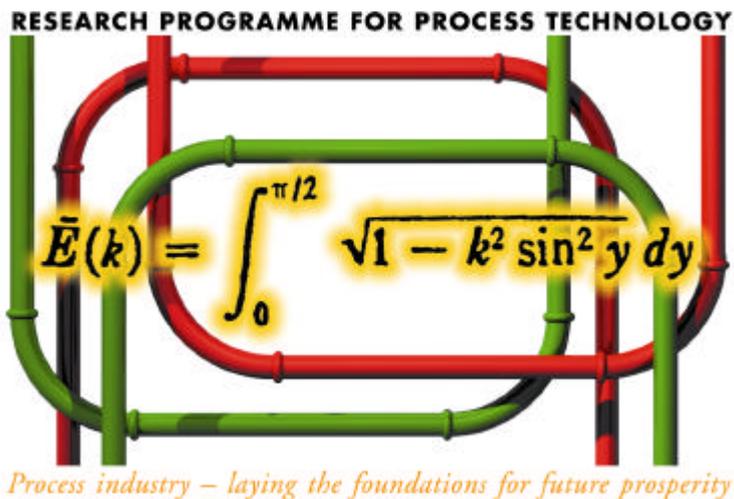


RESEARCH PROGRAMME FOR PROCESS TECHNOLOGY 1999 -
2002

RESULTS OF THE 1st YEAR

2nd RESEARCHER MEETING ON
NOVEMBER 23rd, 2000



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Foreword

The Academy of Finland launched the Research Programme for Process Technology (PROTEK) in 1999. Preparatory work was carried out by a group with members from universities, industry, the Chemical Industry Federation and the National Technology Agency. Being conscious that the increase in applied, industrial research demands ever more understanding of the basic chemical and physical phenomena, PROTEK has concentrated on three main themes:

- basic process phenomena
- process simulation, modelling and optimisation
- development of research methodology

An important objective of the programme is to intensify interaction and co-operation between universities and industry, and to facilitate the transfer of know-how between different disciplines. Researcher training using industry as a source of research motives can lead to successful utilisation of both basic and applied knowledge. The final objective of PROTEK is to improve the quality of industrial processes and, in the long term, promote the competitiveness of the process industry products while focussing on environmental, economic and safety considerations.

In the programme, FIM 15 million has been allocated to fund nine research groups or consortia for three years. Most of the groups begun work in August 1999. The research themes are various, including bioprocessing, burning, catalysts, modelling and pulping.

This booklet summarises the first year's work of all the participating groups. Publications, patents and degrees have been produced, connections created between universities, laboratories and industry, and many international contacts have taken place. Despite the diversity of the research themes, there are common interests in the methodologies and approaches. Connections between groups and consortia make the separate projects a true research programme. The purpose of this survey is for its part to bring the groups more acquainted with each other's work and to present the contents of the programme to all the interested ones.

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Progress report 1.8.1999-31.7.2000 of the project:
**Modelling and developing of efficient process configurations
combining reaction and distillation**

Finnish name:
**Reaktioita ja tislausta yhdistävien prosessien kehittäminen ja mallinnus
Project 46912**

Professor Juhani Aittamaa

Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design
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Researchers in the project:

Ph.D student *Kaj Jakobsson*

Collaboration

During the project close collaboration with Neste Engineering Oy has taken place in model development. M.Sc. Sini Pakkanen completed her M.Sc. Thesis (Prosessilaskennan ratkaisumenetelmien kehittäminen, HUT Laboratory of Chemical Engineering and Plant Design, 2000), her advisor was Lic.Sc. (Tech.) Antti Pyhälähti from Neste Engineering.

Results of the project

Interesting chemical systems have been identified for processes combining reaction and distillation. These chemical systems serve as benchmark cases for the development of the software tools both for reactive distillation and side reactor/separator concept. The chemical systems are MTBE production, iso-Octene–production and TAME – production. The first prototype has been developed of the new unit model of the side reactor/separator concept. In this approach the model equations of the column and the reactors are solved simultaneously in steady state. This new tool is based on an already existing reactive distillation model. The model of the column is based on ideal stages. The side reactors are modelled as a sequence of CST – reactors. The modelling allows in the side reactor block two phases (liquid/vapour). The reactor stages can also be used as temperature controllers. The new model has been able to solve the benchmark cases successfully and has been proven to be faster and more robust than the existing tools.

Conference presentations

Jakobsson, K., Aittamaa, J., Gorak, A., Kenig, E., A Synthesis and Design Tool for Reactive Distillation, EFCE 2nd European Congress of Chemical Engineering, Montpellier France 5-7 Oct 1999.

Jakobsson, K., Pakkanen, S., Pyhälähti, A., Aittamaa, J., Modelling of a Combination of a Side Reactor and a Distillation Column, Nordic Reaction Systems Seminar, CTU, Göteborg 19-20.6.1999.

Visits

Prof. M. Oljuic, Delft University, Netherlands 21.6 2000

Prof. R. Krishna, University of Amsterdam, Netherlands 22.6 2000

ANNUAL REPORT on the period from August 1999 to July 2000

Rapid and specific DNA-based methods for determinations of bacteria as tools to control and monitor industrial food processes

Project number: 46921

Professor Tapani Alatossava

University of Oulu, Biotechnology Laboratory / REDEC of Kajaani
Salmelantie 43, FIN-88600 Sotkamo, Finland

Scientists involved in the project:

Tilsala-Timisjärvi, Anu, Ph.D., post-doctoral scientist
Brandt, Kirsi, M.Sc., graduate student (genetics)
Munsch, Patricia, Ph.D., post-doctoral scientist
Ravin, Viktor, Ph.D., post-doctoral scientist (supported by a grant of the EC Biotech2 programme).

Description on the collaboration:

On the field of *lactic acid bacteria* (LAB) research there has been an intensive collaboration with prof. G. Tannock, Univ. of Otago, New Zealand and his laboratory. The work concerns applicability of the species specific primers developed previously in the project laboratory (Univ. of Oulu) for identification of *Lactobacillus* isolates from dairy products, silage and gastrointestinal tract. Furthermore, development of PCR- based strain-specific identification methods for dairy and probiotic *Lactobacillus casei* and *Lb. rhamnosus* strains has been performed partially through a collaboration research project coordinated by VTT Biotechnology and supported by Tekes, National Technology Agency of Finland. In this project there are participants from Finnish food industry and from Finnish research and university organizations.

Concerning Staphylococcus and Streptococcus bacteria a research collaboration with prof. S. Pyörälä (Univ. of Helsinki) and her group as well as with a Finnish biotechnology company has started.

On the field of Pseudomonas bacteria research there has been a close collaboration with four European scientists and their laboratories: Dr. J.-M. Meyer / Univ. Louis Pasteur- Strasbourg, France, Dr. L. Gardan / INRA d'Angers-Beaucouzé, France, Dr. K. Johnstone / Univ. of Cambridge – Cambridge, United Kingdom, and Prof. H. Budzikiewicz / Univ. of Cologne – Germany.

Summary of results:

- 1) PCR-based identification of industrially important *Propionibacterium* species has been developed (Tilsala-Timisjärvi & Alatossava, a manuscript submitted).
- 2) A novel phase sequence-based identification approach for *Lactobacillus casei*-group strains has been discovered and further characterized (Brandt *et al.*, *Micron* 32(2001)(in press); Brandt & Alatossava, a manuscript submitted) .
- 3) A novel insertion-sequence (IS) element in *Lactobacillus delbrueckii* chromosome has been discovered and further characterized (Ravin & Alatossava, a manuscript in preparation).
- 4) Siderotyping of mushroom pathogenic *Pseudomonas* isolates has been developed (Munsch *et al.*, *Appl. Environ. Microbiol.* 66(2000)(in press)), and a novel *Pseudomonas* pyoverdine has been characterized (Fernandez *et al.*, a manuscript in preparation).
- 5) Potential DNA sequences and primers for PCR-based identifications of plant and animal pathogenic and food spoilage *Staphylococcus* and *Pseudomonas* species has been determined (Tilsala-Timisjärvi *et al.*, *Milchwissenschaft* 55(2000)488-492; Munsch *et al.*, manuscripts in preparation).

Publications:

- Tannock, G.W., Tilsala-Timisjärvi, A., Rodtong, S., Ng, J., Munro, K. & Alatossava, T. (1999) Identification of *Lactobacillus* isolates from the gastrointestinal tract, silage, and yoghurt by 16S-23S rRNA gene intergenic spacer region sequence comparisons. *Appl. Environ. Microbiol.* 65:4264-4267.
- Walter, J., Tannock, G.W., Tilsala-Timisjärvi, A., Rodtong, S., Loach, D.M., Munro, K. & Alatossava, T. (2000) Detection and identification of gastrointestinal *Lactobacillus* species by using denaturing gradient gel electrophoresis and species-specific PCR primers. *Appl. Environ. Microbiol.* 66:297-303.

International visits:

Dr. P. Munsch has visited altogether about six weeks the laboratory headed by Dr. Gardan (INRA d'Angers, Beaucouzé) in France, and performed an experimental DNA taxonomy research in this laboratory.

Other publication activities:

Two patents assigned by Oulutech Ltd. (Oulu) has been accepted:

- Alatossava, T., Tilsala-Timisjärvi, A. & Forsman, P. (inventors). DNA-sequence-based diagnosis of mastitis from a milk sample. New Zealand Patent 332047 (accepted Nov 12, 1999).
- Alatossava, T., Tilsala-Timisjärvi, A. & Forman, P. (inventors). DNA-sequence-based diagnosis of mastitis from a milk sample. Australia Patent 716675 (accepted Dec 23, 1999).



Modelling phase interactions in process engineering

Project 46897

Professor Kari Heiskanen

Helsinki University of Technology
Mechanical Process Technology and Recycling
P.O.B. 6200, FIN-02015 HUT, Finland

Researchers in the project:

R. Kalapudas

N. Schreithofer

M. Miettinen

Dr V. Kirjavainen

During the report time the project was supposed to prepare measurement methods. This has been done and the project is almost on time.

Task 4.2.1 Atomic force microscopy (sub-task resp. N. Schreithofer)

The construction of the new AFM device has advanced slightly slower than planned due to lack of investment money and due to the delayed delivery of the Queensgate piezo and its controller. The piezo arrived three months later than promised. The piezo is now operational. It has a z-direction movement of 70 μm which is double of the originally proposed. Its estimated resolution is better than 0.1 nm.

During construction a decision was made that the position of the piezo and the laser are to be changed in relation to the sample holder. In the new design the piezo and the laser are on the top and the z-direction movement is downwards. The sample holder will be on the bottom. This change was made due to the risk that water entering the piezo can destroy it. The change caused some problems with the laser beam focusing but by redesigning the optical path they were solved.

The set-up is lacking only some minor parts before first tests can be started. One major part that we cannot afford is a microscope having a far field optical plane. We are at the moment experimenting using a CCD camera and ordinary camera zoom lenses and macro-rings. The preliminary results look promising and the final set-up is planned that way.

It is assumed that the AFM construction is ready, slightly delayed, in November.

The main point has been that the device has been financed from the overhead obtained from other projects and this has caused quite a stress on HUT laboratory finances and caused delays as no money has been available at times.

Task 4.2.2 Induction time measurements (sub-task resp. R.Kalapudas)

The induction time device had a faulty circuit board. It is now repaired during the visit of Mauno Miettinen to Virginia Tech University and Professor Yoon. The device is up and running. Measurements have been performed with HCl cleaned quartz and the times measured are well above 2 s but with already at 1×10^{-5} mol/l dodecylamine, the induction times are 4-5 ms, even below 3 ms which is the device resolution at the moment. Experiments are continuing to test 160-200 μm particles instead of 125-200 μm .

We are discussing to further develop the measurement by attaching onto it a CCD camera and camera lenses in the same way as we have tried in the AFM. This would allow a faster and more accurate analysis. No decisions have been taken yet.

TASK 4.2.3 Adsorption cell (the resp. of the sub task is M. Miettinen)

A method to purify amine via recrystallisation from ethanol has been tested and in use.

Two different methods to analyse adsorption has been developed, but there seems to be still some questions to be solved before we can rely on the results. The first method is based on methyl yellow and colorimetric measurement and the other on a modified LECO carbon analyser. Tests have been performed at different concentrations and with different particle sizes as well as with different ageing of the sample.

The two methods give rather different results and the reason is unclear. Work continues to solve this discrepancy. The difference is typically such that with colorimetric measurement the calculated adsorption coverage is close to double.

The carbon analyser shows a two peak behaviour (see appendix). The second peak appears always at 90 seconds heating in 470°C . The first peak appears at 45 seconds only at higher concentrations indicating a less bound surface layer of amine on quartz. It is a physi-sorbed layer that has a different orientation. The results show at this stage that the adsorption onto fine particles ($\sim 20\mu\text{m}$) has a different final equilibrium concentration than the coarser particles (20-250 μm). This should not be so. It has been agreed that narrow size fractions of 5-10; 10-20 and 20-50 μm will be prepared and their adsorption measured. This part is crucial for our further measurements.

Much discussion has gone to the cleaning of the samples. We have now used hydrochloric acid but there is a doubt that the surface structure has been damaged due to the treatment. There is AMF evidence that in fact hydrochloric acid affects the surfaces and probably also the temperature when on the surface ? quartz starts to change to ? quartz. As can be seen in AFM measurements the crystals of ? quartz are much smaller and grow to fill crevices in the ? quartz surface. This will be studied further with the ESCA of Turku University. If so then we have to continue testing surface cleaning methods.

The main emphasis of the project is now to clarify the problems in surface adsorption analytical methods.

Task 4.2.4 Contact angle measurement (sub-task resp. Dr V. Kirjavainen)

The work is delayed by purpose and will be started after the surface cleaning and the analytical problem is solved.

Task 4.2.6 Experimental designs (sub-task resp. Dr K. Heiskanen)

Experimental designs will be made after preliminary experiments can be made with the AFM. It will be ready before the end of the year.

Material selection

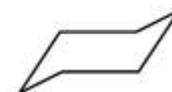
The first sample material has been selected even if the task timetable called it to be done during this summer. We have obtained pure quartz samples from Brasil and from Arizona.

Other tasks

The literature survey has been performed but did not yield any new and unknown data.

The project was reported at the Fine Particle Research Institutes annual meeting (organised by TU Delft) in Scheveningen, The Netherlands, in August 2000 as a progress poster. (poster as annex)

The project has sent an “Measurement of bubble particle interaction forces by AFM based technique” abstract to the 6 world Congress of Chemical Engineering, no answer yet.



The Academy of Finland

Research Programme for Process Technology (PROTEK)

Project 46937



Annual Consortium Report 1999 – 2000

Fundamental Studies for Improving Submodels in Combustion Modeling

Project leader: Professor Mikko Hupa

Åbo Akademi University, Combustion and Materials Chemistry
Lemminkäinenkatu 14-18 B, FIN-20520 TURKU, Finland

This project is run jointly in a consortium consisting of Åbo Akademi Process Chemistry Group – Combustion and Materials Chemistry (ÅA), VTT Energy – Aerosol Technology Group (VTT) and the University of Oulu – Department of Chemistry (OY). The project covers the research areas: ASH, FUEL and TURBULENCE-CHEMISTRY. The research activities in ASH are run in close cooperation between all three partners, the FUEL part is run by Åbo Akademi Process Chemistry Group in cooperation with the Technical University of Vienna and the TURBULENCE-CHEMISTRY activities within the project are worked out at Åbo Akademi Process Chemistry Group together with VTT Energy.

Research personnel:

<i>Rainer Backman</i>	ÅA	<i>Jouni Hokkinen</i>	VTT
<i>Anders Brink</i>	ÅA	<i>Jorma Jokiniemi</i>	VTT
<i>Pia Kilpinen</i>	ÅA	<i>Lars Kjälman</i>	VTT
<i>Christian Mueller</i>	ÅA	<i>Jouni Pyykönen</i>	VTT
<i>Bengt-John Skrifvars</i>	ÅA	<i>Risto Laitinen</i>	OY
<i>Maria Zevenhoven</i>	ÅA	<i>Laura Nuutinen</i>	OY
<i>Ari Auvinen</i>	VTT		

The research work within the consortium is coordinated by Åbo Akademi Process Chemistry Group and followed up in annual project meetings held at the different sites of research (08/1999 Turku, 08/2000 Oulu, 08/2001 Espoo, 08/2002 Turku). In between these annual meetings, working meetings are held focussing on the different research topics (ASH: 3 meetings, FUEL: 1 meeting, TURBULENCE-CHEMISTRY: 1 meeting). Within the first year of the project good progress has been made in all three working areas. However, the activities in the FUEL part started delayed due to personnel changes in Åbo Akademi Process Chemistry Group. By this point of time this delay is almost vanished due to starting up a close co-operation with the Technical University of Vienna.

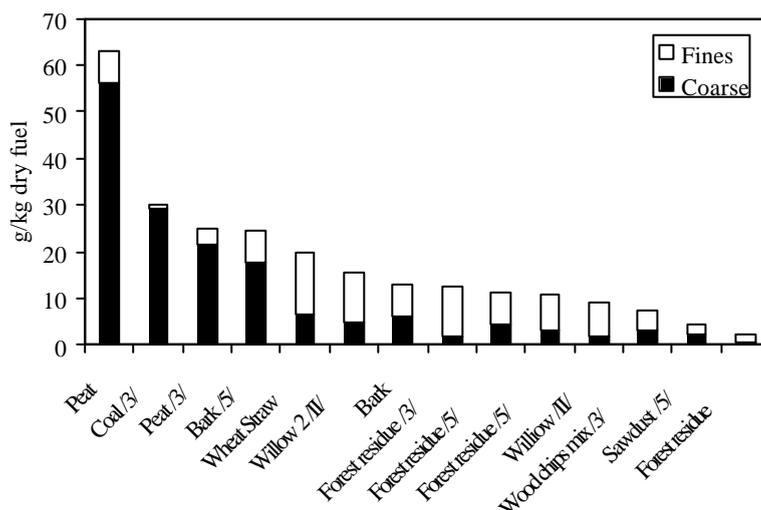
Results of the research:

ASH

The goal of the work done in this part of the project (ÅA,OY) is to increase the detailed knowledge about how ash behavior in a full-scale combustion unit can be predicted in a more reliable way than today, using advanced fuel analysis. The specific focus is formulated in the following four statements:

1. To further develop the novel ash behavior prediction tool where the advanced fuel analysis method “selective chemical dissolution analysis“ is coupled with “multi-component, multi-phase thermodynamic equilibrium analysis“.
2. To study if the “selective chemical dissolution analysis“ method can be simplified by using other solvents or by combining solutions.
3. To study the effectiveness and reliability of different detection methods of the ash forming elements in the different solutions.
4. To study the relevance of the different solution fractions with respect to ash behaviour problems in full scale combustion

The statements 1, 3 and 4 have been addressed during this reporting period. In total 14 different fuels have been analysed using the chemical dissolution analysis. Partly the underlying data were produced within this project, partly within TEKES based projects, e.g. in the national programmes LIEKKI and CODE. A summary of the chemical dissolution analysis results is shown below. As can be seen, the amount of easy-leachable elements varies strongly depending on what fuel is analyzed. One can also see that similar fuels such as different samples of bark or forest residue show considerable differences in their ash element amounts and distributions in the fuel. For example “Bark 5“ contains some 6,6 g/kg (db) easily leachable ash forming elements and 17 g/kg (db) inert ash, while another sample of Bark named “Bark“ had some 7,0 g/kg (db) easily leachable ash forming elements but only some 5,9 g/kg (db) inert ash. Similar differences can be seen with the Forest residue samples.



Summary results of the chemical dissolution analyses. The elements leached out in water and acetate fractions are summed up to the “fines“ fraction shown in the figure. Elements leached out in HCl and those elements not leached out at all summed up to the “coarse“ fraction.

At VTT Energy the ash related work focuses on an improved understanding of effects of submicron particles and vapour deposition on the deposit layer strength and on its re-entrainment to the flow. Within the first year of this project the applicability of radioactive tracer techniques in aerosol and deposition measurements have been tested. Gamma scanning techniques can be used on-line to observe the deposit behaviour during an experiment. This procedure provides some very useful and unique data that are supplemented by aerosol measurements at the inlet and the outlet of the experimental set up.

Since the first experiences have been promising, it was decided to use these techniques in this project even though this means extra time for the build-up and testing of the experimental system that consists of a flow in a straight cooled pipe. The build-up phase is now in progress and it is planned to start the experimental work next year.

For system testing as well as for the first experiments, a mixture of inert particles (copper) and NaCl vapour will be used to create deposit layers. Inert particles will be generated with a dry-aerosol generator and NaCl formed by vaporisation from a furnace vessel. Before the experiments, copper and/or NaCl will be activated in a Triga reactor into short lifetime isotopes. During the experiment, the heat exchange tube can be monitored with five gamma detectors. One detector scans a 17 cm long section of the tube. Once a deposit is formed, an additional high-velocity air stream will be fed into the heat exchanger tube. The idea is to monitor with gamma detection and filter collection the re-entrainment of deposited material. Different ratios of inert particles and NaCl vapour will be used. With five detection points, it should be possible to monitor possible deposit movement (via re-entrainment and re-deposition) as well. After each experiment the activity profile will be measured with a high resolution using a germanium detector.

Next to the described experimental work, theoretical studies were performed within the 1999/2000 period. Those studies focused on the transport of a condensable amount of vapour species in porous deposits taking into account the variation in saturation vapour pressures at the contact point or the neck between adjacent particles. The difference in vapour pressures leads under the conditions investigated to sintering via vapour phase transport.

FUEL

One of the key advantages of fluidised bed combustion is its potential of burning a wide variety of fuels and even fuel mixtures in an efficient, clean and reliable way. However, the properties of the fuels vary a lot, and thus, the combustion chamber conditions and the emission formation tendency may also vary within a wide range. A mathematical tool is being developed during the last years for studying the nitrogen oxide emission formation in circulating fluidised bed combustors (CFBC). With this model different fuels and fuel mixtures can be compared with regard to their nitrogen oxide emission formation tendencies at typical FBC conditions.

For the efficient use of this predictor certain fuel-specific values are needed as input data in addition to the conventional ultimate and proximate analyses. For this purpose combustion experiments in a laboratory FBC will be carried out during 2000/2001 (ÅA) within the project. This is done in collaboration with the Technical University of Vienna. The specific objectives of the experiments will be to establish a fuel-database for nitrogen components including the split of volatile- and char-nitrogen, and the share of different fixed-nitrogen components in the volatiles (NH₃, HCN, NO). In addition, insight into fuel-specific characteristics of char reactivity and fragmentation will be obtained that can be included in submodels of the predictor.

TURBULENCE-CHEMISTRY

The last subtask within this project covers modelling of turbulent reactive flows with special focus on a turbulence-chemistry interaction model applicable to industrial scale combustion processes in the long run (ÅA, VTT). Following an advanced evaluation of the current situation in this field of research the recently by R. Bilger developed Conditional Moment Closure Method (CMC) was chosen as most promising approach for predicting turbulent reactive flows including complex chemical kinetics. Preliminary results for reactive jet flames have been achieved by applying a simplified CFD-code for parabolic flows combined with different chemical approaches ranging from global 4-step kinetics to detailed elementary reaction schemes for methane combustion.

The next step within this project is now the extension of the simplified fluid-dynamic model to elliptic flows as they occur in technical applications. Next to the plain extension to more complex flow patterns and three dimensions the available code needs to be further developed with regard to the inclusion of radiative heat transfer and the treatment of chemical reactions in the near wall regions of a confined flow. In the final stage of the project the developed submodel will be connected by an interface to the commercial CFD-code FLUENT.

Publications:

- Brink, A., Mueller, C., Kilpinen, P., Hupa, M.: *Possibilities and Limitations of the Eddy Break-Up Model*, Comb. Flame 123:275-279, 2000.
- Mueller, C., Brink, A., Kilpinen, P., Hupa, M., Kremer, H.: *Modeling of an Industrial Scale Gas-Burner Using Finite-Rate Chemistry – Options and Restrictions Resulting from Eddy-Break Up Based Models*, Int. J. on Environmental Comb. Technol., 2000, (to appear).
- Zevenhoven, M., Skrifvars, B.-J., Yrjas, P., Hupa, M., Nuutinen, L., Laitinen, R.: *Searching for improved characterization of ash forming matter in biomass*, 16th Int. Conf. on Fluidized Bed Combustion, Reno, 2001 (accepted for publication).
- Pyykönen, J., Jokiniemi, J.: *Modelling aerosol dynamics and transport in boundary layers*, J. Aerosol Sci., 2000 (submitted for publication).

Consortium:

**Expert system for crystallization and filtration processes
(46918)**

Person in charge of research: Act Professor Sirkka-Liisa Jämsä-Jounela
Helsinki University of Technology, Laboratory of Process Control and Automation
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**Optimization of Reaction Crystallization Process
(46919)**

Prof. Juha Kallas
Lappeenranta University of Technology, Laboratory of Process Engineering
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**Optimization of Reaction Crystallization Process; Filtration Properties and
Dewatering (46920)**

Docent Marja Oja
Lappeenranta University of Technology, Laboratory of Chemical Technology
P.O.B. 20, FIN-53851 Lappeenranta

Project 46918

Name: Expert system for crystallization and filtration processes

Research team

Sirkka-Liisa Jämsä-Jounela
Tatu Kuitunen
Jerri Kämpe
Carlos Quiros (1.8.1999-31.7.2000)

Project cooperation and other funders

Consortium: LUT, Lab of Chemical Engineering; LUT, Laboratory of Process Engineering;
HUT; Laboratory of Process Control and Automation

TEKES Technology Programme of Process Integration
“ Integrated Process Monitoring and Fault Diagnosis Systems “
Larox Oyj and Fortum Oyj

Progress and research results

The intelligent control system of the pressure filter has been designed and is currently under development. The overall system consists of the modeling, classification, economic, fault diagnosis and control modules.

The *modeling module* contains models of the different operating stages of the filter. For the filtration which occurring in the feed stage and partly in the pressing stage a model developed by Holdich (1996) is used for predicting the filtrate volume. The Terzaghi-Voigt- model is used for predicting filtrate volume in the consolidation phase of the pressing stage. The *classification module* utilizes the neural network to classify the feed and the states of the process. The *control module* is an upper level control that gives setpoints to the basic control loops. The *economic module* optimizes the operation of the pressure filter in order to maximize the throughput of the equipment which, in turn, minimizes the cost of filtration per tonne of dry cake. The *fault diagnosis module* detects process disturbances and equipment malfunctions. It consists of a diagnostic application and a database containing knowledge of the normal operation. The intelligent control system has been implemented using the PC based InTouch system (Wonderware). The fault diagnosis system has been implemented with Java®.

The system was tested with the off-line data from a pilot filter. First the predicting capability of the modelling module was tested. According to the results, the model is able to predict the filtrate build-up accurately. The system has been also tested with fault case data from the pilot filter. It is capable of diagnosing the faults from the data in real time. In fault cases the system gives suggestions to the operators about the appropriate action. The remote support system is under development.

Publications

- Jämsä-Jounela, S-L., Oja, M., Modelling module of the intelligent control system for the variable volume pressure filter, *Filtration&Separation* **37** (2000) No 2, 39-49.
- Jämsä-Jounela, S-L., Kuitunen, T., Quiroz, C., Kämpe, J., Fault diagnosis and remote support system for the variable volume pressure filter, Proceedings of the 4th Symposium on Fault Detection, Supervision and Safety for Technical Processes, Safeprocess 2000, Budapest 2000, pp. 985-991.
- Jämsä-Jounela, S-L., Kuitunen, T., Quiroz, C., Kämpe, J., Fault diagnosis system for the variable pressure filter, *Proceedings of IFAC Workshop on Future Trends in Automation in Mineral and Metal Processing*, Helsinki 2000, pp. 450-455.
- Jämsä-Jounela, S-L., Quiroz, C., Intelligent process monitoring system, *Proceedings of the 28th Conference on Automation and Telecommunication in Mines and Processing Plants – Coals and Minerals*, Szecyrk 2000, pp. 133-138.
- Jämsä-Jounela, S-L., Paavola, E., Kuitunen, T., Kämpe, J., Modern fault diagnosis system for the variable volume pressure filter, *Proceedings of ECC'99*, VDI/VDE-Gesellschaft Mess- und Automatisierungstechnik (GMA), Karlsruhe 1999.
- Jämsä-Jounela, S-L., Tóth, S., Kuitunen, T., Kämpe, J., Fault diagnosis system for the variable volume pressure filter, *Proceedings of the 14th World Congress of IFAC*, vol.ed. T. McAvoy, W. Marquardt and S-L. Jämsä-Jounela, International Federation of Automatic Control, Beijing 1999, pp. 397-402.

Communication of information

- Jämsä-Jounela, S-L., Paavola, E., Kuitunen, T. and Kämpe, J. Modern fault diagnosis system for the variable volume pressure filter, *Automaatio 1999*, ed. R. Heinonen, Finnish Automation Society, Helsinki 1999, pp. 430-435.

Project 46919

Time period 1.1.2000-28.08.2000

Name: Optimization of reaction crystallization process (Kiteytysprosessin optimointi)

Research team

Prof. *Juha Kallas* (responsible leader)

Hannu Alatalo 1.1.2000 -

Henry Hatakka 1.1.2000 -

Co-operation in project

Deliverer of particle size analyzers (MTS)

- Development and testing of new type of analyzers

MUREA-project (TEKES)

- Åbo Academi, Kemira Agro (Kemira Chemicals and ProfMath)
- Industrial process to study

Results

In-line particle size analyzers and image analysis software are bought and tested.

Hannu Alatalo:

Parameterized geometry file of mixing tank with shaped bottom, 6-blade Rushton turbine and baffles for CFD-calculation with FLUENT. Geometry is created with journal-file commands of GAMBIT. Created geometry is going to be used in simulations of local conditions of crystallizer.

Henry Hatakka:

Simple model for reactive crystallization is created. The model is based on the continuous population balance and it includes nucleation and crystal growth. First stage experiments are done during the researcher visit in Martin-Luther-Universität in Halle (MLU) 3.6.-28.8.2000. Barium sulphate was produced in small-scale crystallizer. Three different reactions were used; barium chloride with ammonium sulphate, potassium sulphate and copper sulphate. Both homogeneous and heterogeneous reactions were studied, ie. all three different sulphates were fed both solid particles and aqueous solution in separate experiments. Crystal size distribution was analyzed during the time from start-up to steady-state or from step change to steady-state. These results are going to be used in testing and developing of the model.

Visits

Researcher exchange program with two universities (LUT and MLU), Academy of Finland project number 48351:

- Henry Hatakka in MLU 3.6-28.8.2000
- Crystallization group from MLU in LUT 14-15.8.2000

Non-academic reporting and publications

Co-operation information change with Kemira

Reporting of results of particle size analyzers for development of the analyzers (MTS)

Project 46920

Name: Optimization of Reaction Crystallization Process; Filtration Properties and Dewatering

Background and Objectives

The crystallization process is closely related to the separation of crystals from the solute. In reaction crystallization process the filtration characteristics of crystalline product can change periodically due to operation parameters of the plant, system conditions and physical characteristics. The current demands of the cost effectiveness, a better cake dewatering and purity demands of the final product have increased the use of the membrane filter presses. This project will provide background information the filtration properties of different crystalline products during dewatering by classifying the products into different categories on the basis of the dewatering properties. This information can be utilized in designing the reaction crystallization and the separation of the crystals from the mother liquid.

Research team

Docent, D.Sc. (Tech.), *Marja Oja*

M.Sc. (Tech.) *Oili Niemelä* 1.10.1999 –24.2.2000

M.Sc. (Chem.) *Marja Luomala* 1.4.2000 –

Student *Kati Pöllänen* 15.5. – 31.7.2000

Project cooperation

Consortium: LUT, Lab of Chemical Engineering; LUT, Laboratory of Process Engineering; HUT; Laboratory of Process Control and Automation

LUT Centre for Separation Technology (CST)

MTS, Messtechnik Schwartz GMBH, Germany

Results

The purity of final product in the whole process depends in addition to the dewatering properties also on the washing properties of the obtained filter cake. Soluble substances can be removed from filter cakes by two principal operations: dewatering and washing. In many cases the first operation is to dewater the cake and then wash the cake. The residual liquid can be removed by compressing the cake or displacement the retained filtrate by gas (usually by air). In some applications the washing can take as much as 80% of total cycle time. Therefore it is important to know the washing characteristics of the obtained filter cakes. The literature survey of the washing models suggested that a good model for cake washing is an axial dispersion model that leads to a fair agreement between experimental and theoretical calculations.

The mode of filtrate removal is selected on basis of the characteristics of the crystalline product. The characteristics of the product depend on the primary properties of the particles such as particle size distribution, shape, density, surface properties and others, and on the primary properties of suspension such as solid concentration, density, temperature, viscosity, pH and chemical composition. If one primary property of the particles or the liquid varies, the dewatering and washing properties of the crystalline slurry may change significantly and a functional solid liquid separation system can become inefficient.

In order to optimize the solid liquid separation of the crystallization process the characteristics of the slurry has to be available before setting the process parameters of the separation. Therefore the particle size and shape distribution should be measured on-line. The particle size distribution is measured using active three-dimensional laser beam scanning method (MTS Psya 522 model SD). The shape was measured with on-line particle image analyzer (MTS PIA 4000 LUT). The results obtained with on-line measurement were compared with the results measured off-line. The off-line size distribution was measured using laser diffraction method (Coulter LS 130) and the shape parameters were measured from the images acquired by video camera from the optical microscope using image analysing program (AnalySIS 3.0). The results showed that on-line measurements did not give reliable results and the analyzers have to be modified for the measurement of crystalline product. This was done in co-operation with the manufacturer of the analyzers.

The off-line image analysis of the crystalline product showed that the particles can be classified into two classes: plate-like and rod-shaped particles. In this analysis particles were in the position of greatest stability. The portion of plate-like particles was smaller. It is known that it is difficult to dewater and wash plate-like materials. Therefore it is important to find a method for measuring the portion of plate-like particles on-line. This can be done by analyzing the images obtained on-line with off-line image analysing program. The results can be analyzed to give the relevant parameters needed for the shape classification. These parameters should then be measured on-line.

Future

The crystallization group will begin the experimental work and the filtration group will obtain material for the filtration tests. The parameters for the dewatering and washing models are measured separately using laboratory scale piston press filter. The models are evaluated using the dewatering and washing results obtained with a full size test filter. The slurries are classified on the basis of the accuracy and the reliability of the parameters and simulation models. The filtration models may need some modifications to include the influence of the crystalline products, because particle shape is an important factor in crystallization as well as in solid liquid separation.

6. Publications

- Jämsä-Jounela S-L., Oja M., *Modelling module of the intelligent control system for the variable volume pressure filter*, *Filtration&Separation* **37** (2000) No 2, 39-49
- Oja M. and Martin H., *Filter Cake Compression: Modeling of Consolidation Period*, 8th World Filtration Congress, Brighton, 3-7 April, Vol. 1, (2000), 54-56
- Oja M., *On-line Measurement of Particle Size Distributions*, 6th Nordic Filtration Symposium, 21-22.8.2000, Lappeenranta
- Oja M. and Laaksonen M., *Pressure Filtration Process Modeling with Methods of Neural Computing*, IFAC MMM Workshop, 22-24.8.2000, Finland, 486-488

Kinetic modeling of dehydrogenation of $C_3 - C_5$ alkanes

Project numbers: SA 46914, 46915, 46916 and 46917

The project coordinator: Professor Outi Krause

Helsinki University of Technology, Department of Chemical Technology
P.O.B. 6100, Fin-02015 HUT, Finland

Cooperation:

The project is a cooperation between four groups:

- Industrial Chemistry, Helsinki University of Technology (Prof. *Outi Krause*)
- Physics, Helsinki University of Technology (Dr. *Jouko Lahtinen*)
- Physical Chemistry, University of Helsinki (Prof. *Markku Räsänen*)
- Process Chemistry, Åbo Akademi University (Prof. *Tapio Salmi*) and Physics, University of Turku (Prof. *Juhani Väyrynen*)

The project group held the kick-off meeting on August 26, 1999 in Otaniemi. The research groups presented their research plans, which were discussed in detail. After that the project group met two times during the year. In addition, some meetings for smaller groups of researchers were arranged to discuss thoroughly some of the obtained results. From the beginning of the year 2000 the same chromia catalysts have been studied in three groups, creating a need for an even closer cooperation.

In addition to financing from the PROTEK program, support from the Graduate School in Chemical Engineering, from the Graduate School of Material Physics and from the Graduate School LASKEMO has been received.

Visits abroad and from abroad

Dr Bert Weckhuysen, from the Catholic University of Leuven in Belgium, visited Finland August 23 through August 29, 1999. One of his specialities is the characterisation of oxide surfaces. He held a seminar entitled "Raman spectroscopy in the characterisation of oxide catalysts" at the University of Helsinki. In addition, he discussed with the individual groups and joined the kick-off workshop.

Resources and Results

The researchers working in the project are mentioned in the sections describing the results of each group.

Two licentiate's theses have been completed

- Ms. Elina Harlin, HUT, September 1999
- Mr. Kalle Kauraala, HUT, May 2000

and one master's thesis

- Ms. Sanna Airaksinen, HUT, December 1999.

Dehydrogenation on supported oxide catalysts;

Laboratory of Industrial Chemistry, HUT

The researchers of the project were Ms. *Elina Harlin*, Lic. Sc. (Tech.), Ms. *Sanna Airaksinen*, M.Sc. (Tech.) and Ms. *Jaana Kanervo*, M.Sc. (Tech.). All are postgraduate students.

Results

Alumina-supported vanadium oxide catalysts were studied in the dehydrogenation of butane. The reduced oxides V^{3+}/V^{4+} were active in the reaction. The activity of the VO_x catalyst was higher after the CO reduction than after the H_2 reduction, because of water formation and the adsorption of OH groups on the active sites during the H_2 reduction. Before the vanadium oxide on the catalyst was reduced, it was active in the oxidative dehydrogenation forming alkenes and water. [1]

The dehydrogenation on chromium oxide catalysts was studied with the aim of developing a kinetic model for the dehydrogenation reaction. The activity measurements in the isobutane dehydrogenation were performed under various process conditions. The mathematical modelling was begun with simple kinetic expressions and will be extended to more detailed ones in the future. Also, the deactivation behaviour of the chromium oxide catalysts has been studied. FTIR spectroscopy has proven to be a valuable tool in assessing the stabilities of these catalysts. With this method, the catalytic activity during one dehydrogenation test can be measured almost continuously, see Figure below.

It was observed that the oxide catalysts reduce during the first minutes on stream. Therefore the reduction kinetics of the supported chromium oxides were studied with TPR experiments. A methodology was developed to treat the dynamic measurement data and the parameters of the kinetic models were estimated. [2]

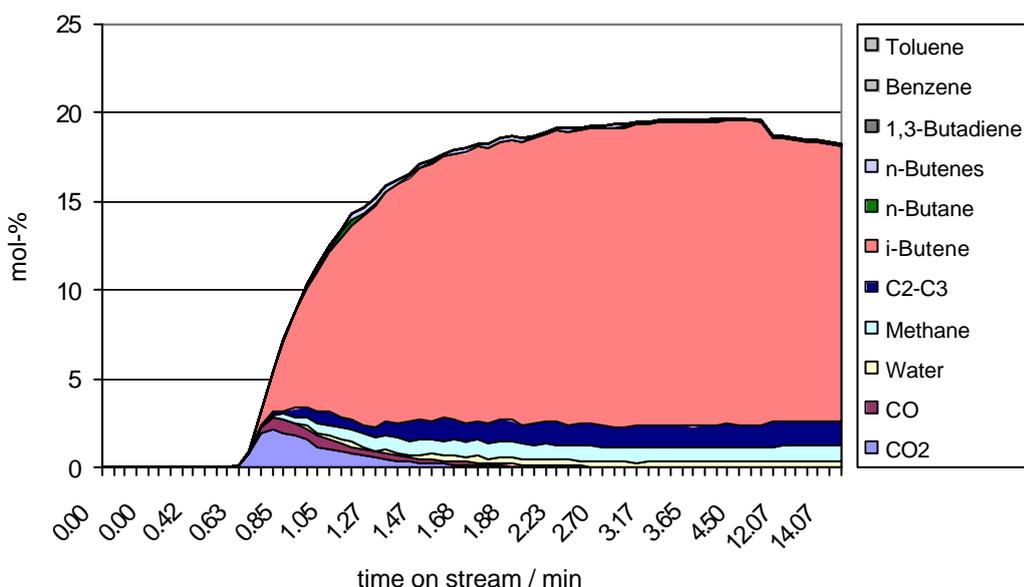


Figure. A typical product distribution in the dehydrogenation of isobutane.

ESCA studies of model and real catalysts

Laboratory of Physics, HUT

The researchers of the group were Mr. *Kalle Kauraala*, Lic. Sc. (Tech.), postgraduate student, Ms. *Karin Habermehl*, M.Sc, postgraduate student and Mr. *Mårten Eriksson*, Mr. *Jani Sainio*, Mr. *Olli Pakarinen* and Mr. *Jukka Katainen*, graduate students.

Single crystal surfaces

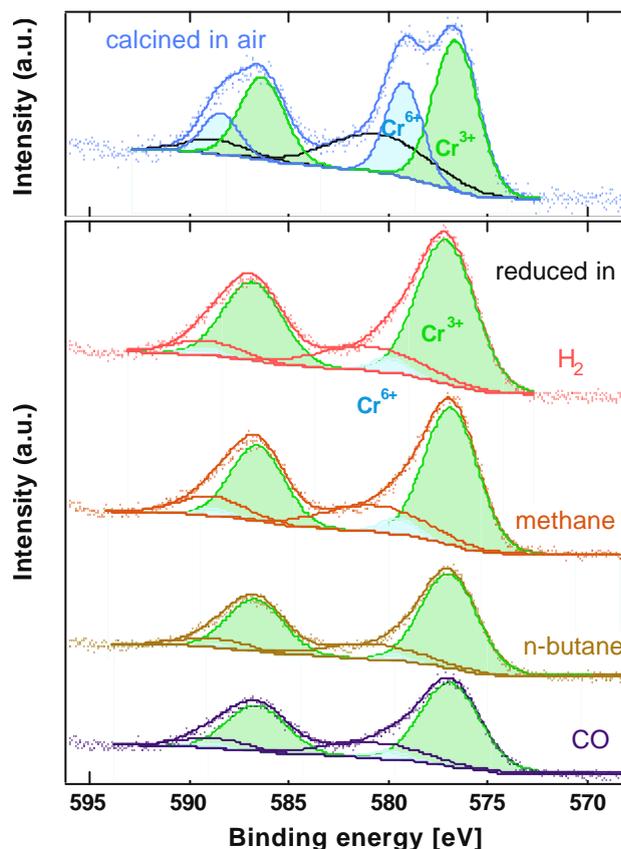
We have studied the adsorption and desorption of pentane on Co(0001) single crystal surface. The adsorption takes place below 180 K, but whether dissociation takes place already during adsorption is unknown. The desorption takes place around 220 K and several hydrocarbon fragments are seen during desorption.

Model catalyst surfaces

We have prepared a model catalyst surface on a NiAl (110) single crystal. When this surface is exposed to oxygen in vacuum, an ordered γ -Al₂O₃ layer is formed with a thickness of 4.5 Å. Chromium is then evaporated on this surface in vacuum. This far we have investigated the layer growth of Cr and Cr₂O₃ on the oxide surface. The results indicate three-dimensional growth in both cases. The Cr on the surface can easily be oxidised to Cr₂O₃ in vacuum but no CrO₃ has been detected. If the oxidation is done below 500°C, annealing of the surface results in reduction of the Cr₂O₃ to metallic Cr.

Characterisation of supported catalysts

The chemical state of Cr in a set of supported CrO_x/ γ -Al₂O₃ catalysts has been studied with ESCA (Electron Spectroscopy for Chemical Analysis). One catalyst made using Atomic Layer Deposition (ALD), one made by impregnation, and two commercial catalysts have been measured. All samples were calcined in air prior to ESCA measurements. The calcined samples were then reduced in H₂, CO, CH₄ or n-butane in an *in situ* reaction. After calcination the fraction of Cr⁶⁺ is between 20% and 30% in all the catalysts, the ALD-catalyst showing the highest fraction. After reduction only Cr³⁺ is seen on the surface and in this regard all the catalysts are identical. The ESCA spectra of the impregnated catalyst after calcination and reduction are shown in the adjacent figure.



Raman spectroscopic studies on group VI alumina supported oxide catalysts

Laboratory of physical chemistry, UH

The researchers of the group were Dr. *Leonid Khriachtchev* and Mr. *Martti Paakkunainen*, M.Sc., postgraduate student.

Results

The samples

Typical samples, provided by the consortium, include $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{CrO}_x/\gamma\text{-Al}_2\text{O}_3$ powders which have a layer of molybdenum or chromium oxides, respectively, on the surface of the alumina support.

The methods

The samples were principally characterised by using Raman spectroscopy, but some thermogravimetric analyses and quantum mechanical calculations were also carried out. The Raman measurements were performed using a homemade *in-situ* quartz cell. The cell can be heated up to (650 ± 20) °C, and various gas-phase reagents can be introduced to the sample when the Raman spectrum is recorded. The gases are fed into the cell through Brooks mass flow controllers. About 20 mg of each sample was pressed into a thin wafer and mounted on the sample holder in the *in situ* cell.

The results

The structures of $\text{Mo}/\text{Al}_2\text{O}_3$ and $\text{Cr}/\text{Al}_2\text{O}_3$ catalysts can be analysed by using Raman spectroscopy at various stages of catalysis. Isolated species, polymeric species and crystalline structures were readily differentiated.

As evidenced by thermogravimetry, when the temperature was increased, water desorption occurred at elevated temperatures, the total amount of water being between 5 and 9 wt-%, depending on the sample.

Ab initio quantum mechanical study shows that the calculations for cyclic Mo_xO_{3x} species, $x=3-5$, can be used to explain their experimental infrared spectra.

The plans

In future we intend to investigate intermediate structures of the catalysts using Raman spectroscopy. Resonance Raman enhancement technique will be applied to the catalyst studies to selectively enhance vibrations of various intermediates. Reduction studies will be made with thermogravimeter, and quantum mechanical calculations will be extended to real catalysts. Diffuse reflectance spectroscopy will be employed as a supplementary method.

Kinetics, mechanism and transport phenomena in heterogeneous catalysis

Process Chemistry (ÅA) and Laboratory of Physics (UT)

The researchers of the project were Prof. *D.Yu. Murzin*, Dr. *Ahmad Kalantar Neyestanaki*, Mr. *Henrik Backman* and Mr. *Hannu Karhu*.

Results

Pd and Pt catalysts with varying metal contents (1-5 wt-%) were prepared on two types of carriers: γ -Al₂O₃ and knitted silica-fibre. The catalysts were prepared by impregnation from solutions of H₂PtCl₆, PdCl₂, Pt(NO₃)₂ and Pd(NO₃)₂. The activities of the catalysts were investigated in gas-phase hydrogenation of o-xylene in a differential tube reactor at temperature ranges of 430-520 K (with 10 K interval) and H₂ and o-xylene partial pressures of 0.19-0.38 bar and 0.04-0.10 bar in argon. Prior to the experiments the catalysts were reduced *in situ* in H₂-flow at 673 K. The catalysts were characterised by N₂/H₂-adsorption, H₂/o-xylene-TPD and XPS.

Detailed kinetic measurements were carried out over the 1 wt-% Pt/Al₂O₃ catalyst. Additional experiments were performed to ensure that the data are obtained in the absence of diffusion limitations. A typical kinetic run exhibited a deactivation of ca. 30% during the first 20 minutes and steady-state operation was reached. Volcano shaped dependency of the rate on temperature was observed with the rate passing through the maximum at 460 K. The reaction order towards o-xylene was found to be close to zero, whereas the order towards H₂ increased with temperature from 0.9 at 430 K to 3 at 520 K. The results showed an increased *cis/trans* 1,2-DMCH ratio by increased hydrogen concentration at the given operation temperature. The *cis/trans* ratio decreased by increasing the operation temperature. The Pt/Al₂O₃ catalysts, prepared from nitrate precursor exhibited higher activities in o-xylene hydrogenation compared to the corresponding catalysts prepared from the Cl-precursor. This was attributed to the chlorine inhibition. The XPS studies indicated the presence of chlorine on the catalysts prepared from the Cl-containing precursor even after reduction in H₂-flow at 400°C. The effect of metal loading and reduction temperature on the hydrogenation rate was studied. The amount of H₂ desorbed from the catalysts reduced at different temperatures was correlated to the hydrogenation rate.

The adsorption and reaction kinetics of aromatic components, particularly regarding the multi-centred adsorption have been modelled theoretically. A kinetic model based on advanced reaction mechanism of o-xylene hydrogenation over Pt/Al₂O₃ catalysts was developed.

The Pt/knitted silica-fibre catalyst exhibited high activities in xylene hydrogenation. Xylene conversion of 98.5% was achieved over Cl-free 5 wt-% Pt/silica-fibre catalyst at 460 K and H₂ and o-xylene partial pressures of 0.6 and 0.06 bar. Further work on this topic will include an effort to improve the dispersion of silica-fibre catalysts.

The construction of an *in situ* reaction cell next to the XPS vacuum chambers for combined XPS and gas-phase hydrogenation of xylene is under construction. The system is expected to be ready soon. The kinetic measurements of xylene hydrogenation over Pd/alumina catalysts are currently being carried out.

Publications:

- Harlin, M.E., Niemi, V.M., Krause, A.O.I., Alumina-Supported Vanadium Oxide in the Dehydrogenation of Butanes, *J. Catal.* **195** (2000) 67-78.
- Krause, A.O.I., Airaksinen, S.M.K., Kanervo, J.M., Dehydrogenation of Light Alkanes on Supported Chromium Oxide Catalysts, ACS National Meeting, Washington, August 20-24, 2000, keynote lecture
- Su, X., Kung, K.Y., Lahtinen, J., Shen, R.Y., Somorjai, G.A., 1,3- and 1,4-cyclohexadiene Reaction Intermediates in Cyclohexene Hydrogenation and Dehydrogenation on Pt(111) Crystal Surface: A Combined Reaction Kinetics and Surface Vibrational Spectroscopy Study Using Sum Frequency Generation, *J. Mol. Catal. A: Chemical* **141** (1999) 9-19.
- Smeds, S., Salmi, T., Murzin, D.Yu., Kinetics of mesitylene hydrogenation, *Appl. Catal. A*, **185** (1999) 131-136
- Murzin, D.Yu., Catalysis involving multi-centered species on nonuniform surfaces, 1. Adsorption, *React. Kinet. Catal. Lett.* **70** (2000):2, 219-226
- Murzin, D.Yu., Salmi, T., Catalysis involving multi-centered species on nonuniform surfaces, 2. Kinetics, *React. Kinet. Catal. Lett.* **70** (2000):2, 227-234

Catalysis and separation technology based on cross-linked enzyme crystals

Project number: 46910

Professor Matti Leisola

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Professor Marja-Liisa Riekkola

Responsible project leader in University of Helsinki
Laboratory of Analytical Chemistry
P.O.B. 55, FIN-00014 University of Helsinki, Finland

Research group members:

Ph.D. *Jouni Jokela*, Laboratory of Bioprocess Engineering
M.Sc. *Johan Finell*, Laboratory of Analytical Chemistry
M.Sc. (Tech.) *Antti Vuolanto*, Laboratory of Bioprocess Engineering

Cooperation of the partners and funding from other parties:

Collaboration of the two partners in this project has been exceptionally intensive, because all the experimental research concerning the study of the catalytic and separation properties of the cross-linked enzyme crystals have been done in the Laboratory of Bioprocess Engineering so that the researchers from both laboratories have worked in daily contact. Part of the research concerning the crystallization and cross-linking of the enzymes has been done in the laboratory of the third partner, Macrocrystal Oy.

Tekes, the National Technology Agency has also financed this project until the end of the year 1999.

Scientific results:

Cross-linked enzyme crystals offer the possibility to develop totally novel catalysis and separation technologies. At its best crystallization of an enzyme and concomitant cross-linking of the crystals produces materials strong enough to be packed into an HPLC-column using traditional high pressure packing methods. Xylose isomerase (XI) from *Streptomyces rubiginosus* has been proven to be an optimal enzyme for this kind of purposes in analytical and large scale applications according to the properties listed below:

- Almost spherical crystal form makes possible high density packing into the column without disintegration of the crystals, which would block the flow through the column.
- For the analytical applications it is possible to prepare small size (~10 µm) crystalline material having a relatively narrow size distribution profile.
- Cross-linking with glutaraldehyde and lysine remarkably increases the mechanical stability of the XI-crystals and decreases the water solubility making them suitable packing materials for HPLC-columns.
- Production costs of cross-linked XI-crystalline material are relatively low because XI is an industrial enzyme produced in bulk scale, *Str. rubiginosus* xylose isomerase itself is a low cost enzyme and the cross-linking chemicals are not expensive.

We have shown that cross-linked xylose isomerase crystals (CLXIC) packed into an HPLC-column are able to separate molecules smaller than 1000 Da based on the size exclusion mechanism originating from the porous nature of the crystals. Xylose isomerase crystals are less porous than some other cross-linked enzymes or many commercial size exclusion supports, the characteristic of which could be partly responsible for the high mechanical strength of this material. The CLXIC-column separated all the n-alcohols tested (C₁ ... C₈). The increasing retention of n-alcohols together with the increasing chain length is most probably related to the quantity and quality of hydrophobic moieties of enzyme crystal surface exposed to the surrounding solvent. From the natural L-amino acids and the corresponding D-amino acids only aromatic and heterocyclic amino acids are clearly retained with the CLXIC-material. Retention does not correlate with the hydrophilic/phobic nature of these amino acids, so some other interactions are responsible for the behaviour of these amino acids. Experiments with the L- and D-amino acids have so far shown that CLXIC-material does not contain structures capable of effective chiral separation of amino acids. However, the CLXIC-material shows chiral selector properties towards many tetrose and pentose sugars and D- and L-arabitol. These observations clearly show that the chiral separation of CLXIC-material is based on the interaction between the substrates or substrate analogs of the enzyme and its active center. In addition of the chiral separation of D- and L-arabitol, other sugar alcohols are also selectively retained on the CLXIC stationary phase.

Crystallization together with the cross-linking in some cases destroys the catalytic activity of a soluble enzyme. However, xylose isomerase is almost completely active also in a CLC-form leading to a CLXIC-column in which even the reactions of weakest substrates are detectable. In these experiments we found two new tetrose substrates, D- and L-threose, one new pentose substrate, L-lyxose and two new hexose substrates, L- and D-mannose for this xylose isomerase enzyme. Because almost all the tetrose, pentose and hexose sugars have different retention towards the CLXIC-material the substrate is simultaneously isomerized and the reaction mixture components are partially separated in the CLXIC-column.

Xylanase II from *Trichoderma reesei* is another enzyme that was crystallized, cross-linked and packed into a column (i.d. 5 mm) in order to study the possible applications of CLEC's. Cross-linked xylanase crystals (CLXC) were much more fragile than CLXI-crystals and the crystal form, tetragonal sheet, was not optimal for column packing purposes. Because of this fragility of the xylanase crystals, cross-linking was made after the crystals were packed into the column. This cross-linking technique may give an extra rigidity to the CLXC-filling. The retention behaviour of small, neutral polyethylene glycol (PEG) molecules and the n-alcohols (C₁ ... C₈) in CLXC-column was similar than in the CLXIC-column. CLXC-column separated also PEG molecules with high molecular weights (from 1000 Da to 318000 Da) but the pores inside the crystals cannot be solely responsible for this separation. One explanation for this phenomenon could be that the xylanase crystals of different sizes (~1...40 µm)

together with the cross-linking of these crystals inside the column create another porous structure outside the xylanase crystals.

Xylan is the natural substrate of xylanase II enzyme. Xylanase hydrolyses the glycosidic bonds between the xylose units from which xylan is constituted. The insolubility of native xylan makes its use in column applications impossible, so we studied the behaviour of soluble xylooligosaccharides in the CLXC-column. In all experiments xylotetraose was hydrolyzed at least to xylobiose and xylose, but with long reaction times and column lengths, xylotetraose was totally hydrolyzed to xylose. Xylobiose behaved identically with xylotetraose in these experiments. Addition of xylose into the eluent did not inhibit hydrolysis of xylotetraose in the CLXC-column. Xylose and xylobiose were separated during the hydrolysis reaction in the CLXC-column due to the lack of interaction of xylose with the CLXC-material. Elution behaviour of xylose was identical with other pentose sugars while xylobiose eluted later than the pentoses and other disaccharides. Also soluble xylanase hydrolyzed xylotetraose and xylobiose, when high enzyme/substrate ratios (0,1 ... 20 w/w) and long reaction times (30 min...24 h) were used, but CLXC-column produced relatively more xylose through a mechanism which is not yet fully understood.

To our knowledge, the hydrolysis of xylobiose by xylanase has not been reported in the literature before.

Endoglucanase III is the third enzyme which is crystallized and cross-linked during this project but these crystals were mechanically so fragile that columns were blocked even at low flow rates.

Publications:

Leisola M and Jokela J. Process for the preparation and simultaneous separation of enzyme-catalyzed products. International Patent Application no PCT/F100/00702, Filing day 18.8.2000.

Pastinen O., Jokela J., Eerikäinen T., Schwabe T. and Leisola M. Cross-linked glucose isomerase crystals as a liquid chromatographic separation material. *Enzyme Microb Tech* 26 (2000) 550 - 558.

Leisola M., Jokela J., Finell J. and Pastinen O. Simultaneous catalysis and product separation by cross-linked enzyme crystals. *Biotechnology and Bioengineering*, In press.

Visiting scientists:

Prof. Ken Izumori, Faculty of Agriculture, Kagawa University, Japan	4.9.2000
Dr. Julian Cooper and David Hopkins from British Sugar Ltd, Great Britain	28.9.2000

Activity Report on
Alkaline Delignification of Lignocellulosics

Project 46924

Responsible Person Professor Bruno Lönnberg

PROTEK Project of Åbo Akademi University
Faculty of Chemical Engineering, Laboratory of Pulping Technology
Porthansgatan 3, FIN-20500 TURKU, Finland

Researcher

Mr. *M.M.A. Quader*, M.Sc., graduated from Asian Institute of Technology in Bangkok, Thailand. Mr Quader is accepted by Åbo Akademi University as Ph.D. Student of Pulping Technology (will join the International Ph.D. Programme in Pulp and Paper Science and Technology, PaPSaT).

Research Partners

Åbo Akademi University has worked together with Ahlstrom Machinery, Kymmene and Rintekno with the aim of developing a new sulphur-free, alkaline delignification process named IDE (after: impregnation, delignification and extraction). As the companies have changed (Andritz-Ahlstrom and UPM-Kymmene) there will also occur changes in the future industrial consortium.

Aim of Project

The aim of this project is to develop a new chemical pulping process, which provides higher pulp yields and better pulp bleachability, and a pulp as strong as those obtained with current alkaline pulping processes (kraft). The new pulping concept requires that no sulphur in any form should be used in the pulping liquors.

Results

The study started with special prehydrolyses before impregnation as to discover a catalytic effect by process technological means. If successful, this would improve the process without introduction of catalysts, e.g. AQ and EDA. The hypothetical approach was to “loosen” the bonds between lignin and hemicelluloses/cellulose as to speed up the delignification. It was demonstrated that a common 15 min steaming was not effective, while prehydrolysis by “water-cooking” at various temperatures led to some effects. However, from an economic point of view, it is not yet possible to determine the best result by certainty, but some further tests should be carried out. The problem is that high prehydrolysis temperature well decreases the kappa number after the IDE cook, but unfortunately also decreases the pulp yield below reasonable levels.

After this initial phase, the impregnation conditions were changed beyond normal limits, as to reveal possible effects on delignification without application of catalysts. Because low impregnation temperatures ensure the chemicals to impregnate into the wood material with simultaneously minimum reactions and hence consumption in a premature stage, temperatures as low as 60° C were tested. It was seen however that 80° C was an optimum for the case studied, i.e. to provide the best combination of pulp yield and residual lignin content (kappa

number) as regards the final delignification result obtained by a subsequent oxygen stage after the IDE stages. The screenings were rather high compared with the common IDE levels, but not higher than for current pulping processes, which unfortunately would be the case, if the impregnation temperature would be decreased further. The total yield was now about 51 % for the spruce wood used at a corresponding kappa number of about 40. This is high, but on the other hand the pulp yield is normally higher relative to the kappa number, and thus a selective oxygen stage would give good yields after the oxygen treatment, which was about 18, i.e. well below levels useful for a common ECF bleaching system.

It appears that the IDE process could be further developed by application of quite low impregnation temperatures for high pulp yields and relatively low kappa numbers, but by introducing instead an oxygen delignification stage which is selective and hence would result in acceptable pulp strength values, as was demonstrated.

Models in process development: selection, validation and integration

PROJECT 46909

Project leader: Ilkka Turunen, professor

Lappeenranta University of Technology, Laboratory of Process System Engineering
P.O.B. 20, FIN-53851 Lappeenranta, Finland

Project personnel

<i>Ilkka Turunen,</i>	Prof.	Project leader
<i>Esko Lahdenperä,</i>	Lic. Tech.	Research Scientist
<i>Arto Laari,</i>	M.Sc.	Research Scientist

Brief summary of the project goals

Modelling of unit operations at different levels of detail is studied in the project by the aid of three test cases. Real measured data from industry or from pilot plants are used to estimate the model parameters and validate the models. The modelling is carried out at different mechanistic levels, from simple models to very detailed ones. Also different competitive theories are used to describe the physical phenomena. Conclusions will be made e.g. about adequate modelling approach at different stages of process life-cycle, mainly from the viewpoint of practical process development.

Results

Extraction in a sieve-plate column.

The work was started with simple steady state model of the column, using empirical correlation for plate efficiency. The parameters of the correlation were estimated from industrial data. The fit was good but validity region of the model was restricted according to the experimental range.

Dynamic experiments were carried out with a small pilot column to allow more alternation in process conditions. Based on these experimental results, following two models are under development:

- dynamic model where plate efficiency has been correlated with flow velocities of both phases
- dynamic model where mass transfer is described with a very detailed, mechanistic approach

Gas-liquid reaction in a concurrent bubble column.

Models with and without axial dispersion have been completed for a test reaction. Measurements of gas hold-up are currently going on to improve the models. Experimental program to measure bubble size distribution is planned for further improvement.

Gas-liquid-solid reactor (KATAPAK-reactor)

A relatively detailed model was developed. Because of the multitude of phenomena involved, it was necessary to study different phenomena separately with mock-up experiments and combine the submodels. CFD was needed to evaluate flow velocities inside the catalyst pockets.

The model will be improved by more detailed description of gas-hold up, gas-liquid mass transfer and velocity distribution in catalyst bed. These are currently studied experimentally in another project, financed by TEKES.

Publications

Piironen, M., Haario, H., Turunen, I., Modelling of Katapak reactor for hydrogenation of anthraquinones. Accepted for publication in Chemical Engineering Science.

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