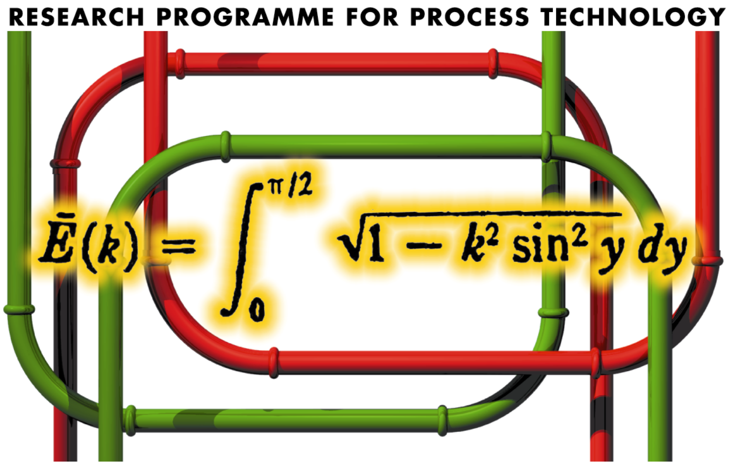
RESEARCH PROGRAMME FOR
PROCESS TECHNOLOGY 1999 - 2002

RESULTS OF THE 2nd YEAR

3rd RESEARCHER MEETING ON NOVEMBER 22nd, 2001



Process industry – laying the foundations for future prosperity

Contents

Foreword

The Research Programme for Process Technology (PROTEK) of the Academy of Finland has now been running over two years, since it began in August 1999. The results of the second year (from August 2000 to July 2001) are presented in this booklet. Good productivity has been continued within publications, scientific degrees, connections created between universities, laboratories and industry, and many international contacts. There are minor changes in the structure of the groups due to management changes and reorganisation of some consortia. The projects are presented in alphabetical order following the names of the project leaders.

The budget of the programme is 15 million Finnish marks and funding time is three years. The composition of the programme was planned by a programme committee having members from the Research Council for Natural Sciences and Engineering and Research Council for Environment and Natural Resources (nowadays Research Council for Biosciences and Environment) of the Academy, National Technology Agency (Tekes), Finnish chemical industry, universities, and the Chemical Industry Federation of Finland. In 2002 the programme will be internationally evaluated.

PROTEK has concentrated on three main themes:

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

The research themes are various, including biotechnical processes, burning, catalysts, thermodynamics, modelling and pulping. 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.

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Progress report 1.8.2000-31.7.2001 of the project:

1. Modelling and developing of efficient process configurations combining reaction and distillation

Finnish name:

Reaktioita ja tislausta yhdistävien prosessien kehittäminen ja mallinnus

Project number: **46912**

Professor Juhani Aittamaa

Helsinki University of Technology
Laboratory of Chemical Engineering and Plant Design
Kemistintie 1, P.O.B. 6100, FIN-02015 HUT, Finland

Researchers in the project:

Kaj Jakobsson, Ph.D student, Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design

Collaboration

Collaboration with Neste Engineering Oy has taken place in model development with Lic.Sc. (Tech.) Antti Pyhälahti and Dr. Kari Keskinen.

Kaj Jakobsson acted as the instructor of the M.Sc. thesis of Tuomas Ouni "Optimisation of reactor-separator-recycle system" Helsinki University of Technology, Laboratory of Chemical Engineering and Plant Design. This diploma project was done in the Tekes' (National Technology Agency) project "Dimerointireaktioiden kineettinen mallintaminen ja prosessin optimointi".

Collaboration with Dr. Liisa Rihko-Struckman in Max-Planck-Institut für Dynamik komplexer technischer Systeme was done in order to find new chemical systems for processes combining reaction and distillation.

Results of the project

During the first year of the project a prototype model of a process combining reaction and distillation was developed. The main improvement of the new model is that the steady state model equations of the column and the reactors are solved simultaneously. Present modelling of reactors and separators is based on separate models that are often very difficult to solve because of the strong interaction of the units. Simultaneous solution is expected to be more reliable and faster.

During this reporting period the prototype has been further developed. The focus of the development was directed to generation of good initial values for the independent variables of the model. Good initial point for the solution algorithm is of great importance when Newton's solution method or some of its relatives is used. Three initialisation models have been implemented:

1. Initial compositions are obtained by calculating the reactor blocks of the model using the average feed compositions. The compositions of the reactor effluent are distributed linearly in the column depending on their relative volatility. The temperatures are obtained from multicomponent flash calculations that give the boiling point of the mixture.
2. Average feed compositions are used as the initial compositions and mass balance calculation is done to obtain the flows. Temperatures are set at the boiling point of the mixture.
3. The initial values of a previous simulation are used.

Because the new model is aimed as a tool for optimisation of large-scale process configurations combining reaction and distillation the question of the description of real distillation plates is relevant. The rate-based approach has dominated the recent development of distillation modelling. However, in the project we showed that for small-scale real plates the rigorous efficiency approach described the real plate behaviour as well as the rate-based model. This is not surprising since the two models are based on the same multicomponent Maxwell-Stefan mass transfer theories. The rigorous efficiency calculations are fairly easy to implement into an ideal stage model. The efficiency model used is even applicable to large-scale plates. Rate based models for large scale plates are still under development.

The suitability of production of *tert*-octyl methyl ether for process configuration combining reaction and distillation was investigated.

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.

Publications and conference presentations

Jakobsson, K., Pyhälahti, A., Pakkanen, S., Keskinen, K., Aittamaa, J., Modelling of a Side Reactor Configuration Combining Reaction and Distillation, ECCE 3rd European Congress of Chemical Engineering, 2nd International Symposium on Multifunctional Reactors, June 26-28, 2001, Nuremberg.

Jakobsson, K., Pyhälahti, A., Pakkanen, S., Keskinen, K., Aittamaa, J., Modelling of a Side Reactor Configuration Combining Reaction and Distillation, Submitted to Chem.Eng.Sci Special issue of 2nd International Symposium on Multifunctional Reactors June 26-28, 2001.

Jakobsson, K., and Aittamaa, J., Comparison of plate efficiency estimation models to experimental results of pilot scale: a case study, Accepted for presentation in 2001 AIChE Annual meeting, November 4-9, 2001, Reno, NV.

L. K. Rihko-Struckmann, R. S. Karinen, K. Jacobsson, A. O. I Krause and J. R. Aittamaa, The Production of a Novel Oxygenated Gasoline Component, EFCATS 5th European Congress on Catalysis, 2-7 Sep, University of Limerick, Ireland.

2. 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:

Brandt, Kirsi, M.Sc., graduate student (genetics)
Munsch, Patricia, PhD.
Ravin, Victor, PhD
Riipinen, Katja, M.Sc., graduate student (genetics)
Tilsala-Timisjärvi, Anu, Ph.D.

Description on the collaboration:

Concerning the lactic acid bacteria (LAB) research an intensive international collaboration has been done with Prof. G. Tannock (Univ. of Otago, New Zealand) and Dr. R. Raya (Cerela, Argentina) and their groups. The samples from Emmental cheese processes for the project have been obtained by Valio Ltd.

The research collaboration and consulting on DNA-based identification of mastitis bacteria and their pathogenicity and resistance factors have been continued with prof. S. Pyörälä (Univ. of Helsinki) and her group as well as with a Finnish biotechnology company.

The research collaboration on the field of DNA-based taxonomy and identification of mushroom pathogenic *Pseudomonas* species has been done especially with Dr. K. Johnstone (Univ. of Cambridge, United Kingdom). A methodological collaboration on *Pseudomonas* genome analysis has been started with Prof. Ritzenthaler (CNRS-Toulouse, France) and his group.

This research has been supported also by two grants from the EU regional funds and Oulu province.

Summary of the results:

1. Three new IS elements (ISLdl1, ISLdl2 and ISLdl3), which vary in copy numbers and in locations in the genome of Lb. delbrueckii strains, have been discovered. This source of DNA polymorphism could be applied to design sets of primers for multiplex PCR reactions in order to identify and monitor specificly Lb. delbrueckii starter strains interested.
2. Additional sequence data on Lb. rhamnosus phage Lc-Nu genome have been determined and further applied to reveal amount of DNA polymorphism among the strains of Lb. casei –group species. Using this approach strain-specific primer pairs for PCR-based identification of three probiotic Lb. rhamnosus strains including also strain GG have been developed.
3. New mushroom pathogenic *Pseudomonas* species has been discovered and a PCR-based identification method for this species has been developed.
4. Various methods, commercial products and kits for isolation of DNA from cheese and fermented milk samples have been tested and further modified in order to develop simple and rapid protocols for PCR-based analysis of dairy starters and spoilage bacteria in milk and milk products.

Publications:

Tilsala-Timisjärvi, A., Forsman, P. & Alatossava, T. (2000) Bovine mastitis diagnosis from milk by a polymerase chain reaction-based method. Milchwissenschaft 55:488-492.

Munsch, P., Geoffroy, V.A., Alatossava, T., & Meyer, J.-M. (2000) Application of siderotyping for characterisation of *Pseudomonas tolaasii* and *"Pseudomonas reactans"* isolates associated with brown blotch disease of cultivated mushrooms. Appl. Environ. Microbiol. 66:4834-4841.

Brandt, K., Tilsala-Timisjärvi, A. & Alatossava, T. (2001) Phage-related DNA polymorphism in dairy and probiotic *Lactobacillus*. Micron 32:59-65.

Tilsala-Timisjärvi, A. & Alatossava, T. (2001) Characterization of the 16S-23S and 23S-5S rRNA intergenic spacer regions of dairy propionibacteria and their identification with species-specific primers by PCR. Int. J. Food Microbiol. 68:45-52.

International visits:

Prof. G. Tannock (Univ. of Otago, New Zealand) has visited altogether about four weeks in Dec ´00 – Jan ´01 at Univ. of Oulu, and performed an experimental research together with the scientists of this project on the stain-specific identification of probiotic *Lactobacillus.*

3. Modelling phase interactions in process engineering

Project number **46897**

Project leader: Professor Kari Heiskanen

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

Researchers involved in the project:

Reijo Kalapudas	*MINVTT*
Vesa Kirjavainen	*MEKTKK*
Jaakko Leppinen	*MINVTT*
Mauno Miettinen	*MINVTT*
Nóra Schreithofer	*MEKTKK*

Cooperation:

This project is run in a consortium consisting of:

Laboratory of Mechanical Process- and Recycling Technology at Helsinki University of Technology (MEKTKK);

VTT Chemical Technology, Mineral Processing (MINVTT).

During the reporting time, the project was supposed to partially perform Task 2. and 3. and complete Task 4, as described in the submitted application.

Task 2 to obtain second partial objective (direct force measurements)

1. *Material selection (sub-task responsible Prof. K. Heiskanen)*

The test material selected was pure quartz from Arkansas and Brazil. It has also been decided that artificial silica and borosilicate glass spheres will be used for AFM force measurements. This experimental material was chosen because it was considered necessary to test and understand the basic phenomena of the particle-bubble interactions. Measuring with spherical particles gives the possibility to normalise the measured force and fit the measurement data to the available theoretical calculations.

2. *Preliminary characterisation (sub-task responsible V. Kirjavainen)*

The selected quartz samples were subjected to thorough study in order to determine the surface properties.

The shape of both Brazil and Arkansas quartz particles were evaluated using SEM images. Both samples were found suitable for AFM force measurements.

Surface cleaning methods with ethanol, HCl, HNO_3 and NaOH have been tested. The samples were analysed with ESCA, XRD, FTIR and AFM in order to determine the effect of different cleaning methods on the surface properties of quartz. NaOH treatment was finally chosen because it results clean and smooth surfaces. This method will be used for cleaning the samples before induction time measurements and AFM force measurements.

3. *Adsorption measurements (sub-task responsible M. Miettinen)*

Adsorption measurements have been performed at MINVTT and at the Laboratory of Environment and Mineralogy (LEM) in Nancy, France, during the visit done by N. Schreithofer.

Purified amine was used and different size fractions from each batch of Arkansas and Brazil quartz was tested. The analysis of the adsorbed amount was analysed from the solution by UV/VIS spectroscopy method and directly from the quartz surfaces using combustion analysis and IR spectroscopy. Combustion analysis is a new method for analysing adsorbed species directly from the mineral surfaces. Two research papers are planned to be published, one on the effect of surface treatment methods on the surface properties of quartz, and an other on the adsorption of amine studied by IR spectroscopy and combustion analysis technique.

4. *Contact angle measurements (sub-task responsible V. Kirjavainen)*

For completing this subtask, the available microscope objective – photo objective – CCD camera system built into the new AFM based instrument is planned to be used. These measurements will be started soon.

5. *Atomic force microscopy (sub-task responsible N. Schreithofer)*

The development and construction of the experimental device working on AFM principle has been finished, although the first measurements were performed about 3 months later than promised due to the break down of the piezo translator and the controller unit. These units have been sent back to the manufacturer and fixed. The instrument is now operating and force measurements are performed with it on everyday basis. Discussions with researchers from acknowledged research groups revealed that this instrument is unique of its kind and may open new possibilities in study of surface phenomena.

The instrument was first tested by doing force measurements between mica sheets and borosilicate glass spheres. The instrument proved to function very well.

At present interactions between hydrophobized silica spheres and air bubbles are under study. The particles are hydrophobized, using 1,1,1,3,3,3-hexamethyl-disilazane. The experiments are performed in ultra-pure water. The measurements showed an unexpectedly long jump-in distance, which was also confirmed by the images captured by the CCD camera. Violent deflection of the air bubble was also captured. The available theories does not give explanation for the observed phenomenon, and therefore the decision was taken that the future research work will emphasis on the study and understanding of it, due to its novelty and overriding importance in interactions between particles and air bubbles.

Task 3 to obtain third partial objective (solid-gas force balance modelling)

Due to its complexity, the completion of this task was delayed. It was suggested that the data of the force measurements and the adsorption tests would be put into the international forum opening new possibilities for further theoretical developments.

Task 4 to obtain fourth partial objective (film rupture studies)

1. Induction time measurements (sub-task responsible R. Kalapudas)

Induction time measurements are done also at the moment. A more advanced technique for counting the particles attached to the air bubble is planned to be developed. The technique is based on image analysis.

2. Induction time interpretation

The interpretation of the results is in progress.

Publications

N. Schreithofer, K. Heiskanen, New experimental design for direct force measurements between particles and air bubbles, with special interest on natural mineral particles. Proceedings of 6th World Congress of Chemical Engineering, 23-27 Sept. 2001, Melbourne, Australia.

Visits

Nóra Schreithofer has visited:

University of Siegen, Prof. Hans-Jürgen Butt's group to discuss about the new experimental setup;

Laboratory of Environment and Mineralogy (LEM) in Nancy, France, where she performed adsorption tests, zeta-potential measurements and had several discussions about the different issues connected to the research work done at HUT and got very thorough explanations about the theoretical background of the experimental techniques developed and used at LEM for surface characterization of minerals;

University of Melbourne and University of South Australia where renown research groups work in the field of colloidal interactions with special interest on interactions between particles and deformable surfaces such as air bubbles and oil droplets.

The Academy of Finland
Research Programme for Process Technology (PROTEK)
Project number **46937**

Annual Consortium Report 2000 – 2001

4. Fundamental studies for improving submodels in combustion modeling

Project leader: Professor Mikko Hupa

Åbo Akademi University, Combustion and Materials Chemistry
Lemminkäinengatan 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:

Rainer Backman	*ÅA*	*Jouni Hokkinen*	*VTT*
Anders Brink	*ÅA*	*Jorma Jokiniemi*	*VTT*
Pia Kilpinen	*ÅA*	*Lars Kjäldman*	*VTT*
Christian Mueller	*ÅA*	*Jussi Lyyränen*	*VTT*
Bengt-Johan Skrifvars	*ÅA*	*Jouni Pyykönen*	*VTT*
Maria Zevenhoven	*ÅA*	*Risto Laitinen*	*OY*
Ari Auvinen	*VTT*	*Laura Nuutinen*	*OY*

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 (08/2000 Oulu, 11/2001 Espoo). In between these annual meetings, working meetings are held focussing on the different research topics. Within the second year of the project good progress has been made in all three working areas.

Results of the Research Activities:

ASH

The goal of the work done in this part of the project by ÅA and OY is to increase the detailed knowledge about how ash behaviour 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 behaviour prediction tool where the advanced fuel analysis method, a selective chemical dissolution analysis, is coupled with a 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 23 different fuels have been analysed using the chemical fractionation procedure. Partly the underlying data were produced within this project, partly within Tekes based projects, e.g. in the national programmes LIEKKI and CODE and the international co-operation funded by Tekes/DOE. A summary of the deposit behaviour of 23 fuels is reported in the Academic Dissertation “Ash forming matter of biomass fuels“. A summary of the chemical dissolution analysis results is shown below (Figure 1).

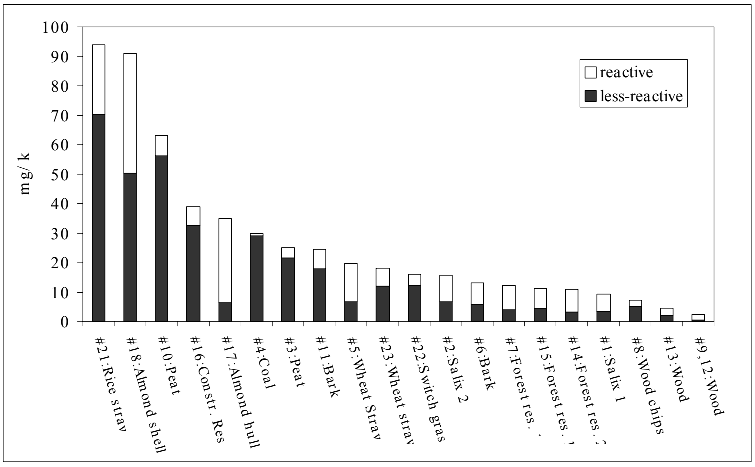


Figure 4.1 The distribution of ash forming matter in different fuels

As can be seen, the amount of easy-leachable elements varies strongly depending on what fuel is analysed. Marked differences were seen in the distribution of the ash-forming elements in the various fuels. In geologically older fuels, more ash-forming elements were present as excluded and/or included minerals. In relatively young fuels, up to half of the amount of ash-forming elements was present in the soluble fraction after leaching with water and ammonium acetate.

The present study shows that the easily leached elements are the main constituents of fine fly ash and consequently a reasonable approximation of fly ash compounds.

Prediction of the presence of a molten phase in fly ash, together with the reactive amount, total ash composition, melt range, T_{15}, and maximum amount of melt, permits ranking of fuels in order of deposit formation tendencies (Figure 2). In the present study, the ranking of fuels as less-problematic < problematic was as follows: coal < peat < wood derived fuels < annual crops < agricultural waste, which very well corresponds to general practical experiences with these fuels.

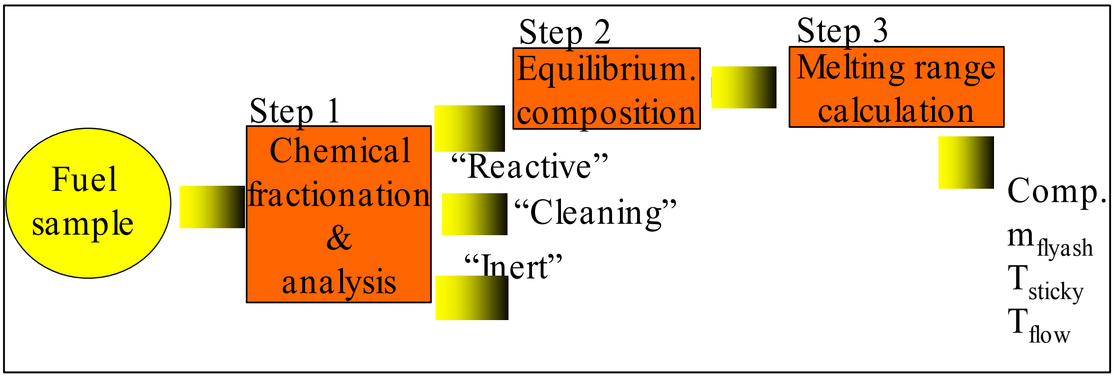


Figure 4.2 Simplified prediction scheme

Fractionation experiments with bark showed marked differences in analytical results from different laboratories (Figure 3). This led to extra efforts for analysis at OY.

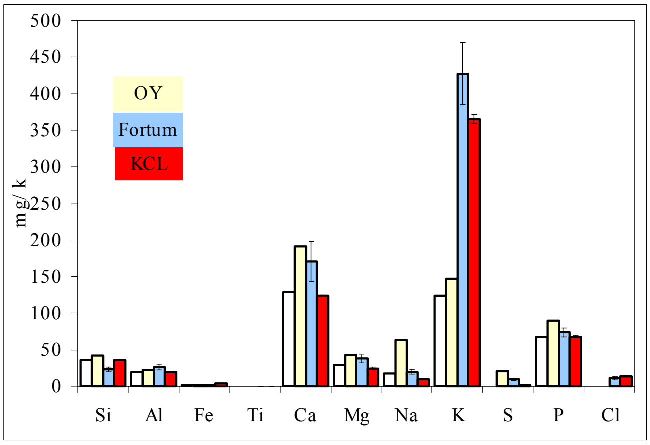


Figure 4.3 Differences in analytical results (Bark #6 leached with water)

VTT Energy has continued during this reporting period on the development of radioactive tracer measurements for real-time deposition studies. The tests with these techniques were carried out at the end of 2000. The tests indicated that the application of radioactive techniques is not quite straightforward. Nonetheless, they still hold promise for the future.

In our test experiments, radiotracer was added into the generated test aerosol that was fed into a deposition test system. The accumulation of the deposited material was measured on-line with five sequential scintillation detectors. As the test system, we had a simple straight cooled pipe. To enable the estimation of the fraction of aerosol deposited in the cooled tube, outflowing aerosol was collected to a filter, the activity of which was monitored with a sixth detector.

The radiotracer materials have to be activated in a nuclear reactor. The produced radioactive isotope must have a relatively short half-life (less than 20 hours), so that the used equipment can be easily disposed of. For the same reason, the activated isotope may not have long lived daughter nuclides and the level of impurities in the material must be low. In order to avoid excess activity, a high-energy gamma has to be produced in a significant fraction of the decays. Alkalines, potassium and sodium, can easily be activated into a suitable short-lived isotope. The half-life of ^{24}Na and ^{42}K are 14.959 h and 12.36 h respectively. The biggest problem with potassium is its natural long lived ($T_{1/2}$ = 1.27E9 y) radioactive isotope ^{40}K. The difficulty with sodium is that almost all decays (99.94%) also yield a 2754 keV γ-ray. This will increase the dose of the laboratory personnel, because it is practically impossible to shield such a high-energy gamma. An easy starting material that fulfills all the requirements was copper. The active isotope, ^{64}Cu, has a suitable half-life of 12.7 h. It has only a very weak, 0.47%, characteristic gamma peak at 1346 keV.

The calibration of the sequential detectors is a five-step process. Firstly, the background noise needed to be corrected. This is simply done by measuring the level of the noise with each detector. The second step is to perform an efficiency calibration. The pulse rate coming from a standard calibration source has to be measured with all detectors, because each scintillation detector has a different sensitivity to radiation. Thirdly, the decay rate of the sample has to be taken into account especially, when short-lived isotopes are applied in the experiments. There is also a need for an energy calibration if several radionuclides are to be measured. Lastly, the effect of the lead shielding has to be taken into account.

In the test experiment, the nitrogen flow rate was 100 l/min (NTP), of which 20 l/min was directed through the aerosol generator. The temperature of the gas was 200°C at the inlet of the tube. The aerosol was produced from copper powder using a dry powder generator. The flow rate of the coolant water was 1 l/min and the inlet temperature was 30°C. The activity measurements were started five minutes before the aerosol feed. Each measurement lasted for 30 seconds and the duration of all measurements was 60 minutes.

The deposition profile in the heat exchanger was estimated from the measured activity data using the shielding function obtained from the calibration. The accumulation of the deposit in the 85cm long cooled section is presented in figure 4. High deposition rate values close to the outlet may be due to its close proximity to the filter. Even though the detectors measuring the tube are well shielded from the filter, some pulses penetrate always through the shielding. This can lead to a significant error in deposition measurements, because the activity collected into the filter is much higher than what is deposited into the tube. Overall, relatively even deposition profiles were expected from the test experiment. The fluctuation in the results is probably due to insufficient activity, the effects of the shielding, and differences among the detectors.

The results of the test experiment demonstrated that additional efforts are required until the radioactive tracer methods can be used with reliability in these kinds of experiments. Therefore, we decided not to continue with the radioactive measurements within the context of the PROTEK program. Further development can be done in other on-going and future projects, while in 2001 we have started more conventional experiments in order to meet the objectives of this project within the available time.

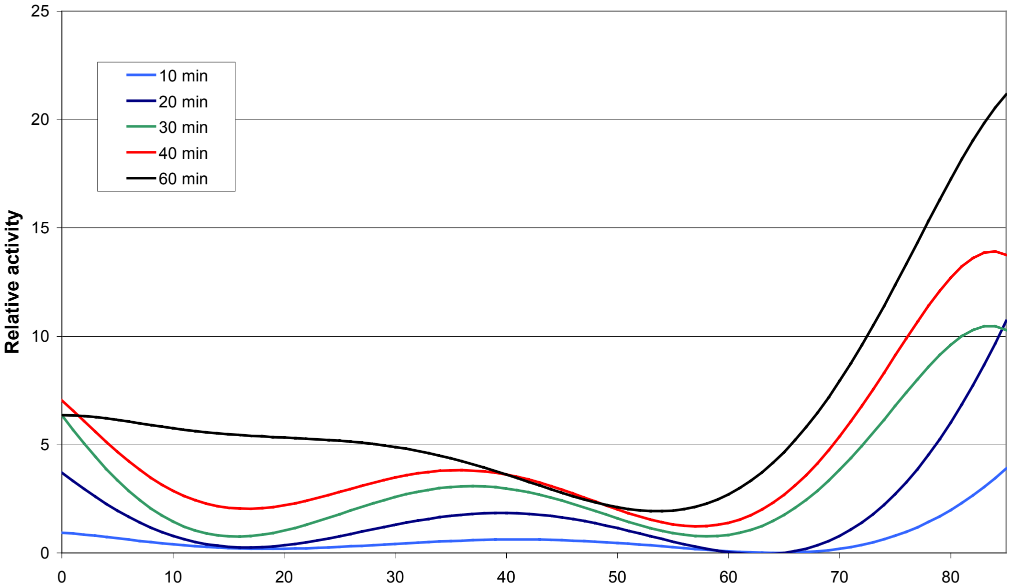


Figure 4.4 Distance from the beginning of the cooled section [cm]

The studies within 2001 have only started at the beginning of October and part of the work planned for this year will be delayed till the beginning of 2002. Our current studies consist of experiments of the ability of alkali species to plug small flow channels. Perforated plates form the small flow channels. In the first experiments, pure Na_2SO_4 was observed to plug the flow channels very rapidly while pure NaCl plugged them at a lower rate. Plugging is measured by observing the pressure differences in the system. In the future experiments, chemical composition will be varied. In addition, we try to use our models, partly developed in this project, to understand the relevance of the experimental observations for real-scale boilers.

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. Besides different coals, wood and other biomasses as well as various waste-derived fuels have been successfully demonstrated in a number of FBC units. 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. Ever tightening emission limits necessitate further development work for the reduction of the emissions from FBC including the components like NO_x and N_2O. To render FBC technology economically attractive, the emission reduction has to take place in the FBC furnace itself.

A mathematical tool is being developed for studying the nitrogen oxide emission formation in circulating fluidised bed combustors (CFBC). The model is based on detailed homogeneous and heterogeneous chemical kinetics and a simplified, one-and-a-half-dimensional hydrodynamics with presumed temperature distribution. With the model different fuels and fuel mixtures can be compared in regard to their nitrogen oxide emission formation tendency at typical FBC conditions (Figure 5).

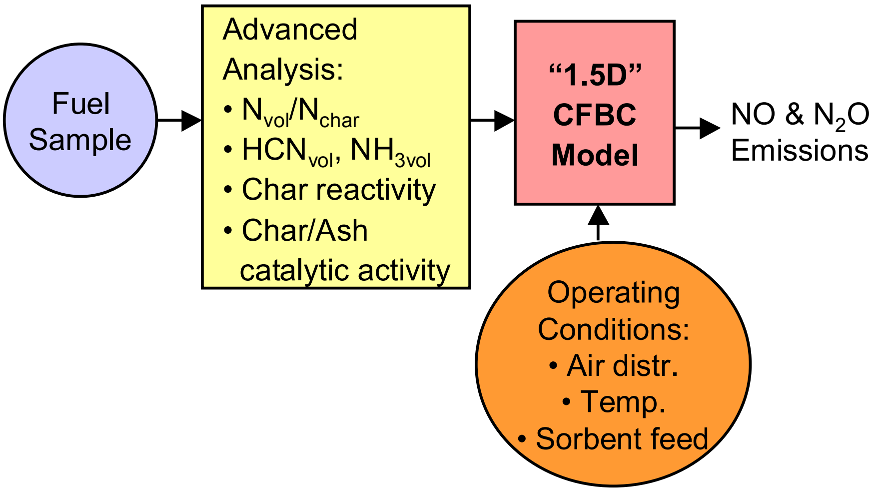


Figure 4.5 Principle of CFBC nitrogen oxide emission tendency prediction

Certain fuel-specific values are needed as input data to the predictor in addition to the conventional ultimate and proximate analyses. Especially, information is needed on the behaviour of fuel-nitrogen including fuel-nitrogen split into volatiles (vol-N) and char (char-N), and the share of different fixed-nitrogen components in the volatiles (NH_3, HCN, NO). Knowledge is also needed on the reactivity of char including char-carbon oxidation to CO and CO_2, and char-nitrogen oxidation to NO, N_2O, N_2, as well as the catalytic activities of char and ash in their reactions with nitrogen components (NO, N_2O, NH_3, HCN). These values can be experimentally determined at various laboratory reactors, and for many conventional fuels much of this data is already available. The data is then used in a comprehensive, one-and-a-half-dimensional CFBC chemistry model that calculates under given operating and boiler conditions the NO and N_2O concentrations in the CFBC furnace and in the flue gases.

Within this project combustion experiments in a laboratory FBC will be carried out during 2000-2002. This is done in collaboration with Vienna University of Technology. The objectives are especially to establish a fuel-database for N components including the split of vol-N and char-N, and the share of different fixed-nitrogen components in the volatiles (NH_3, HCN, NO). In addition insight into char reactivity and fragmentation behaviour will be obtained. These all are essential input into the CFBC model. About ten fuels will be tested including coals, peats, biomasses, and wastes.

The combustion tests will be performed in a FBC formation rate unit (diameter 35 mm, height 240 mm). It is made of quartz glass to minimise possible catalytic effects on the reactor wall and to allow visual observation of the combustion process. It operates in the range of bubbling and slugging fluidization. The FRU has electrical heating shells that produce a uniform temperature. Depending on the fuel a single fuel particle or batches of fuel particles will be used. In the flue gas CO_2, CO, CH_4, HCN, NH_3, NO, NO_2, and N_2O will be measured continuously by FTIR. Preliminary tests with Polish coal, salix, and rice straw have shown good results on the suitability of the reactor for the fuel characterisation tests.

TURBULENCE-CHEMISTRY

The last subtask within this project deals with the development and application of an advanced turbulence-chemistry interaction model – the Conditional Moment Closure Method (CMC) – that allows inclusion of detailed chemical kinetics to CFD-based combustion simulations. The work is performed at ÅA with support from VTT Energy.

During the last reporting period first results for a laboratory jet flame applying CMC have been presented. Those results were obtained with 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. Since than considerable effort has been spend to develop a concept to combine CMC with the commercial CFD-code Fluent.

The concept includes next to Fluent a newly developed code solving the CMC equations in the mixture fraction space and a separate interface combining both algorithms. First results with this concept using a global 4-step kinetic scheme are obtained for a laboratory methane jet flame. In this context the CFD-code Fluent is used to obtain flow and mixing field information on the flame. These are in first instance the velocities u and v, the turbulence quantities k and ε and mixture fraction ξ and mixture fraction variance g (Figure 6). The interface connecting both codes is responsible for converting these quantities into conditional quantities; conditional to a location in mixture fraction space:

$$\langle u|\eta\rangle, \langle v|\eta\rangle, \langle \chi|\eta\rangle \qquad \text{with } \eta = \langle \eta|\xi(x,t)\rangle$$

The first two variables describe the conditional velocities and the latter one the conditional scalar dissipation. Based on theses quantities the simplified CMC transport equations for chemical species and enthalpy is solved in the η-space:

$$\langle \rho \cdot u_i|\eta\rangle \frac{\partial Q_i}{\partial x_i} = \langle \chi|\eta\rangle \frac{\partial^2 Q_i}{\partial \eta^2} + \langle \omega_i|\eta\rangle$$

The discretisation in η-space follows the generation of control volumes, conversion of partial differential equations into a set of algebraic equations and integration of these algebraic equations over the control volumes. Convective fluxes are approximated by a power-law scheme and diffusive fluxes by linear interpolation. The coefficient matrix is solved implicitly using a TDMA solver.

The solution in η-space provides a conditional density, which is the variable relating CMC and CFD solutions. The conditional density is converted to a conventional average by the interface and passed to Fluent. The figures below show O_2 and CO_2 species distributions in η-space (Figure 7) and the corresponding methane distribution in the flame (Figure 8).

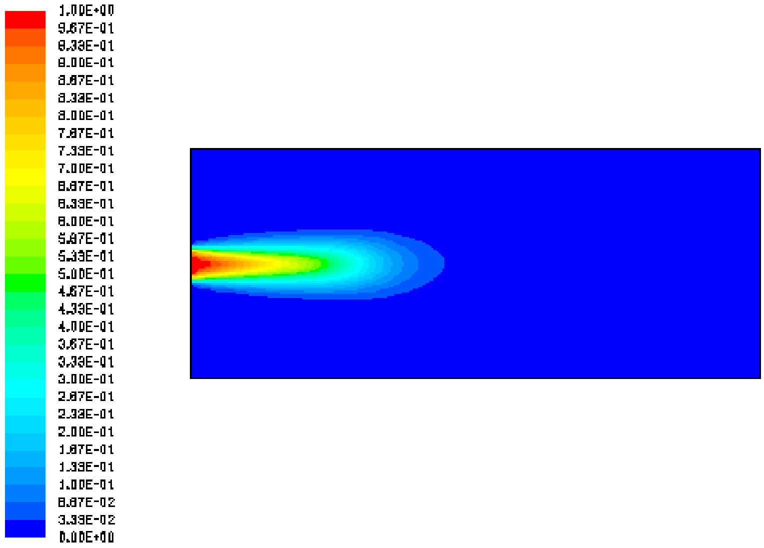
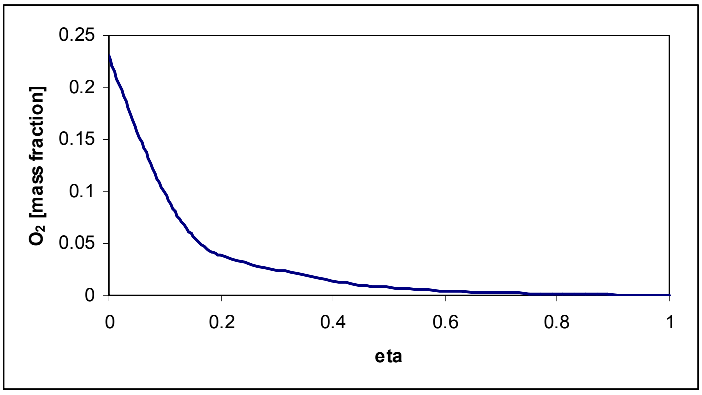


Figure 4.6 Mixture fraction distribution in methane jet flame [mass fraction]



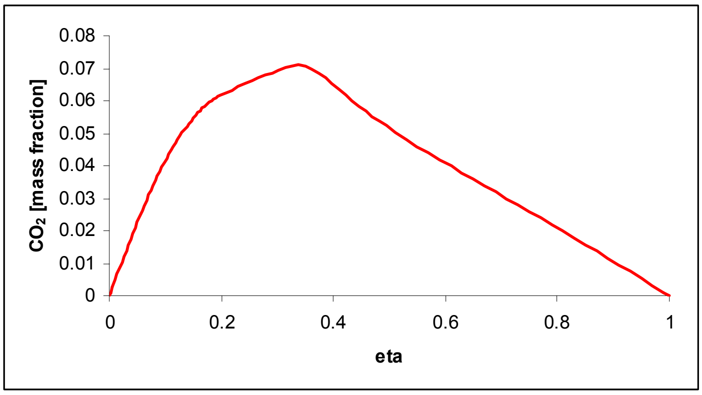


Figure 4.7 O_2 and CO_2 distribution in η-space at x = 5 cm

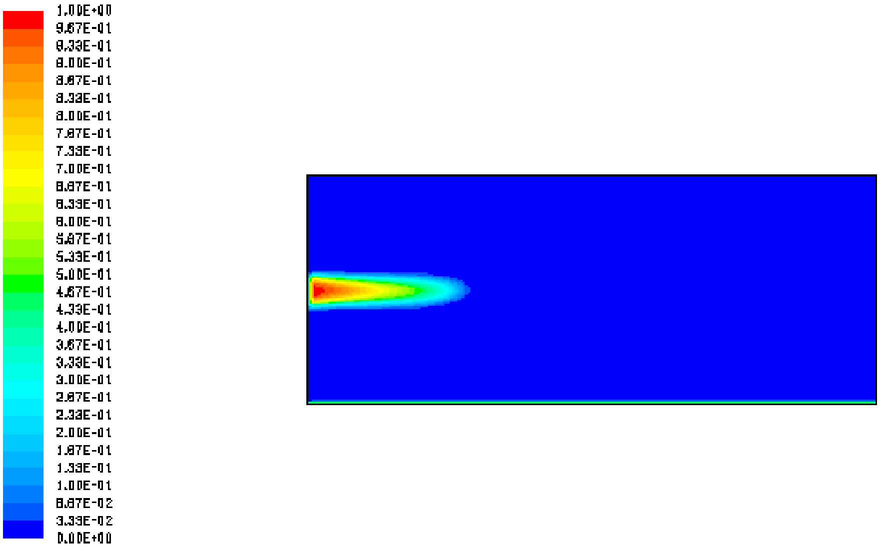


Figure 4.8 CH_4 distribution in methane jet flame [mass fraction]

Publications:

Zevenhoven-Onderwater, M.F.J.: *Ash forming matter in biomass fuels*, Academic dissertation, Åbo Akademi University, Report 01-03, 2001.

Zevenhoven, M.: *The prediction of deposit formation in combustion and gasification of biomass fuels*, Åbo Akademi University, Report 01-02, 2001.

Zevenhoven, M., Skrifvars, B.-J., Yrjas, P., Hupa, M., Nuutinen, L., Laitinen, R., *Searching for improved characterization of as forming matter in biomass* (paper 73), Presented at the 16th International Conference on Fluidsed Bed Combustion, Reno/Nevada, 2001.

Pyykönen, J., Jokiniemi, J.: *Modelling alkali chloride superheater deposition and its implications*, submitted for publication in *Fuel Process. Technol.*, 2001.

Kilpinen, P., Kallio, S., Hupa, M.: *Advanced modeling of nitrogen oxide emissions in circulating fluidized bed combustors: parametric study of coal combustion and nitrogen compounds chemistries*, Presented at the 15th International Conference on Fluidsed Bed Combustion, Savannah/Georgia, 1999.

Kilpinen, P., Kallio, S., Konttinen, J., Mueller, C., Jungar, A., Hupa, M., Åmand, L.E., Leckner, B.: *Towards a quantitative understanding of* NO_x *and* N_2O *emission formation in full-scale circulating fluidised bed combustors*, Presented at the 16th International Conference on Fluidsed Bed Combustion, Reno/Nevada, 2001.

Mueller, C., Keihäs, J., Brink, A., and Hupa, M.: *Application of the Conditional Moment Closure (CMC) method to a turbulent non-premixed flame including chemical kinetics*, Topical Meeting on Modelling of Combustion and Combustion Processes, Turku, 2000.

5. Kinetic modelling of dehydrogenation of C_3-C_5 alkanes

Project numbers: **SA 46914, 46915, 46916**

Project coordinator: **Professor Outi Krause**
Helsinki University of Technology, Department of Chemical Technology, P.O.Box 6100,
FIN-02015 HUT, Finland

Co-operation

The project is a co-operation between three groups:

Industrial Chemistry, Helsinki University of Technology (Prof. Outi Krause)

Physics, Helsinki University of Technology (Docent Jouko Lahtinen)

Physical Chemistry, University of Helsinki (Prof. Markku Räsänen

The groups have held meetings at regular intervals to discuss the results of the groups and to synchronise research activities optimally.

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

Visits abroad and from abroad

Professor Krause and Ms. Sanna Airaksinen visited Catholic University of Leuven, in Belgium from November 30 to December 1, 2000. The purpose of the visit was to meet and discuss with Dr. Bert Weckhuysen, a specialist in oxide catalysts and Ms. Riikka Puurunen, a visiting researcher from the laboratory of Industrial Chemistry, HUT.

Professor Krause visited Catholic University of Leuven also May 15, 2001.

Mr. Jani Sainio visited Dublin City University in Ireland from September 1 to November 30, 2000.

Resources and results

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

Two master's theses have been completed:

Mr. Mårten Eriksson, HUT, May 2001

Mr. Jani Sainio, HUT, June 2001.

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.), Ms. *Jaana Kanervo*, M. Sc. (Tech.) and Ms. *Riikka Puurunen*, Lic. Sc. (Tech.). All are post-graduate students.

Results

Alumina-supported vanadium oxide catalysts were studied by modifying them with Mg and Zr in order to influence the acid-base character of the catalyst and thereby the activity and selectivity in dehydrogenation. The Zr modification did not have an effect on the activity. With Mg modification the activity decreased but the selectivity to butenes increased.

The reaction kinetic modelling studies with i-butane dehydrogenation over chromium oxide catalysts were continued. The dehydrogenation reaction was best described with a model which assumed the slow step of the reaction to be the adsorption of the alkane on the catalyst. Also the deactivation behaviour of the chromium oxide catalysts was studied. The two catalysts used had different stabilities in dehydrogenation (Figure 1). This was suggested to be related to their oxidation state distributions. We also studied the catalysts' stabilities in several cycles of dehydrogenation and regeneration. No clear difference was found between the catalysts but TPR experiments suggested that the surface structure was more stable on the commercial catalyst than on the catalyst prepared with Atomic Layer Deposition method (ALD-catalyst).

The active sites on the metal oxides studied are considered to be reduced metal cation centres. The reduction of the chromium oxide catalysts was studied by kinetic modelling of H_2-TPR data. The catalysts were suggested to reduce according to a nuclei growth mechanism taking place in two dimensions. The methodology and models developed were further sophisticated and will in future be applied to vanadium oxide catalyst studies.

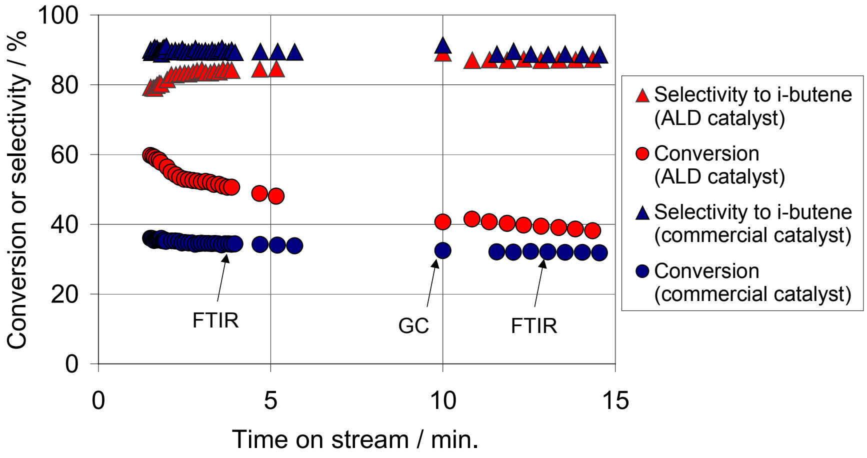


Figure 5.1 Activities of two CrO_x/Al_2O_3 catalysts in the dehydrogenation of i-butane.

ESCA Studies on 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, Mr. *Jani Sainio*, M.Sc, postgraduate student from July 1, 2001, Mr. *Mårten Eriksson*, Mr. *Olli Pakarinen*, Mr. *Jukka Katainen* and Mr. *Olli Himanen*, undergraduate students.

Single crystal surfaces

We have studied the adsorption and desorption of benzene on Co(0001) single crystal surface. The adsorption takes place already at room temperature but at 180 K a well ordered adsorption structure can be observed. The desorption takes place above room temperature and several hydrocarbon fragments are seen during desorption. The study of the adsorption structure is in progress.

Model catalyst surfaces

We have prepared a model catalyst surface on a NiAl (110) single crystal. When this surface is oxidized in vacuum, the Ni-atoms diffuse under the surface and an ordered Al_2O_3 layer is formed with a thickness of 4.5 Å. The structure of the layer resembles γ-Al_2O_3, with crystal size of millimeters. On this Al_2O_3 surface we evaporate Cr in vacuum. This far we have investigated the layer growth of Cr and Cr_2O_3 on the oxide surface. The results indicate 3D growth in both cases. The metallic Cr can easily be oxidized to Cr_2O_3 in vacuum but no CrO_3 has been detected. If the oxidation is done below 500°C, annealing of the surface results in reduction of the Cr_2O_3 to metallic Cr.

Catalyst characterization

The ESCA (Electron Spectroscopy for Chemical Analysis) studies of supported CrO_x/Al_2O_3 catalysts have been continued. The samples include two commercial catalysts, one impregnated catalyst and one made using Atomic Layer Deposition (ALD) method. The samples were first calcined and then reduced with H_2, CO, CH_4 or n-butane in the *in situ* reaction cell. The fraction of Cr^{6+} after calcination is between 20% and 30% of the Cr content with the ALD-catalyst showing the highest fraction. After reduction only Cr^{3+} is seen on the surface. No Cr^{2+} has been detected on the reduced samples.

Raman spectroscopic studies of CrO_x/Al_2O_3 and MoO_x/Al_2O_3 catalysts;

Laboratory of Physical Chemistry, UH

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

Results

CrO_x/Al_2O_3 and MoO_x/Al_2O_3 catalysts have been studied under oxidative and reducing atmospheres. The samples, provided by Laboratory of Industrial Chemistry at HUT, included two 13% CrO_x/Al_2O_3 samples (one made by impregnation, the other by ALD-method) and seven MoO_x/Al_2O_3 samples of different Mo concentrations. Calcination and reduction were done either at 560 °C (Mo samples) or 590 °C (Cr samples). Raman spectroscopy was used to characterize the catalyst surface structure at different stages of sample treatment. Measurements were made at 50 °C after each treatment. H_2, CO, CH_4, and 2-methylpropane were used as reducing gases. In literature, the assignment of the oxidation state of the Cr spectra is controversial.

Examples of measured Raman spectra are shown in Figure 2. Aided by the XPS measurements done in the Laboratory of Physics at HUT the Raman bands of the reduced Cr spectra (Fig. 2B) are confidently assigned to Cr^{3+} species. The versatile capabilities within this consortium allow also similar approach to solve the open questions on the assignment of the Raman spectra of the Mo species.

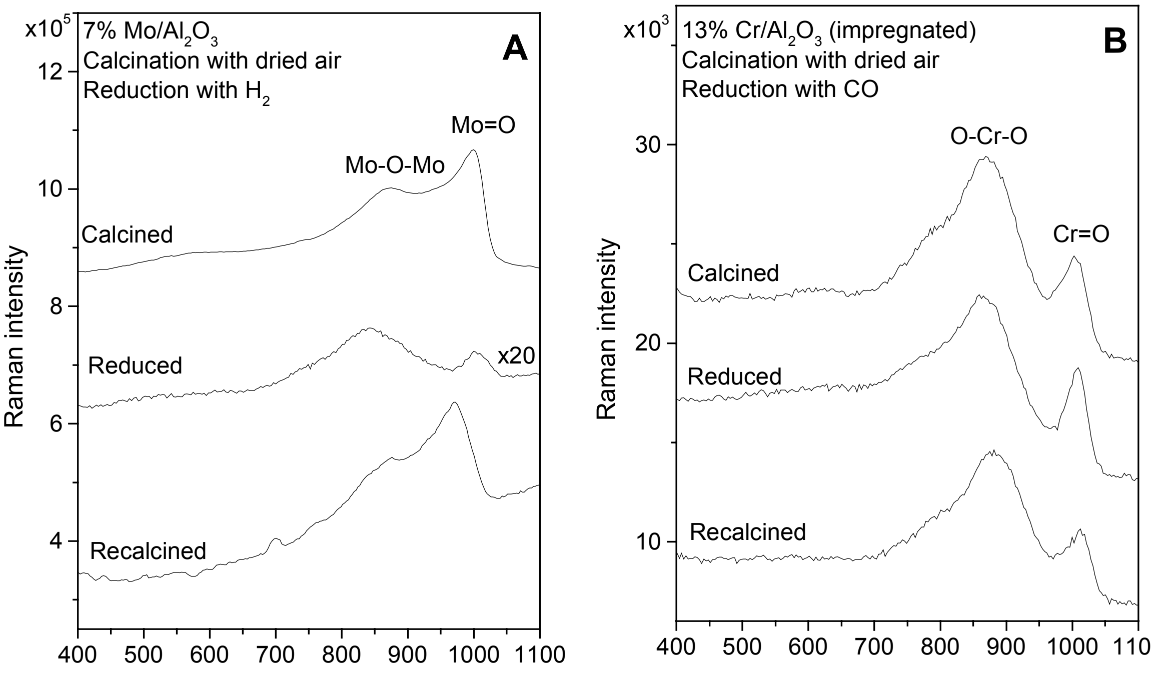


Figure 5.2 Raman spectra of calcined, reduced, and recalcined 7% MoO_x/Al_2O_3 catalyst (A) and 13% CrO_x/Al_2O_3 impregnated catalyst (B). Measurement time 1000 s, resolution ~15 cm^{-1}, excitation wavelength 514 nm.

Publications

Harlin, M. E., Niemi, V. M., Krause, A. O. I., Weckhuysen, B. M., Effect of Mg and Zr Modification on the Activity of VO_x/Al_2O_3 Catalysts in the Dehydrogenation of Butanes, accepted for publication, *J. Catal*. 2001.

Airaksinen, S. M. K., Kanervo, J. M., Krause, A. O. I., Deactivation of CrO_x/Al_2O_3 catalysts in the dehydrogenation of i-butane, *Stud. Surf. Sci. Catal*. **136** (2001) 153-158.

Kanervo, J. M., Krause, A. O. I., H_2-TPR kinetics; case study on the reduction of a CrO_x/Al_2O_3 catalyst, *Stud. Surf. Sci. Catal*. **133** (2001) 593-598.

Habermehl-Cwirzen, K., Katainen, K., Lahtinen, J., Hautojärvi, P., The Adsorption of Benzene on Co(0001), submitted to *Surface Science*.

Eriksson, M., Sainio, J., Lahtinen, J., Chromium Deposition on Ordered Alumina Films – an XPS Study of the Interaction with Oxygen, submitted to *Journal of Chemical Physics*.

Paakkunainen, M., Khriachtchev, L., and Räsänen, M., *In Situ* Spectroscopy of MoO_x/Al_2O_3 Catalysts, ICAVS-1, Turku, Finland August 19-24, 2001, poster presentation.

6. Catalysis and separation technology based on cross-linked enzyme crystals

Project number: 46910

Professor Matti Leisola
Coordinator and responsible project leader in Helsinki University of Technology:
Laboratory of Bioprocess Engineering
P.O.B. 6100, FIN-02015 HUT, Finland

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

Research group members:

Ph.D. *Jouni Jokela*, Laboratory of Bioprocess Engineeriring

M.Sc. *Johan Finell*, Laboratory of Analytical Chemistry

M.Sc. (Tech.) *Antti Vuolanto*, Laboratory of Bioprocess Engineeriring

Co-operation in the project:

Helsinki University of Technology, Laboratory of Bioprocess Engineering and University of Helsinki, Laboratory of Analytical Chemistry have worked together with Macrocrystal Oy in the field of crystal preparation and with University of Joensuu, Department of Chemistry in the field of crystal structure determination and enzyme-substrate interactions.

Scientific results:

We have continued to study the application of enzyme crystals as a LC separation material. Subtilisin, protease from *Bacillus subtilis*, was crystallized, cross-linked with glutaraldehyde/lysine and packed under low pressure into short glass columns (ID 5mm). Cross-linked subtilisin crystals (CLSC) separated polyethylene glycols and n-alcohols C 1...6 similarly as other enzyme crystals (xylose isomerase and xylanase) tested during this project. Rod shaped CLS-crystals were not as strong as polygonal cross-linked xylose isomerase crystals (CLXIC) but they were usable with low eluent flow rates. The slow solubility of the CLS-crystals prevented further separation experiments with this material but anyway few amino acids had affinity towards CLSC-material and also chiral D/L separation was seen with one amino acid.

The separation of nucleosides and nucleic acid bases has been tested with CLXIC-column and we are presently continuing this promising study.

Stability and conversion efficiency of CLXIC-column in the isomerization reactions was studied by feeding D-glucose solution into the column with or without recycling. In recycling mode the CLXIC-column preserved better its stability. The apparent activity measured directly from the column was lower compared to the situation, where the activity was measured in a batch reactor. One reason to this difference could be channeling of the CLXI-crystal packing in the column reactor. Also in the test where L-arabinose or L-ribulose, which was produced from commercial ribitol by resting cells of *Acetobacter aceti*, was fed into the CLXIC-column reactor, the conversion efficiency decreased as a function of time.

One important parameter governing the efficiency of a heterogeneous catalyst is diffusion. The small size of the pores in the enzyme crystals, especially in CLXI-crystals, creates restricted diffusion even with small monomeric sugar molecules. We have measured this phenomenon in batch reactor by using D-glucose as a substrate and by different sizes (20 ... 83 µm) of CLXI-crystals. Preliminary results show that the isomerization activity decreases linearly 0.5%/µm of crystal diameter when compared to the soluble xylose isomerase activity. This means that in the 40 µm CLXIC-material most of the activity of the soluble enzyme is present but in a highly compact form.

In a previous report we introduced the high efficiency of a column packed with cross-linked xylanase crystal (CLXC) to hydrolyse xylo-oligomers. When we further analysed the results, the flow rate of eluent proved to be the most important factor in controlling the observed reaction rate in the CLXC-column. At higher flow rates, the mass transfer into the pores of the CLXC-material is enhanced. It seems also that in CLXC-column environment, where enzyme/substrate ratio is maximal, xylose is neither a substrate nor an inhibitor.

Publications:

J. Finell, J. Jokela, M. Leisola and M.L. Riekkola. Total hydrolysis of xylotetraose and xylobiose by soluble and cross-linked crystalline xylanase II from Trichoderma reesei. Submitted in BMC Biotecnology, 2001.

J. Jokela, O. Pastinen, M. Leisola. Isomerization of pentose and hexose sugars by an enzyme reactor packed with cross-linked xylose isomerase crystals. Submitted to Enzyme Microb Technol 2001.

Visits:

Ivan Smajlovic, IAESTE-trainee from Yugoslavia, 1.9. - 31.10.2000.

Vice-president and founding member of International Society of Rare Sugars (ISRS), Matti Leisola, was invited to the foundation ceremony held in Japan 10.4.2001.

Consortium:

7. Optimization of reaction crystallization process

Project numbers: **46918, 46919, 46920**

Consortium coordinator: Marja Oja

Lappeenranta University of Technology
Department of Chemical Technology
P.O.B. 20, FIN-53851 Lappeenranta

Co-operation

Consortium: LUT, Laboratory of Chemical Engineering (Marja Oja); LUT, Laboratory of Process Engineering (Juha Kallas); HUT; Laboratory of Process Control and Automation (Sirkka-Liisa Jämsä-Jounela)

LUT Centre for Separation Technology (CST)

MTS, Messtechnik Schwartz GMBH, Germany

Filtration Properties and Dewatering

Research team

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

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

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

Student Kati Pöllänen 15.5. – 31.7.2000

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.

Results

Experimental set-up. The crystallization group produced the dicalcium phosphate dihydrate (DCPD) slurries for the experiments. Eleven DCPD-slurries were selected for the filtration experiments. Two of them were produced using normal process chemicals. The samples for the filtration tests were collected at the steady state of the crystallization. Five of the slurries were filtered immediately after the collection of the sample and the rest of the samples were allowed to age before filtration experiments. The concentration of the test slurries was 12 - 13 % by weight. The slurries were filtered with a laboratory scale piston press filter, where the height of filtration chamber was adjusted to 100 mm and the pressure rise time to two seconds. The filtration pressures were from 0.5 to 3 bars. In all experiments the filtration phase was followed by an expression phase with 4 bars pressure. The filter medium in all experiments was a new filter cloth.

Characterisation of slurries. The particle size distributions in the crystalliser were measured on-line using MTS PsyA 3D-ORM analyser. The size distributions of the sample slurries and filter cakes were measured using Coulter LS130 analyser, and the particle shape parameters were measured from the images acquired by video camera from the optical microscope using image analysis program (AnalySIS 3.0).

Filtration characteristics. The specific cake resistances of the process chemical slurries are higher than the others. The specific resistance of the fresh slurry (Fig. 1) increases when the residence time of the crystallization increases. The same trend can be seen also for the aged slurries, but the average level of the resistance is somewhat higher due to the smaller mean size. However, the mean size does not explain the differences, because the range is only from 25 to 34 microns. The compressibility coefficient seems to be directly related to the width of the particle size distribution (d_{90}- d_{10}). The pressure dependence of the average cake porosity is very weak.

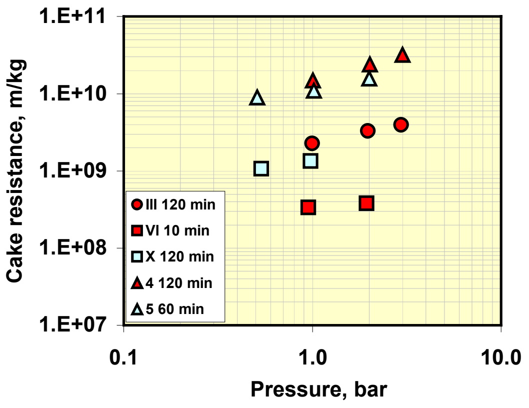


Figure 7.1 Cake resistance

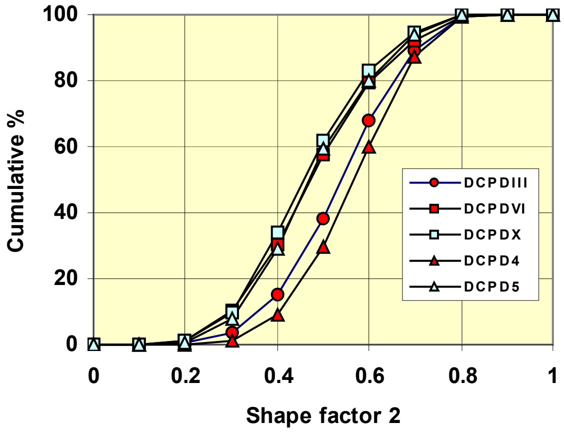


Figure 7.2 Shape factor

Shape characterisation of the crystals. The nine shape factors used in characterisation were the ratios of the characteristic diameters. The preliminary shape analysis (Fig. 2) indicates that the most characteristic feature of the crystals defining the filtration properties of the slurry is the elongation of the particles. Longer residence time seems to shorten the particles and make them smoother. However, the particle size is the most important factor that defines the filtration resistance. Therefore, the shape should be connected to the particle size using SOM.

Future

The slurries are classified on the basis 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 crystallisation as well as in solid liquid separation.

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: Modelling 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 Modelling with Methods of Neural Computing, IFAC MMM Workshop, 22-24.8.2000, Finland, 486-488

Expert system for crystallization and filtration processes

Reporting period: 1.8.2000 – 31.7.2001.

Research team

Sirkka-Liisa Jämsä-Jounela (leader)

Tatu Kuitunen

Jerri Kämpe

Timo Ryynänen

Jouni Lipiäinen

Project cooperation and other funders

Consortium: LTKK, Laboratory of Chemical Engineering; LTKK, Laboratory of Process Engineering; TKK; 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 developed. 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.

During the reporting period the economic, optimising control strategy for the pressure filter has been designed. The model-based control strategy utilizes the on-line models of the different filtration stages and the optimising algorithm of filtration times and capacity.

Publications

Jämsä-Jounela, S-L., Kämpe, J., Ryynänen, T., Remote support system of the pressure filter, *10th IFAC Symposium on Automation in Mining, Mineral and Metal Processing*, ed. M. Araki, IFAC, Tokyo 2001, pp 337-342.

Jämsä-Jounela, S-L., Vermasvuori, M., Haavisto, S., Kämpe. J., Industrial Applications of the Intelligent Fault Diagnosis System, ACC2001, Arlington, Virginia, USA.

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,* Szcxyrk 2000, pp. 133-138.

Communication of information

Jämsä-Jounela, S-L., Ryynänen, T., Kämpe, J., Painesuodattimen etävika-diagnostiikkajärjestelmä, Automaatiopäivät 2001,ed. L. Yliniemi, Suomen Automaatioseura, Helsinki 2001, pp. 469-474.

Ryynänen, T., Modelling pressure filter, Tutkimusraportti , TKK, Prosessien ohjauksen ja automaation laboratorio, 2001.

Optimization of reaction crystallization process

Finnish name: Kiteytysprosessin optimointi

Responsible leader Prof. Juha Kallas

Time period 29.8.2000-31.07.2001

Researchers

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

CRYSOPT

- Thematic Network in Crystallization (31 participants from nine various EU countries)

Results

In-line particle size analyzers were tested and developed further on.

Hannu Alatalo:

Flow simulation with three different feed locations was done. The geometry of simulated system consisted of the tank with a shaped bottom, 6-blade Rushton turbine, baffles, two feed pipes, product removal pipe and particle size measuring probe. Preliminary calculations of flow and particle tracks for premixed feed pipe were conducted. Reaction system of phosphoric acid and calcium hydroxide was studied.

Henry Hatakka:

The model created for reactive crystallization was tested with experimental results for $CaCO_3$ precipitation obtained in previous project. The model is based on the continuous population balance and it considers only nucleation and crystal growth; the reaction is assumed to be a fast ionic reaction and no agglomeration is involved. The model is developed within the MODEST –modelling and estimation package.

Precipitation of dicalcium phosphate dihydrate (DCPD) was selected as a process to be studied. The effects of residence time, temperature, mixing velocity and feed arrangements on crystal size distribution were studied. Analytically pure phosphoric acid (H_3PO_4) and calcium hydroxide ($Ca(OH)_2$) were used in experiments. Produced DCPD was used in subsequent filtration experiments. Experiments with industrially available lower purity phosphoric acid (Kemphos Bio) initiated also, but were stopped because of the in-line crystal size analysis problems. The obtained experimental results are to be used in testing and developing of the model.

The effect of feed arrangements was found to be the most dominant to increase particle size in produced DCPD, especially, when using premixed feeding. The other controlling parameters have almost negligible effect on size distribution of DCPD crystals formed. The study of the influence of the feed arrangements on crystal size distribution is to be continued.

Publications

Poster in BIWIC2001 (held in 19th and 20th of September) is accepted. The title of the abstract is "Effect of Feed arrangements on Reactive Crystallization of DCPD" and authors are Henry Hatakka, Marjatta Louhi-Kultanen and Juha Kallas.

Visits

Researcher exchange program with two universities (LUT and Martin-Luther-Universität Halle-Wittenberg), Finnish Academy project number 48351:

- Uta Lüdecke from MLU in LUT 4.-13.12.2000

Non-academic reporting and publications

Co-operation information exchange with Kemira

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

Activity report 2001 on the PROTEK Project

8. Alkaline delignification of lignocellulosics

Responsible Person Professor Bruno Lönnberg

Åbo Akademi University
Faculty of Chemical Engineering, Laboratory of Pulping Technology
Porthansgatan 3, FI-20500 Turku/Åbo

Researcher

Mr. *M.M.A. Quader*, M.Sc., graduated from the Asian Institute of Technology in Bangkok, Thailand. Mr Quader has been accepted by Åbo Akademi University as a Ph.D. Student of Pulping Technology.

Research Partners

Åbo Akademi University (ÅAU) developed the sulphur-free IDE pulping concept in co-operation with the Finnish pulp and paper companies. The pulping concept is further developed, and ÅAU is focusing on catalysis of the delignification, since soda processes are slow.

Aim of Project

The aim of this project is to develop the new chemical pulping process named IDE to improve its rate of delignification. The pulping concept requires that no sulphur is introduced, which implies that the risks for corrosion are limited and hence black liquor gasification may be applied to improve the energy balance.

Results

The study carried out on a laboratory scale indicated that delignification provided high kappa numbers when reducing the impregnation temperature, Figure 1. However, extremely low temperatures and long times seemed to achieve a stabilised level that certainly requires oxygen delignification before final bleaching.

Prehydrolysis of the chips by water cooking appeared to affect the delignification very significantly, particularly when high temperatures were applied, Figure 2.

A comparison of IDE pulp with kraft and soda-AQ pulps again revealed that the IDE pulp had slightly longer and more slender fibres. The bleachability of the IDE pulp was comparable with that of the reference pulps, Figure 3. Its final pulp yield again was clearly better by about 2 percentage units, Figure 4. The beatability was equal with that of the soda-AQ pulp, but better than that of kraft. The pulp strength again was clearly lower than the strength of kraft pulp.

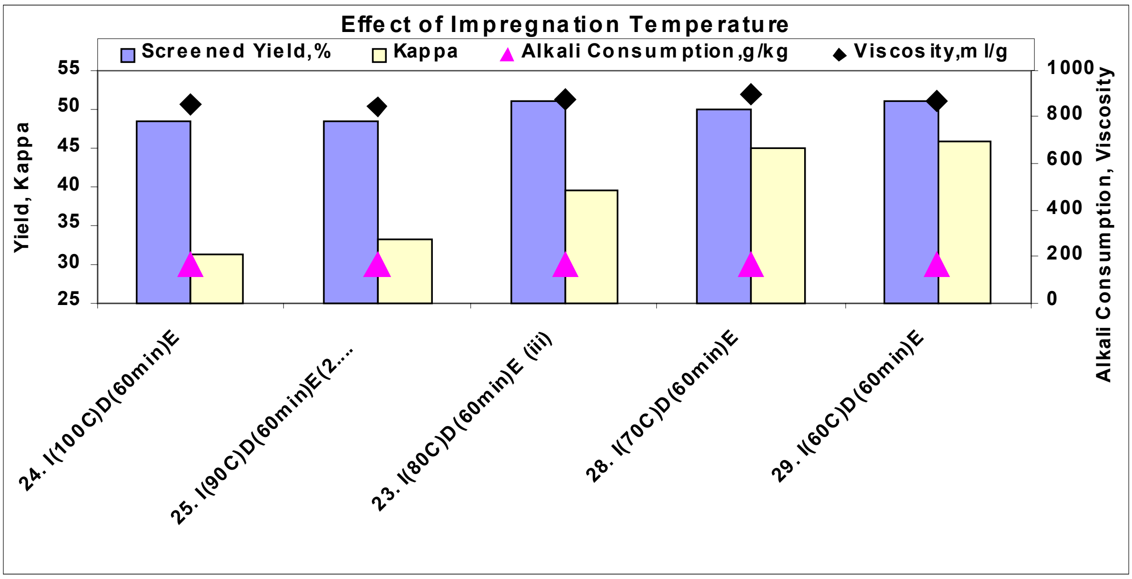


Figure 8.1 Impregnation temperature in IDE cooking. Key: I(100C) means impregnation at 100° C; D(60min) means delignification for 60 min.

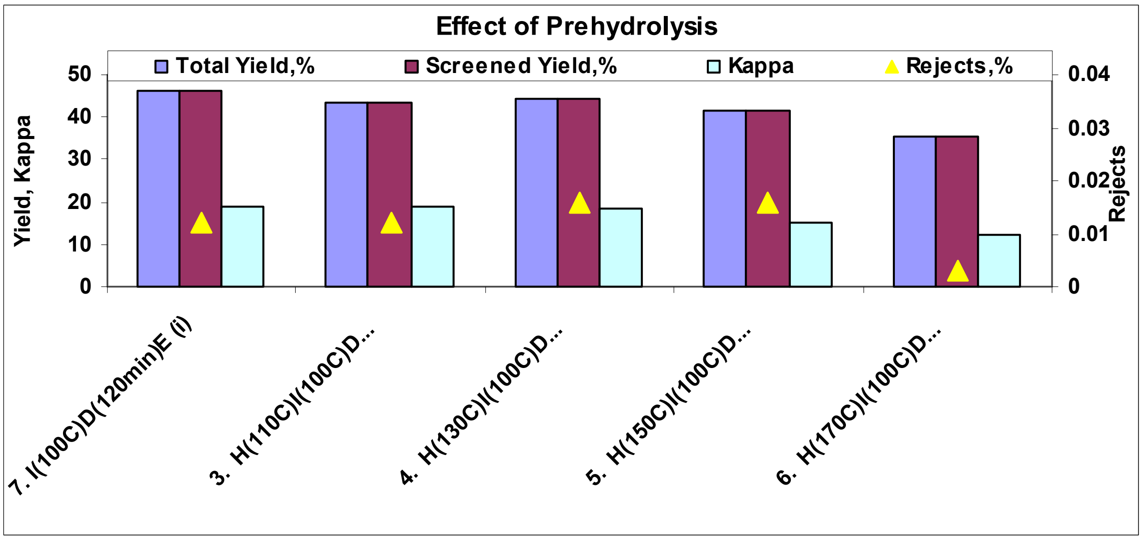
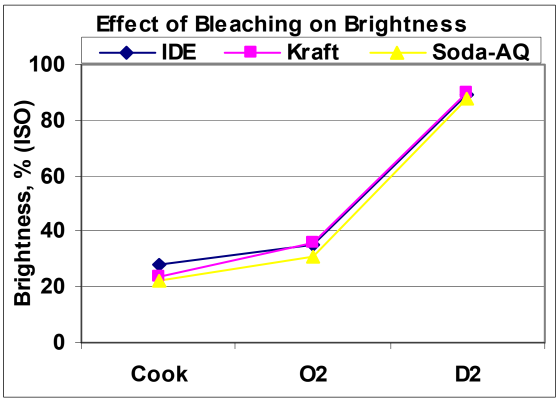


Figure 8.2 Prehydrolysis of the chips prior to IDE cooking. Key: See Figure 1; H(110C) means hydrolysis at 110° C.



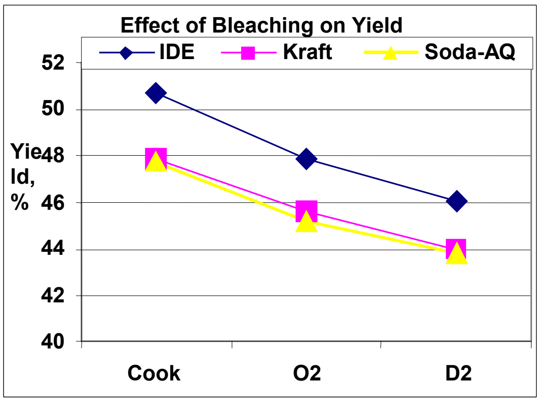


Figure 8.3 Cook, oxygen treatment and ECF bleaching of IDE pulps.

Figure 8.4 Cook, oxygen treatment and ECF bleaching of IDE pulps.

9. Kinetics, mechanism and transport phenomena in heterogeneous catalysis

Project number **46917**

Professor Tapio Salmi

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Background and organisation

The research work was continued during 2001 as a collaborative effort between Åbo Akademi (ÅA) and University of Turku (TY). The project leaders were professor *Tapio Salmi* (ÅA), professor *Dmitry Murzin* (ÅA) and professor *Juhani Väyrynen* (TY). The researchers of the project were docent *Ahmad Kalantar Neyestanaki* (ÅA, postdoc), FM *Hannu Karhu* (TY/ÅA postgraduate student) and *Henrik Backman* (ÅA, undergraduate student)

Scientific results of the project

Detailed kinetics of gas-phase hydrogenation of o-xylene was studied in a continuous flow fixed bed reactor over different catalysts prepared at the laboratory of industrial chemistry (ÅA). In addition, dehydrogenation and epimerization of the products, *cis* and *trans* 1, 2-dimethylcyclohexane (1, 2-DMCH), were investigated and the corresponding kinetic parameters were determined. The catalysts used are presented in Table 1.

Table 9.1 The catalysts used in the o-xylene hydrogenation.

	Support material		
Active metal	SiO_2	Al_2O_3	Silica-fibre
Pt	●	●	●
Pd	●	●	
Ni		●	

The hydrogenation experiments were carried out under atmospheric pressure and temperature range of 360 – 520 K. The reactants concentrations were varied between 0.19 - 0.74 bar (for hydrogen) and 0.04 - 0.1 bar for o-xylene. The dehydrogenation and epimerization reactions were investigated in the same temperature range as o-xylene hydrogenation. The H_2, *cis*1.2-DMCH and *trans* 1,2-DMCH partial pressures were 0.19 - 0.76 bar, 0.77 mbar and 0.14 mbar, respectively.

At ÅA the catalysts were characterized by N_2-adsorption, H_2-adsorption, H_2/o-xylene/TPD and EDXA. The XPS analysis was carried out for all catalysts at TY (FM Hannu Karhu).

Generally, the hydrogenation of o-xylene exhibited a similar pattern over all the catalyst. A maximum in hydrogenation activity *vs.* temperature was observed (Fig. 1) at all the H_2/o-xylene molar ratios investigated. The nature of the catalyst is determining the T_{max} in the o-xylene hydrogenation activity (Fig. 1). The *cis*-to-*trans* 1, 2-DMCH ratio was found to depend on the nature of the catalyst, temperature and the reactants concentration. More *trans*-isomer is being formed over Pd than Pt.

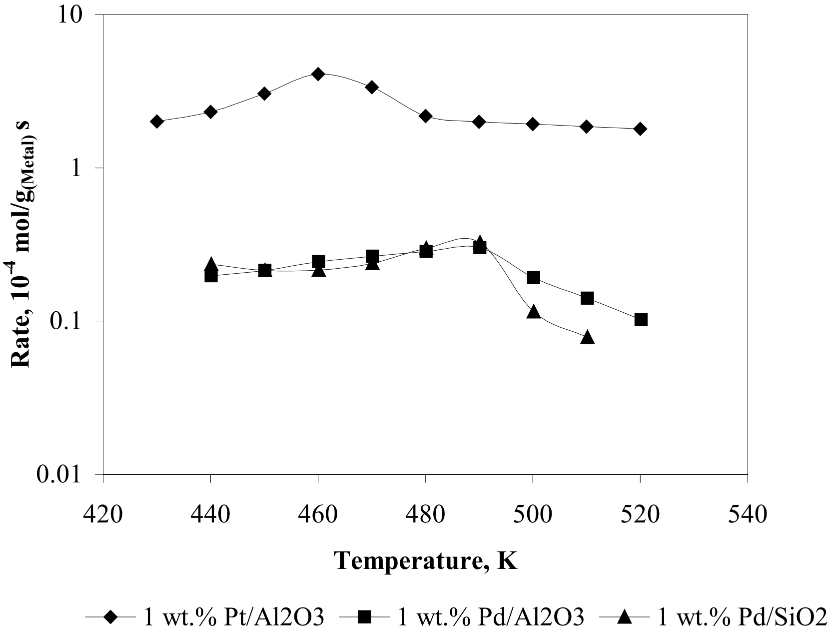

Figure 9.1 The temperature dependency of o-xylene hydrogenation. $p_{H2} = 0.37$ and $p_{o\text{-xylene}} = 0.06$ bar.

Dehydrogenation and epimerisation of *cis* and *trans* 1, 2-DMCH was found to take place in considerable rates over silica and alumina supported Pt and Pd catalysts. Dehydrogenation and epimerisation reactions are faster over platinum than palladium.

The application of the knitted silica-fibre as a support for gas-phase hydrogenation of o-xylene was studied. Different knitted silica-fibre supported platinum catalysts were prepared and employed. Complete conversion of o-xylene was achieved. The activity of the fibre catalyst, in terms of turnover number, was found to be comparable to that of a conventional Pt/alumina catalyst. The fibre catalyst, on the other hand, exhibited less pressure drop induction and mass transfer limitations.

Preliminary kinetic modelling, based on plausible surface reaction mechanism, was carried out and the model gave a good explanation of the experimental data (*e.g.* Fig. 1). Detailed kinetic modelling is under progress.

The construction of "*in situ* XPS (ESCA) reaction chamber" was completed at TY. The o-xylene hydrogenation over single crystals combined with XPS will be carried out during 2001.

The results of the project achievements were reported in three international conferences. Three full-length papers have been submitted to international journals. For more details, please refer to the list of publications.

List of publications

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Kalantar Neyestanaki, A., Backman, H., Mäki -Arvela, P., Wärnå, J., Salmi, T., Murzin, D., Yu., Kinetics and modelling of o-xylene hydrogenation over Pt/γ-Al_2O_3 catalysts, Submitted for publication in *Chemical Engineering Journal*, 2001.

Kalantar Neyestanaki, A., Mäki-Arvela, P., Toukoniitty, E., Backman, H., Klingstedt, F., Salmi, T., Murzin, D., Application of New Metal Impregnated Knitted Silica-Fiber on Catalytic Oxidation and Hydrogenation Processes, *to be published in the proceedings* of the 19th ORCS conference, San Antonio, USA, April 4-18, 2002.

Backman, H., Katalysisk hydrering av o-xylene på Pt- och Pd- katalysatorer, *diploma work* at the Laboratory of Industrial Chemistry, Faculty of Chemical Engineering, Åbo Akademi, 2001.

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Kalantar Neyestanaki, A., Backman, H., Mäki -Arvela, P., Wärnå, J., Salmi, T., Murzin, D. Yu., Kinetics and modelling of o-xylene hydrogenation over Pt/γ-Al_2O_3 catalysts. *Oral presentation* at the XV International Conference on Chemical Reactors (CHEMREACTOR-15), June 5 - 8, 2001. Helsinki, Finland.

Kalantar Neyestanaki, A., Mäki-Arvela, P., Backman. H., Karhu, H., Wärnå, J., Salmi, T., Murzin, D., Yu., , Väyrynen, J., Gas-phase hydrogenation of o-xylene over Pd-catalysts-kinetics and stereoselectivity. *Poster presentation* at EUROPACAT V, September 2 - 7, 2001. Limerick, Ireland.

Karhu, H., Kalantar Neyestanaki, A., H., Väyrynen, J., Ollonqvist, T., Salmi, T., ESCA study of catalyst reduction under flowing hydrogen. *Poster presentation* at EUROPACAT V, September 2 - 7, 2001. Limerick, Ireland.

Kalantar Neyestanaki, A., Mäki-Arvela, P., Toukoniitty, E., Backman, H., Klingstedt, F., Salmi, T., Murzin, D., Yu., Application of New Metal Impregnated Knitted Silica-Fiber on Catalytic Oxidation and Hydrogenation Processes. *Oral presentation*. To be given at the 19th ORCS conference, April 14 - 18, 2002. San Antonio, USA.

10. Models in process development: selection, validation and integration

Project number **46909**

Project leader: Ilkka Turunen, professor

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Project personnel

Ilkka Turunen,	Prof.	Project leader
Arto Laari,	Lic. Tech.	Research Scientist
Esko Lahdenperä,	Lic. Tech.	Research Scientist
Kalle Saastamoinen,	M.Sc.	Research Scientist

Brief summary of the project goals

Modelling of unit operations at different level of details is studied in the project by the aid of several 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.

Collaboration

Collaboration with Kemira Chemicals Oy, Oulu Research center has taken place in order to obtain real test cases for modelling purposes.

Results

Modelling of sieve-tray extractor has been continued. Four different modelling approaches with different degree of detail has been completed. A comparative study of model quality is being carried out.

Modelling of concurrent bubble column has been continued as well. After validating simple plug flow and axial dispersion model, CFD approach has been started. Population balance of gas bubbles will be included. For this purpose, bubble coalescence and break-up is being studied and modelled in another project in the same laboratory. Modelling of multitubular airlift reactor (a modification of bubble column) has been taken as an additional test case in the project.

The completed model of the gas-liquid-solid reactor (KATAPAK) has to be improved by including CFD-model of the phenomena inside the catalyst pockets. This stage is waiting for experimental results to be obtained from another project.

Publications

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