulate matter) and CO_2. The use of diesel fuel in fuel cell systems requires (pre)reforming of diesel into a hydrogen or methane rich gas. However, catalytic reforming of diesel fuel causes either deactivation of catalysts or formation of coke due to sulphur content and aromatic compounds in the diesel fuel. To this end an alternative process for reforming of diesel fuel is investigated, gasification of diesel in supercritical water.

In order to improve the dynamic response to load changes a battery is added to the system design, resulting in a fuel cell – battery hybrid system.

The aims of this project are development of a supercritical diesel reformer and optimisation of the hybrid fuel cell system design.

Project description

To investigate the process performance an experimental set-up of a supercritical water gasification reformer is designed and built. In supercritical water, diesel is converted into a hydrogen-rich gas, at a temperature of approximately 650°C and a pressure of 300 bara without any catalysts. After cooling down, a gas/water separator and gas clean-up, the hydrogen-rich gas can be used in a fuel cell. The liquid phase will be recycled into the reactor. Experiments and modeling have shown the optimal conditions for conversion of diesel in supercritical water. To optimise hybrid system design, performance and control a dynamic simulation model is developed.

Results

The results of experiments with maritime diesel fuel are promising, a carbon conversion up to 85% and an energy conversion up to 92% have been obtained. A kinetic model of the process is being developed.

In order to optimize hybrid system design, performance and control, a dynamic simulation model is developed. System studies have been carried out in order to assess various combinations of the supercritical reformer with fuel cells. An optimal system with regard to simplicity and efficiency seems a combination of the supercritical reformer with a solid oxide fuel cell. Overall system efficiency (LHV) of more than 42% is calculated when using diesel as fuel. The efficiency can be further increased when the solid oxide fuel cell will be integrated with a simple cycle gas turbine. This makes the technology interesting in various military applications, in the range from 10 kW (APU) to 1 MW (hotel load on board of naval ships).

Acknowledgement

This research project is carried out by TNO Science and Industry, Netherlands Defence Materiel Organisation, University of Twente and SPARQLE BV. It is financially supported by SenterNovem and the Ministry of Defence.

A new technology for fast pyrolysis of biomass: -development of the PyRos reactor-

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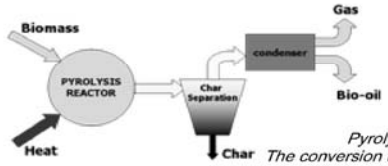
Introduction



Pyrolysis: The conversion to condensable liquids, gases and char by heating the material in an oxygen free environment.

Flash pyrolysis is a process with the aim of high oil yields, up to 75 % of liquids. This process can be characterized by:

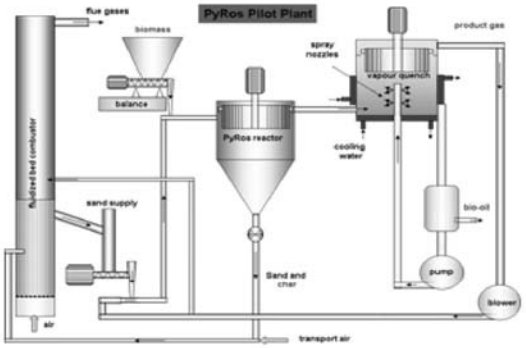
- high heating rates of the particles (< 2 sec)
- temperature between 450 and 600 °C
- short gas residence time at high temperatures (< 1sec)

The produced bio-oil from the process - with a five time higher energy density compared to the biomass - can be easily stored and transported. So the production and use of the bio-oil can easily decoupled in time and place.

The major problem of present reactors for flash pyrolysis are the carry-over of char, causing the following problems:

- solids in the oil
- increase of the viscosity over time by catalytic action of char
- alkali concentrated in the char dissolves in the oil (pH = 2 -3)

The PyRos process



In the PyRos-process (patented by TNO NL99/00688) the pyrolysis is implemented in a cyclonic reactor with a integrated hot gas filter (the rotational particle separator, RPS, US-patent US5073177). In this way a particle free bio-oil can be produced. The biomass and the inert heat carrier are introduced as particles in the cyclone, the solids are transported by recycled vapours from the process.

By centrifugal force the particles are moved to the periphery of the cyclone where the pyrolysis process takes place. Evolved vapours are transported rapidly to the centre of the cyclone and leave the cyclone by the rotating filter.

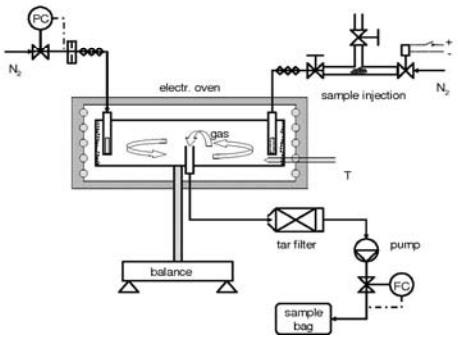
The hot vapours are quenched with cooled bio-oil and separated in a second RPS used as demister for small droplets and aerosols. The remaining gases and char can be used to heat up the heat carrier and transportation gas.

Features of the PyRos reactor are:

- high heat transfer rates
- short gas residence time
- controllable particle residence times
- particle free vapour production
- integration of reactor and particle filter
- compact/low cost reactor

Experimental

- Mathematical modeling to scale up the process
- 30 kg/hr Pilot plant a fully integrated pilot plant with char/gas combustion, inert heat-up and liquid collection.
- Kinetic measurements on a novel TGA at flash pyrolysis conditions



Green Refinery Feed *via* Catalytic Flash Pyrolysis of Biomass

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OSPT theme	: Energy Conversion Processes	Research school	: OSPT
		Period	: 02/2008 – 01/2012
Supported by	: STW (GSPT)		

Introduction

Flash pyrolysis is a promising route for thermo-chemical conversion of wood, agricultural waste or biomass in general, yielding a bio-oil that can be a potential substitute for transportation fuels. However, the bio-oil obtained from conventional flash pyrolysis has low quality in term of high oxygen content. The oxygenate components are mainly responsible for most of deleterious properties of the bio-oil: high viscosity, non-volatility, high acidity. Research on catalytic after-treatment of the bio-oil has not shown any promising results because of fast de-activation of the catalyst. In this work, a novel approach is introduced for the production of high quality bio-oil where flash pyrolysis and catalysis are integrated in a single reactor. Integrated catalytic flash pyrolysis of biomass offers the possibility to improve the quality and stability of the oil by *in-situ* de-oxygenation and cracking. The high quality bio-oil obtained by catalytic pyrolysis of biomass may be used as a co-feedstock for conventional refineries and in this way the existing infrastructure can be utilized for the production of sustainable transportation fuels.

Experimental Set-up

A continuous bench scale unit of 1kg/hr feedstock capacity is built up to study the effect of the key process variables on *in situ* catalytic flash pyrolysis of biomass. The reactor is a cylindrical quartz tube of 3.3 m length with an internal diameter of 5 cm. The reactor is heated electrically and is operated in a temperature range of 400 °C to 550 °C. Premixed feedstock (catalyst & biomass) enters the reactor at its top. Under inert atmosphere the thermo-chemical conversion of biomass particles takes place in a few seconds yielding a gas composed of condensables (bio-oil) and non-condensables.

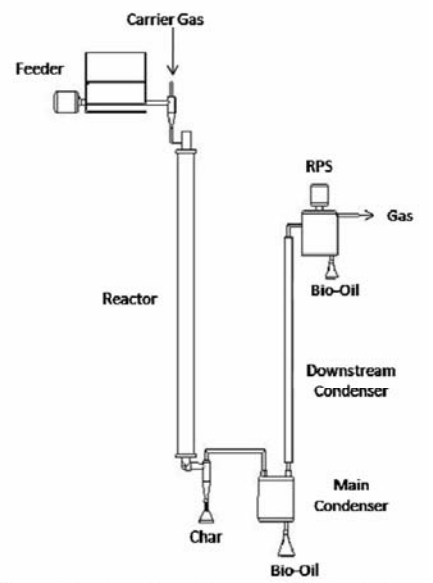

Figure: Schematic of the experimental setup

Results

The unit demonstrated good operating stability and flexibility for varying operating conditions. Preliminary experiments conducted with zeolites based acidic catalysts have shown that both the pyrolysis of biomass and the de-oxygenation of product vapours can be achieved in a single reactor and an improved quality bio-oil can be produced using catalysts *in situ* during the pyrolysis process.

Acknowledgement

This project is sponsored by STW, TNO, ABEMARLE, BIO^{e}CON and PETROBRAS.

Biomass gasification in supercritical water

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OSPT theme	: Energy Conversion Processes	Research school	: OSPT
Supported by	: Senter Novem	Period	: 09/2007 – 09/2011

Biomass gasification in supercritical water

Biomass gasification in supercritical water is the conversion of biomass in supercritical water. At approximately 600˚C and the corresponding water pressure of 300 bar, organic compounds are converted into a gas containing hydrogen, methane and carbon dioxide.

Current Situation

The research done on biomass gasification in supercritical water so far mainly focused on the composition of the product gases and the conversion as a function of the process conditions ("proof of principle" and "operation window").
A better understanding of the fundamental phenomena playing a role in biomass gasification in supercritical water is essential for an adequate reactor- or process design.

Applications

Anticipated applications of biomass gasification in supercritical water are:

- The on-site production of hydrogen in industry, vehicles, buildings.
- The production of renewable hydrogen as a clean fossil fuel.
- The production of a methane rich gas.

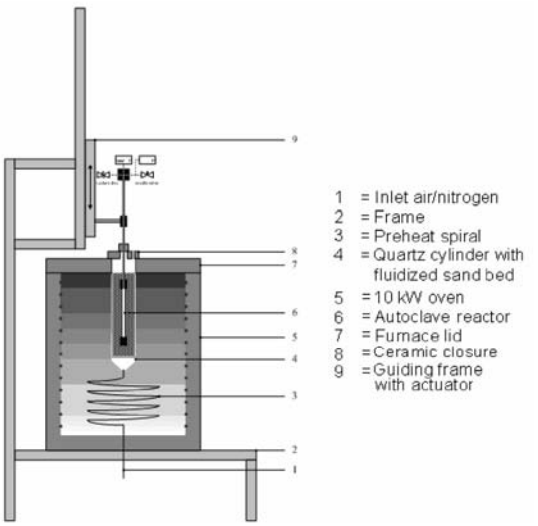

Figure 1: Scheme of experimental set-up.

Research topic

This research will focus on the development of a new type of reactor for the thermal conversion of biomass in supercritical water. First a bench-scale batch reactor on a balance will be built and tested for doing kinetics measurements (figure 1). Furthermore the following subjects will be investigated:

- Integrated heat transfer
- Measurements of kinetics
- Development of a process model

Project objectives

On base of the results of this project new design rules for the thermal conversion of biomass in supercritical water will be developed to obtain higher throughputs, higher gasification efficiencies and a high quality gas.

Acknowledgement

This project is sponsored by Senter Novem. This project is integrated in the framework of research institute IMPACT.

Ignition of municipal solid waste on a grate

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		Research school	: OSPT
Supported by	: TNO	**Period**	: April 2006 – April 2010

Introduction

The goal of this project is to investigate the ignition behavior of a packed bed of municipal solid waste (MSW) on a moving grate (figure 1). The effect of several parameters like primary air flow and calorific value of the waste particles on the ignition are investigated.

When the ignition mechanism is understood better, the fire in the furnace of MSW incineration plants can be controlled better and the waste can be incinerated more efficiently.

A theoretical as well as an experimental approach is used.

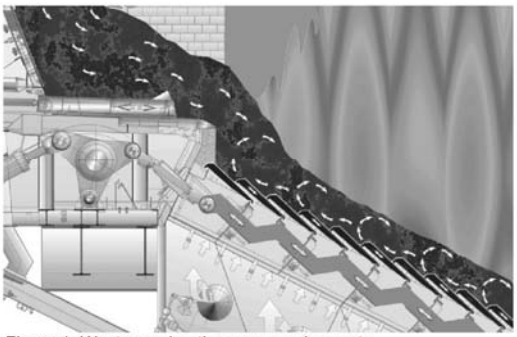

Figure 1. Waste combustion on a moving grate. Source: www.martingmbh.de

Overview and Results

Four different subjects are considered to investigate ignition in a packed bed of a solid fuel:

- *Gas phase combustion in an inert packed bed*. A combustible gas mixture is fed through a packed bed of alumina spheres. The gas mixture is ignited at the bottom of the bed. The location of the flame is measured. Experiments and modeling show that a premixed gas flame inside an inert packed bed is likely to travel downstream. Close to stoichiometric combustion, flashback might occur.
- *Auto-ignition of a packed bed by an hot air stream.* Preheated air is fed though a packed bed of a solid fuel (wood for example). The time needed for ignition and the critical air temperature for ignition are measured. An air temperature of only 230°C is needed to ignite wood. Char can be ignited with an air temperature of even 180°C.
- *Piloted ignition of a solid fuel.* A slab of either wood or a plastic is radiatively heated. A spark is created above the sample to ignite the evolving gases. The time to ignition as a function of radiative heat flux is measured. For heat fluxes below 30kW/m^2 ignition times increase dramatically. Also moisture content has a large influence on the ignition time.
- *Ignition front movement within a burning packed bed.* A packed bed of wood is ignited from the top. The air needed for the combustion is fed from below. The location of the ignition and combustion are measured by thermocouples. Modeling showed that radiation from the burning wood char is the main heat transfer mechanism responsible for the movement of the ignition front. It appears that the gas flame on top of the packed bed does not influence the front movement.

Acknowledgment

The EU project NextGenBioWaste sponsors this research. The goal of the NextGenBioWaste project is to improve the efficiency of renewable energy production and reduce harmful emissions of municipal waste and biomass incinerators.

Advanced biomass combustion on a grate

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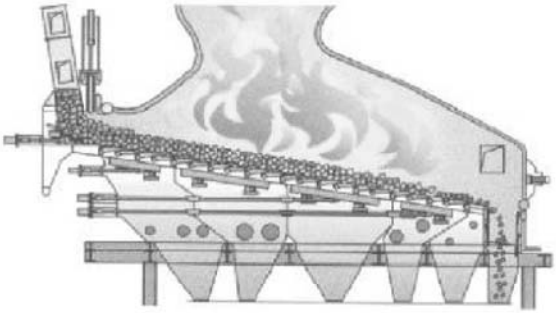
		Research school	: OSPT
Supported by	: Association of Waste Companies (VA)	**Period**	: January 2009 – January 2013

Introduction

Sustainable energy is an issue of great importance for our society. Of all sustainable energy sources, biomass and residues of biomass represent the main ones. The most frequent way of utilizing those sources is combustion. In addition, generation of municipal wastes increases rapidly, and that represents the main motive for investigating the possibility of using waste as energy source. Current technology is based on grate furnaces, where chemical energy of the fuel is converted into electricity, and in some cases into electricity and heat (cogeneration) used for various purposes. The efficiency of energy conversion is in a range of 20-30%, but in last few years new developments emerged, that could improve that efficiency even higher than 30%. The researches in this area are inclined toward better overall energy efficiency, reduced emissions and better ash quality.

Description

The conversion of solid fuels in grate furnaces, with ignition from the top of the fuel bed have been investigated. New approach in this area could be turned toward ignition from the bottom by preheated air. The goal of this research is to determine whether this way of ignition is applicable in current technology, as well as its influence on emissions, bottom ash quality, combustion rate, and combustion flexibility.



Acknowledgement

This research project is financially supported by Association of Waste Companies (VA)

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Bioprocess Engineering Groups

The Bioprocess Engineering laboratory participates in the gradate schools OSPT, VLAG en BSDL.

The bioprocess engineering chair group develops new biotechnological processes for manufacturing of healthy food ingredients, biofuels, biopolymers, pharmaceuticals, and biopesticides. The challenge is to make high-quality products in a sustainable and economic way, to avoid overexploitation of natural resources and the environment and maximize the chances of utilization by existing and new biotech companies.

Our research is focused on production of biomass and specific biomass ingredients and enzymatic conversions at high efficiencies and high volumetric productivities, in some cases integrated with isolation of the product. An integrated approach is used in which the production system (the bioreactor) is improved, the molecular metabolism is controlled, and the best strains are selected or improved. Using this approach, the bioprocess is studied at different scales ranging from the complete bioreactor to the biochemistry inside the cells. Models are used as a tool to understand the complex behavior of the biological system as such and of the interaction with the physical transport processes in a bioreactor, and ultimately to allow better design and operation of the bioreactor. There are 3 areas of expertise in our research (figure 1): bioreactor design, cellular processes, and modeling. Strong application areas for the coming years are expected to be: marine biotechnology, industrial biotechnology (biofuels and green chemicals), animal cell technology.

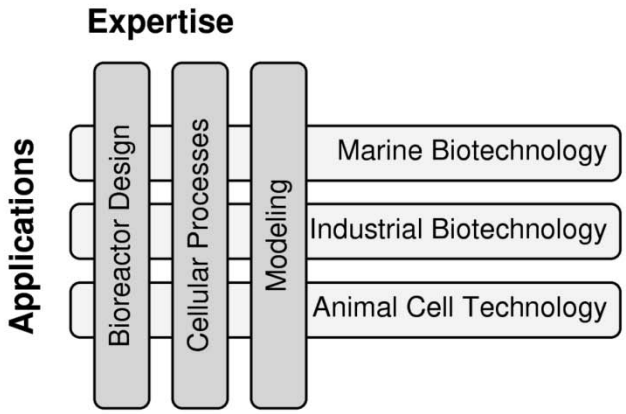

Figure 1: An integrated approach of expertise in research and application area of the bioprocess engineering chair group.

Expertise

Bioreactor design

Bioreactor design is the most classical topic in bioprocess engineering. Our position in this area is unique as we focus on specific bioreactors such as in solid state fermenters without a continuous liquid phase present, photobioreactors, in which light is used as an energy source

and multiphase bioreactors in which the bioconversion and product recovery are integrated. We have up-to-date experimental facilities for bioreactor studies in the areas indicated, which allow us to study the bioconversion on different scales and to use rapid methods like for example the acceleration-stat to study process dynamics.

Cellular processes
The whole cell can be considered as a reaction network. We focus on the relation between metabolic fluxes and reactor conditions. Changes in the rates through various metabolic routes in response to different environmental conditions or genetic manipulations give indications with respect to certain bottlenecks. Flux models are developed for organisms like micro-algae, sponges, and animal cells.

Modeling
Mathematical models are used as a tool to understand the complex interactions in the cell and between the cell and its surroundings (the bioreactor). Models are developed to describe e.g.:

- Gradients in bioreactors (e.g. in solid state fermentation, immobilized biocatalysts, light and oxygen gradients in photobioreactors),
- Heat and mass transfer (e.g. evaporative cooling, food uptake by sponges, light transfer in photobioreactors)
- Metabolic fluxes (e.g. for medium design for animal cell cultures, prediction of effects of nutraceuticals on metabolism in mammalians, synthesis and accumulation of lipids or carotenoids in microalgae.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Production of chemicals and feed ingredients by processing lignocellulosic rest streams using organic acids

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OSPT theme	: Products & Processes	**Research school**	: VLAG
Supported by	: CCL Research	**Period**	: Sept 2005 – Dec 2009

Introduction

When producing chemicals by fermentation, readily fermented raw materials like sugar and starch derived from crops are often used. However, cheaper carbohydrate rich streams from agriculture, like corn stover, wheat straw, or forestry could be utilized. This lignocellulosic plant biomass requires pre-treatment in order for the subsequent enzymatic hydrolysis of plant cell wall polysaccharides into fermentable sugars to be efficient[1]. A standard pre-treatment is dilute sulphuric acid in combination with heat, but this leads to the formation of compounds such as furfural and 5-HMF that inhibit ethanol yeast fermentation and will also generate inorganic waste[1,2,3]. The organic maleic acid has been mentioned as a possible alternative as its application results in high sugar yields and in smaller amounts of the inhibiting byproducts[4]. Within this project, the possibilities for producing value-added chemicals and animal feed ingredients, such as lactic acid, fumaric acid, ethanol and lysine, are researched. The aim is to use organic acids in the pre-treatment of the lignocellulosic plant biomass.

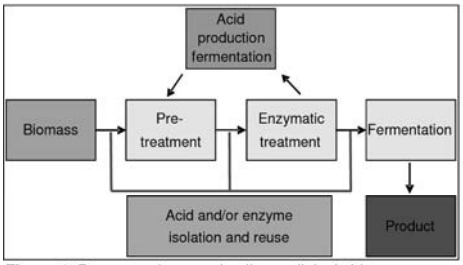

***Figure 1**. Process scheme using lignocellulosic biomass.*

Approach

The different stages in the process (see Figure 1) are focused upon separately. The sugar degradation in the pre-treatment, the fermentative production and recycle of the organic acid are focal points, but also the valorisation of the side stream plays a key role.

State of affairs

In experiments that mimic pre-treatment conditions it was found that organic acids cause less arabinose degradation than the stronger sulphuric acid. It was also shown that specific acid catalysis does not apply to degradation in presence of maleic and fumaric acid. The degradative behaviour of maleic acid did not exceed that of water, while that of fumaric acid was even less (see Figure 2). This makes application of fumaric acid advantageous for lignocellulosic ethanol production processes[5].

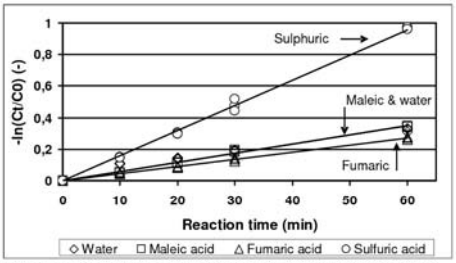

***Figure 2**. Degradation of arabinose at elevated temperatures.*

Acknowledgement

This research project is financially supported by CCL Research.

References

1. Mosier, N. et al., Biores. Techn., 2005. 96(6).
2. Lawford, H.G. and J.D. Rousseau, Appl. Biochem. and Biotechn., 2003. 106(1-3).
3. Lloyd, T.A. and C.E. Wyman,. Biores. Techn., 2005. 96(18).
4. Mosier, N.S. et al., Biotechn. Progress, 2001. 17(3).
5. Kootstra, A.M.J. et al., Biochem. Eng. J., 2009. 43

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Maximal butanol yield by directed engineering

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Introduction

The need to reduce CO_2 emissions has promoted the use of renewable resources as starting material for the production of fuels and chemicals. The acetone-butanol-ethanol fermentation (ABE fermentation), which has been once industrial, has a great potential for the production of butanol from lignocellulosic biomass. Butanol represents an important source of additives to be blended with existing fuels, and therefore contributes to meeting the increasing demand for renewable fuels (figure 1). Next to that it is also a widely used solvent and chemical feedstock. However, to again make the ABE process economically viable there are some improvements to be achieved; higher butanol yields and higher volumetric productivity to reduce recovery costs.

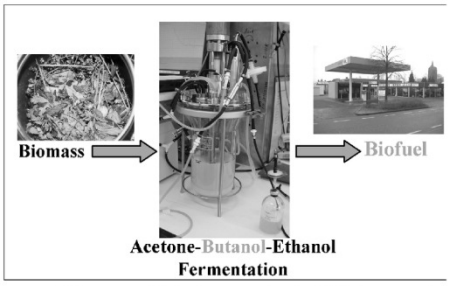

Figure 1: Biomass to biofuel conversion by ABE fermentation.

Aim

We want, by means of genetic engineering of existing acetone-butanol-ethanol-producing Clostridial species, to increase the butanol yield and reduce by-product formation of acids and acetone.

Research

Genetic tools are being developed to engineer a *Clostridium acetobutylicum* strain with a single-route fermentation pathway. This single-route mutant should convert glucose into 1-butanol, with a theoretical maximum yield of 1 mol BuOH/mol glucose.

The wild type metabolic network includes enzymes that catalyse competing reactions whose production is at the expense of butanol production. These products include acids such as lactate, acetate, and butyrate, but also solvents like ethanol and acetone. Enzymes involved in these reactions are our first knock-out targets.

Generated (multiple) knock-out mutants of *C. acetobutylicum* will be characterized in batch fermentations (laboratory scale 1-2 L bioreactors), by functional genomics (DNA Microarray analysis) as well as by routine physiological analyses.

Future research

First our gene knock-out system is being optimised and validated. This will give us the ability to generate mutants with multiple knocked out genes. Metabolic modelling of these mutants should provide us with information on further optimisation of the metabolic pathways involved in butanol formation.

This project is financially supported by the Netherlands Ministry of Economic Affairs and the B-Basic partner organizations (www.b-basic.nl) through B-Basic, a public-private NWO-ACTS programme (ACTS = Advanced Chemical Technologies for Sustainability).

AGROTECHNOLOGY & FOOD SCIENCES GROUP WAGENINGEN UR

Photosynthetic cell factories: Milking of carotenoids from *Dunaliella*

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Introduction

Carotenoids, a group of natural, fat-soluble, yellow to red pigments, are mainly found in plants, algae and photosynthetic bacteria, where they play an important role in photosynthesis. They protect the cell from damage by light and oxygen.

Due to its capacity of accumulating large amounts of carotenoids, the alga *Dunaliella salina* is used worldwide as main source of natural β-carotene to meet with the increasing demand by food, pharmaceutical and cosmetic industries. Hejazi and co-workers (1) developed a new method for simultaneous production and extraction of carotenoids from *Dunaliella salina*. In a two-phase bioreactor, cells are cultivated under stress conditions so that they start to produce and accumulate a high quantity of carotenoids in fat globules. These are extracted from the cells to the organic phase (dodecane) in a constant process, the so-called milking of micro algae (fig. 1).

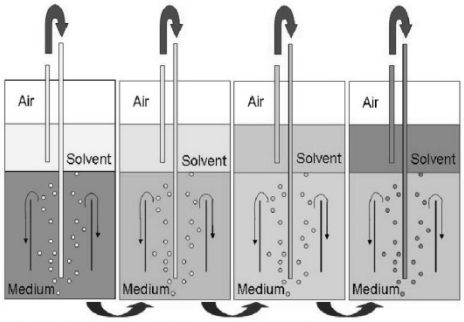

Figure 1: Milking after application of stress

Aim

The aim of this research project is to gain insight in the extraction procedure. This is of importance for the optimisation of the milking process.

Results

We studied the extraction profiles of carotenoid production and extraction, when cells were exposed to various stresses, viz, low temperature, high light intensities or a combination of both. Results showed that the various stresses did influence the pattern of carotenoids produced under stress (2). However the pattern of extracted carotenoids did not vary too much. In case of gentle mixing during milking, only all secondary carotenoids were extracted. More vigourous mixing resulted in increased cell death and thus also in extracted chlorophylls.

Current research

Next to studying the extraction at macroscopic level, we will also look at the production, location and extraction of the carotenoid containing globules at cell level. For this various microscopic techniques will be used.

So far only wild-type strains of micro algae are used. The quality of strains obtained from micro algae collection banks is often very poor. Therefore we will select the best carotenoid producing cells. Flow cytometry based cell-sorting will be used for the selection process using carotenoid induced fluorescence for detection.

References

1. Hejazi, M.A., C. de Lamarliere, J.M.S. Rocha, M. Vermue, J. Tramper and R.H. Wijffels 2002 Biotechnology and Bioengineering 79:29-36.
2. Kleinegris, D.M.M., M. Janssen, W. Brandenburg, R.H. Wijffels. Submitted for publication.

Acknowledgement

This research project is financially supported by STW-VICI (WLM.6622).

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

stw

Photosynthetic cell factories: Development of high efficiency photobioreactors

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OSPT theme	: Products and processes	**Supported by**	: STW-VICI (WLM.6622)

Aim

Study the productivity and the primary metabolism of *Chlamydomonas reinhardtii* in a controlled lab-scale photobioreactor as a function of different cultivation conditions. The obtained results can be used for designing large scale photobioreactors.

Chlamydomonas reinhardtii

This green micro-alga (Fig.1) is used as a model organism to study the effects of for example oxygen concentration on the primary metabolism. The genome of *Chlamydomonas reinhardtii* is sequenced and with this we can construct a metabolic model to visualise the effect of different cultivation conditions.

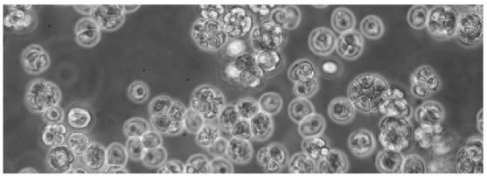

Figure 1. *Chlamydomonas reinhardtii*

Spinning tube-in-tube photobioreactor

To investigate the effect of different cultivation parameters we designed a lab-scale photobioreactor, the spinning tube-in-tube photobioreactor (Fig. 2).

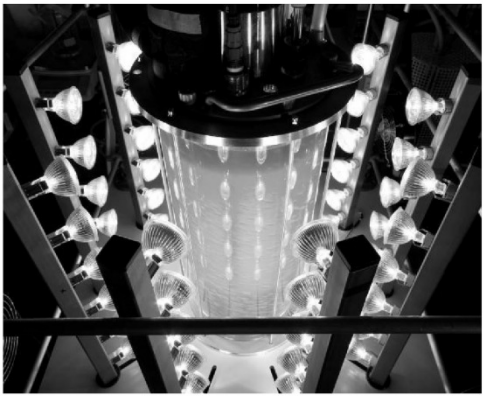

Figure 2. Spinning tube-in-tube photobioreactor

Mixing is provided by rotating the inner tube, enabling us to uncouple aeration and mixing. The algae grow in the annular gap of 10 mm and light is provided by 60 halogen lights (max. light intensity 1500 μmol m^{-2} s^{-1}).

On-line data acquisition

Cultures are monitored on-line as shown in Fig. 3. The obtained gas data can be translated into consumption and production rates as shown in Fig. 4. From these data the productivity can be calculated.

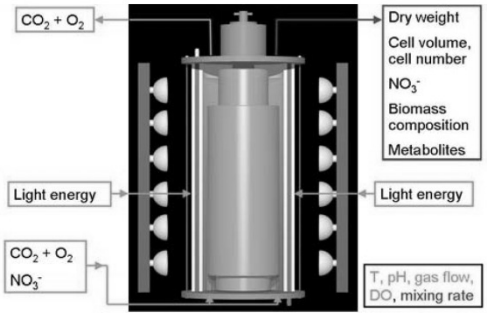

Figure 3. On-line (blue) and off-line (red) measurements during cultivations

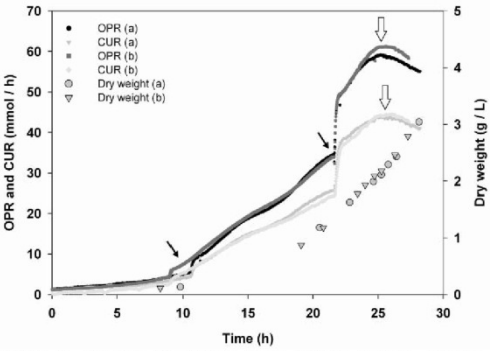

Figure 4. Oxygen production rates (OPR), carbon dioxide consumption rates (CUR) (in mmol h^{-1}) and dry weight concentrations (in g L^{-1}) for duplicate batch experiments (a and b) at a mixing rate of 70 rpm. Closed arrows indicate the time points of stepwise light increase. Open arrows indicate the time points with the maximal productivity and minimal quantum requirement for oxygen evolution and carbon dioxide fixation.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Cultivation of microalgae in photobioreactors for shellfish in the nursery phase

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OSPT theme	: Products and processes	**Research school**	: VLAG
Supported by	: Zeeuwse Tong and HZ	**Period**	: 2008-2013

Introduction

Chaetoceros muelleri (Figure 1) is used to a high extent as feed for shellfish. It is believed to be very shear sensitive and is therefore typically cultivated in open tank systems or bubble columns. For production cost reasons, it would be an advantage to be able to cultivate the algae in tubular photobioreactors (PBR's). However, application of a tubular PBR could lead to a shear stress that would be detrimental for *Chaetoceros muelleri*.

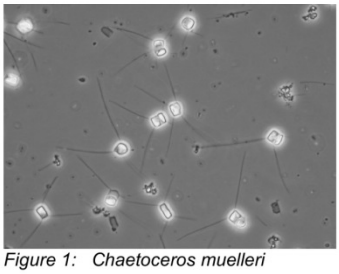

Figure 1: Chaetoceros muelleri

Objectives

The objective of this project is to find an optimal design for a tubular PBR in which a shear sensitive species like *Chaetoceros muelleri* can be produced.

Methods

Effect of shear stress

To select a suitable recirculation pump for the construction of a tubular PBR, it is important to know the level of shear stress that can be tolerated by the algal species. Quantifiable shear stress is applied to the algae in shear cylinders (Figure 2). The effect of the shear stress is measured as a percentage of viable cells by different viability staining methods and physiological assays.

Figure 2: Shear cylinders

Effect of tube diameter

Methods to determine the optimum diameter of the tubes of the PBR will be developed. Small diameter tubes will result in higher biomass densities, but at the same time shear stresses could be higher.

Effect of oxygen accumulation

Maximum permissible length of the PBR depends on dissolved oxygen accumulation, because oxygen at a certain level will have an adverse effect on the growth. Oxygen tolerance of *Chaetoceros* and oxygen accumulation in outdoor tubular PBR's will be measured.

Effect of harvesting regimen

There are two important points to consider for the determination of the optimum harvesting regimen: dilution rate and time of harvesting during the day.

Acknowledgment

The project is supported by Hogeschool Zeeland and the Zeeuwse Tong project.

logo

photo

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B-Basic
Bio-based Sustainable Industrial Chemistry

Screening of Enzymes for Production of Biobased Monomers

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OSPT theme	: Polymerization technology	**Research school**	: VLAG
Supported by	: NWO & B-Basic	**Period**	: 09 2006– 08 2010

Introduction

Enzymatic polymerization has emerged as a field of remarkable interest for production of green plastics (biomers, Fig. 1) with new properties and outnumber of applications in chemical and pharmaceutical industry among others. Among these bio-like products, the lactones or cyclic ester oligomers (CEOs, Fig. 2.a) become outstanding building blocks for synthesis of outnumbers of biomers. Those cyclic molecules find application in ring opening polymerization technique (ROP, Fig 2b, Fig. 1.b) that has several advantages over polycondensation (PC). Remarkable characteristics in ROP are absence of by-products that reduce the reaction efficiency, formation of higher molecular weight products, and diminution of costs in downstream processing stages. Therefore lower costs routes for synthesis of raw material for ROP applications become an issue of great interest.

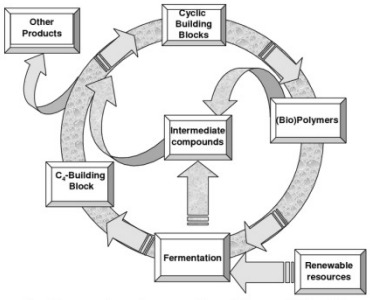

Figure 1. General scheme for bio-sustainable polymer production.

Aim

The aim of this project is to develop novel enzymatic synthesis of CEOs , that might be candidates for ring-opening polymerization applications.

Research

The research approach is divided in two large parts. Initially the confirmation of the reaction is done and the conditions were the reactant conversions were the most significant are used for larger scale synthesis. Subsequently a product separation and characterization is carried out using standard techniques such as HPLC, NMR, IR, MS, and MALDI-TOF.

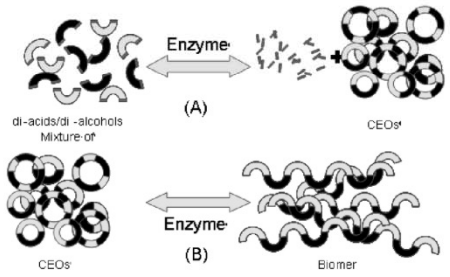

Figure 2. (a). Synthesis of cyclic ester oligomers (CEOs) from acid and alcohol. (b). Ring opening polymerization from CEOs.

Acknowledgement

This research is funding by the Netherlands Ministry Economic Affairs and the B-basic partner organization through B-basic, a public-private NWO – ACTS program.

Harvesting of microalgae for oil extraction

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OSPT theme	: Products and Processes	**Research school**	: VLAG
Supported by	: Wetsus	**Period**	: NOV 2008 – NOV 2012

Introduction

In commercial algae production harvesting is generally done by centrifugation. However, the costs and energy demands for harvesting the algal biomass by these methods are high. In the technical and economical analysis on microalgae for biofuels it was shown that the investment costs for the centrifuges contributed upto 34% of the total investment on equipment. The study also showed that the centrifuge used 48.8% of the total energy consumption.

In a feasibility study on sustainable co-production of fine chemicals and energy from microalgae several harvesting methods were evaluated*. This evaluation showed that induced flocculation combined with flotation or sedimentation and subsequent further dewatering by centrifugation and filtration is the most promising cost and energy efficient alternative method for harvesting microalgae.

Problem definition

Flocculation can be achieved in different ways (induced flocculation, auto- and bioflocculation or electroflocculation). However flocculation of the algal biomass is poorly understood. The optimal conditions of the algae and the culture medium for effective flocculation are often unpredictable. This makes it difficult to find ways to control the harvesting process.

Aim

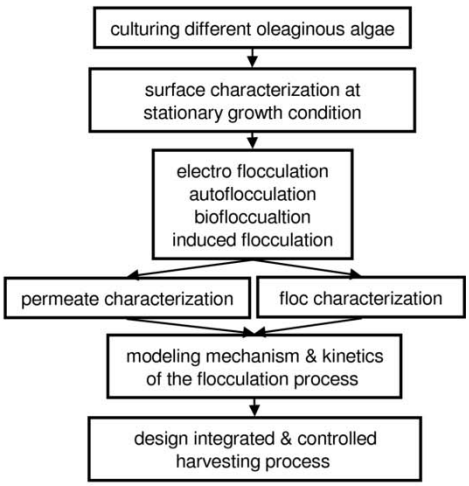
The aim of our work is to develop pre-concentration processes for different oleaginous algae based on induced flocculation, electroflocculation, bio- and autoflocculation.

Experimental work

The algae differ in cell size, cell shape, cell wall thickness and show different algal surface properties. We will investigate the effect of these parameters on the different flocculation processes and on the resulting algal aggregate size and size distribution, and aggregate density.

Modeling and design

We want to derive mechanistic as well as kinetic models for the flocculation of algae based on the experimental results from our tests and validate the models. The derived mechanistic models should predict the effectiveness of the flocculation method for a given algae and the size and density of the algal flocks obtained. The kinetic model should predict the dynamics of algal flocculation at given medium and cell conditions. These models will help us to develop effective integrated harvesting processes for the different algae studied.



*Reith, J. H. 2004. Duurzame co-productie van fijnchemicaliën en energie uit micro-algen. Openbaar eindrapport E.E.T. project K99005/398510-1010

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Secreted expression of self-assembling proteins in *Pichia pastoris.*

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SPT theme	: Products and Processes	**Research school**	: VLAG
Supported by	: B-Basic	**Period**	: Sept 2006 – Sept 2010

Introduction

Molecular self-assembly is a powerful approach for fabricating novel supramolecular architectures with well defined functionalities. By observing the processes by which supramolecular architectures are assembled in nature (Figure 1), we can begin to exploit self-assembly for the synthesis of entirely novel synthetic materials. However, the biologic production of these proteins is often a challenge due to the repetitiveness of the protein sequence and to their self-assembly properties. Gene instability, absence of suitable chaperons and unwanted intracellular assembly of supramolecular structures are just a few of the problems one might encounter when trying to use biological production hosts to successful produce these proteins.

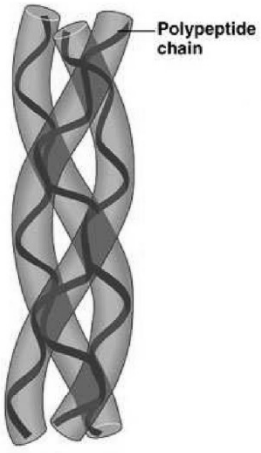

Figure 1 – Collagen self-assembling.

Aim

This project aims at the successful secretion of self-assembling heterologous proteins in *Pichia pastoris.*

Research

Improvement of the production host compatibility with the designer protein or, production of non-interacting (soluble) precursor molecules, followed by *in-vitro* modification into the mature self-assembling form.

Acknowledgement

This research project is financially supported by B-Basic.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Immortalized sponge cell culture

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		Research school:	VLAG
Research group:	Food and Bioprocess Engineering	**Period**:	Jan 2008 – Jan 2012
OSPT theme:	Products and processes	**Supported by:**	IP/OP and VLAG

Introduction

The seas and oceans have been recognized as very potent sources for the medicines of the future. Marine sponges are the champions with respect to the number and diversity of the thousands of bioactive secondary metabolites that have been discovered in the marine environment during the last decades (Newman and Cragg 2004; Sipkema et al. 2005). Since harvesting sponges for bioactive compounds is neither environmentally and economically feasible, an alternative strategy for the bulk production of sponge based bioactive compounds is necessary (Pomponi 2006). Large-scale in vitro sponge cell culture may provide a well-defined and controllable environment for the production of chemicals and other bioproducts of interest. However, due to significant gaps in our understanding of culture conditions for marine invertebrate cells, all attempts to maintain a normal or immortalized marine invertebrate cell line have been unsuccessful (Rinkevich 2005).

Aim

The aim of this project is to develop immortalized sponge cell cultures for the production of marine-derived bioproducts.

Research

Immortalizing will be achieved by extending the life span of sponges by introduction of the immortalizing agent hTERT (human Telomerase Reverse Transcriptase). This gene has proven to be an effective life span extending agent with high efficacy in numerous studies of mammalian cells. The target sponges will be, *Axinella corrugata*, which produces stevensine, *Dysidea avara*, which produces avarol, *Xestospongia muta* and *Haliclona oculata*.

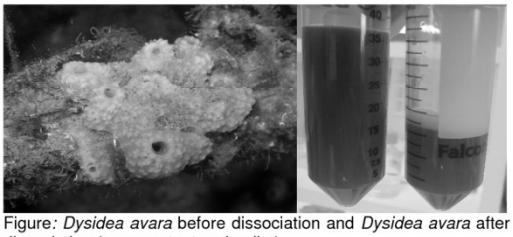

Figure*: Dysidea avara* before dissociation and *Dysidea avara* after dissociation (supernatant and pellet).

Acknowledgements

This project is in collaboration with the Laboratory of Microbiology and Harbor Branch Oceanographic Institution and is financed by the Graduate School VLAG and IP/OP.

References

Newman,D.J. and Cragg,G.M. 2004. Advanced preclinical and clinical trials of natural products and related compounds from marine sources. Current Medicinal Chemistry 11: 1693-1713.

Pomponi,S.A. 2006. Biology of the Porifera: Cell culture. Canadian Journal of Zoology 84: 167-174.

Rinkevich,B. 2005. Marine invertebrate cell cultures: new millennium trends. Mar. Biotechnol. 7: 429-439.

Sipkema,D., Franssen,M.C.R., Osinga,R., Tramper,J., and Wijffels,R.H. 2005. Marine sponges as pharmacy. Mar. Biotechnol. 7: 142-162.

Production of *Beauveria bassiana* spores for control of malaria mosquitoes in Solid-state fermentation

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OSPT theme	: A2: New process principles and production systems	**Research school**	: VLAG
		Period	: June 2007 – Aug 2010

Introduction

Malaria is one of the most deadly diseases worldwide. It causes 1 to 3 millions deaths each year. The disease is transmitted by female anopheles mosquitoes from one person to another. Lab-application of *Beauveria bassiana* spores showed high virulence on tested mosquitoes. For field-application, huge amount of spores as well as scale-up is required. One drawback though in scaling-up solid state fermentation (SSF) is the lack of a deeper understanding about the physiology and kinetics of growth and sporulation of the *B. bassiana* bioconversion reaction

SSF in trays/bags is attractive because it requires low technology and relatively cheap investments. However, these systems require steep gradients to drive the internal heat and mass transport. So far, little is known on the sensitivity of *B. bassiana* growth and spore formation in such gradients.

Aim

Currently we are working on a medium solution containing glucose, yeast extract and peptone which gave high spore yield compared to other media. However, little in known concerning when and why spores formation occurs. According to one of the hypotheses, the formation appeared to be induced by depletion of the nitrogen source and supported by the presence of excess carbon source. In this project, the hypothesis is tested by growing *B. bassiana* on a media containing glucose, yeast extract and peptone and studied in time in order to understand the stoichiometric and kinetics of growth and sporulation of B. bassiana.

In this project, we also study the gradients in the tray/bag SSF bioreactor and their influence on the B. bassiana performance for the production of spores. Mathematical models as a tool are used to simulate temperature and gas composition profiles and to predict the safe layer thickness for maximum growth and sporulation of B. bassiana. Later on, the model is validated by measuring the temperature and gas composition profiles occurring at different depths within the tray bed when B. bassiana is cultivated in a properly controlled lab-scale tray reactor. Predicted and measured temperature and composition concentrations of several locations within the bed will then be compared.

A tray/bag is a layer of solids in which a fungus grows. Oxygen is supplied by diffusion and is consumed by the fungus which produces heat and carbon dioxide which are then transported out of the bed layer by conduction and diffusion, respectively.

In the beginning of fermentation, temperature and oxygen are location independent. During growth, temperature and gaseous concentration gradients develop within the bed causing steep gradients leading to zones with high temperature and low concentrations.

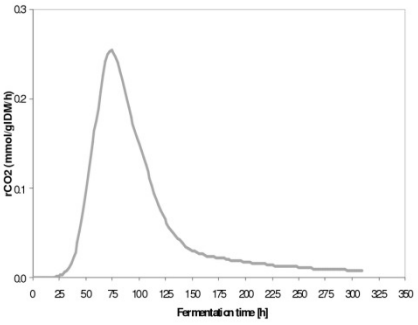

Figure 1: Time course of the carbon dioxide production rates of *B. bassiana* cultivation on medium containing glucose, yeast extract and peptone

Chemoenzymatic peptide synthesis

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OSPT theme	: Products and Processes	**Research school**	: VLAG
Supported by	: NWO	**Period**	: August 2008 – August 2012

Introduction

Peptides have an increasing importance in health care and nutrition. Currently the most mature technology for peptide synthesis is chemical synthesis. The disadvantages of chemical synthesis are, however, lack of specificity and environmental burden. These disadvantages can potentially be overcome by enzymatic peptide synthesis. Yet enzymatic peptide synthesis still has to be developed further in order for it to become commercially feasible.

Project description

The overall aim of the project is to develop low-cost versatile chemo-enzymatic strategies for the synthesis of peptides using a combination of enzymes. Our focus is to evaluate the suitability of available enzymes and to define and optimize suitable bioreactor configurations and process conditions for peptide synthesis.

Approach

One of the enzymes involved in the peptide synthesis is a peptidase, which has the ability to cleave and thereby deactivate other enzymes. One way to prevent degradation is by physical separation of the enzymes. A novel approach for this separation has been developed by the group of Prof. Cohen Stuart. Lindhoud *et al.* (Biomacromolecules **8**: 2219, 2007) were able to encapsulate enzymes in complex core coacervate micelles. This method will be tested for our system.

Micellar immobilization of enzymes and characterization of the immobilized enzymes (e.g. investigating the operational stability of the micelles) will be studied. Furthermore, a reactor design for the peptide synthesis will be proposed.

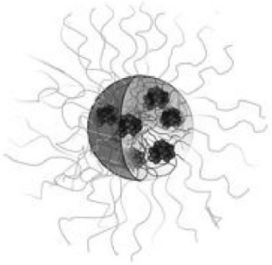

Figure 1: Complex core coacervate micelle encapsulating enzyme molecules

Acknowledgement

The research is carried out in collaboration with university groups from Groningen and Nijmegen and DSM. It is financially supported by NWO-ACTS-IBOS (ACTS: Advanced Chemical Technologies for Sustainability; IBOS: Integration of Biosynthesis and Organic Synthesis).

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Universidad de Huelva

"Harnessing the sun for microalgae cultures": Photobioreactor design, operation and control for high irradiance areas.

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OSPT theme	1. Products and Processes	**Period**:	May 2006 – May 2010

Introduction

The use of microalgae for production of high value compounds and biofuels, as well as their use in bioremediation and in animal and human feeding, is currently catching the attention from investors. However, the production cost for microalgae is still one of the main bottlenecks limiting large scale production. Since microalgae are photosynthetic organisms, the efficient use of light is a prerequisite for successful industrial production processes.

Aim

The aim of this project is to maximize the photosynthetic efficiency of the growing microalgae in a flat panel photoreactor prototype in which outdoor sunlight conditions can be simulated.

Research

Under outdoor conditions, the daily solar cycles determine the main algae growth conditions in the photobioreactors: light and temperature regimens. While temperature can be controlled, light availability becomes the dominant factor determining the productivity.

Since outdoor conditions can be simulated in the reactor, it is operated in Huelva (Andalucía, Spain) to profit from the high-irradiance clear-sky conditions.

The study of different factors involved in the productivity, as the dilution rate at different intensities will be studied. This will allow us to define an optimal control strategy to maximize the productivity of this kind of panelar reactor.

Figure 1: Simulation of outdoor conditions inside reactor with photon flux density and temperature control

Chlorella sorokiniana was selected as reference strain due to its high specific growth rate, 0.27 h^{-1} and its tolerance to high irradiance, high temperature and high CO_2 concentrations. The lamps used to simulate high photon flux densities (PFD) were red light emitting diodes (LEDs), which provide a narrow band wavelength with low power consumption and homogeneous photon flux densities.

Acknowledgements

The research project is supported by LGem, Techno Invent, Technogrow BV and University of Huelva, Spain.

WAGENINGEN UNIVERSITY
AGROTECHNOLOGY AND
FOOD SCIENCES

Production of fungal spores for control of malaria mosquitoes

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OSPT theme	: Products and Processes	**Period**	: 05-2006 – 05-2010

Introduction

Malaria is a deadly disease killing over 2 million people each year. Malaria parasites are transferred from human to human by malaria mosquitoes. Currently chemical insecticides are employed as a method for malaria mosquito control, but there is increasing resistance in mosquitoes against those insecticides. A promising alternative is the in-house application of spores of entomopathogenic fungi such as *Metarhizium anisopliae* to control mosquitoes and decrease the human-to-human transfer rate of malaria. For country-wide application a cheap, large scale production method is needed. For this we make use of solid state fermentation (SSF) as fungi usually are easier to grow and form better quality spores (conidia) in SSF.

The aim of this project is to develop a cheap, large scale production system for production of conidia of *M. anisopliae*. The first stage is the identification of a suitable substrate and fermenter type; thereafter the focus will be on the maximization of the productivity through better understanding of solid state fermentation.

Research

Based on small scale experiments with a number of substrates in Petri dishes and in aeration tubes we decided to use hemp impregnated with a rich nutrient solution as the substrate for SSF of M. anisopliae (Figure 1). It is feasible to use such defined substrates as a cost estimate indicated that substrate amounted to less than 10% of the total production cost.

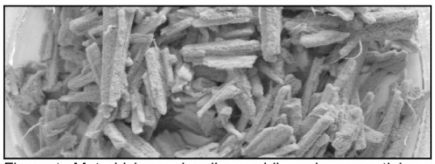

Figure 1: *Metarhizium anisopliae* conidia on hemp particles

Experiments in mixed SSF-fermenters indicated that growth is severely affected by mixing. Therefore we use packed beds, in which temperature can be controlled accurately by evaporating water (evaporative cooling). We use this established system to investigate different aspects of solid state fermentation that influence the performance of the fungus and the productivity of the fermentation.

Current research focuses on decreasing the required fermentation time, thus increasing productivity. Conidia formation is followed in time to determine the best moment for harvesting the conidia, while a number of inoculation methods are being tested to obtain a fast initiation of the fermentation (Figure 2).

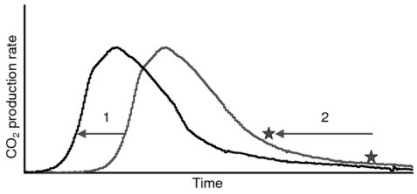

Figure 2: Decreasing total fermentation time by (1) optimizing the inoculation method and (2) optimizing the moment of harvesting.

Future research

In many SSF processes there is an initial period of exponential growth, which rapidly makes place for non-exponential, often linear, growth. The cause for this behaviour is as of yet unknown. Future research will focus on the identification of this growth limiting factor. A model will be constructed to describe the depletion of nutrients in the outer layer of the support (hemp) particles to investigate the role of diffusion in the deviation from exponential growth. Such knowledge may be used to modify the system to allow a longer exponential growth phase and thus a shorter fermentation time.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Metabolomics of carotenoid biosynthesis in the alga *Dunaliella salina*

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	Dr. C.H.R. de Vos	**Research school**	: VLAG
Research group	: Bioprocess Engineering WUR	**Supported by**	: STW-VICI
OSPT theme	: Products and processes	**Period**	: May 2005 – May 2009

Introduction

The alga *Dunaliella salina* is a photosynthetic microorganism, which is capable of accumulating large amounts of carotenoids (up to 15% of dry weight). These secondary metabolites are yellow to red pigments and possess valuable antioxidant activity. Due to these properties carotenoids have several applications in food, feed, pharmaceutical and cosmetic industry.

The elevated carotenoid production in *Dunaliella salina* is reported to be a reaction to certain environmental stress conditions (e.g. high light intensity, high salinity; see Fig. 1). The underlying mechanisms of this response, however, are not fully understood. The reason for this is that, due to the unknown genome sequence and the lack of a genetic engineering system for *Dunaliella salina*, stress response is usually just studied by measurement of carotenoid concentration.

Fig. 1: Non-stressed (left) and stressed (right) Dunaliella salina. The latter accumulate large amounts of carotenoids (orange/red pigment).

Project description

The aim of this project is to use metabolic profiling strategies to create a better understanding of the effects of physiological conditions on the carotenoid metabolism in *Dunaliella salina*. Ideally, this will generate leads for maximization of carotenoid production in this alga.

Dunaliella salina will be cultured under various environmental conditions and as many different metabolites as possible will be detected in the extracts in an unbiased manner. The obtained metabolic profiles of the different physiological conditions can be directly compared. In this way we will gain detailed insight in the pathways, which respond to the applied stress conditions. In addition, the metabolites of the carotenoid biosynthetic pathways will be extracted and analyzed under favorable conditions. The exact amount of these metabolites can be accurately quantified by using reference compounds, rendering a more accurate picture of the stress-induced differences in carotenoid metabolism in *Dunaliella*.

Using RT-PCR methods we will selectively analyze the expression of genes, which are active at the most important key points of the biochemical pathways. These genes will be selected based upon the information present in algae genomic databases. We will also use plant-based databases and use homology comparisons for sequence information and the design of effective primers. In addition, enzyme concentrations will be determined and linked to the gene-expression and metabolite data.

Acknowledgement

This research project is financially supported by STW-VICI (WLM.6622).

Oxygen production in photobioreactors: a biological approach

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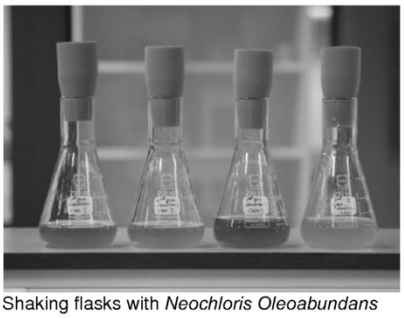
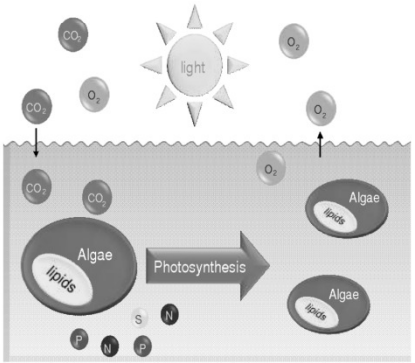
OSPT theme	: Products and Processes	**Research school**	: VLAG
		Period	: Sept. 2008 – Sept. 2012

Introduction

Microalgae receive much attention because of the need for sustainable biofuels. However, the production technology must be improved to make this technology economically feasible.
The most important issue appears to be the reduction of the energy input to build and operate large-scale algae production plants. A lot of energy is required to remove the photosynthetically produced oxygen (O_2) by means of gas transfer.



Shaking flasks with *Neochloris Oleoabundans*



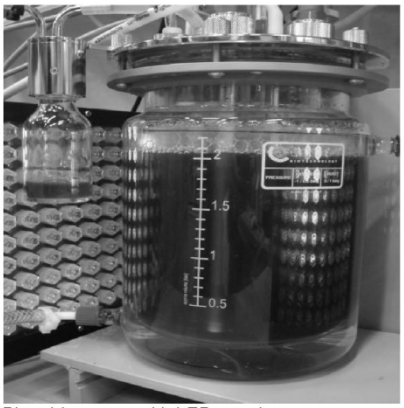
Schematic representation of liquid/gas phase (CO_2 / O_2) and photosyntesis on microalgal duplication

Technological challenge

High O_2 partial pressure inhibits photosynthesis because of photoinhibition and photorespiration. Development of an energy efficient and economically feasible process for O_2 removal.
The research approach will first relay in biological studies. Subsequently, physical studies will be performed to develop new O_2 removal technologies.

Objective

Demonstrate the possibility for spontaneous degassing of O_2 in photobioreactors and determine the critical O_2 partial pressures needed to induce this process. Set up a generic selection procedure to improve the O_2 tolerance of microalgae. Improve the O_2 tolerance of given microalgae strains and determine the physiological changes induced.



Photobioreactor with LED panel

Carbon dioxide supply in photobioreactors: a biological approach

wetsus
centre of excellence for sustainable water technology

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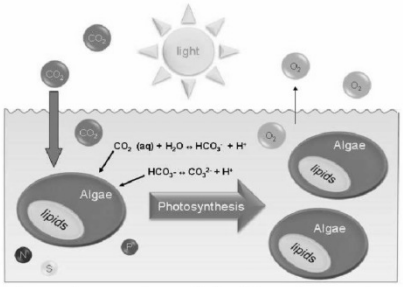
Supported by	: TTIW Wetsus	**Period**	: Sep-2008 - Sep-2012

Motivation

Microalgae are sunlight-driven cell factories that convert carbon dioxide to potential biofuels, foods, feeds and high value compounds. They have been receiving more attention recently due to the need for sustainable biofuels. However, the production technology already existing must be improved to make biofuel production from microalgae oil an energy efficient and economically feasible process.

The most important issue appears to be the reduction of the energy input to build and operate large-scale algae production plants. A lot of energy is required to supply carbon dioxide and to remove the photosynthetically produced oxygen by means of gas transfer.



Schematic overview of liquid and gas phase transport of O_2 and CO_2 during microalgal duplication.

Inorganic carbon can be stored as bicarbonate (HCO_3^-) under alkaline-saline conditions. In these conditions.

Mono Lake, alkaline-saline lake in California.

carbon dioxide transfer from the gas phase to the liquid phase could be done at a low energy input.

Technological challenge

The challenge of this research is the development of an energy efficient and economically feasible process for carbon dioxide transfer in highly productive lipid-rich microalgae. This project completely depends on species that both grow under alkaline-saline conditions and produce storage lipids. A biological approach is taken to find and select such microalgae from existing culture collections and alkaline-saline environments. The selected strains will be characterized for their performance under reference conditions of high pH, high salt concentration and moderate light. Furthermore, they will be evaluated for their lipid productivity and lipid composition as a function of those variables.

Post-treatment of municipal wastewater using algae

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OSPT theme	: Products and Processes	**Research school**	: VLAG
Supported by	: Wetsus	**Period**	: Dec 2008 – Dec 2012

Introduction

As part of the European Water Framework Directive the effluent demands of, among others, nitrogen and phosphorus will become stricter in the near future.

N	10	mg/L	current
	2.2	**mg/L**	**new**
P	2	mg/L	current
	0.15	**mg/L**	**new**

Current and future effluent demand for nitrogen and phosphorus

As a result of this development, post-treatment will be needed in the wastewater treatment plants. A system using algae forms a good post-treatment system. Algae take up nitrogen and phosphorus to assimilate into biomass, using readily available CO_2 and sunlight as carbon source and energy source.

Biofilm of Chlorella on a polycarbonate plate

Algal biofilms offer several advantages over suspended systems as:

- biomass is easier to harvest
- no suspended matter in effluent
- low energy requirement (no mixing)
- vertical placement is possible (giving higher photosynthetic efficiency due to light dilution)

Technological Challenge

The goal of this project is to develop an algal photo-biofilm system for the post-treatment of municipal wastewater. This reactor is primarily aimed to remove residual nitrogen and phosphorus in wastewater.

The challenge is to develop a process with high nitrogen and phosphorus removal during both day and night. And in addition to minimize the land requirement for this biosolar process by obtaining a high photosynthetic efficiency.

Secondly, the symbiotic relationship between algae and bacteria in a biofilm can be used. In this scenario algae and bacteria provide each other with O_2 and CO_2, while cleaning the effluent.

Acknowledgement

This research is carried out within TTIW Wetsus.

Expression screening of newly designed protein polymer genes

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OSPT theme	: Products and processes	**Research school**	: VLAG
Supported by	: B-Basic	**Period**	: Sept 2005 – Sept 2009

Introduction

Expression screening of newly designed protein polymer genes (EXSPANDS) is a project aimed at increasing predictability of protein polymer building block expression. By testing the expression of a selected set of polypeptides in a limited number of suitable expression hosts, we attempt to derive a set of guidelines for future expression of similar polypeptides.

One of the selected protein polymer building blocks is elastin like polypeptide. Elastin like polypeptides (ELPs) are designer polypeptides inspired by hydrophobic regions of elastin, these polypeptides are known for their elasticity, biocompatibility, and inverse phase transition behavior in solution. Heating solutions of ELPs above a transition temperature gives protein aggregation, a feature that can be used for a multitude of applications like; protein purification, controlled drug delivery or drug targeting.

Expression of Elastin like polypeptides

The expression of elastin like polypeptides has been described in literature for various expression systems, but up to date *E. coli* remains the most successful the expression host. In this expression system ELP is produced inside the cells, when using a hyper expression protocol volumetric expression levels of 200-400 mg l^{-1} are obtained. We have recently found that secreted expression of ELP is possible in *Pichia pastoris* expression cultures, by using the α-factor signal sequence.

Fermentor setup used for P. pastoris cell cultures

Future prospective

We are now focusing on the production of elastin based biomaterials. We want to design and produce new elastin building blocks (or combine elastin with other protein blocks) to get polypeptides that have more suitable properties for biomaterial applications.

The production of such building blocks starts at DNA level, with the production of genes encoding for different block types. The blocks are then combined with genes of other block types, or with the same block type to create a gene encoding for a larger polypeptide. The genes are then placed into *Pichia pastoris* and produced in methanol induced fed batch cultures in 2 l fermentors. The expressed genes can often be purified from the fermentation broth by using their distinct protein properties.

Acknowledgement

This project is financially supported by the Netherlands Ministry of Economic Affairs and the B-Basic partner organizations (www.b-basic.nl) through B-Basic, a public-private NWO-ACTS programme (ACTS = Advanced Chemical Technologies for Sustainability).

AGROTECHNOLOGY & FOOD SCIENCES GROUP
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Growth inhibition of *Monodus subterraneus* by free fatty acids

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Research school	: VLAG	**Period**	: 2000-2009 (50%)

Introduction

Monodus subterraneus is a freshwater microalga, which produces high concentrations of eicosapentaenoic acid (EPA, 20:5ω3) and is regarded as one of the most promising algal EPA producers. For commercial EPA production, high volumetric productivities are needed to reduce photobioreactor size and downstream processing costs.

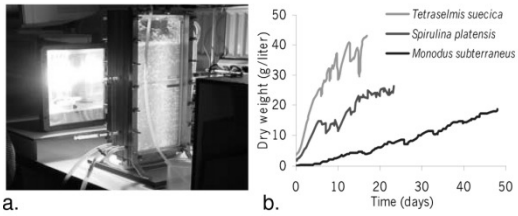

Fig. 1 a. Flat panel photobioreactor
b. Typical batch runs for several strains

In flat panel photobioreactors microalgae can be grown at high cell densities (Fig. 1). However, at these high biomass concentrations a reduction of productivity is observed. It has been suggested that this reduction in productivity is caused by compounds released by the microalgae.

Aim

We hypothesized that this auto inhibition was caused by fatty acids released by the microalgae. Our aim was to investigate if free fatty acids produced by *Monodus subterraneus* inhibited growth of this species.

Results

Several fatty acids were tested on their growth inhibitory properties. Here, the growth inhibition test of EPA is shown (Fig. 2). This figure shows that growth of *Monodus* was inhibited with increasing EPA concentration.

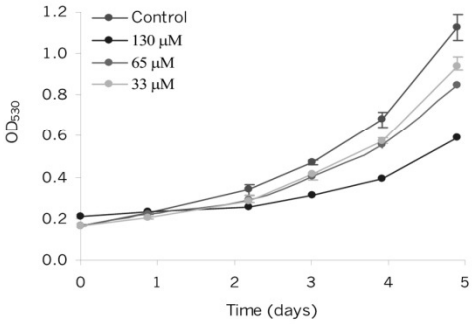

Fig. 2. Effects of different concentrations of EPA (20:5ω3) on growth (measured as OD_{530}) of Monodus.

Most fatty acids at saturated concentrations inhibited *Monodus subterraneus* to some extent. To compare the different fatty acids, the concentration at which 50% inhibition (IC50) occurred was calculated. Palmitic acid (16:0) and oleic acid (18:1ω9) were strongest inhibitors causing 50% growth inhibition at concentrations of 0.4 μM and 3 μM, respectively.

Conclusion

In high cell density cultures of *Monodus subterraneus*, palmitic acid and oleic acid are likely to cause growth inhibition, since they are also present in *Monodus*.

Effects of O_2 concentrations on growth and fatty acid composition of *Nannochloropsis* sp.

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OSPT theme	: Product and Process	**Research school**	: VLAG
Supported by	: Royal Thai Government	**Period**	: 18 May 2005 – 18 May 2010

Introduction

Nannochloropsis sp. is extensively cultured for aquaculture for its high level of poly-unsaturated fatty acids (PUFA). In large-scale production of the microalgae accumulation of O_2 is one of the most severe problems. High O_2 concentrations compete with CO_2 for the photosynthetic enzyme RuBisCo at low light as well as at high light intensities. In addition, high O_2 concentrations combined with high light intensity will stimulate photoinhibition and cause photooxidation. This will reduce biomass productivity and may influence product quality.

Within photobioreactor systems the microalgae will experience dynamic changes in oxygen concentrations and it is not clear, how algae respond to these dynamic changes.

Aims

For optimal design of closed tubular photobioreactors for growth and production of *Nannochloropsis* sp., we need to investigate the effects of oxygen on growth and PUFA content of *Nannochloropsis* sp. at different light intensities and reveal the effects of dynamic changes in O_2 concentration on growth and fatty acids composition.

Approach

A flat panel photobioreactor set-up (figure 1) is operated in turbidostat mode. This set-up enables us to quantitatively reveal the effects of oxygen and possible oxygenated products on the growth and PUFA content in *Nannochloropsis* sp. at controlled and constant light conditions as well as at controlled changing light conditions. The effects will be investigated at reactor level as well as on molecular/cellular level.

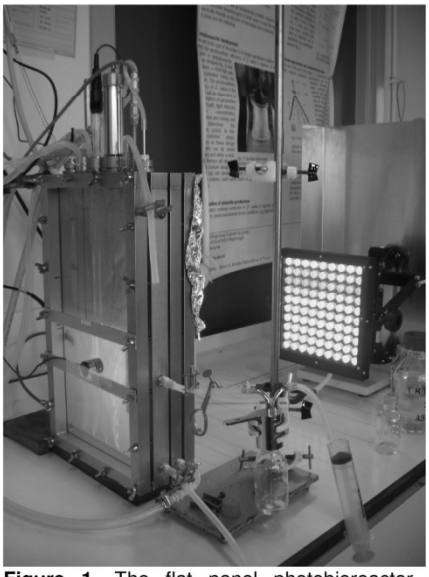

Figure 1. The flat panel photobioreactor for growing *Nannochloropsis* sp. is operated in turbidostat mode.

Acknowledgement

This research project is carried out within the framework of the VLAG. It is financially supported by Royal Thai Government.

Agrotechnology and Food Sciences Group

Research Group

Valorisation of Plant Production Chains

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Ir. Maarten Kootstra
Ir. Tijs Lammens
Dianika Lestari
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Ir. Bas Meussen
Anna Steinle (DE)
Yinglai Teng
Dr.ir. Jac Aarts
Dr. Hamdy Saad
Yessie Sari

Activities of the Group
The Wageningen University, Chair of Valorisation of Plant Production Chains (WU-VPP) is a multidisciplinary research group within the Agrotechnology and Food Science Group (AFSG) performing scientific and applied research aiming at the development of economically and environmentally sound (bio)chemical, enzymatic and biological conversion and fermentation processes. These processes are based on plant raw materials and should substitute fossil resources of bulk chemicals. Key components of the research are the definition of measures to reduce industrial energy consumption on a global scale, to fully exploit available and as yet uncovered cheap resources of agricultural (waste) streams, and to decrease CO_2 emissions and pollution.

The group's projects are organized around a number of central themes:

- Energy, exergy and economy aspects of plant-based production processes
- Biorefinery
- Biomass utlization
- Bioconversion
- Nitrogen-rich bulk chemicals
- Fermentation and process technology
- Enzymatic conversions
- Separation and extraction technologies
- Metabolic engineering.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
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Production of chemicals and feed ingredients by processing lignocellulosic rest streams using organic acids

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OSPT theme	: Products & Processes	**Research school**	: VLAG
Supported by	: CCL Research	**Period**	: Sept 2005 – Dec 2009

Introduction

When producing chemicals by fermentation, readily fermented raw materials like sugar and starch derived from crops are often used. However, cheaper carbohydrate rich streams from agriculture, like corn stover, wheat straw, or forestry could be utilized. This lignocellulosic plant biomass requires pre-treatment in order for the subsequent enzymatic hydrolysis of plant cell wall polysaccharides into fermentable sugars to be efficient[1]. A standard pre-treatment is dilute sulphuric acid in combination with heat, but this leads to the formation of compounds such as furfural and 5-HMF that inhibit ethanol yeast fermentation and will also generate inorganic waste[1,2,3]. The organic maleic acid has been mentioned as a possible alternative as its application results in high sugar yields and in smaller amounts of the inhibiting byproducts[4]. Within this project, the possibilities for producing value-added chemicals and animal feed ingredients, such as lactic acid, fumaric acid, ethanol and lysine, are researched. The aim is to use organic acids in the pre-treatment of the lignocellulosic plant biomass.

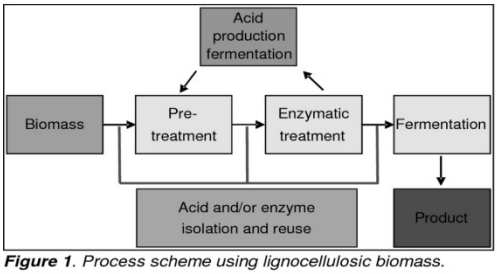

***Figure 1**. Process scheme using lignocellulosic biomass.*

Approach

The different stages in the process (see Figure 1) are focused upon separately. The sugar degradation in the pre-treatment, the fermentative production and recycle of the organic acid are focal points, but also the valorisation of the side stream plays a key role.

State of affairs

In experiments that mimic pre-treatment conditions it was found that organic acids cause less arabinose degradation than the stronger sulphuric acid. It was also shown that specific acid catalysis does not apply to degradation in presence of maleic and fumaric acid. The degradative behaviour of maleic acid did not exceed that of water, while that of fumaric acid was even less (see Figure 2). This makes application of fumaric acid advantageous for lignocellulosic ethanol production processes[5].

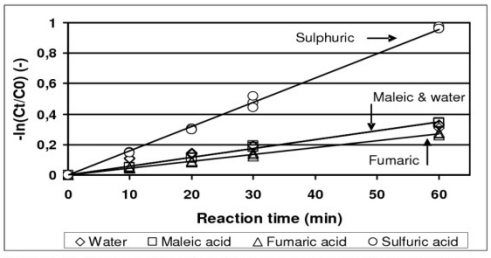

***Figure 2**. Degradation of arabinose at elevated temperatures.*

Acknowledgement

This research project is financially supported by CCL Research.

References

1. Mosier, N. et al., Biores. Techn., 2005. 96(6).
2. Lawford, H.G. and J.D. Rousseau, Appl. Biochem. and Biotechn., 2003. 106(1-3).
3. Lloyd, T.A. and C.E. Wyman,. Biores. Techn., 2005. 96(18).
4. Mosier, N.S. et al., Biotechn. Progress, 2001. 17(3).
5. Kootstra, A.M.J. et al., Biochem. Eng. J., 2009. 43

AGROTECHNOLOGY & FOOD SCIENCES GROUP
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Multistage countercurrent protein extraction of *Jatropha curcas* press cake

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OSPT theme	: Products & Processes	**Research school**	: VLAG
Supported by	: KNAW	**Period**	: Nov 2006 – Nov 2010

Introduction

Jatropha curcas is grown mainly for oil production. After oil removal, *Jatropha* press cake contains approximately 24% protein (DM). Due to the present of toxic compound in press cake, *Jatropha* protein application will be focused on non food or technical, such as adhesives, and coatings. Therefore, this research aims to obtain high protein recovery from *Jatropha curcas* press cake at low solvent to solid ratio by using multistage countercurrent extraction at room temperature, in order to produce large amount of protein with minimum cost.

Methods

Countercurrent extraction of *Jatropha* press cake were carried out by using batch extractions sequences shown in *Figure 1*.

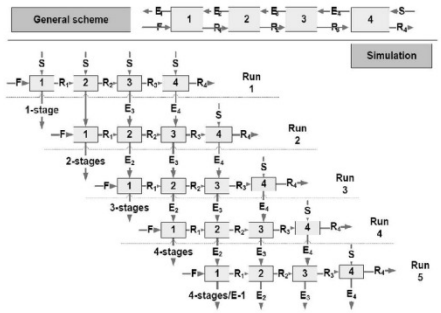

Figure 1 *Four stages countercurrent extraction* (*1, 2*)

Results

Countercurrent protein extraction at room temperature by using 0.055 M NaOH at solvent to solid ratio of 4 g/g successfully improves protein recovery from *Jatropha curcas* press cake one-stage extraction. Not only improves protein recovery from 35 to 70%, but also improves protein concentration in extract flow from 32 to 63 mg/mL.

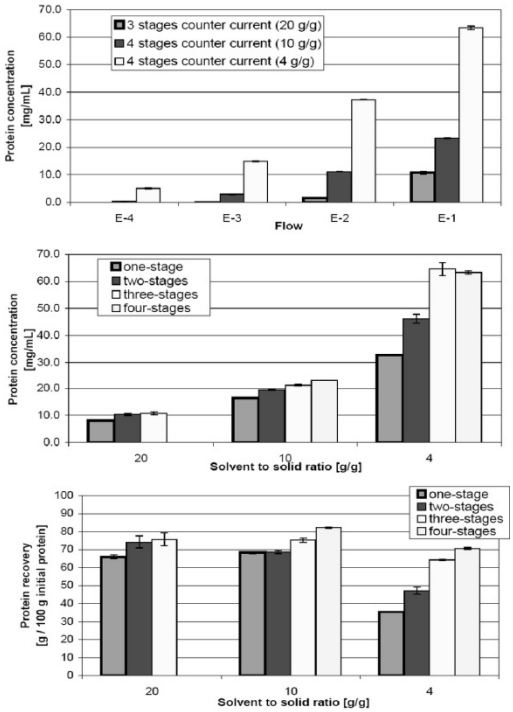

Figure 2 *Protein recovery and protein concentration obtained by using countercurrent extraction*

Acknowledgement

The authors are grateful to the KNAW for the financial assistance.

References

1. Adupeasah, S. P., Diosady, L. L., and Rubin, L. J. (1993) A MULTISTAGE HYDROCYCLONE STIRRED-TANK SYSTEM FOR COUNTERCURRENT EXTRACTION OF CANOLA OIL, *Journal of the American Oil Chemists Society 70*, 755-762.
2. Moure, A., Franco, D., Sineiro, J., Dominguez, H., and Nunez, M. J. (2003) Simulation of multistage extraction of antioxidants from Chilean hazelnut (Gevuina avellana) hulls, *Journal of the American Oil Chemists Society 80*, 389-396.

WAGENINGEN UNIVERSITY
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A novel process route for the production of building blocks for chemicals from protein sources using electrodialysis

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OSPT theme	: Separation Technology	**Research school**	: VLAG
Supported by	: STW	**Period**	: Apr 2008 – Apr 2012

Introduction

Amino acids (AA) are very interesting feedstocks for the chemical industry because of the functionality they contain[1]. They can be obtained from hydrolysis of cheap protein wastes or side streams obtained from bioethanol production for example, and separated by electrodialysis (ED). However, to increase the efficiency of ED of AA's with the similar isoelectric points (pI), modification or removal of charged groups such as -COOH is required. For example, specific enzymatic reactions can be considered. Both modification and separation technology will be integrated into one process route for the production of chemicals which are traditionally made from petroleum industry (see Figure 1).

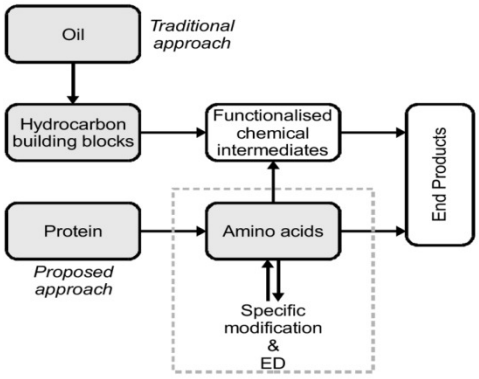

Figure 1. *New route for producing chemicals.*

Approach

A possible route starts with the hydrolysis of protein into a mixture of 20 standard AA's. Followed by ED, the mixture can be separated into acidic, basic and neutral AA groups. The present research is focusing on the specific modification and separation of basic AA's: arginine (Arg) and lysine (Lys). L-lysine decarboxylase (LDC) may be used to achieve this.

As shown in Figure 2, LDC can specifically convert Lys to cadaverine (Cad.)[2,3,4] while Arg is not affected. Such a reaction can be carried out either in buffer (pH = 6.0) or without buffer. At the pH = 10.76 (pI of Arg), Arg has no charge while Cad. is positively charged[5]. Thus ED can be applied to remove Cad. from Arg.

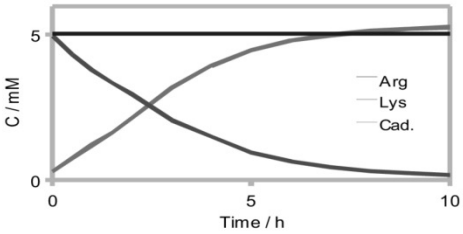

Figure 2. *Arg + Lys with LDC (buffer free).*

Acknowledgement

This project is financially supported by STW and carried out jointly with University of Twente.

References

1. Scott et al., Appl. Microbiol. Biotechnol. 2007, 751, (75). 2. Gale & Epps, Biochem. J. 1944, 232 (38). 3. Soda & Moriguchi, Biochemical and biophysical research commuinication 1969, 34 (34). 4. Soda & Moriguchi, Meth. Enzymol. 1971, 667 (17). 5. Kvašnicka & Voldřich, J. Chromatogr. A 2006, 145 (1103).

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Aqueous *Jatropha curcas* oil extraction assisted by pure culture of new *Bacillus licheniformis* strain

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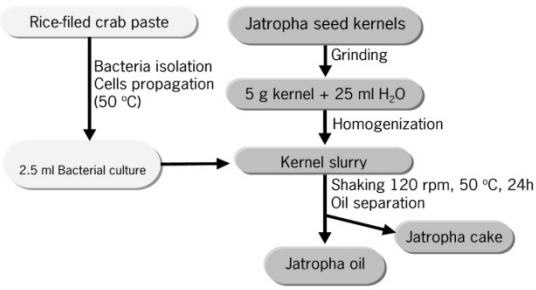
Introduction

Aqueous oil extraction assisted by enzymes or proteolitic microbial cells has attracted attention due to its mild conditions, clean process, and lower investment costs[1, 2]. The process also allows prompt removal of some toxins or antinutritional compounds from certain oilseeds[3, 4]. A new method of aqueous Jatropha oil extraction assisted by bacterial culture is reported here. Strains isolated at higher temperature (50 °C) from the gut of rice field crab was used to extract Jatropha oil from unheated Jatropha seed kernels.

Methods



Results

Four different rodlike bacteria were isolated from pasted crabs: BK21, BK22, BK23 and BK24. Fig. 1 shows screening results of selected bacteria strains on unheated Jatropha kernel slurry. BK23 gave best oil yield to be 51%, while BK21 and BK22 each gave lower oil yield (45%). In contrast, BK24 liberated only 6% oil from jatropha kernel slurry.

A 16S rRNA sequence of strain BK23 was determined. The similarity rank analysis showed that BK23 is closely related to members of the genus Bacillus; therefore we propose the assignment of this isolate as *Bacillus licheniformis* strain BK23

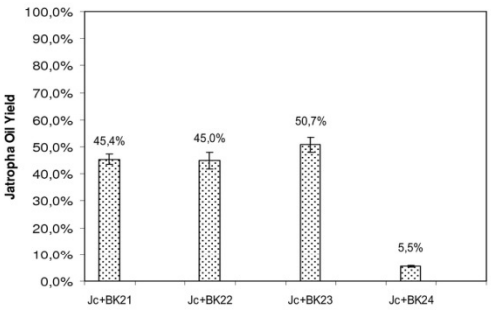


Fig. 1. Screening results of selected bacteria strains on Jatropha kernel slurry incubated at 50 °C for 24 hours. Jc=*Jatropha curcas* kernel.

If BK23 cells were firstly propagated in nutrient broth, culture addition into kernel slurry released 47% oil at 37 °C and 60% at 50 °C.

Conclusions

BK23 is shown capable of releasing oil from unheated (raw) Jatropha kernels. Process optimization in the future is important to improve oil yield that is applicable for commercial process.

References

1. Rosenthal, A.; Pyle, D. L.; Niranjan, K., Aqueous and enzymatic processes for edible oil extraction. *Enzyme and Microbial Technology* **1996,** 19, (6), 402-420.
2. Man, Y. B. C.; Karim, M.; Teng, C. T., Extraction of coconut oil with Lactobacillus plantarum 1041 IAM. *Journal of the American Oil Chemists Society* **1997,** 74, (9), 1115-1119.
3. Cater, C. M.; Rhee, K. C.; Hagenmai.Rd; Mattil, K. F., Aqueous extraction - alternative oilseed milling process. *Journal of the American Oil Chemists Society* **1974,** 51, (4), 137-141.
4. Caragay, A. B., Pacing technologies in the fats and oils industry. *Journal of the American Oil Chemists Society* **1983,** 60, (9), 1641-1644.

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Food Process Engineering Group

The Food Process Engineering laboratory participates in the gradate schools OSPT, VLAG en BSDL.

The Food Process Engineering group is active in the field of synthesis and purification of high-value food ingredients and in new structuring processes for food products. An important aspect is the development of new experimental and modeling methods to characterize and quantitatively describe the behavior of the complex media that foods are (e.g., concentrated, polydisperse suspensions and multi-component emulsions, or non-ideal granular media), with the help of various techniques, amongst others lattice-Boltzmann methods, which give the possibility to design the process from the phenomena inside the product stream.

Food structuring. The mild and low-energy preparation of monodisperse emulsions with the help of new, micro-technological systems is studied in a number of projects.
Another important area is structuring of biopolymer-based products. A new type of equipment has been developed that for the first time allows detailed study of the changes in the material under well-defined shear fields and types of very high intensity. Several projects look into structuring with protein, starch, protein/starch mixtures, and protein/starch/fat mixtures.

Food grade synthesis and purification of food ingredients. We aim to produce specific, high-value ingredients for food products. This is achieved through the application of enzymatic conversions, often under non-conventional conditions, in combination with new separation processes, and through new fractionation technology, based on the application of micro-technological (microsieve) technology.

Mild Isolation and Fractionation of Biomacromolecules from Agro- and Biofeedstocks

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Introduction

Membrane technology has led to significance importance with wide number of applications in recent decades and with emergence of ideal membrane cascades (Fig. 1) for downstream processing (DSP) [1, 2]. Membrane cascades gaining importance for the separation of the macromolecules and small molecules [3]. Membrane filtrations are giving growing competition to variants of chromatography for final polishing stages of DSP. Most of them suffer from the high capital cost, low space velocities and dependence on concentration diffusion within absorbed pores. Slow diffusion is a problematic for the macromolecules for which the choice of the suitable absorbents is severely limited. Membranes can greatly increase transport rates by convection relative to those only by diffusion. However, the most efficient membrane filter cannot provide the best separation performance with respect to chromatographic processes. Thus, it is a conviction that integrated membrane cascade system with different configurations might over come this problem [1, 2].

Aim

Development of membrane cascades to fractionate small molecules.

Scope definition

A general model will be developed with the minimum amount of input parameters for the design of a membrane cascade. The model will be validated on the lab scale. Cascade membrane systems will be tested on pilot scale.

Research Approach

1) Single stage Experiments: flux and rejection evaluation
2) Development of the membrane single stage and cascade model
3) Cascade experiments and model validation

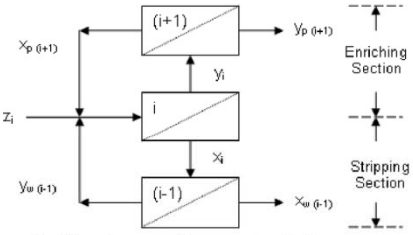

Figure 1: Membrane Cascade Scheme

Ideal cascade condition:

(i) $y_{i-1} = x_{i+1} = z_i \quad (i = 2, 3, ..., n-1)$

(ii) $\beta = y_i(1-z_i)/z_i(1-y_i)$ is constant

when condition 1 and 2 are met, α is constant and $\beta = \sqrt{\alpha}$; where, x_i, y_i, z_i stream compositions, β is head separation factor and $\alpha = y_i(1-x_i)/z_i(1-y_i)$ is stage over all separation factor.

Acknowledgement

This research project is sponsored by Dutch Separation Technology Institute (DSTI).

References

[1] E. N. Lightfoot, *Separation Science and Technology* **2005**, *40*, 739

[2] E. N. Lightfoot, T. W. Root, J. L. O'Dell, *Biotechnology Progress* **2008**, *24*, 599.

[3] B. Van der Bruggen, M. Mänttäri, M. Nyström, *Separation and Purification Technology* **2008**, *63*, 251

Modelling and design of membrane fractionation of milk

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Supported by	: Micro-Ned	**Period**	: April, 2006 – April, 2010

Introduction

Milk is used as a starting material for the manufacture of many dairy products. However, the functionality of the various components in milk (e.g. whey protein, casein and fat) could be utilized more effectively if they were available as separate components. Therefore, the fractionation of milk is of interest, not only for improvement of product quality but also for economic reasons. The selectivity and efficiency of current membranes are not sufficient to make the fractionation process a reality. Recently, micro sieves have become available: a new type of membrane with low flow resistance, and defined uniform pore size. The properties are such that the fractionation of milk seems possible on commercial scale.

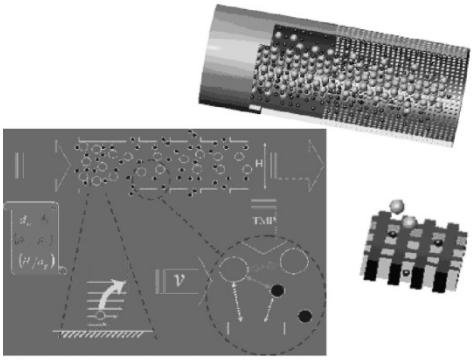

Fig 1: Particle migration phenomena

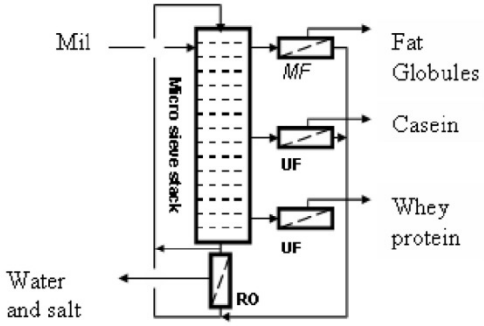

Fig.2: Membrane fractionation stack

Objective

The objective of this project is to study the different interactive parameters influencing particle migration in pressure driven flows and as a result see how the later phenomena can be used to mitigate the existing ***selectivity*** and ***flux*** problems in membrane separation. The ultimate aim is to use the potential of such particle movements in the design of membrane fractionation stack for milk and other areas of applications.

Approach

The research anticipated to encompass three stages:

1. Experimental investigation of the different parameters (some of them indicated in figure 1)
2. Develop models at mesoscopic scale which can be used for engineering design based on Lattice Boltzmann.
3. Design of fractionation stack.

Mild Fractionation of Suspensions and Emulsions

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Introduction

In the food industry, fractionation of components from foods with the aid of membranes is increasingly performed. A large disadvantage of fractionation with membranes is accumulation of components on or near the membrane, causing reduced flux. This cake layer formation is called fouling. The cake is not infinitely increasing in height, since there is also back-transport of particles from the cake towards the bulk. One of the back-transport mechanisms is shear-induced diffusion. This phenomenon occurs when particles are subjected to shear, which is created due to local differences in velocity. Particles diffuse towards the bulk, where low shear is present.

Besides investigating shear-induced diffusion as back-transport mechanism, studies also looked at particle distribution of suspensions under the influence of shear. In these studies it was concluded that larger particles migrate with a larger diffusion coefficient than the smaller particles (*figure 1*). In this way shear-induced migration enables separation on size of the feed flow and makes it useful for fractionation.

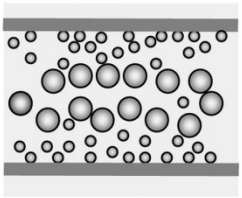

Figure 1: Size separation based on shear-induced diffusion

Aim of the project

The aim of the DSTI project is to obtain process conditions, system geometries and design under which fractionation of particles, using shear induced diffusion, is optimal.

Approach

As a start, fractionation experiments will be performed with membrane systems (*figure 2*)

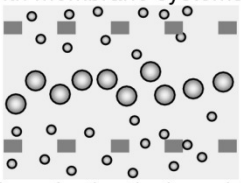

Figure 2: Membrane fractionation by applying shear-induced diffusion

The larger particles (green) will migrate to the centre of the channel, while the smaller particles (red) will migrate over a shorter distance. The pores are larger than the particles, in order to minimize the effect of fouling on the membrane. Optimization of the fractionation yield, by changing process conditions like feed flow velocity and feed concentration, will be aimed for.

Additionally, a method to quantify shear-induced diffusion will be developed, by online measurement of the particle and fluid behaviour. From the data, knowledge will be obtained about the optimal process conditions and system geometries. The improved or new system acquired, should lead to increased fractionation efficiency and reduced fouling under mild processing conditions. This, in turn, reduces energy use and saves costs of separation in food industries, like dairy and beer.

Acknowledgement

This project is carried out within the framework of DSTI and is conducted in cooperation with Norit X-Flow, Friesland Foods and Royal Cosun.

AGROTECHNOLOGY & FOOD SCIENCES GROUP
WAGENINGEN UR

Fractionation of suspensions and colloidal solution with Deterministic Ratchet

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Introduction

Nowadays microfluidic devices are quite popular for cell/DNA sorting and fractionation. Deterministic ratchets seem most promising for fractionation application of concentrated suspensions based on particle size with less particle accumulation [1].

Deterministic ratchets [2] consist of periodic arrays of obstacles. The feature of an array of obstacles is that each next row of obstacles is shifted with $\Delta\lambda$ perpendicular to the flow direction (see figure 1). The shift $\Delta\lambda$ is a fraction of λ, the distance from centre to centre of the obstacles ($\Delta\lambda < \lambda$).

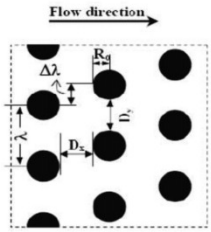

Figure 1. Geometric parameters are defined with 3 obstacle rows in a periodic cell.

Aim of the project

The aim of this research project is to fractionate more concentrated suspensions and colloidal solution by the ratchet devices.

The fractionation of deterministic ratchets follows the flow line sieving principle. The flow field between the obstacles in the pore is divided into number of flow lanes ($N=\lambda/\Delta\lambda$) which are separated by dividing streamlines via stagnation points (obstacles) inside the microchannel. The number of flow lanes is also equal to the number of obstacle rows in one periodic cell.

The fractionation is based on the radius of particle, r_p and the critical lane width, D_c. D_c, a fraction of D_y, is used to determine the movement of particles (see figure 2).

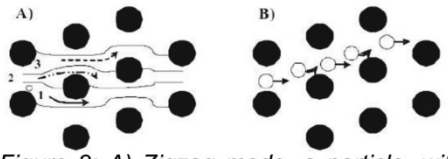

Figure 2: A) Zigzag mode, a particle, with radius smaller than the lane width, follows streamline following lane 1, 3, 2 and back to lane 1. B) Displacement mode, a particle, with radius larger than the lane width of lane 1, moves in the initial lane.

Research

Devices are simulated by using Lattice Boltzmann methodology. This will lead to basic design guidelines on the ratchet geometry, dynamic flow patterns, concentration regimes and interparticle interactions that are important.

Based on the results of the simulation, a number of ratchets will be manufactured, which will probably imply the application of micromachining on scales smaller than one micrometer.

The ratchets will be experimentally tested with microscope connected with high speed camera, in which particles can be followed and analyzed via image analysis.

Reference

[1] T. Kulrattanarak, R.G.M. van der Sman, C.G.P.H. Schroën, R.M. Boom. Adv. Colloid Interface Sci., 142 (2008) 53-66.
[2] L.R. Huang, E.C. Cox, R.H. Austin, J.C. Sturm. Science, 304 (2004) 987-990.

Acknowledgement

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AGROTECHNOLOGY & FOOD SCIENCES GROUP
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Lactose hydrolysis and enzyme immobilization

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Introduction

Next to hydrolytic activity of β-galactosidase (EC 3.1.2.23), which converts lactose into galactose and glucose, the enzyme possesses transgalactosylic activity and converts lactose into galacto-oligosaccharides (GOS). (Boon 2000; Bruins 2003) The mechanism of lactose hydrolysis and transgalactosylation is shown in Figure 1.

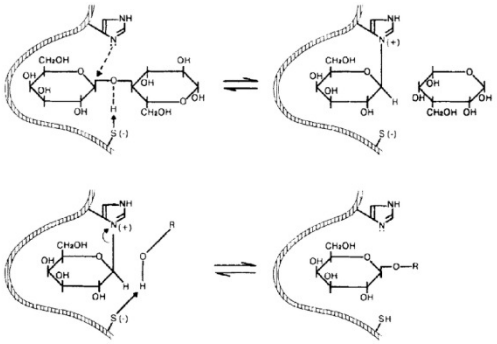

Figure 1. Mechanism of lactose hydrolysis and transgalactosylation (Prenosil et al. 1987).

GOS consist of a mixture of oligosaccharides with degree of polymerization (DP) 1 up to DP 10 with a varying amount of galactose molecules attached to a lactose molecule. GOS have several health benefits and can be used as prebiotics (Boon 2000; Bruins 2003). Furthermore, some GOS are naturally present in human breast milk and can be used as an ingredient for infant nutrition (Boon 2000).

Aim of the research

The final aim of this CCC project is to optimize GOS production by constructing a process that results in a higher oligosaccharide yield and a lower lactose content.

Approach

The enzyme preparation used is a β-galactosidase from *Bacillus circulans*. The focus will be at determination of the kinetics of the enzyme preparation. This will be performed in micro reactors. Next, a kinetic model will be constructed, which can be used to make predictions on oligosaccharide yield.

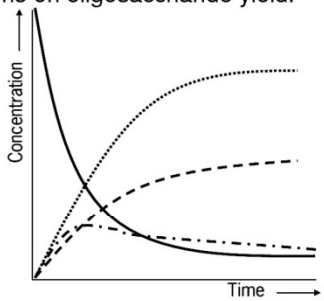

Figure 2. Lactose conversion into glucose, galactose, and trisaccharides in time. Symbols: — lactose; ····· glucose; – – galactose; – · – trisaccharide. Adapted from: Bruins (2003).

Subsequent process optimization might include other reactor concepts, increase of the substrate concentration, and change of pH and temperature.

Acknowledgement

This project is carried out within the framework of the Carbohydrate Competence Center (CCC) in cooperation with FrieslandCampina Domo and the University of Groningen (RUG).

References

Boon, F. (2000). *"Enzymatic synthesis of oligosaccharides."* Process Engineering. Wageningen University. PhD thesis.

Bruins, M. E. (2003). *"Oligosaccharide production with thermophilic enzymes."* Process Engineering. Wageningen University. PhD thesis.

Prenosil, J. E., E. Stuker, and J. R. Bourne (1987). *"Formation of oligosaccharides during enzymatic lactose: Part I: State of art."* Biotechnology and Bioengineering 30(9): 1019-1025.

New food-grade microencapsulation systems produced with microtechnological devices

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Introduction

Targeted and controlled delivery of drugs or probiotics is a major goal for the pharmaceutical and food industry. For efficient smart delivery, microcapsules should have sufficient (mechanical) stability, a well defined permeability to the encapsulated material, present a release trigger mechanism, and ideally be monodisperse. Also, especially for food applications, its shell has to be food-grade and inexpensive.

Recently, there has been an increased interest in using self-assembled colloids and polymers at emulsion droplet interfaces to form microcapsules. In the conventional method to produce them emulsion droplets are used as 3D colloidal "templates", whose size and shape determine the morphology of the obtained particle aggregates. Unfortunately, current approaches rely on bulk emulsification methods that produce microcapsules with a broad size distribution, and further these methods are restrictive with respect to the materials employed. On the other hand, methods that exploit the great potential of interfacial assembly for producing microcapsules have been hampered by the lack of understanding of the self-assembly process.

Aim

The main goal of this project is to develop new food grade microcapsules based on electrostatic layer-by-layer adsorption on emulsion droplets, using combinations of oppositely charged proteins, polysaccharides and/or colloidal particles, together with microchannel processing technology. The production of the microcapsules will be approached experimentally and computationally.

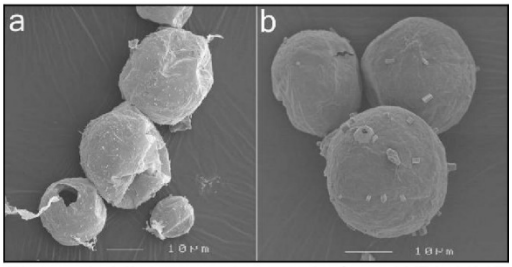

Figure 1: Microcapsules made from WPI, HMP and WPI-fibrils with (a) three layers and (b) seven layers

References

Sagis, L.M.C., de Ruiter, R., Rossier Miranda, F.J., de Ruiter, J., Schroën, C.G.P.H., van Aelst, A.C., Kieft, H., Boom, R., van der Linden, E. *Polymer microcapsules with a fiber-reinforced nanocomposite shell*. Langmuir **24**, 1608 (2008)

Acknowledgement

The project is a collaboration project between the Food Physics group and the Food Process Engineering group of Wageningen University, and part of the national research initiative MicroNed. Francisco J. Rossier Miranda is personally sponsored by the Programme AlBan, the European Union Programme of High Level Scholarships for Latin America, scholarship No.E05D060840CL.

Flow-induced structuring of protein-rich foods

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OSPT theme : Product and Processes
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Introduction

Structured and concentrated protein-rich foods gain increased interest due to health and aesthetic reasons. A high protein intake is reported to slow down sarcopenia progression in elderly people, to provide more satiety than carbohydrates and fat, and to contribute to body weight regulation. However, the formation of multi-level structures in concentrated protein systems is not yet optimal, which leads to poor sensory and texture properties, and stability problems. The latter is caused by extensive protein-protein interactions present in concentrated protein systems leading to water syneresis and product hardening.

Objective

The objectives of this project is to get insight into the dependency of structure formation to protein concentration in protein-rich products and to understand the mechanisms driving product hardening. Well-defined flow is utilized to understand underlying mechanisms of structure formation in highly concentrated systems.

Research

Whey protein isolate (WPI) is used as a model protein in this project with the gel as the model product. During the initial stages of this project, we study the rheological properties of the starting material and the mechanical properties of the model product in time. We prepared the products with different process conditions under shear flow. We expect that the rheological properties influence protein interactions under shear, which lead to differences in structure formation. An in-house developed shearing device, which is an upscale of a cone-plate geometry of a rheometer, is used in this project.

Results show that shear flow slightly reduced hardness of the fresh gel (Fig.1). However, the hardness levels between un-sheared and sheared gels were comparable after three days storage.

Obviously, mechanisms of hardening process can not be counteracted solely through mechanical processing, suggesting the importance of an inherent WPI-property.

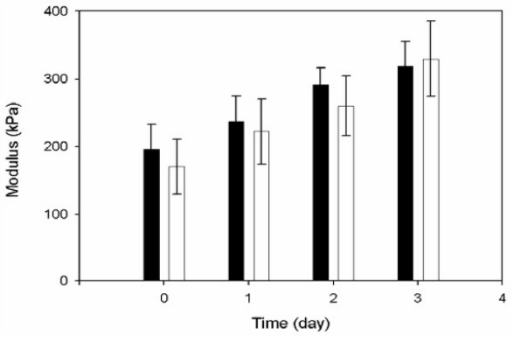

Fig 1. Hardening of unsheared (■) and sheared (□) gels upon storage.

Currently, we are investigating modifications of WPI in order to influence the mechanical properties of the model product.

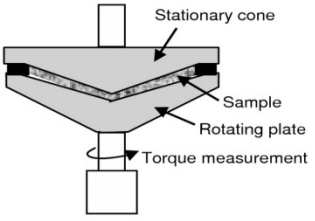

Fig2. Schematic picture of a shearing device with well-defined flow.

Acknowledgement

This research is financially supported by Top Institute Food and Nutrition (TIFN).

Massive parallelization of multi-chamber microreactors for selective reaction and separation

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OSPT theme	: Separation Technology	**Research school**	: VLAG
Supported by	: NWO (PoaC)	**Period**	: Feb. 2006 – Jan. 2010

Introduction

Microreactors can be characterized by large specific interfacial areas, short diffusion distances and laminar flows. As a result, microreactors are suited for in situ separation of products.
To increase total production we can scale-up the microreactors in parallel while maintaining the advantageous properties. In this PoaC project we explore the opportunities of the microreactor. Current research focuses on new techniques for reaction analysis and separation.

Project aim and description

This project's aim is to develop modular assemblies with up-scaled micro-fluidic devices for gas-liquid as well as liquid-liquid systems where contact between different phases can be controlled and optimized. It involves mainly enzymatic processes in polymeric micro-fluidic devices with a focus on reaction and separation.
Besides enzymatic processes, virtual prototyping is used in order to provide fluid dynamics and design rules for micro fluidic devices. These devices are currently fabricated by micromilling in porous polymer layers. These polymer layers are stacked with a membrane in between to form flat plate membrane microreactors. This fabrication method offers the opportunity to quickly build and test new microreactor designs and the polymeric structures have an unprecedented flexibility for a microreactor. The advantageous property can be used for rolling and stacking of these chips in modular assemblies.

Current research: mass diffusion in liquids

Although it is not widely known, mass diffusion has been examined experimentally and theoretically for the separation of liquid mixtures (F. O. Shuck 1963). Properties of liquids as viscosity, density and polarity among others make the introduction of a so called enhancer for mass diffusion less straight forward than in gaseous mixtures (Geboers et al. 2007). Ideally such an enhancer is inert, well described and does not affect the separation if only for the retention.
A membrane to control mass transfer between liquid phases would apply to the description as a static enhancer. Such membranes commonly are inert for the solutes and they have a characteristic permeability for each component. Therefore, membranes can be characterized as enhancers. They exhibite a larger friction with one of the components of the mixture than with the others, provided that the membrane does not exclude components (e.g. has a very low permeability or high retention).
We are developing a device for mass diffusion separation that utilizes the described principle. Hence only two solutes are required and issues with introducing a liquid enhancer can be avoided.
We are interested in the possibilities of purifying a mixture of oligosaccharides in a co-current aqueous flow by removing the lower molecular weight saccharides through various MF and NF membranes.

Acknowledgements

This research was carried out within the Dutch initiative "Process on a Chip" (PoaC), part of the framework Advanced Chemical Technologies for Sustainability (ACTS). We acknowledge the Dutch organization for scientific research (NWO) for the financial support.

References

F. O. Shuck, H. L. T. (1963). "Separation of liquids by mass diffusion." AIChE Journal 9(4): 442-447.

Geboers, M., P. Kerkhof, et al. (2007). "FricDiff: A novel separation concept." Separation and Purification Technology 56(1): 47-52.

WAGENINGEN UNIVERSITY
AGROTECHNOLOGY AND
FOOD SCIENCES

The formation and deformation of protein structures with visco-elastic properties

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Introduction

People suffering from celiac disease—gluten intolerance—cannot enjoy the structural and functional properties gluten provides in many foodstuffs. Despite a lot of research on alternative gluten free cereals, no cereals with a structure equivalent to that of wheat have been found. Due to increasing intolerance for gluten, a need is raised for the production of breads without the gluten allergenic ingredients.

The low quality of gluten free wheat products is caused by the fact that gluten proteins are a major structure-builder, which can not be replaced without a detrimental effect on product quality. Only with a gluten protein analog—a biopolymer system with similar functional properties as the gluten-proteins matrix it is possible to make quality gluten free wheat products.

Aim

In this study, we investigate how a protein structure should be processed to obtain an aggregate that has comparable functionality as gluten. The formation of protein structures with comparable functionality as gluten particles may fill the gap of quality gluten free products.

Research

The gluten network is a very complex network, and the real structure is still unclear. Nevertheless, we think that we can consider the gluten network to be built up by protein particles (or aggregates) that interact with each other. The strength of those particles is governed by the chemical bonds and physical interactions at molecular scale. In this project, we try to mimic those gluten particles by aggregated formed with other proteins. To get insight in the necessary micro-aggregate properties, the effect of different types of micro-aggregates on the properties of the final protein structure is investigated.

Small micro-aggregates are formed by shearing a phase separating protein/carbohydrate solution. The phase separation of the solution causes proteins to concentrate in one phase, so the protein molecules prefer to cluster and form physically linked aggregates. Stirring will break the formed aggregates into droplets, leading to small protein beads. Variation in concentration, type of carbohydrate, shearing speed and temperature results in different protein aggregates. The effect of the variations of the protein aggregates on their ability to form a network is analysed. The network structure is visualized by microscopy and rheological properties of the formed network are measured.

Future research

When the effect of the protein type, size of the micro-aggregate and shape of the micro-aggregate is clarified, further research will focus on the influence of chemical bond formation. By chemical modification of the surface of the micro-aggregates, the effect of additional sulphide-groups or surface charge on the final protein structure will be analyzed.

Later we will investigate the effect of shearing and kneading on the protein network in the presence of starch particles and water. This is the first step to evaluate the potential of protein aggregates as gluten replacers.

Acknowledgement

'This research was financially supported by the Graduate School VLAG.

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Separation and Isolation of Minor Components

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OSPT theme	: Separation Technology	**Research school:**	VLAG
Supported by	: SenterNovem	**Period**	: July 2007 – July 2011

Introduction

Many product or even waste streams in the food industry contain components that may be interesting for e.g. functional foods. These product streams are typically large in volume and contain only a small amount of the component of interest. In order to efficiently remove the component, a robust and highly selective separation process should be developed.
A method to selectively capture a target component from a mixture is the use of protein-based affinity ligands. These ligands are specifically designed for the target component and often have strong binding characteristics. However, these ligands should be efficiently regenerated.

Aim

This project focuses on the development of a novel separation process for large (continuous) process streams containing small amounts of the target component. The process is based on the use of protein-based affinity ligands to capture the component of interest.

Research

Bovine serum albumin (BSA) is used as a model target component to investigate the adsorption and desorption process. Special focus will be put on the desorption process, since the ligand binds very strongly to its target component.
Several configurations for affinity adsorption (packed bed, expanded bed and membrane adsorption) have been investigated using mathematical modeling.
Both batch and packed bed experiments are used to characterize the adsorption and desorption behaviour at different pH and temperature. The packed bed experiments are performed using an Äkta Purifier chromatography system (GE Healthcare).

Whey is used as a model feed stream to extract BSA from. The influence of other components in whey, α-lactalbumin and β-lactoglobulin in particular, is investigated.
Based on the outcome of these experiments, a process will be developed based on adsorption (and desorption) performance and robustness.

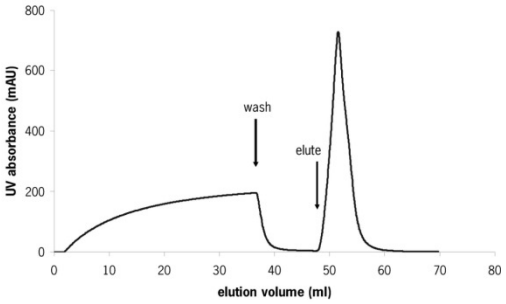

Figure 1: Example of BSA adsorption and desorption in a packed bed

Acknowledgements

This research project is carried out in cooperation with FrieslandCampina Research, DSM Biotechnology Center and BAC.

Mild Fractionation of Suspensions and Emulsions

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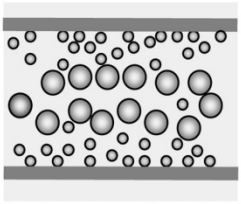
Supported by	: DSTI	**Period**	: January 2008 - January 2012

Introduction

In the food industry, fractionation of components from foods with the aid of membranes is increasingly performed. A large disadvantage of fractionation with membranes is accumulation of components on or near the membrane, causing reduced flux. This cake layer formation is called fouling. The cake is not infinitely increasing in height, since there is also back-transport of particles from the cake towards the bulk. One of the back-transport mechanisms is shear-induced diffusion. This phenomenon occurs when particles are subjected to shear, which is created due to local differences in velocity. Particles diffuse to regions with low shear.

It was found that the shear-induced migration of the particles depends on the particle size. Larger particle migrate at a higher rate, with higher diffusion coefficient, compared to smaller particles. Therefore, shear-induced migration enables separation based on particle size. This makes it useful for fractionation of suspensions with variable particle sizes.



Size separation based on shear-induced diffusion

Shear-induced migration dominated flow over a membrane results in less large particles close to the membrane. Therefore, larger pores can be used to remove small particles while retaining larger ones.

Aim of the project

The aim of the DSTI project is to obtain process conditions, system geometries and designs under which fractionation of particles, using shear-induced diffusion, is optimal.

Approach

The potential of shear-induced migration as basis for a less fouling-sensitive separation and fractionation process will be investigated by a mathematical model. The model will incorporate the most relevant physical processes.

As a start a continuum-based model for the flow and filtration of a monodisperse suspension will be used. The model will be extended to bidisperse systems. The bidispersity has several implications on the flow behaviour. These implications require development of new model components to capture the complex behaviour of polydisperse suspensions. The model will be validated with experiments.

The model can be used to study the effect of process designs. The gained insight should lead to increased fractionation efficiency and reduced fouling under mild processing conditions. This, in turn, reduces energy use and saves costs of separation in food industries, like dairy and beer.

Acknowledgement

This project is carried out within the framework of DSTI and is conducted in cooperation with Norit X-Flow, Friesland Foods and Royal Cosun.

Emulsification with microstructures

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OSPT theme	: Products and Processes	**Research school**	: VLAG
Supported by	: Economic Affairs, provinces Gelderland & Overijssel	**Period**	: February 2005 – September 2009

Introduction

Emulsions have been utilized in various industries, such as food, cosmetics or pharmaceutics. Well known examples are margarine, mayonnaise, sun cream, paints and, more recently, drug delivery systems. Commonly used emulsions are water in oil (W/O) or oil in water (O/W) emulsions. But also double emulsions (an emulsion in an emulsion), are of great relevance.

The most important properties of the emulsions are determined by their droplet size and droplet size distribution. A relatively new technique to produce emulsions is membrane emulsification. Advantages of membrane emulsification are control over droplet size and -distribution, low shear stresses, and low energy consumption. A promising new variant is microchannel emulsification (MCE; Figure 1), in which spontaneous droplet formation takes place. Because this process is not yet well understood, there is still room for improvement. In this research, design parameters such as channel dimensions are related to droplet formation.

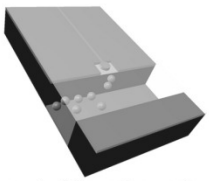

Figure 1: Microchannel emulsification

Aim

The aim of the project is to gain a thorough understanding of the microchannel emulsification process. The ultimate goal is to derive design rules for microchannel emulsification systems.

State of affairs

The effects of several design parameters were investigated by experiments and by simulation. The calculated and simulated droplet diameters are comparable. The current model is of such quality that it allows us to do a preliminary investigation on the break-up mechanism, and more specifically the pressure gradients in the system. The pressure gradients in the oil during the droplet formation are a result of changes in capillary and hydrodynamic pressures. In Figure 2, an example of a screenshot of a simulation result is depicted. The pressure curves at various time steps allow us to evaluate the exact function of the terraces in relation to pressure differences in the system, and this is currently investigated further.

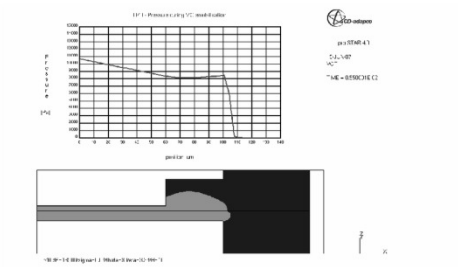

Figure 2: Screenshot VOF-simulation

Acknowledgement

This research project is carried out in cooperation with several project partners: Royal Friesland Foods, Nanomi, Demcon, and others.

Uniform, small-sized droplets: from mechanisms to large scale production

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OSPT theme : Products and Processes
Supported by : SENTER
Research school: VLAG
Period : March 2005-March 2009

Introduction

A lot of foods, drugs, and personal care products are emulsion-based, and it is assumed that the mean droplet size and size distribution of these emulsions are important factors to control product properties like shelf life and texture. In industry, the production of monodisperse, small-sized emulsion droplets is a problem. Conventional emulsification methods may achieve high production rates, but cannot control droplet size. Micro technology could be a solution; monodisperse droplets can be produced in microdevices. However, the production rates of these microdevices are limited unless they can be placed in parallel.

The main challenge of this project will be to develop a (new) micro emulsification technique to produce uniform emulsion droplets, which not only works on a lab scale, but can also be scaled up to meet industrial demands.

Research

In order to meet industrial demands we first have to understand how droplet formation in a single device works, and is influenced by various parameters; e.g. flow rate, interfacial tension, and viscosity. In this project glass microdevices with various geometries are used to study shear-based droplet formation. Hexadecane-in-water is chosen as a model system. Shear-based droplet formation in a microdevice can be visualised using a high-speed camera connected to a light microscope. Figure 1 shows pictures of shear-based formation of a droplet in a microdevice with a T-junction. Hexadecane is introduced from the vertical channel and water is introduced in the horizontal channel.

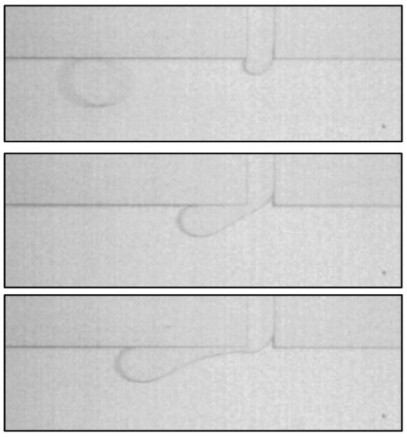

Figure 1: Hexadecane droplet formation in MilliQ water in a microdevice with a T-junction (van der Graaf, Steegmans, et al., Coll & Surf A 266, 2005, 106)

At the junction, a hemispherical interface is formed (figure 1(a)). The hexadecane droplet grows, and is deformed by the cross-flowing water, until it is connected to the junction with a long thin neck (figure 1(b) and (c)). When the neck breaks a droplet is formed and the process starts again.

In the future, more work shall be done on understanding shear-based droplet formation in a single microdevice, on parallelisation of microdevices, and on improving the stability of the uniform emulsion droplets.

Acknowledgement

This research project is part of the national research initiative MicroNed.

Shear induced separation of starch-gluten systems

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OSPT theme	: Separation Technology	**Research school**	: VLAG
		Period	: Dec 2006 – Dec 2010

Introduction

This project investigates a new separation method for wheat dough into its constituents gluten and starch.
The separation occurs when dough is exposed to well-defined plain shear. The separation process is based on the fact that the gluten fraction in dough has viscoelastic properties. Compared with traditional separation, which is based on kneading and washing, the current process offers important potential advantages; water and energy consumption is decreased, while improved gluten properties can be expected.

Objective

The aim of this project is to study the shear induced separation in more detail. The separation mechanism and phenomena related to this will be investigated. We aim at the development of new separators or applications for industry.

Approach

The separation process will be studied using a lab scale shearing device, which configuration is based on a cone-plate rheometer. The shearing device is described in more detail by Peighambardoust *et al.* (2006) and Manski *et al.* (2008*)*. The device allows well defined deformation of concentrated biopolymer systems. Shearing wheat dough in this device leads to a protein enriched fraction.

State of affairs

During the initial stage of the project, the influence of process parameters like shear rate, processing temperature and processing time were investigated. The separation is studied by measuring the protein content over the height of the device. The outcomes of that study suggested that the separation mechanism comprised two steps. First gluten aggregates are formed, followed by the migration of them to the apex of the cone (step 2).
By determining the rheological properties of the starting material, for instance the viscoelasticity, the driving mechanism for the separation process will be further unravelled. It can be expected that the properties of the starting material will have an influence on the separation behaviour. Nevertheless, we found that a broad range of flour types could be separated, implying a generic applicability of the new separation principle for wheat flour.

Even without optimisation of the shearing device, a separation enrichment of around 60% protein in the apex of the cone was already obtained when a flour was used that possessed a protein content of 11% (depleted fraction around 3% protein). Therefore, we concluded that the separation indicates promising opportunities for industrial application.

References

- Peighambardoust, S.H., van der Goot, A.J., Boom, R.M., Hamer, R.J., (2006) Microstructure formation and rheological behaviour of dough under simple shear flow, Journal of Cereal Science, 43, 183-197
- Manski, J.M., van der Zalm, E.E.J., van der Goot, A.J., Boom, R.M., (2008) Influence of process parameters on formation of fibrous materials from dense calcium caseinate dispersions and fat, Food Hydrocolloids, 22, 587-600
- Van der Zalm, E.E.J., Van der Goot, A.J., Boom, R.M., 2009. Influence of process conditions on the separation behaviour of starch-gluten systems. Submitted.

Professors

List of abbreviations

AFS	Agrotechnology & Food Sciences	WUR
AS	Applied Sciences	TUD
CEC	Chemical Engineering and Chemistry	TU/e
ET	Engineering Technology	UT
ME	Mechanical Engineering	TU/e
3ME	Mechanical, Maritime & Materials Engineering	TUD
MPS	Mathematics and Natural Sciences	RuG
ST	Sciences & Technology	UT

PhD Index

Keywords