Department of Separation Processes

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Fields of research

- Hydrodynamics of two phase flow in micro/macro channels
- Sulfur dioxide oxidation, sulfation and sulfonation
- Kinetic studies of heterogeneously catalyzed reactions in microreactor
- Design of counter-current vibrating plate extractor (VPE)
- Fluorinated hydrocarbons as potential solvents in liquid-liquid extraction processes
- Supercritical fluid extraction of biologically active substances
- Kinetics of supercritical fluid extraction
- Chemical and enzymatic reactions in supercritical CO_2
- Mass transport in polymeric membranes, mutual influence of permeating substances
- Mass transport through ionic liquid membranes
- Membrane separation of methane and CO_2 mixtures
- Separation of racemic mixtures
- Separation of gasoline vapors from air by supported ionic liquids membranes
- Description of the flow of condensable gas through the porous medium

Applied research

- Hydrodynamics of annular gas-liquid flow
- Application of microreactors for gas phase catalytic reactions
- Liquid-liquid extraction of luminophores, recycling of Y and Eu
- Liquid-liquid and supercritical fluid extraction and refining of plant extracts
- Purification of biogas by supported liquid membrane
- Extraction of insecticides from plants

Research projects

Flexible, fast and future production processes (F^3 Factory)

(V. Jiřičný, jiricny@icpf.cas.cz; FP7 collaborative large integrated project, Theme NMP-2008-3.2-1; supported by EU under Contract No. CP-IP 228867-2 F^3 Factory)

The goals of the projects are in improvements of EU chemical industry's competitive position by development modular continuous plant (F^3 Plant) which combines world scale continuous plant efficiency, consistency and scalability with the versatility of batch operation. Based on the extensive hydrodynamic study, the microsulphonator pilot plant prototype was designed, manufactured and tested in ICPF. Together with Procter&Gamble, ICPF participated in the upgrade of the industrial pilot plant with the aim of installing the new microsulphonator reactor. During 2013 the microsulphonator was installed into Procter&Gamble pilot plant and its operation was successfully tested. The obtained product reached two our of three target quality criteria. ICPF team also tested the advanced method for the SO_2 analysis (defined in 2012) in the pilot plant installation, and participated in the pilot plant experiments with the pilot plant microreactor for sulfur dioxide catalytic heterogeneous oxidation.

Pressure drop during the annular gas-liquid flow

(J. Křišťál, kristal@icpf.cas.cz; research contract with Procter&Gamble)

Based on the successful pilot plant tests during the F^3 Factory project, Procter&Gamble was interested in the continuation of our cooperation within the research project focused on the hydrodynamic measurements of annular gas-liquid flow. The existing experimental unit was modified to accommodate the larger reactors and the hydrodynamic experiments were carried out in the area of interest of the commercial partner. The most important evaluated parameters were pressure drop and flow regime.

Application of microreactors for gas phase catalytic reactions

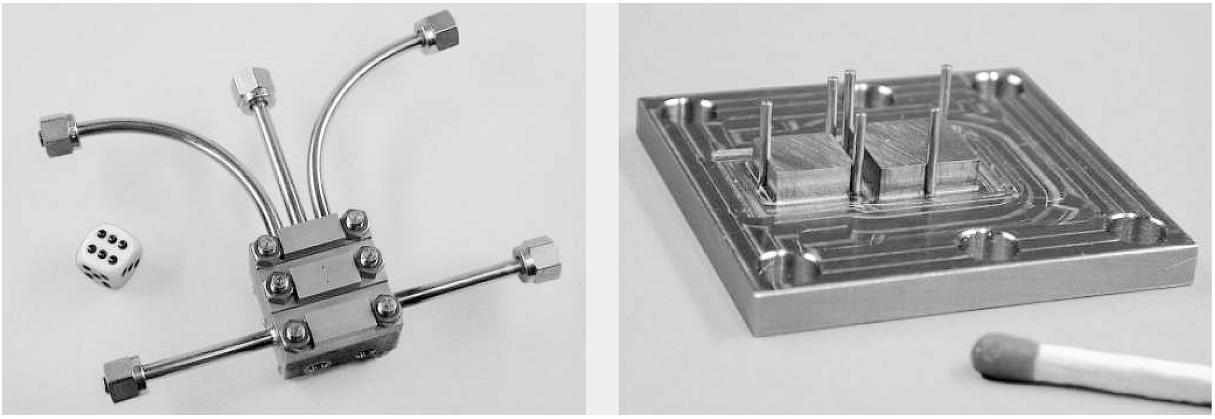
(P. Stavárek, stavarek@icpf.cas.cz; research contract with Momentive Specialty Chemicals)

The feasibility of application of microreactors was assessed and evaluated for the gas phase catalytic oxidation reaction. Based on this feasibility study, the preliminary design of an experimental laboratory apparatus was prepared.

Synthesis methylchoride in a microreactor

(Z. Vajglova, vajglova@icpf.cas.cz; study stay at Åbo Akademi University, Finland)

A reactor setup consisting of two stainless steel microreactors (Gas Phase Micro Reactor with mixer, GPMR-mix, by Microinnova Engineering GmbH, Austria) coupled in series was used for production of methyl chloride by hydrochlorination of methanol. The influence of temperature on the methanol conversion and selectivity towards methyl chloride were investigated. A maximum conversion of 97.6 % and a selectivity of 98.8 % could be reached, which is close to the calculated thermodynamic equilibrium. Comparison with results obtained from a single microreactor and a modified setup of the two microreactors revealed that the serial coupling resulted in a dead volume with a blind activity which cannot be neglected when describing the setup. Furthermore, separation of gaseous products using condensers was investigated and as well as the composition of obtained gas and liquid phase.



Gas Phase Micro Reactor (GPMR) with mixer and internal heating cooling (left)
Top housing plate of reactor with mixer and reactor stack (right)

Applications of liquid-liquid extraction in recovery of rare earth metals

(A. Heyberger, heyberger@icpf.cas.cz; joint project with University of KwaZulu-Natal, Durban, Republic of South Africa; supported by ICPF)

The object of this project was to perform laboratory and pilot plant tests for recycling of luminophores from waste compact fluorescent light bulbs (CFLs). The process consists of selective extraction of valuable yttrium and europium and removal of toxic mercury. The experimental results were used as a basis for the design of the pilot plant unit with counter-current vibrating plate extractor (VPE) at cooperating University. Common patent was applied. [Ref. 20]

Pilot plant unit for recovery of luminophores

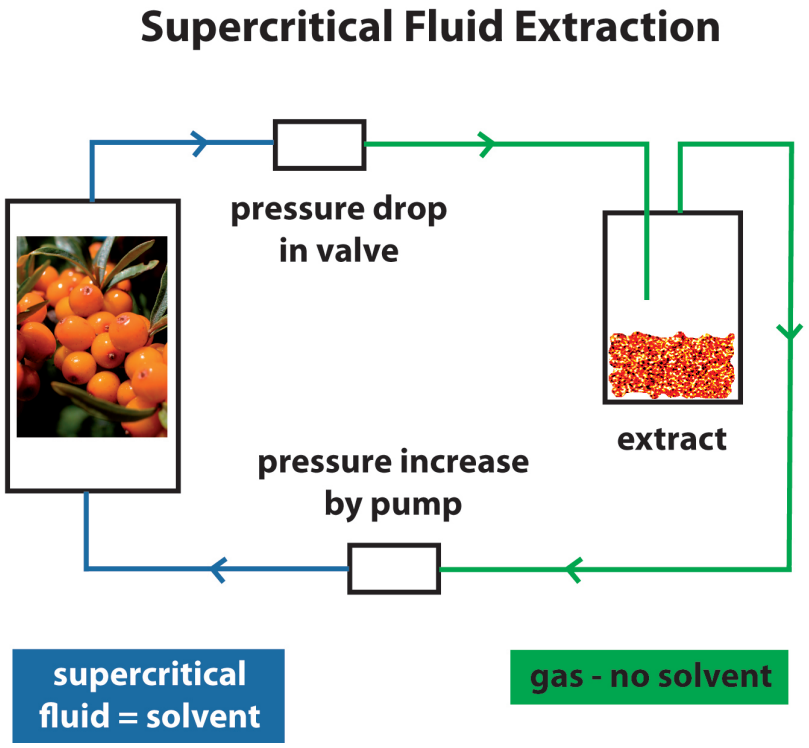
Research and development of new products for complex plant protection

(M. Sajfrtová, sajfrtova@icpf.cas.cz; joint project with Matoušek CZ a.s., Crop Research Institute; supported by TACR, project No. TA01010578)

New preparations for eco-agriculture are being developed on the basis of hydrodistillates and supercritical extracts from tropical plants with high content of the biologically active substances.

Plant material supplied from South Africa is submitted to supercritical fluid extraction, hydrodistillation and maceration in order to assess the suitability of the methods used for obtaining extracts with maximum biological activity. The supercritical fluid extraction is conducted under different experimental conditions. The insecticidal activity (antifeedancy, acute toxicity, and chronic toxicity) of isolates is measured on larvae of *Spodoptera litoralis*. Antifungal bioassay is carried out on the isolates as the inhibition effect on the growth of model pathogenic and toxinogenic fungi. The chemical composition of isolates is determined by GC/MS technique. [Refs. 11, 12]

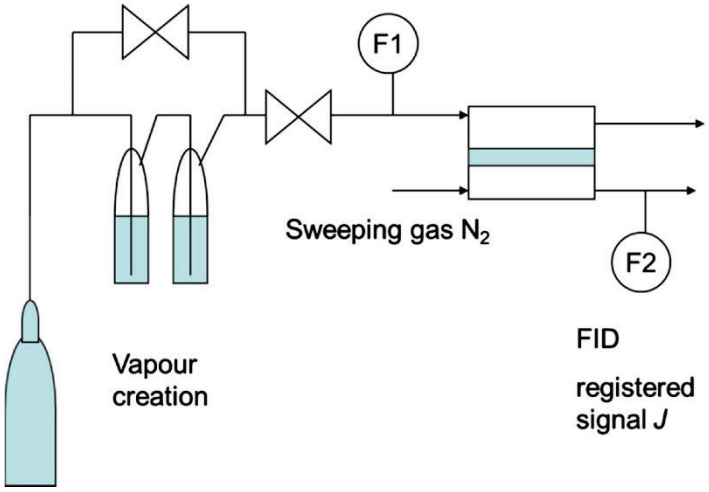
Solubility of isolated components in supercritical CO_2 is measured using the dynamic method and the extraction kinetics is simulated by phenomenological models. [Refs. 1, 8, 13]



Study of polymeric membrane swelling and make use of this effect for increasing its permeability

(P. Uchytil, uchytil@icpf.cas.cz; joint project with IMC, supported by the GACR, project No. P104/09/1165)

The location of the phase change inside membranes and swelling of the membrane material during toluene transport in a polyethylene membrane were investigated. The special experimental sweeping-gas set-up was proposed and constructed to obtain all transport parameters in polymeric membranes (flux, diffusivity and sorption). Study of an addition of a convenient substance was performed on several types of membranes that were prepared in cooperation with the foreign partner (Prof. S.-Y. Suen). On the basis of the obtained results new membrane separation process was designed and the high separation efficiency of gas separation was experimentally verified and applied for patent. [Refs. 9, 10, 21]

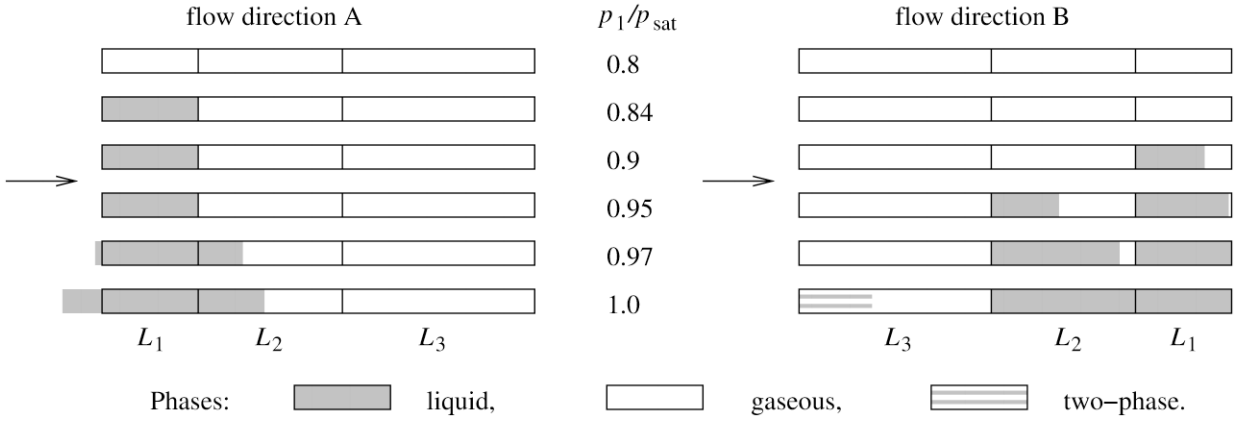


Sketch of the permeation apparatus

Flow of saturated vapors through porous membranes

(J. Řezníčková, reznickova@icpf.cas.cz; joint project with Institut für Strömungsmechanik und Wärmeübertragung Technische Universität Wien; supported by MEYS, MOBILITY, project No. 7AMB12AT010)

Mathematical model of the vapors flow through asymmetric porous membranes was developed. The flow is modeled using the energy balance and accounting for capillary condensation, for the transport of the enthalpy of vaporization, and for the temperature variation due to the Joule-Thomson effect. Transport of isobutane through an asymmetric ceramic membrane consisting of three different layers has been investigated. In the case studied, the mass flow rate can become several times larger in one flow direction than in the other flow direction. It depends on the state of vapor saturation and on the porous structure of the membrane in which direction the mass flow rate becomes larger. The large differences in the mass flow rate occur if the fluid condenses in one or in several parts of the membrane in one flow direction, but it does not condense or condenses in different parts of the membrane in the other flow direction. This finding may be generalized. For the flow of a vapor which is in a state close to saturation, the mass flow rate through an asymmetric membrane in one flow direction may differ very much from the mass flow rate in the other direction.



Phase state of the permeant in the membrane layers for both flow directions at different upstream relative vapor pressures, for $p_1 - p_2 = 0.5$ bar. Thicknesses of the individual layers are not to scale

Separation of volatile organic compounds (VOCs) from air

(P. Izák, izak@icpf.cas.cz; joint project with ICT Prague; supported by GACR, project No. P106/10/1194)

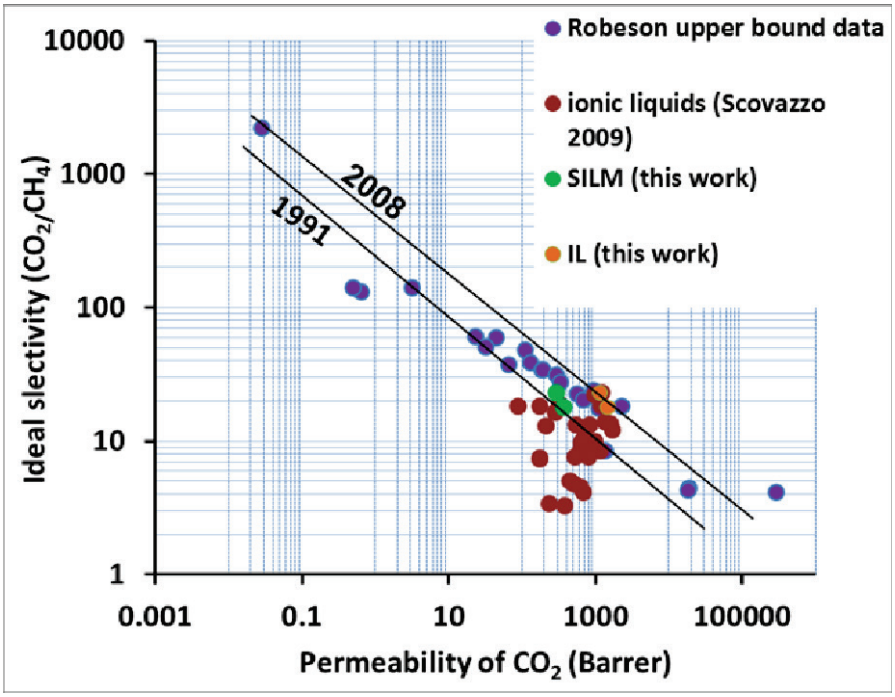
Aim of this project is a development and application of membrane techniques to increase the affectivity of classical separation processes with help of computer simulations and theoretical modeling. In most of processes the goal of separation techniques is to recycle vapor phase, which was lost in a sweeping gas.

Ionic liquid polymer gel membranes based on poly(vinylidene fluoride-co-hexafluoro-propylene) (p(VDFHFP)) were prepared by solvent casting from a solution in acetone. The membranes contain from 20 wt. % to 80 wt. % of pure or mixed ionic liquids based on the imidazolium cation: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) and 1-hexadecyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([HdMIM][TFSI]). The gas transport through the membranes prepared in this study was evaluated in the temperature range of 20 - 60 ºC, which includes the melting point of the high temperature ionic liquid [HdMIM][TFSI]. These permeation measurements show a significant increase of the permeability in the presence of the IL mixture, especially for carbon dioxide. This suggests a potential application in gas separation membranes, for instance for natural gas treatment or for CO_2 sequestration from flue gas [5].

In addition, we present a novel method for the treatment of raw sorption kinetic data recorded by a gravimetric sorption apparatus equipped with calibrated quartz (McBain's) spiral balance. The mentioned treatment enables to eliminate overlapping mechanical oscillations of the spiral balance (caused by the initial charging of the sample gas/vapor into the evacuated measuring chamber) and to successfully reconstruct the real elongation of the spiral caused by gas/vapor sorption into a polymer material. This allows to calculate even from highly noised sorption data the accurate values of gas/vapor diffusion coefficients [2].

Molecular dynamics simulations of n-hexane adsorbed onto the interface of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][Tf_2N]) are performed at three n-hexane surface densities, ranged from 0.7 to 2.3 μmol/m^2 at 300 K. For [bmim][Tf_2N] room temperature ionic liquid, we use a non-polarizable all-atom force field with the partial atomic charges based on ab initio calculations for the isolated ion pair [7].

Successful practical application of ionic liquid (IL) membranes requires good understanding of their basic transport properties and the role of the IL itself and its polymeric support. Within this work, two approaches to the calculation of mass transfer coefficients of gases in supported ionic liquid membranes were applied. The first one applies the models and data reported on diffusivity and solubility of gases in pure ionic liquids in the literature, in combination with porosity and tortuosity of the support. The second one is based on fitting of experimental data obtained from two ionic liquid membranes. The results of both approaches were compared and used to predict the properties of ionic liquid membranes. It was found that the model based on data of pure liquids overestimated the mass transfer coefficient signify-cantly. The correlation diagram known as the Robeson plot is frequently used to compare the permeability and selectivity of a new membrane with the already reported data. It combines the Robeson upper bound data with the determined results and the data of pure ionic liquids reported previously [6].



Robeson upper bound data and ionic liquid data

Membrane separation - the more effective separation of a pure enantiomer from a racemic mixture

(P. Izák, izak@icpf.cas.cz; joint project with ICT Prague and IMC; supported by GACR, project No. P106/12/0569)

The goal of the proposal is to develop new membrane separation techniques for successful resolution of racemic mixtures allowing optimization of the therapeutic value of enantiomeric drugs (pharmacological and toxicological) and avoiding their adverse effects. The key objective is to separate enantiomers by a new membrane separation method, based on the proposed supported chiral room temperature ionic liquid membrane, that has never been studied yet. In comparison with classical methods employed earlier, it should show higher efficiency and cost effectiveness in the processes of enantiomer separation. New chiral hyper-branched polyimide membranes modified by end-capping with (+) or (-) – isopinocampheyl-amine were prepared and the careful characterization of the membranes by spectroscopic methods was done. Further, the results of comprehensive research on transport of particular enantiomers through hyperbranched polyimide membranes modified by end-capping with (+) or (-) – isopinocampheylamine and cellulose derivative membranes were described. Diffusion coefficients, total sorption values and separation factors for enantiomers of racemic mixtures were measured. The new pertraction cell for measurement of diffusion coefficient was used.

We developed an all-atom non-polarizable force field for simulations of two chiral room temperature ionic liquids derived from 1-n-butyl-3-methylimidazolium bromide ([bmim][Br]); namely, (*R*)-1-butyl-3-(3-hydroxy-2-methylpropyl)imidazolium bromide (hydroxypropyl) and 1-butyl-3-[(1*R*)-nonyl]imidazolium bromide. The force field adopts the CHARMM parameters for intramolecular and repulsion-dispersion interactions, and it employs reduced partial atomic charges of the ions which we derived by quantum mechanical calculations.

International co-operations

CSIR of Pretoria and Johannesburg, Republic of South Africa: Extraction of essential oils from plant raw materials
Institut für Strömungsmechanik und Wärmeübertragung Technische Universität Wien: Flow of saturated vapors through porous membranes
Institute of Chemical Engineering, Sofia, BAS: High-pressure phase equilibria
Institute of Macromolecules, St. Petersburg, RAS, Russia: Membrane separation
Institute on Membrane Technology, CNR, Italy: Novel composite membranes containing ionic liquid and selected polymers for specific gas/gas, gas/vapor and vapor/vapor separations
KIT Karlsruhe, Germany: Design of pilot plant size microreactor for sulfur dioxide catalytic heterogeneous oxidation
Momentive Specialty Chemicals, Czech Republic: Application of microreactors for gas phase catalytic reactions
National Chung Hsing University, Taiwan: Preparation of Dense Homogeneous Polymeric Membranes and Study on Their Gas Permeation Properties
Otto von Guericke University of Magdeburg, Germany, Max-Planck-Institut für Dynamikkomplexer technischer Systeme. Magdeburg: Mass transport through porous membranes
Procter&Gamble, Belgium: Research and developments of microapparatus characteristics
Procter&Gamble, Belgium: Hydrodynamics of micro reactor for sulfonation
Procter&Gamble, Belgium: Hydrodynamics of annular gas-liquid flow
Technische Universität Wien, Institut für Strömungslehre und Wärmeübertragung, Austria: Flow of saturated vapors through porous membranes
Technical University of Lisbon, Portugal: Supercritical extraction of biological compounds from aromatic plants
University of Colorado, Boulder, CO, USA: Mass transport during vapor permeation and pervaporation, ionic liquids
University of Burgos, Spain: Enzymatic reactions of oil in supercritical CO_2 medium
University of KwaZulu-Natal, Republic of South Africa: Liquid-liquid extraction processes with fluorinated hydrocarbons, recovery of luminophores

Visits abroad

J. Křišťál, Procter&Gamble, Belgium (3 weeks)
V. Jiřičný, Procter&Gamble, Belgium (2 weeks)
P. Stavárek, Procter&Gamble, Belgium (5 weeks)
Z. Vajglová, Åbo Akademi University, Finland (6 months)

Visitors

M. Čársky, University of KwaZulu-Natal, Durban, Republic of South Africa
F. Euzenat, ENSIASET Toulouse, France
A. Palavra, Technical University of Lisbon, Portugal

Teaching

J. Hanika: ICT, Faculty of Chemical Technology, postgradual course “Multiphase Reactors”

J. Hanika: ICT, Faculty of Chemical Technology, course "Pharmaceutical Engineering"
H. Sovová: TU Darmstadt, Life Long Intensive Program "Process Intensification by High Pressure Technologies – Actual Strategies for Energy and Resources Conservation"

Publications

Original papers

[1] Bucic´-Kojic´ A., Sovová H., Planinic´ M., Tomas S.: Temperature-Dependent Kinetics of Grape Seed Phenolic Compounds Extraction: Experiment and Model. *Food Chem.* 136(3-4), 1136-1140 (2013).

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[17] Hanika J.: Decades of German-Czech Common Research on Periodic Operation of Trickle Bed Reactors. In: *Jubiläumsband 60 Jahre Dresdner Verfahrenstechnik*, pp. 194-197, Technische Universität Dresden, Dresden 2013.

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Patents

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