

Characteristics of main research directions investigated at the institute and the achievements 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
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The Institute of Chemical Process Fundamentals (ICPF) is one of six institutes constituting the Section of Chemical Sciences of the Czech Academy of Sciences. The Institute serves as a centre for fundamental research in chemical, biochemical, catalytic, and environmental engineering. Besides these activities, the Institute acts as a graduate school for Ph.D. studies in the field of chemical, biochemical, environmental engineering and processes, physical chemistry, inorganic and organic technology, organic chemistry, industrial chemistry, and biotechnology. The multi-disciplinary character of the Institute's activities is great advantage for complex problem solving and for scientific cooperation with external subjects.

The ICPF research activities are based on a long-term tradition and cover a wide range of fundamental scientific topics. The acquired know-how enables to carry out high-quality research in the fields ranging from pure chemical disciplines (like inorganic, organic, analytical and physical chemistry) over the applied chemistry in homogeneous and heterogeneous catalysis, chemical reaction engineering, and separation and material science to other related technical and technological areas such as hydrodynamics of multiphase flow systems, environmental biotechnology, aerosol formation and transformation, and chemical processes accelerated by laser beams or microwave field. These aspects are very beneficial for the solution complex multidisciplinary projects.

Main research directions of the Institute currently include:

1) Separation Processes in Chemical Engineering

The Laboratory of Separation Processes has acquired highly valued know-how as well as high international recognition in all of its research domains, namely: membrane separation processes; experimental thermodynamics; flow hydrodynamics in packed beds, mathematical modelling and microtechnology; supercritical extraction and liquid/liquid extraction.

The significance and specific contribution of the Laboratory consists in providing the fundamental research in chemical engineering with stress on patenting and application of the results in industrial practice. Particularly, the Laboratory is at the forefront of development of membrane techniques for purifying raw biogas and high-precision instruments and techniques for the measurements of vapour-liquid equilibria at reduced, normal, and elevated pressures. Naturally, the focus of experimental research is shifting continuously towards the systems of relevance to novel chemical and separation processes (new classes of promising solvents such as ionic liquids, systems dealing with polymers, etc.).

All above-mentioned topics are new fields of the research in the CR. Study of the *gas transport through thin liquid film* was started just in 2010. The three patents and four national awards were obtained on separation by the thin liquid membrane in various gas separation cases. The *separation of racemic mixtures* by supported chiral ionic liquid membrane for pharmacy industry is also the subject of investigation.

For *phase equilibria measurements and reliable data processing*, there are no competing researcher groups in the country. Unique computational skills based on mathematical gnostics are used in data processing. Data assessment, experimental

method diagnostics, and model parameter optimization are possible even in cases of a very small size of the data sample for which the assumption of normality of experimental error cannot be verified or is violated. Therefore a project of a research centre for the studies of energy storage materials is in preparation with the Institute of Thermomechanics of the CAS (IT). The team from our Laboratory has contributed to this project by its expertise in thermodynamics and in measurements of thermal properties of solids and liquids by means of the differential scanning calorimetry, whereas the team from the IT has mainly contributed by proposing engineering solutions of energy storage.

The systematic *research of microreactors* has aimed at development of new routes for chemical transformations and process intensification. The efforts are focused on the chemical-engineering design, hydrodynamics and heat and mass transfer characterization of microreactors suitable for heterogeneous processes and kinetic studies; for instance for the gas phase hydrogenation or oxidation reactions.

The *extraction of biologically active compounds from plants with supercritical CO₂* or compressed superheated liquids has been studied along with mathematical modelling of the kinetics of the process. Research has been also directed to foaming polymers using supercritical CO₂ or at preparation of nanostructured metal oxides.

The Laboratory is also focused on the *conversion of waste to valuable metals* in the field of electronic waste and the recovery of biowaste to valuable products for application to cosmetic, food and/or pharmaceutical industry.

2) Aerosol Chemistry and Physics

Research in the Laboratory of Aerosol Chemistry and Physics (LACP) was focused both on the studies on aerosol chemical and physical properties, and on theoretical developments of molecular theory of the fluid phase and molecular and mesoscale simulation methods.

Activities were focused on several areas: experimental studies on atmospheric aerosols, specifically on size resolved chemical composition and highly time resolved particle size distributions; behavior of aerosols in indoor environments especially those considered as cultural heritage, and also transformations of aerosol particles on their route from outdoor to indoor environments; synthesis of nanoparticles via aerosol processes and related adverse health effects of inhaled engineered nanoparticles; kinetics of nucleation and growth both in laboratory and in atmospheric systems; aerosols originated in traffic; sampling of aerosol particles emitted at elevated temperatures and pressures; and theoretical study on influence of surface processes and electromagnetic radiation on nanosystems. Participation in European infrastructure projects EUSAAR/ACTRIS led to a harmonization of atmospheric aerosol measurements on a qualitatively new level. The obtained data allow better aerosol parametrization to be used not only in weather forecasting models but also in the modelling of aerosol influence on regional and global climate.

Development of the molecular theory of fluids with emphasis on water, aqueous solutions, and other systems with associating constituents; development of methodologies of molecular simulations of equilibrium and reacting systems and their applications; mesoscopic computer simulations of polymeric and energetic materials are the main results of modeling and simulation group. A theoretical study of an influence of substrate geometry and heterogeneity on interfacial phase behavior of adsorbed model fluids was also developed.

3) Heterogeneous Catalysis and Reaction Engineering

Department of Catalysis and Reaction Engineering was carried out in the priority areas of catalysis, reaction engineering, surface science, materials engineering,

chemical and environmental technologies, and process development. The main expertise had covered all major aspects of homogenous and hetero-geneous catalysis, materials` science with special focus on texture and morphology studies, transport phenomena, environmental processes, mathematical modelling, nanotechnology, and biotechnology.

Obviously, it is not a simple task to characterize briefly the main research achievements at the Department during the inspected period 2010-2014. In summary more than 200 scientific achievements could be tracked in the form of research papers, books and book chapters, patents, industrial approved technologies, and best available technologies. It must be emphasized that the performed research included also some very fundamental scientific topics, such as principles of molecular templating in the preparation of organized particles, the research of synthesis, thermodynamics, and structural prediction of ionic liquids, and the development of advanced nanostructured photonic electrodes for sensor purposes. In parallel special attention was paid to the environment related processes, mostly focusing on the treatment of water pollution. In this context photochemical oxidation processes with titanium dioxide, with various types of photosensitive phthalocyanines, or with hydrogen peroxide and UVC had been developed from the bench laboratory level up to the half-scale or even up to the industrial full scale. The special focus on the evaluation of production parameters for various types of dyes and pigments must not be also omitted. Some of the special systems were then applied in the industrial development of time sensitive photonic sensors for medical use. It is also necessary to stress a new research area focused on biotechnology.

Catalysis and reaction engineering with focus on the design and construction of various types of reactors is another important activity of our research team. Attention is paid to the parameter of selectivity of a particular hydrogenation catalyst, specifically of Ru/BINAP complexes, driving model reactions in the stereoselective course, to the innovative catalysts with high content of Pt developed within EU IMMEDIATE project for application in automotive industry and also to the synthetic mesoporous silica-aluminas (MSA, which structures had been systematically studied as supports of Pt, Pd and Pd/Pt catalysts for hydrosulfurization, or development of heterogeneous catalysts for the oxidation of volatile organic compounds. Further, the activities directed towards the photochemical and photocatalytic environmental processes, electrocoagulation and sorption techniques together with the combined thermal desorption and catalytic oxidation for soil decontamination is necessary to stress. Nanotechnology focused on photoactive nanostructures preparation and application predesign by mathematical modelling and newly biotechnology completes the main research areas of the Department.

4) Hydrodynamics of Multiphase Reactors

The basic research has been focused on the behavior of multiphase dispersed systems, namely on the transport of mass and momentum. The goal is to understand the key underlying mechanisms governing their behavior.

In particular, the gas-liquid, gas-liquid-solid, liquid solid and gas-solid systems were studied. These basic studies have the following specific applications: aerated and sparged vessels, bubbly flows and bubble layers, foams and foaming, flotation columns, three-phase (bio)reactors and contactors, sedimenting tanks, powders and granular media - flow and rheology.

It was applied the multi-scale approach: (i) large scales (e.g. hydrodynamics of bubble columns, flow regimes and stability, mass transfer, beer over-foaming, bubble production and rise in lakes), (ii) small scales (e.g. bubble formation, rise, oscillations,

coalescence and breakup, bubble motion in non-circular micro-channels), (iii) intermediate scales (bubble-bubble interactions, bubble-solids interaction in flotation). Three complementary ways for our investigations were used: (i) experimental measurements, (ii) theoretical modelling (physically based simplified models) and time series analysis (non-linear dynamics), and (iii) numerical simulations (Computational Fluid Dynamics - Fluent, CFX; DEM for granular materials).

For experimental evaluation of the multi-phase flow characteristics, the visualization methods (PIV, micro-PIV, hot-film/wire anemometry, high-speed cameras) and electrodiffusion diagnosis (characterization of wall-turbulence, flow recirculation zones or measuring the shear stress on the wall) were used, coupled with the rheology testing of both liquid systems (complex fluids, micro-dispersions) and granular media (flowability, internal friction, cohesion), supplemented with surface tension measurements (static, dynamic) to study interfacial phenomena due to the presence of surfactants. Hydrophones are used for hydro-acoustics essays.

The fundamental knowledge can then be used for design, prediction and optimization of the equipment working with multiphase systems, which are employed in almost all technologies (flow features and mass and heat transport).

5) Analytical and Material Chemistry

Department provides analytical support to all departments of the Institute. Analytical laboratory is well equipped for the qualitative and quantitative analysis of organic compounds and their mixtures (NMR, LC-NMR, HRMS, LC-MS, GC-MS, HPLC). It can also provide analysis of inorganic compounds and heavy metals (AAS, MP-AES, SEM, UV-VIS spectrophotometer). The original research is focused on development of new separation approaches and methods. New pulse sequences are designed in order to precisely determine the value and sign of various spin-spin coupling constants e.g. $^nJ(^{13}\text{C}-^{13}\text{C})$ and $^nJ(^{29}\text{Si}-^{13}\text{C})$. LC-NMR hyphenation is frequently sought-after technique and it is a subject of many collaboration and joint projects.

Substantial part of the department is formed by organic/organometallic laboratories. These laboratories went through rigorous reconstruction in 2013 and they can provide dignified and save workplace for contemporary research in the field of organic synthesis. Besides traditional synthesis of new types of carbohydrates, cyclopentadienyl catalysts, carbosilane dendrimers, and the new ambitious topic of materials for molecular electronics have been emerged. The new, highly motivated workgroup is focused on synthesis of the new helicene and phenacene derivatives. This workgroup developed a new approach to the synthesis of helicenes and the procedure has been patented in cooperation with industrial partner which launched a production of racemic helicenes in 2014.

Novel materials are also synthesized in the workgroup of laser chemistry. New nanostructured C, Si, Ge materials are prepared using IR and/or UV laser assisted deposition. New nano-objects (nano-wires, nano-spirals, nano-sheets), multilayers and nano-composites were prepared in this way. Last workgroup of the Department is focused on the application of immobilized biocatalysts in organic-inorganic matrices as various optical sensors.

6) Environmental Processes

Research in Environmental Process Engineering Laboratory (EPEL) has been focused on modern technologies for sustainable power generation and various aspects of environmental protection, exploitation of Brownfields, pollution abatement and recycling processes for waste materials. Other research activities have been directed towards applications of the electrodeless discharge lamps in photochemistry and

photocatalysis in microwave fields and applications of such technique in organic synthesis. Valuable applications of selective microwave heating were exploited in recycling of the waste plastics, repairs of the asphalt roads, drying of the detergents, and the soil decontamination, etc.

Laboratory was established by unification of several research groups dealing with combustion/gasification research, hydrometallurgy, waste recycling and research of microwave chemistry and heating effects. The main activities of EPEL with various aspects of protection of the environment, and applications of new techniques for such purpose, can be assessed in four directions as it follows:

- Clean combustion and co-combustion technologies with reduction of pollutants (SO_2 , NO_x , N_2O , POP, heavy metals) and CO_2
- Gasification and co-gasification technologies with deep gas cleaning for advanced applications (fuel cells, catalytic processes) and development of small and medium gasifiers with integral production of fuel gas for gas engines
- Waste related research aiming at recovery of valuable materials, metals, non-metallic elements and energy (recycling and recovery of plastics, recovery of critical elements, e.g. REM from electronic and electrical waste, urban mining)
- Research (chemistry, catalysis and synergetic treatment) and Applications of microwave based technologies (mainly for environmental utilization)

Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Eduard Hála Laboratory of Separation Processes

The laboratory has acquired highly valued know how as well as high international recognition in all of its research domains, namely the experimental thermodynamics, membrane separation processes, supercritical extraction, liquid/liquid extraction, and flow hydrodynamics in packed beds, mathematical modelling and microtechnology. The significance and specific contribution of the Laboratory consists in providing the fundamental research in chemical engineering with stress on patenting and application of the results in industrial practice. Research is aimed at the development of experimental methods for investigation of phase equilibria, membrane separations, supercritical and liquid/liquid extractions, microreactors. Particularly, the Laboratory is at the forefront of development of membrane techniques for purifying raw biogas and high-precision instruments and techniques for the measurements of vapour–liquid equilibria at reduced, normal, and elevated pressures. Naturally, the focus of experimental research is shifting continuously towards the systems of relevance to novel chemical and separation processes (new classes of promising solvents such as ionic liquids, systems dealing with polymers, etc.). In the laboratory several topics were explored and they are described in detail below:

Topic W1: Phase Equilibria in Systems of Low Molar Mass Components

Methodology of measurement and development of experimental techniques for vapour–liquid equilibrium (VLE) determination is a traditional research of the group. This research started in the late 1940s by Professor E. Hála and co-workers, and it was transformed later into the “Prague thermodynamic school”. Their first book (Pergamon Press, 1958, 1968) became the basic world textbook dealing with all related problems: besides of the thermodynamic description and prediction of phase equilibria with new approaches, it includes also mathematical processing of data, measurement and control of system variables, and the first bibliography of published data. All those items have been supplemented, extended and continued since the group became integrated into the ICPF (1964). As a result, many scientific papers and books were published with high international impact; the last large publication is represented by two volumes of Landolt-Börnstein Encyclopedia (2008). The group gained worldwide reputation in high quality measurements, accurate interpretation, and statistically sound data processing.

During the last 100 years, data for more than 20000 VLE systems have been published yielding approximately 300000 experimental points what was partly sufficient to enable for example the development of the UNIFAC group contribution prediction method, however many data are still missing in this database. In the 1990s, the group has been involved in the large IUPAC project dealing with alkane + alkanol + ether systems. In parallel, the best software in the world was developed for very reliable data processing.

VLE data have been measured also during 2010–2014 in binary and ternary systems of compounds with selected functional groups as a natural continuation of the above mentioned IUPAC project. Investigated systems were: *tert*-amyl methyl ether + *tert*-butanol + isooctane, isooctane + isobutanol + 4-methyl-2-pentanone, isopropanol + isooctane + 2,4-dimethyl-3-pentanone, and dimethylbutane + diisopropylether + 3-methyl-2-butanone. All binary data were correlated using the Wilson and the NRTL models and subsequently used for successful prediction of data for ternary systems.

Complex combination of phase and chemical equilibria has already been experimentally studied earlier. Recently, these investigations were completed by the data determined isothermally in the system with chemical reaction (transesterification), namely in the quaternary ethyl ethanoate + ethanol + propyl ethanoate + propanol system and in all six binary subsystems. Good prediction was achieved with use of correlated NRTL binary parameters.

This topic can continue for many years by supplementing the database with new data, particularly if practically all once-leading European and American labs have quitted experiments since measurements are “difficult and expensive”; it is easier to use prediction methods which unfortunately do not always lead to the reliable results. In final stage, a pilot plant (= unavoidable experiment again) must be run to verify the design of separation unit.

Results: 5 papers, 4 presentations at international congresses. Total number of citations of mentioned papers is 8 (WoS).

Bernatová S. et al., J. Chem. Eng. Data 56(4), 783–788 (2011). Bernatová S. et al., Fluid Phase Equilib. 307(1), 66–71 (2011). Pavlíček J., et al., Fluid Phase Equilib. 328, 61–68 (2012). Pavlíček J. and Wichterle I. 45(1), 83–89 (2012). Pavlíček J. et al., Fluid Phase Equilib. 344, 59–64 (2013).

Topic W2: Vapour–Liquid Equilibria in Systems Containing Polymer

This topic has been split from the topic W1 and it represents the extension to systems containing components with high molecular weight. The demand for the data of such systems has been raised in connection with polymeric flow improvers necessary for facilitation of oil transport. New data were necessary to develop/improve prediction methods based on the group contribution concept. The phenomena of vapour–liquid equilibria (VLE) is essentially the same as for low molar weight components, however experimental techniques had to be modified due to problems with smooth boiling, and downsized because polymers were available in small amount only.

The first microebulliometer for total pressure measurement was developed, tested and used to measure the component activities in mixtures of polymers with organic solvents in 2010. During five years, this still has been three times redesigned to enable measurement even under more unfeasible conditions. At the beginning, several polymeric flow improvers such as copolymers of octadecyl methacrylate or dodecyl methacrylate with acrylic acid or with 1-vinyl-2-pyrrolidone were investigated with several organic solvents (toluene, hexane, chloroform). Later, this ebulliometric techniques has been successfully used for VLE measurements of other systems like the poly(acrylic acid) + water, the poly(methyl methacrylate) + acetone or 2-butanone, and the polystyrene + toluene system. All those data have been measured at three isotherms in the region of low polymer concentrations and correlated using the

UNIQUAC-FV model. The three prediction models (the GC-Flory EoS, the UNIFAC-vdW-FV, and the Entropic-FV model) were tested against the new experimental data.

Novelty of the topic: Several stills were developed and designed for total pressure measurement by ebulliometric method. This technique has not been practically used and described earlier in literature. In parallel, three correlation and prediction methods were successfully applied to the newly obtained data.

Results: 6 papers, 1 book, 7 presentations incl. one keynote lecture at congresses, gold medal awarded at international exhibition INOVA 2011. As the by-product, one book was published during this period. Total number of citations of mentioned papers is 5 (WoS).

Pavlíček J. et al., Fluid Phase Equilib. 297(1), 142–148 (2010). Bogdanić G. and Wichterle I. J. Chem. Eng. Data 56(4), 1080–1083 (2011). Pavlíček J. et al., Fluid Phase Equilib. 358, 301–303 (2013). Pavlíček J. et al., Chem. Biochem. Eng. Q. 28(4), 447–450 (2014). Pavlíček J. et al., Chem. Biochem. Eng. Q. 29(1), 45–48 (2015). Bogdanić G. et al., Polimeri 31(3–4), 153–156 (2010). Bogdanić G. et al., Collection of Miscibility Data and Phase Behavior of Binary Polymer Blends Based on Styrene, 2,6-Dimethyl-1,4-Phenylene Oxide and of Their Derivatives. 124pp., Research Signpost, Trivandrum (2010).

Topic W3: Volumetric Studies

Densities, molar excess volumes, and speed of sound were investigated within three projects granted by the Czech National Foundation for period 2003–2011. The aim was to provide reliable thermodynamic data for liquids and liquid mixtures dealing with both the environmental problems and (bio)fuels. Experimental data were measured, correlated and subsequently used for modelling and prediction of pressure–volume–temperature state behaviour.

Since 2010, the data were determined and processed in several ternary systems containing (toluene + 2,2,4-trimethylpentane) with alcohols or methyl *tert*-butyl ether, including all binary subsystems. Measurements were carried out isothermally. Densities of heterocyclic compounds (pyridine, picolines) were measured up to pressure 40 MPa. Adiabatic compressibility was evaluated, too. An extensive review of excess volumes for systems composed with mesitylene, has been prepared. The topic has been entirely ceased after retirement of J. Linek (leader of the above mentioned projects) in 2012 and after reorganization of the whole department.

Results: 7 papers, 8 presentations. Total number of citations of mentioned papers is 10 (WoS).

Morávková L. et al., J. Chem. Thermodyn. 42(1), 65–69 (2010). Morávková L. et al., J. Chem. Thermodyn. 42(7), 920–925 (2010). Morávková L. et al., J. Chem. Thermodyn. 43(12), 1906–1916 (2011). Houšková H. et al., Fluid Phase Equilib. 337, 156–164 (2013). Morávková L. et al., J. Chem. Thermodyn. 64, 137–150 (2013). Morávková L. et al. J. Chem. Thermodyn. (in press). Morávková L. and Sedláková Kem.Ind. 62(5–6), 159–170 (2013).

Topic W4: Thermodynamic Properties and Liquid Phase Behaviour in Systems of Ionic Liquids

In this topic, experimental studies of phase equilibria in binary and multicomponent mixtures of gases and liquids and of thermodynamic and thermophysical properties of pure liquids and liquid mixtures are addressed at the Research Group of Thermodynamics of Task-Specific Materials (TTSM) along with the

experimental data processing, i.e. their critical assessment and model parameter optimization. Task-specific materials and particularly ionic liquids (ILs) are studied in terms of their structure-property relationships and application potential of this promising class of compounds.

Over the past five years, six original papers in peer-reviewed journals, one full paper in conference proceedings, and one review were published. For example, a homologous series of ammonium-based ILs was studied from the point of view of their use as co-solvents in reaction media in asymmetric hydrogenations. The main goal of this project was to investigate the influence of the main solvent methanol on the degree of hydrophobicity of the ionic liquids for an efficient recycling of the catalyst and product separation. In addition, interesting structure-property relationships were found both for pure ILs and in their mixtures with methanol.

A similarly motivated study was carried out to evaluate the suitability of water as extraction medium in the removal of IL synthesis precursors 1-chlorobutane and 1-methylimidazole from [bmim][PF₆]. LLE in pseudoternary systems of these organic solvents, water, and the IL were measured in a study of intensification of the use of ILs as reaction co-solvents in asymmetric hydrogenations. A method of chemical analysis by means of UV-Vis spectrophotometry was developed to allow for a simultaneous determination of concentrations 1-methylimidazole and imidazolium-based ILs that show overlapping UV spectra. In 2013—2014, an interacademic exchange project with the partner CNRS laboratory Thermodynamics of Intermolecular Interactions of the Institute of Chemistry Clermont-Ferrand (Dr. P. Husson) was completed. A range of novel ILs with a differing structure of the alkyl substitution group on the cation was studied to investigate the alkyl substituent structure on the physicochemical properties of pure ILs and their mixtures with water. Thermodynamic and transport properties of pure ILs were measured and reported on in a recent paper published in *Fluid Phase Equilibria*. Two more papers (thermal properties of pure ILs, and excess properties and LLE in systems IL+water) are in preparation and will be submitted to peer-reviewed journals in 2015.

Since 2014, TTSM is currently running a MEYS project LD14090 From task-specific solvents to energy storage. Thermodynamics of ionic liquids at the service of their applications. The project team consists of members of TTSM and GAMOS groups of the ICPF and is to some extent linked to the above-described interacademic project, focusing on the structure-property relationships of a range of IL with oligoether functional groups and on their application potential as electrolytes.

In the IUPAC Project # 2011-065-3-500 Database on liquid-liquid equilibria of binary mixtures of ionic liquids and molecular compounds a compilation of available literature data was made and a web-based database interface (Ionic Liquids LLE Internet Accessible Storage - ILLIAS) is under construction. A volume of the Solubility Data Series (*Journal of Physical Chemistry and Reference Data*) will be published during 2016.

In all the described projects, thermodynamic modelling of the studied properties using GE models and robust regression methods based on mathematical gnostics were used. The mathematical gnostics enables us not only to obtain reliable model parameters, but also to critically assess data where statistical methods fail.

Results: 7 papers, 9 presentations. Total number of citations on all above mentioned papers belonging to the topic was 22 (WoS).

A. Andresova, et al., *Fluid Phase Equilib.* 371, 41 (2014); K. Machanová, et al., *Fluid Phase Equilib.* 363, 156 (2014).; M. Bendová, et al. *J. Solut. Chem.* 41, 2164 (2012); K. Machanová, et al., *J. Chem. Eng. Data* 57, 2227 (2012); K. Machanová, et al. *Procedia Engineering* 42, 1229 (2012); J. Jacquemin, et al., *ChemPhysChem* 13, 1825 (2012); I. Černá, et al., *Chem. Eng. Proc.: Process Intensification* 50, 264 (2011).

Topic W5: Study of the Mass Transport in Polymeric Membranes and in Ionic Liquids

In the recent decades, membrane separation processes such as **pervaporation and vapor permeation** have evolved from prototypes in the laboratory to a utilization at large scale plant for industrial operations with significant technical and commercial impact. The knowledge of the transport of permeated substances in membranes is essential for the proposition of membranes separators.

Apparatus for consecutive measurements of permeability, diffusivity and solubility of vapors in polymer film during a single experiment was developed. The main advantage of this sweeping-gas apparatus with a new type of a permeation cell is the possibility to determine an amount of permeates sorbed in a membrane in the steady state of a vapor permeation process without any need of manipulation with the membrane. Permeate sorption data in the steady state provide important information about transport mechanism in polymeric membranes. Solubility, diffusivity and permeability of toluene vapors in a low-density polyethylene (LDPE) membrane were measured using this new type of permeation apparatus. The simple **semi-empirical model** of toluene transport in a polyethylene membrane based on relation between experimentally obtained effective diffusion coefficients and concentration dependent diffusion coefficients evaluated from experiments on new permeation apparatus was proposed. Pervaporation transport of binary mixtures of four butanol isomers (1-butanol, 2-butanol, isobutanol and *tert*-butanol) with water through polyethylene membrane was studied.

New method of diffusivity evaluation in polymeric membranes based on probability theory and statistical analysis from the first two statistical moments was proposed. The difference from assumption of Fick's second law is possible to detect.

Separation of carbon dioxide from binary gas mixtures and also from raw biogas by polymeric membranes and by ionic liquids was studied.

New and **patented method** for **purification of raw biogas** by thin film swollen composite membrane was invented in E. Hála Laboratory of Separation Processes. This method was approved in pilot plant and based on this small industrial unit was constructed. This research was awarded by: **E.ON Global Energy Award, category: Company, Award of ERSTE Corporate banking, Award of Ministry of the Environment of the Czech Republic, Price of Kapsch, Invention – Technical Science – Czech Head 2014.**

In this field of the research it was collaborated with prof. S.-Y. Suen, National Chung Hsing University, Taichung, prof. R. Noble, University of Colorado, Boulder, USA and Dr. S. Kononova, Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia and Dr. J. Jansen, Institute on Membrane Technology, ITM-CNR, Italy.

Results: 31 papers, 7 book chapters, 3 patents, 57 presentations. Total number of citations of our papers belonging to the topic is 204 (WoS).

Kononova S.V., et al., *Crystallogr. Rep.* 56(3), 502-507 (2011). Petříčková R., et al., *J. Membr. Sci.* 369(1-2), 466-473 (2011). Setničková K., et al., *J. Membr. Sci.* 66(22), 5566-5574 (2011).

Uchytíl P., et al., *J. Membr. Sci.* 383(1-2), 262-271 (2011). Liang Ch.-Y., et al., *Sep. Purif. Technol.* 92, 57-63 (2012). Petříčková R., et al., *Sep. Purif. Technol.* 107, 85-90 (2013). Řezníčková J., et al., *J. Membr. Sci.* 435, 46-51 (2013). Uchytíl P., et al., *J. Membrane Sci.* 470, 451-457 (2014). Kohoutová M., et al., *Desalin. Water Treat.* 14(1-3), 78-82 (2010). Randová A., et al., *e-Polymers* 1-6 (2010). Randová A et al., *Chem. Pap.* 65(5), 652-656 (2010). Vopička O., et al., *Eur. Polym. J.* 46(1), 123-128 (2010). Jansen J.C., et al., *Macromolecules* 44(1), 39-45 (2011). Poloncarzová M., et al., *Angew. Chem.-Int. Edit.* 50(3), 669-671 (2011). Randová A., et al., *J. Appl. Polym. Sci.* 119(3), 1781-1787 (2011). Bernardo P., et al., *Sep. Purif. Technol.* 97(SI), 73-82 (2012). Friess K., et al., *J. Membr. Sci.* 415, 801-809 (2012). Izák P et al., *Procedia Eng.* 44, 429-431 (2012). Kárászová M., et al., *Sep. Purif. Technol.* 89, 212-216 (2012). Lísál M., et al., *Phys. Chem. Chem. Phys.* 14, 5164-5177 (2012). Friess K., et al., *Ind. Eng. Chem. Res.* 52(31), 10406-10417 (2013). Jansen J.C., et al., *Sep. Purif. Technol.* 109, 87-97 (2013). Kárászová M., et al., *Sep. Purif. Technol.* 118, 255-263 (2013). Lísál M., et al., *J. Chem. Phys.* 139(1), 014704 (2013). Dolejš P., et al., *Sep. Purif. Technol.* 131, 108-116 (2014). Kárászová M., et al., *Sep. Purif. Technol.* 132, 93-101 (2014). Lísál M., et al., *J. Mol. Liq.* 189(SI), 85-94 (2014). Morávková L., et al., *Chem. Pap.* 68(12), 1739-1746 (2014). Randová A., et al., *Eur. Polymer J.* 61, 64-71 (2014). Randová A., et al., *J. Membrane Sci.* 475, 545-551 (2014). Sedláková Z., et al., *Membranes* 4(1), 20-39 (2014). Izák P., et al., Chapter 12: Pervaporation and Permeation Taking Advantage of Ionic Liquids. In: *Handbook of Membrane Research: Properties, Performance and Applications.* (Gorley, S.V., Ed.), pp. 387-402, Nova Science Publishers, New York 2010. Friess K et al., Chapter 4: Transport of VOCs in Polymers. In: *Volatile Organic Compounds.* (Hanks, J.C. - Loughlin S.O., Ed.), pp. 119-147, Nova Science Publishers, New York 2011. Izák P., Kárászová M.: Kapitola 7: Pervaporace. Chapter 7: Pervaporation. In: *Membránové procesy.* (Palatý, Z., Ed.), pp. 219-236, VŠCHT Praha, Praha 2012. Kárászová M., et al., Chapter 3: Biogas Upgrading for the 21st Century. (Litonjua, R. - Cvetkovski, I., Ed.), Nova Science Publishers, New York 2012. Bobák M., et al., Kapitola 5: Průmyslové aplikace dělení plynů a par. Chapter 5: Industry Application of Separation Gas and Vapors. In: *Membránové dělení plynů a par.* (Šípek, M., Ed.), pp. 103-131, Vydavatelství VŠCHT, Praha 2014. Izák P., Žák M.: Kapitola 7: Pervaporace. Chapter 7: Pervaporation. In: *Membránové dělení plynů a par.* (Šípek, M., Ed.), pp. 153-160, Vydavatelství VŠCHT, Praha 2014. Kárászová M., Izák P.: Kapitola 6: Bioplyn. Chapter 6: Biogas. In: *Membránové dělení plynů a par.* (Šípek, M., Ed.), pp. 133-152, Vydavatelství VŠCHT, Praha 2014. Petříčková R., et al., Method for Separating Gas from a Gas Mixture on a Membrane Wall. Pat. No. PV 2012-725. Applied: 12.10.25. Izák P., Poloncarzová M., Vejražka J.: A Process for Enriching Biogas from Sewerage Plants or Agricultural Basic Industries in Methane and an Apparatus for Carrying Out the Same. Pat. No. 303106/PV 2010-437. Applied: 10.06.02, Patented: 12.02.23. Izák P., Poloncarzová M., Vejražka J.: The Method and Apparatus for Gas Mixture Separation. Pat. No. 303107/PV 2010-438. Applied: 10.06.02, Patented: 12.02.23.

Topic W6: Flow of Condensable Gases Through Porous Membranes

Separation of gaseous mixtures can be achieved by condensation. The separation principle is, that in a liquid and in a gaseous mixture which are in thermodynamic equilibrium with each other the components have a different composition. Condensation can be achieved by (i) removal of heat, (ii) capillary condensation or (iii) the Joule-Thomson effect. It is well known that in membranes with small pores sizes, condensation can occur due to capillary condensation.

The capillary condensation of vapors through porous membranes was investigated theoretically and experimentally. The mass flow was measured for a range of pore diameters between 20 and 200 nm and for a range of upstream conditions and pressure differences. New apparatus for study of condensable gases transport was proposed and constructed.

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. This finding was not till now described in literature. 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.

Results: 3 papers, 4 presentations. Total number of citations of our papers belonging to the topic is 2 (WoS).

Loimer T., et al., *J. Membr. Sci* 383(1-2), 104-115 (2011). Uchytíl P., et al., *J. Membrane Sci.* 470, 451-457 (2014). Loimer T., et al., *PAMM Proc. Appl. Math. Mech.* 14, 685 – 686 (2014)

Topic W7: Supercritical Fluid Extraction of Bioactive Compounds from Plants and its Mathematical Modeling

The extraction with supercritical CO₂ (scCO₂) is particularly suitable for the separation of bioactive compounds from plants because of advantageous properties of the solvent: low critical temperature and pressure, inertness, easy separation from extract, non-toxicity, and availability in high purity and at low cost, to name the most important ones. Its products are applied in food and cosmetic industry but the theory of this process is not yet complete from chemical engineering point of view and thus the optimization of extraction conditions is a matter of experience and trial-and-error procedures, particularly when the composition of extracts from plants as complex mixtures is considered. The research in the group of supercritical fluid processes was focused on the effects of extraction conditions and the extract composition and its insecticidal activity.

The relationship of extraction conditions, extract composition, and activity of extracts against pest insects was examined not only for the supercritical fluid extraction but also for Soxhlet extraction with organic solvents and hydrodistillation. The optimal method and its conditions were determined to achieve different insecticidal activities of the extracts on insects as high acute mortality, chronic mortality, antifeedance, and others. The extraction and chemical analysis were carried out in the ICPF and the insecticidal assays were conducted in the team of R. Pavela at the Crop Research Institute. The paper of Pavela et al. (2010) concerns the insecticidal activity of *Tanacetum parthenium*, while the paper of Sajfritová et al. (2013) presents generalization of the results of long-term research with recommendations for obtaining highly efficient extracts using hydrodistillation and supercritical fluid extraction.

As the acute toxicity of plant isolates was found to be closely related to their content of volatile oil, the research was particularly focused on the scCO₂ extraction of volatiles from plants. Initially, the kinetics of volatile oils extraction from aerial parts of plants was measured by our Portuguese colleagues and modelled using the experience of the ICPF group (Grosso et al., 2010). The further research was carried out completely in the ICPF. The importance of the solute-matrix interaction was taken into account in a novel mathematical model for the extraction from aerial parts of plants

(Sovova, 2012). In the recent paper (Sajfrtova et al., 2014), the scCO₂ extraction of volatiles from seeds was combined with extract fractionation in order to obtain fractions enriched with different bioactive substances.

Another direction of the research concerns the different kinetics of scCO₂ extraction for individual extract components. Thus, the extraction of beta-sitosterol as a minor component in vegetable oil was studied experimentally (Sajfrtova et al., 2010) and its kinetics was calculated using a novel model, which includes multicomponent phase equilibrium (Sovova et al., 2010). The equilibrium was modelled by our Bulgarian colleagues. The model for extraction kinetics was also modified to simulate experimental data from the solvent extraction of polyphenols from grape seed, measured by our Croatian colleagues (Bucic-Kojic et al., 2013).

Moreover, the results of our research and study of relevant literature were summarized in an extensive review paper on scCO₂ from plants where the parts on the kinetic models and extracted plants were written by us and the part on the high pressure equilibrium by our Bulgarian colleague (Sovova and Stateva, 2011). The importance of solute-matrix interaction was emphasized in the paper of Sovova (2012a) and a simplified model for scCO₂ extraction kinetics was developed (Sovova, 2012b).

Results: 11 papers, 16 presentations. Total number of citations on all above mentioned papers belonging to the topic was 111 (WoS).

Pavela R. et al., Ind. Crop. Prod. 31(3), 449-454 (2010). C. Grosso et al., Chem. Eng. Sci. 65(11), 3579-3590 (2010). Sajfrtová M. et al., Int. J. Mol. Sci. 11(4), 1842-1850 (2010). Sovová H. et al., J. Food Eng. 101(2), 201-209 (2010). Sovová H. and Stateva R.P. Rev. Chem. Eng. 27(3-4), 79-156 (2011). Sovová H. J. Chromatog. A 1250(SI), 27-33 (2012). Sovová H. Am. J. Anal. Chem. 3(12A), 958-965 (2012a). Sovová H. J. Supercrit. Fluids 66(SI), 73-79 (2012b). Bucić-Kojić A. et al., Food Chem. 136(3-4), 1136-1140 (2013). Sajfrtová M. et al., Ind. Crop. Prod. 47, 69-77 (2013). Sajfrtová et al., J. Supercrit. Fluids 94, 160-164 (2014).

Topic W8: Liquid-liquid Extraction

Liquid-liquid extraction is a powerful technique for separation of valuable components from diluted solutions. It has been extensively used for refining of liquid products and intermediates, as well as for purifying waste waters from industrial plants and recovering valuable components.

There are two preconditions of a successful extraction process: a selective, stable and non-expensive solvent and an efficient, flexible and reliable extractor. Whereas the choice of solvent strongly depends on the particular extraction task, a flexible, high-performance extractor should be applicable to a wide range of liquid systems and conditions. The vibrating plate extractor VPE, developed in ICPF, meets their requirements.

VPE is a counter-current extraction column provided with a system of reciprocating perforated plates of special construction. Design and arrangement of the unique extractor contribute to the high extraction efficiency and high specific throughput of VPE. Several extraction pilot plant units were designed and constructed for processes serving for recovery of valuable components that are hardly accessible and/or with ecological impact on natural resources.

With the financial support of the Czech Ministry of industry and trade (FI-IM5/075), new recycling technology for precious and special metals from electrical and electronic waste was studied. The project concerned recovery of luminophores from waste CRT screens. Pilot plant unit was built in the factory site of Safina, a.s. Vestec

and the chemical process of reclaiming of europium and yttrium was patented (Gruber et al., 2011).

The project „Recovery of compact fluorescent lamps (CFL) and toxic mercury removal from input phosphors“ (TACR, TA02021290) dealt with finding complex method of recycling waste from used CFLs – from their pulverization through separation for glass, metals and luminophores up to mercury separation and its transformation to a chemically stable form to prevent its subsequent emissions. Main goal was to isolation of valuable components (yttrium and europium oxides) for their reusage for new CFLs. Two pilot plant extraction units were constructed in ICPF CAS and Durban (South Africa). The commercial unit in Durban was designed to process 4800 bulbs per hour. Patent on the process (Ramjugernath et al., 2013) was applied.

Other research activity was focused on separation of biologically active substances from plants and microalgae. The subject of the contract with Favea Europe, s.r.o was to perform laboratory and pilot plant experiments for refining softwood liquid extracts away from terpene compounds using counter-current extraction column VPE. The experimental results were used as a basis for the design of the main dimensions of operating extractor for technology with refining capacity 13.5 tons per year as a replacement for existing batch production.

Within the project "Biorefinery research centre of competence Bioraf" (TA CR, TE01020080) feasibility of the recovery of valuable substances from plant and algal materials for application in cosmetic or food industry was studied. Extractive separation of lipids and higher unsaturated fatty acids from selected microalgal strains (e.g. *chlorella vulgaris*, *trachydiscus minutus*, *scenedesmus* sp.) was performed. Carotenoids, especially lutein, were isolated from *Calendula officinalis* and *Tagetes* sp. petals. As a potential application of waxes in cosmetics two clones of *Miscanthus* sp. were tested.

Results: 5 papers, 2 patents, 1 research report, 8 presentations. Total number of citations on all above mentioned papers belonging to the topic was 2 (WoS).

Gruber V., Rousková M., Heyberger A., Staf M.: *Method for Reclaiming of Organic Extracts Containing Europium and Yttrium Ions*. Pat. No. CZ302854/PV 2010-928. Patented: 14 December 2011. Ramjugernath D., Williams-Wynn M., Čárský M., Heyberger A., Gruber V.: *Recovery of Yttrium and Europium Compounds*. Pat. No. ZA 2013/02663. Applied: 13.04.15.

Topic W9: Flow Hydrodynamics in Packed Beds, Mathematical Modelling and Microtechnology

The team picked up the threads of previous work in field of processes of heavy industry that was performed in the cooperation with Iron and Steel Institute (ISI) at Dobrá, Czech Republic. The cooperation continued on the subject of a mathematical modeling of a blast furnace based on laboratory and production data. The contribution of the team was in the mathematical model formulation and development, solution and validation to enable the evaluation of the reproducibility of iron ore raw materials. The results were summarized in a paper that has been published just recently: Pustejovska et al. (2015).

V. Jiricny as a co-author summarized the previously collected experimental and theoretical know-how in field of spouted beds and electrochemical reactors in a book chapter (Evans and Jiricny 2010). Our previous grant research of the hydrodynamics in the packed beds under the conditions of periodic modulation of the feed rates has shown its potential in considerable performance improvement of the industrial trickle bed reactors. The subsequent research focused on the analysis of the conditions for

the energy savings by periodic pulsations of inlet gas and liquid velocities. The developed criteria based on functional analysis of mass balances and pressure drop equation has shown the energy savings up to 4% under the conditions of periodic modulation relative to the steady state operations (Akramov et al. 2011).

The research in a promising and fast developing field of microtechnology continued with the topics initiated during the EU project IMPULSE (FP6). In particular, the task dedicated to the team during IMPULSE was a development of a suitable microreactor for the electrochemical alkoxylation reaction. The challenge of this reaction was the gas evolution on the electrodes which had an adverse effect on the uniformity of the current density. The team designed a one-pass electrochemical microreactor with a unique bipolar arrangement of the electrodes. In the related papers (Bouzek et al. 2010, Kříšťál et al. 2012) the developed electrochemical microreactor was experimentally and theoretically analyzed with regard to the performance and process intensification.

In general, the microreactors have unique properties such as high specific surface area which is advantageous for various fast exothermic reactions such as gas-liquid absorptions or three phase catalytic hydrogenations. Based on the operating conditions, fluid properties and microreactor geometry, different flow regimes can be obtained, so the operating window of the microreactor has to be well defined. To characterize the flow regimes and the mixing in the microchannels the current available methods were extensively reviewed in Aubin et al. (2010) providing the information about main principles, applicability and limitations. An experimental study of flow hydrodynamic in microchannel with use of Particle Image Velocimetry (PIV) was performed in cooperation with Toulouse University, Toulouse, France. Our team members performed the experiments at our and partner labs with PIV and developed the image evaluation procedure to characterize the flow patterns in the microreactor, see Zálaha et al. (2012).

Within the FP7 project F3 Factory (2010-2013) the team participated on the development of new intensified reactors for continuous production of surfactants in a cooperation with P&G Brussels, Belgium, Britest, UK and KIT, Germany. The team contribution was in catalyst screening for the SO₂ oxidation, experimental characterization, kinetics determination and design and modelling of the pilot reactor. The team was leading also the development and construction of a prototype of a high intensity contactor for a sulfonation reaction, that has been integrated in the pilot plant installation in BIC, PG, Belgium. The reactor concept was successfully validated during the demonstration phase. The team also participated in the demonstration experiments and their evaluation. The papers summarizing the achievements are now in the preparation.

In 2010 the research team succeeded in application of the Modular Microreaction System (Ehrfeld, Germany) which consisted of several microreactors of unique properties. This initiated the research of microreactors application in order to characterize their suitability for more efficient and intensified operation. For instance, the meander reactor was examined for the enzymatic glycerolysis obtaining very reproducible results in contrast to conventional packed bed reactor, see Drhova et al. (2014). Very encouraging results were obtained with the photo-microreactor for degradation of PBDE (Vajglova et al. in press) and degradation of 4-chlorophenol (Hejda et al. 2014). The continuous photo-microreactor has shown considerably higher process efficiency compared to the batch cuvette (Drhova et al. 2012). The kinetic study of 2-methylpropene hydrogenation was examined in a packed bed microreactor revealing the heat and mass transfer effects leading to the observation of

self-sustained oscillations of 2-methylpropene conversion. The observed oscillations of exceptionally long periods in range of several hours are the subject of the recently submitted paper (Stavarek et al, submitted).

The study of microreactors application to such a wide range of different processes initiated a close cooperation with other departments of our institute and several national universities and research institutes that may serve as a good basis for future applications for common projects.

In the evaluated period the team succeeded to attract the interest from several industrial partners which resulted in contract research projects. The contract research covers topics such as fluid microprocessing and hydrodynamic studies of gas-liquid systems (2009-2014, P&G, Brussels, Belgium), microreactors application for gas-phase catalytic reactions (2013-present, Hexion a.s. Sokolov, Czech Republic) and advanced separation methods for liquid-liquid systems (2013-present, Modelarna Liaz s. r. o., Liberec, Czech Republic). Cooperation with the latter partner already resulted in one patent application (Jiricny et al., 2014).

Results: 9 papers, 1 patent, 9 presentations. Total number of citations on all above mentioned papers belonging to the topics was 86 (WoS).

Pustějovská P. et al., , Steel Res. Int., (86), 320-328 (2015). Evans J.W., Jiříčný V., Spouted Bed Electrochemical Reactors. In: Spouted and Spout -Fluid Beds: Fundamentals and Applications, 269-282 (2011), Cambridge University Press, New York. Akramov T.A. et al., Ind. Eng. Chem. Res. 50(18), 10824-10832 (2011). Bouzek K. et al., Electrochim. Acta 55(27), 8172-8181 (2010). Kříšťál J. et al., Ind. Eng. Chem. Res. 51(4), 1515-1524 (2012). Aubin J. et al., Chem. Eng. Sci. 65(6), 2065-2093 (2010). Zálaha P. et al., Chem. Eng. Sci. 68(1), 640-649 (2012). Drhova M. et al., Chem. Papers 108(11), 1058-1066 (2014). Vajglova Z. et al., Res. Chem. Intermed., in press. Hejda S. et al. Chem. Eng. J. 255, 178–184 (2014). Drhova M. et al., Procedia Eng. 42(SI), 1365-1372 (2012). Stavarek P. et al., Catal. Today, submitted. Jiricny et al., (2014), Pat. No. PV 2014-900. Applied: 2014.12.12.

The scope of research of the Laboratory is logically embedded in the overall research profile of the ICPF. At the interfaces of research topics, the Laboratory cooperates with the Department of Catalysis and Reaction Engineering and the Department of Multiphase Reactors.

Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Laboratory of Aerosols Chemistry and Physics

Topic 1: Particle Size Distributions of Atmospheric Aerosol and their Dynamics

One of the key parameters of atmospheric aerosol (AA) is size of aerosol particles, or rather particle size distribution (PSD). For example, the ability of AA to scatter solar radiation is a nonlinear function of particle size, where maximum effect is connected with sizes similar to the radiation wavelength. The strongest light scattering of visual light is connected to particles of several hundred nanometers in diameter. Both smaller and larger particles interact with the incident light much more weakly. Similarly, the ability of aerosol particles to serve as cloud condensation nuclei is size-dependent, particles with diameters of first tens of nanometers get activated rarely or only at higher supersaturations. If we want to assess the potential adverse health effects of aerosol particles, particle size is a parameter that rules the probability of aerosol particles to deposit in a given region of the respiratory tract. Due to the changing nature of atmospheric aerosol, it is necessary to record longer time series of particle size distribution in high time resolution.

Description of results and share of the team

The series of papers on this topic can be divided into three parts. In the first part we have published our own data on PSD and were interpreting them in the context of the location, meteorological parameters, concentrations of relevant gaseous pollutants, and local/regional emissions. Here belong these papers: Zdimal et al. (2011) described situation in the Eastern Mediterranean region where the marine air masses are strongly contaminated with polluted air coming from Greek mainland and continental Europe; Rimnacova et al. (2011) published a case study on the PSD dynamics at suburbs of Prague analyzing several years long series of PSD data and classifying them into several classes; Zikova and Zdimal (2013) performed a detailed statistical analysis on two-years-long PSD data collected on the rural background site in the Czech Highlands.

In the second part, team members co-authored papers where PSD data from Czech sites were put into regional or European context. Into these studies, the team provided QA/QC data on PSD from Kosetice or Prague, helped with data interpretation and paper structure and actively participated on the preparation of the manuscript. Here belong these papers: Borsos et al. (2012) reported a comparison of three Central European capitals, Prague, Vienna and Budapest, and attempted to explain observed similarities and differences including observed new particle formation events; Asmi et al. (2011) compared PSD recorded during one year on several tens of European aerosol background supersites participating in the EUSAAR/ACTRIS projects, classified sites into several types and showed spatial and temporal variations of submicron aerosol concentrations and provided results of statistical analysis on this unique dataset; Beddows et al. (2014) analyzed the data from European sites by cluster analysis and showed transformations of PSD along typical air mass trajectories.

In the third part, data on PSD from mentioned Czech sites were provided to groups performing regional and global atmospheric modeling to compare different scenarios of possible climate changes. In these papers, contribution of team members was reduced to providing QA/QC data and giving feedback to modelers. Here belong papers by Reddington et al. (2011) and by Mann et al. (2014).

Supporting projects and Students involved

European infrastructure projects EUSAAR, EUCAARI and ACTRIS, Czech Science Foundation (project No. P209/11/1342), one project financed by Norwegian Funds, one bilateral project with Austria and other with Hungary (see projects section of these evaluation materials). Two PhD thesis had been defended on this topic.

Key References

Asmi A. et al. (2011) *Atmos. Chem. Phys.* 11(11), 5505-5538. Reddington C.L. et al. (2011) *Atmos. Chem. Phys.* 11(23), 12007-12036. Řimnáčová D. et al. (2011) *Atmos. Res.* 101(3), 539-552. Ždímal V. et al. (2011) *Water Air Soil Pollut.* 214(1-4), 133-146. Borsós T. et al. (2012) *Sci. Total Environ.* 433, 418-426. Zíková N. and Ždímal V. (2013) *Aerosol Air Qual. Res.* 13, 1464-1474. Beddows D.C.S. et al. (2014) *Atmos. Chem. Phys.* 14(8), 4327-4348. Mann G.W. et al. (2014) *Atmos. Chem. Phys.* 14(9), 4679-4713.

Topic 2: Chemical Composition of Atmospheric Aerosols, its Size Dependence and Dynamics

Chemical composition of atmospheric aerosol is a key factor influencing most of its other properties. The content of water soluble inorganic salts controls hygroscopicity of aerosol and therefore its size changes due to changes of relative humidity in the atmosphere or in the human respiratory tract. Moreover, the content of elemental or black carbon is a main factor influencing if the aerosol heats or cools the atmosphere. On the top of that, the aerosol particle composition may influence the particle growth caused by heterogeneous reactions both in liquid and solid phase. Besides previous factors, the aerosol chemical composition also influences aerosol toxicity at a local level and at the same time decides if a particle would serve as CCN.

The study of chemical composition is also used for determination of the aerosol origin using advanced statistical methods of factor analysis (Positive Matrix Factorization or Multi-Linear Engine). These methods may be supported using size resolved chemical composition data as coarse particles have different origin (mechanical processes) than fine aerosol that arise from gas to particle conversion both in high temperature processes and in secondary aerosol formation in atmosphere. A detailed size distribution studies help to distinguish fresh fine aerosol from an aged one and also long range transported coarse particles from the local ones.

Highly time resolved chemical composition data are important to study dynamics of chemical composition changes of aerosols. It helps to describe both aerosol formation (sources) and transformation during daily cycle and a backward aerosol influence on atmospheric diurnal processes. Moreover, the dynamics of aerosol transport and transformation is closely related to the aerosol health effects.

Description of results and share of the team

The series of papers on this topic can be divided into three parts. In the first part we participated on a Pan-European overview of PM₁₀ and PM_{2.5} chemical composition with one year dataset from Prague-Suchbát (Putaud et al. 2010).

Second part is connected to size resolved characterization of atmospheric aerosol using advanced setting of cascade impactors based on comparison of using

the constant humidity inlets at low and high RH that prevents RH based changes in aerosol size distribution during 24h sampling period (Štefancová et al. 2010) including the detailed characterization of user modified BLPI impactors (Štefancová et al. 2011). Chemical composition of dry size segregated aerosol and the dependence of the size distribution of individual chemical species on the air mass origin was assessed in Schwarz et al. (2012).

Third part of papers deals with highly time-resolved chemical composition. Vodička et al. (2013) studied organic and elemental carbon behavior at Prague suburban site with two hour time resolution. The results showed the EC and OC diurnal trends are strongly influenced by the diurnal change of the boundary layer thickness as well as by the time evolution of the strength of both anthropogenic and natural emission sources. High influence of traffic on EC was shown for all seasons except for winter when additional source was attributed to its midday maximum. Comparison of these data with winter and summer parallel measurement at Košetice site resulted in the first thermal OC fraction based analysis using a new EUSAAR2 protocol (Vodička et al. 2015) showing large influence of volatile OC1 fraction at the urban site in comparison with the rural site. Newly obtained highly time and size resolved chemical composition data are being prepared for publications.

Supporting projects and Students involved

European projects EUSAAR, EUCAARI and ACTRIS, one project of Czech Science Foundation, one financed by Norwegian Funds, one bilateral project with Austria and one with Hungary. On this topic, one PhD thesis was defended and another one is close to submission.

Key References

Putaud J-P. et al. (2010) , *Atmos. Environ.* 44(10), 1308-1320 . Štefancová L. et al. (2010), *Atmos. Res.* 98(2-4), 237-248. Štefancová L. et al. (2011), *Aerosol Sci. Technol.* 45(1), 88-100. Schwarz J. et al.(2012), *Sci. Total Environ.* 437, 348–362. Vodička P. et al. (2013), *Atmos. Environ.* 77, 865-872. Vodička P., Schwarz J., Cusack M., Ždímal V.: Detailed Comparison of OC/EC Aerosol at an Urban and a Rural Czech Background Site during Summer and Winter. *Sci. Total Environ.* 518–519, 424–433 (2015).

Topic 3: Production of Tailored Nanoparticles for Toxicity Studies

Nanoparticles (particles with diameter less than 100 nm) have attracted considerable attention, because they show a quantum size effect, for which the physical and chemical properties are strongly dependent on the particle size. Due to this, nanoparticles have great potential in applications such as ceramic materials, electronic components, sensors, magnetic data storage materials or catalysts. The change of properties of nanoparticles can also affect the toxicity and therefore they cannot be treated the same way as bulk material. Some materials could become toxic, if they are inhaled in the form of nanoparticles. When inhaled, they can deposit in the lungs and then potentially move to other organs as the brain, the liver, the spleen, etc. In spite of that, studies of allocation of inhaled nanoparticles are still rather rare. Recently, an inhalation chamber for study of allocation of nanoparticles in organs of laboratory animals was constructed in the Institute of Analytical Chemistry of the CAS. For these experiments a source of continual generation of nanoparticles in duration of weeks and with appropriate particle number concentration, particle size distribution and also with well-defined composition is necessary. Therefore, methods of long term generation of nanoparticles of various species and characterization of synthesized

nanoparticles were studied in the Laboratory of the Aerosol Chemistry and Physics of the ICPF CAS.

Description of results and share of the team

Testing of the feasibility of nanoparticles synthesis from β -diketonate compounds was performed with nickel acetylacetonate (Moravec et al. 2011). Tests of the whole exposure system in the IACH CAS were performed with nanoparticles generated by oxidation of manganese acetylacetonate (Večeřa et al., 2012). For toxicology studies we tested long term synthesis of Pb/PbO_x nanoparticles by thermal decomposition and oxidation of lead bis(2,2,6,6-tetramethyl-3,5-heptanedionate) and also by evaporation/condensation of metallic lead (Moravec et al., submitted) and TiO₂ nanoparticles by thermal decomposition and oxidation of titanium tetraisopropoxide (Moravec et al., 2014). In these studies we performed long term generation of relevant nanoparticles in externally heated tube reactor in our institute and the know-how obtained was then applied using almost identical aerosol generator at the IACH CAS.

Besides direct nanoparticle generation we also took part in the research of toxicity of nanoparticles released from automotive brakes during braking. This research was performed in cooperation with Technical University Ostrava and our part consisted in recording the dynamics of particle size distributions of released particles using aerosol spectrometers SMPS and APS and size resolved sampling of released particles using Berner low pressure impactor (Kukutschova et al., 2011). Impactor samples were then characterized by several analytical techniques to find out not only composition of released particles but also to determine the key processes producing these particles and assess their potential adverse health effects. We also participated in two experimental campaigns in a chemical plant producing TiO₂ particles. The aim was to estimate the real exposure of workers in the production plant by mapping aerosol number and mass concentrations and by monitoring the dynamics of aerosol number size distributions in the vicinity of key process installations. At the same time, the team of medical doctors was examining various health parameters of workers and controls by taking samples of urine, exhaled breath condensate, and others (Pelclova et al., 2015).

Supporting projects and Students involved

Czech Science Foundation grants No. 104/07/1093, P503/11/2315, P503/12/G147. One PhD student participated on this topic.

Key References

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Topic 4: Characterization of Urban Environment Related Aerosol

Aerosol particles belong among major air pollution sources. A special type of environment is the urban area. Aerosol particles emitted from the road traffic

significantly contribute to high levels of air pollution. Today, these particles represent one of the main sources of air pollution in the urban environment. The particles emitted from road traffic can be divided into two categories – direct and indirect emissions. Direct emissions are emissions from vehicle exhausts, abrasion of car breaks, tyres and pavement and particle resuspension. The indirect emissions include secondary aerosol particles originated by chemical reactions from the gaseous emissions. The aim of our work was to compare the contribution of road traffic emissions to air pollution in places with different traffic density and, at the same time, to identify the individual sources of „traffic“ related aerosol according to their size resolved chemical composition.

Another urban related place is the underground metro, which is considered to be one of the cleanest from an environmental perspective. However, numerous studies have reported higher concentrations of PM on underground platforms and inside the trains themselves than above-ground ambient PM concentrations. Considering the routine use of many passengers on metro systems (during commuting for example), it is important to understand and characterize the air quality in these specific microenvironments in order to determine what type of aerosols passengers are regularly exposed to. The aim of this study is to describe aerosol concentrations and variability, and chemically characterize PM sampled during a 24 hour period on a platform of the Prague underground metro system.

Description of results and share of the team

The measurement campaigns of traffic emissions have been conducted at two different sites within the Prague city (with different traffic intensity) together with simultaneous measurement of the same parameters at the background station located in the suburban area of Prague. Measurements included time and size resolved measurement of aerosol particle number concentration and size resolved measurements of particle mass concentration. All the measurements were performed by the members of our laboratory using the equipment of the laboratory only. Following chemical analysis of the samples obtained using cascade impactors was performed partially in our laboratory (IC analysis) and the elemental analysis at the Nuclear Physics Institute of AS CR. The data evaluation and the paper writing were fully covered by our laboratory. Ondráček et al. (2011) published a study including chemical composition of aerosols on traffic dominated sites where size segregated impactor samples and semi-online OC/EC analysis were used to show that ultrafine particles from traffic are mainly composed of carbonaceous species.

The results obtained from measurement on a metro platform in Prague describe the variation of particle mass and particle number concentration and size distribution for a 24 h period. The measurements published in the paper under review (Cusack et al., 2015) were again fully covered by the instrumentation and people from our laboratory. The following data evaluation and analysis of the ionic composition (IC) was also done in our laboratory. The PIXE (elemental) analysis was performed in the CANAM (Centre of Accelerators and Nuclear Analytical Methods LM2011019) research infrastructure.

Supporting projects and Students involved

Czech Science Foundation (project No. P209/11/1342), European FP7 project HEXACOMM (grant agreement No 315760), project of Ministry of the Interior of the Czech republic (grant No. VF2010201513). One PhD thesis will be defended using the results from this topic.

Key References

Ondráček J. et al. (2011) *Atmos. Environ.* 45(29), 5090-5100. Cusack M., Talbot N., Ondráček J., Minguillón M.C., Martins V., Klouda K., Schwarz J., Ždímal V. (2015): Variability of aerosols and chemical composition of PM₁₀, PM_{2.5} and PM₁ on the platform of the Prague underground metro. *Atmos. Environ.* (sent for publication at the beginning of 2015).

Topic 5: Indoor Air Quality in Heritage and Historic Environments

Aerosol particles in the indoor environment constitute a major class of pollutants, in addition to those occurring in gaseous form. A number of health effects have been identified as being linked to exposure to airborne particles. The other effects are caused by particles deposited on indoor surfaces i.e. settled dust: for example in heritage and historic environments visible dust is unwanted from an aesthetic point of view. Further, there is also evidence on degradative effects on historic objects caused by particles. Thus, to control airborne particles and settled dust information on their sources, composition, dynamics in the indoor air, as well as on effects they cause should be known (Morawska and Salthammer, 2003, Hatchfield, 2005).

Description of results and share of the team

Studies on indoor air quality in heritage and historic environments have been carried out with these aims:

- a) development of evaluation methods for indoor air quality in libraries and archives, targeted at reduction of damages on library and archival collections caused by adverse effects of environment,
- b) gaining detailed knowledge of direct dependences between damage of library and archival collections and surrounding environment, leading to precautions reducing the adverse effects of deteriorated environment.

To determine contribution of outdoor air pollutants and indoor sources to indoor air quality in different types of repositories and archives the detailed characterization of indoor air was performed in two libraries and two archives (three naturally ventilated, one with HVAC) in the Czech Republic during four seasons of the year. The measurements were carried out at four locations representing different outdoor environment: rural (the Depository of the Research Library of South Bohemia in Zlata Koruna), small town (the State Regional Archives in Trebon), industrial area (the Library of the Regional Museum in Teplice), and large city (the National Archives in Prague) and included determination of indoor/outdoor (I/O) particle number concentrations and size distributions and monitoring of gaseous pollutants (SO₂, NO₂, O₃, HNO₃, NH₃, formic and acetic acids), temperature, and relative humidity. Further, size resolved sampling of I/O particulate matter (PM) was performed for subsequent chemical analyses that yielded elemental composition (PIXE), water soluble ions (Ion Chromatography) and content of elemental and organic carbon (thermal-optical method, EC/OC Sunset analyzer). The results showed that up to 80% of indoor PM was in submicron range and originated from the outdoor air. Furthermore, activities of the staff were identified as a main source of coarse particles. The dominant component of both fine and coarse fractions was organic matter that made 50-80% of the PM mass. The next most abundant components of fine PM were elemental carbon (soot) and ammonium sulphate and in coarse fraction crustal matter. To find out possible negative effect of dust indoor PM₁ and PM₁₀, particles were deposited on pure cellulose filters (Whatman 1). After artificial aging, the viscosity-average degree of polymerization of cellulose (DP_v) was measured. The decrease of the DP_v of cellulose showed a negative correlation with the deposited mass of sulfate ions in the submicron

dust particles. The monitoring of gaseous pollutants revealed degradation of cellulose based materials (wood, paper) as an indoor source of formic and acetic acids. Further, higher indoor concentrations of gaseous ammonia have been observed compared to outdoor ones. Preliminary results indicate both decomposition of secondary ammonium nitrate that penetrated indoors from the outdoor air and degradation of the organic additives used during building constructions as possible sources.

Supporting projects and Students involved

Projects supported by Norwegian Funds and Ministry of Culture of the CR. One PhD thesis was defended on this topic.

Key References

Hatchfield P.B.: *Pollutants in the Museum Environment, Practical Strategies for Problem Solving in Design, Exhibition and Storage*, Archetype Publications Ltd., London 2005. Morawska L., Salthammer T. (Eds.) (2003): *Indoor Environment, Airborne Particles and Settled Dust*, WILEY-VCH GmbH & Co. KGaA, Weinheim. Andělová L. et al. (2010) *e-Preservation Sci.* 7, 141-146. López-Aparicio S. et al. (2011) *Build. Environ.* 46(7), 1460-1468. Hussein T. et al. (2012). *Aerosol Sci. Technol.* 46(1), 44-59. Smolík J. et al. (2013) *Heritage Science*, 1:7, 1-5. Mølgaard B. et al. (2014) *Indoor Built Environ.* 23(5), 742-756. Mašková L. et al. (2015) *Atmos. Environ.* 107, 217-224. Bartl B. et al. (2015) *Stud. Conserv.* <http://www.maneyonline.com/doi/abs/10.1179/2047058414Y.0000000158>. Chatoutsidou S. et al. (2015) *Build. Environ.* 89, 253-263.

Topic 6: Influence of Surface Processes and Size Effects on Physicochemical Phenomena in Aerosol Systems with Nanoparticles

Gas-to-particle conversion takes place both in different kinds of atmospheric processes (in particular in formation of water drops and smog particles) and in processes of modern technology (for example in nanotechnology). Formation of aerosol nanoparticles is related to such stages as homogeneous nucleation, growth of clusters, their coagulation and coalescence. Above mentioned processes can be influenced by such factors as size effects, external fields (e.g. resonance radiation), the presence in the system of foreign adsorbable gases. Mentioned factors can significantly affect processes taking place in aerosol systems with nanoparticles.

Description of results and share of the team

Physicochemical transformations during formation of aerosol nanoparticles in supersaturated vapor were considered. Size effects in aerosol systems with nanoparticles (clusters) can influence the interaction of gas molecules with the particle surface and activation energies of processes occurring in the nanoparticles. It is known that the rate of homogeneous nucleation depends on the work of the critical cluster formation. In turn, the value of this energy is related to the critical cluster size which is the key parameter in the classical nucleation theory. The problems related to the critical size of particles (clusters) and the rate of homogeneous nucleation in a gas phase taking into account the size dependence of the condensation coefficient of vapor molecules on the nanoparticle surface and the cohesive energy in nano-particles were studied theoretically in (Levdansky et al. 2010a, Levdansky et al., 2014a). It is shown that above-mentioned size effects can lead to an increase in the critical cluster size and accordingly to a decrease in the nucleation rate. The effect of a foreign adsorbable gas on nucleation rate was studied in (Levdansky et al. 2010b).

Size effects can also affect coalescence of nanoparticles, nucleation within nanoparticles, incorporation of a foreign gas by nanoparticles and chemical reactions

inside nanoparticles and on their surface (Levdansky et al. 2010a, Levdansky et al. 2010c, Levdansky et al. 2011, Levdansky et al. 2013a, Levdansky et al. 2013b). It is shown that the rate of chemical reactions inside nanoparticles and on their surface increases with a reduction in the nanoparticle size.

The joint manifestation of size effects that influence processes on the surface of nanoscale objects and processes occurring inside these objects was considered in (Levdansky et al. 2012) by the example of the growth rate of the silicon nanowhisker. In this case size effects influence evaporation and condensation of silicon atoms on the surface of the nanoscale liquid droplet-catalyst (Si–Au liquid alloy) as well as nucleation of Si inside the nanodroplet-catalyst. Influence of the size dependence of the cohesive energy in free nanoparticles on the evaporation rate of nanoparticles was investigated in (Levdansky et al. 2014b). It is shown that experimental data on the evaporation rate of free silver nanoparticles can be interpreted on the basis of the size-dependent cohesive energy in nanoparticles without the assumption of the sufficiently high value of surface tension (that is in contradiction with Tolman theory).

Supporting projects

Two projects of the Science Foundation of the Czech Academy of Sciences and one project of the Czech Science Foundation.

Key References

Levdansky V.V. et al. (2010a) *Int. Commun. Heat Mass Transfer*, 37(6), 593-595. Levdansky (Levdanskii) V.V. et al. (2010b) *J. Eng. Phys. Thermophys.*, 83(2), 401-405. Levdansky V.V. et al. (2010c) *J. Eng. Phys. Thermophys.*, 83(4), 843-848. Levdansky V.V. et al. (2011) *J. Eng. Phys. Thermophys.*, 84(3), 574-578. Levdansky V.V. et al. (2012) *J. Eng. Phys. Thermophys.*, 85(5), 1092-1096. Levdansky V.V. et al. (2013a) *J. Eng. Phys. Thermophys.*, 86(3), 547-550. Levdansky V.V. et al. (2013b) *J. Eng. Phys. Thermophys.*, 86(4), 863-867. Levdansky V.V. et al. (2014a) *J. Eng. Phys. Thermophys.*, 87(5), 1249-1254. Levdansky V.V. et al. (2014b) *J. Eng. Phys. Thermophys.*, 86(4), 469-473.

Topic 7: Structure and Phase Behaviour of Heterogeneous Fluid Systems of Non-Planar Symmetries

Fluids that are subject to an external field or consist of two or more phases exhibit heterogeneous structure. Of particular interest of such fluids are interfacial phenomena that are ubiquitous in nature. Despite an intensive research over the last three decades our understanding of many of their aspects is still very incomplete. The vast majority of early theoretical studies focused on fluid adsorption on idealized planar substrates or between parallel plates. The studies have shown that confining a fluid can dramatically alter its properties and induce completely new examples of phase transitions, scaling behavior and critical phenomena that are absent in bulk fluid. Important examples of this include wetting, pre-wetting and layering at planar walls and capillary condensation, critical point shifts and interfacial delocalization in parallel plate geometries. The phenomenology of these phenomena, as well as their microscopic origin based on the competition between fluid-fluid and wall-fluid forces, is nowadays fairly well understood. More recently, however, there has been increasingly enhanced interest in adsorption and wetting at *micropatterned* surfaces in which the substrate is non-planar or is chemically heterogeneous. This research has been motivated by the recent improvements in surface lithography and related techniques (such as grafting polymer chains onto a substrate) modifying a surface structure on a molecular level. This allows a construction of tailored substrates (or so called “smart surfaces”) for controlled manipulation of adsorbed fluid which plays a central role to the development

of modern technologies, such as microfluidics. At a more fundamental level, however, a study of non-planar substrate models acknowledges a molecular structure of solid surfaces and thus their inherent roughness. The surface roughness reveals new types of interfacial phase transitions and fluctuation effects, as well as surprising connections between adsorption in different geometries.

Description of results

An ultimate goal of our research is to provide a fundamental understanding of the impact of geometry of an external field (a confining wall or substrate) on the phase behavior of the fluid. We have considered several types of non-planar geometries and presented our results in 18 peer reviewed publication, some of the most important of which are:

- a) Spherical geometry: We demonstrated inadequacy of the mechanical route to the surface tension for spherical (curved, in general) interfaces (although frequently used in molecular dynamics simulation studies) neglecting the important influence of fluctuations. While the mechanical route predicts a monotonous decrease of the surface tension with curvature corresponding to positive Tolman's length our results based on new molecular dynamics and density functional theory suggest non-monotonic behavior of the surface tension with a corresponding weak maximum and a negative Tolman's length. A review paper on interfacial phenomena of spherically curved substrates was published.
- b) Wedge geometry: We have shown that wedge geometry induces filling transition the order of which may be different to that of the wetting transition for the same material. In particular, we proposed a way by which a critical surface phase transition, a very rare phenomenon for surface phenomena, can be observed in a laboratory.
- c) Edge geometry: For edge geometries (e.g. concave corners) we have shown that complete wetting near the apex is suppressed for all temperatures., i.e., that the thickness of the adsorbed fluid at the apex is always finite. We predicted the power law according to which the adsorbed fluid thickness increases with the chemical potential difference from its saturation value and showed that this behavior is strongly non-universal.
- d) Groove geometry: We found that the order of condensation in a single deep grooves sensitively depends on temperature, such that below the wetting temperature (on a planar wall of the corresponding material) the transition is first-order and continuous below. In contrast, the groove evaporation is always continuous and we explained this asymmetry by a dimensional analysis. In addition we showed that for the evaporation transition there is "hidden symmetry" with the complete wetting transition occurring at a planar wall.

Supporting projects and Students involved

Czech Science Foundation, projects No. 13-09914S and 13-02938S. One bachelor thesis had been defended on this topic.

Key References

Malijevský A. and Parry A. O. (2013) *Phys. Rev. Lett.* 110, 166101. Sampayo J. G. et al. (2010) *J. Chem. Phys.* 132, 141101. Parry A., Malijevský A. and Rascon C. (2014) *Phys. Rev. Lett.* 113, 146101. Malijevský A. and Jackson G. (2012) *J. Phys.: Condens. Matter* 24, 464121. Malijevský A. (2013) *J. Phys.: Condens. Matter* 25, 445006. Malijevský A. (2012) *J. Chem. Phys.* 137, 214704. Malijevský A. (2014) *J. Chem. Phys.* 141, 184703. Malijevský A. (2014) *J. Phys.: Condens. Matter* 25, 315002.

Topic 8: Molecular-Level Modeling of Aqueous Electrolytes Thermodynamics: Advanced Simulation Methodologies and Applications

Aqueous electrolytes are ubiquitous in environmental, biological, and industrial systems. In addition to experimental data on their properties it has become common nowadays to study and predict their behavior by molecular simulations using various force fields (FF). Typically, infinite dilution electrolyte chemical potentials and the density have been used to determine the FFs parameters. Parameters of different FFs may differ by orders of magnitude pointing to principle deficiencies of the models. Furthermore, attempts to predict chemical potentials at finite concentrations, one of the most important properties of solutions, have been rare for one simple reason: such calculations are both very computationally intensive and technically challenging. Methodologies for chemical potential calculations of electrolytes include a number of different more or less sophisticated methodologies and published solubility results from different research groups for two simple non-polarizable NaCl force fields (FF) compatible with the SPC/E water FF exhibit significant disagreement. Finally, there has been gathered enough evidence that the pairwise models have exhausted their potential and non-additive effects, typically via polarization, must be accounted for.

Description of results

In order to overcome the above mentioned problems, obstacles, and disagreements, we have systematically studied aqueous NaCl electrolytes focusing on performance of available FFs, predictions of solubility, simulation methodologies, and efficient evaluation of other various thermodynamic properties for both non-polarizable and polarizable models with solubility as the most important property. This research was conducted partly within a bilateral CR-USA cooperation project with Dr. Chialvo's group of the Oak Ridge Natl. Lab., and with a close collaboration with Prof. W. R. Smith from University of Ontario, Institute of Technology.

We have developed (i) a Multi-Particle-Move MC (MPM-MC) method which makes it possible to efficiently use the MC methodology even for polarizable models, and (ii) the osmotic ensemble (OEMC) method making it possible to determine the solubility at one MC run. Both techniques have been used in all our simulations and the results were published in 12 papers within the years 2010-2014.

Students involved: Three PhD thesis had been defended on this topic.

Key References

Moucka F., Nezbeda I.: *Mol. Simul.*, 36, 526-534 (2010). Moucka F. et al. *J. Phys. Chem. B*, 115, 7849-7861 (2011). Moucka F. et al.: *J. Chem. Phys.*, 138, 154102-9 (2013). Moucka F. et al.: *Mol. Simul.*, 39, 1125-1134 (2013). Moucka F. et al.: *J. Chem. Theory Comput.*, 9, 5076-5085 (2013). Moucka F. et al.: *J. Chem. Phys.*, 139, 124505-7 (2013). Moucka F., Nezbeda I.: *Fluid Phase Equil.*, 360, 472-476 (2013). Jirsak J. et al.: *Mol. Phys.* 113, 848-853 (2015). Vlcek L. et al.: *J. Phys. Chem. A*, 119, 488-500 (2015). Smith W. R. et al.: *J. Chem. Theory Comput.*, in press. Chialvo A. et al.: *J. Phys. Chem. B*, in press. Smith W. R. et al.: *Fluid Phase Equil.*, in press.

Topic 9: Multiscale Simulations of Polymeric and Energetic Materials

In principle, materials properties of polymeric and energetic materials can be modeled using atomistic simulations. However, for the system size and time scales in hand, the demands of such calculations on even the most sophisticated modern

computers becomes overwhelming. Hence, true multiscale approaches are needed for efficiently representing the polymeric and energetic systems, considering that the formation and reorganization can take place at different time and length scales. In the framework of multiscale modeling, one typically simulates the system at mesoscale using methods such as dissipative particle dynamics. The necessary information in terms of physical interactions among 'super atoms' or 'beads' is given by smaller scale simulations. The development of virtual models based on a multiscale modeling vision and the application of such models for understanding of behavior of the polymeric and energetic systems complements experimental research.

Description of results and share of the team

The series of papers on this topic can be divided into three parts. In the first part we have evaluated behavior of polymeric self-assembled systems in bulk and confinement. In bulk, we predicted the nanostructure of diblock copolymers and hybrid systems based on diblock copolymers and nanoparticles decorated with ligands. We derived phase diagrams as a function of polymer architecture, nanoparticle concentration and ligand decoration. In confinement, we studied nanostructure formation of symmetric and asymmetric diblock copolymers confined between planar surfaces. The nanostructure formation was investigated and characterized by varying the separation width and the strength of the interaction between the surfaces and the diblock copolymers.

In the second part, we have developed a suite of computational tools for particle-based mesoscale simulations of the non-equilibrium dynamics of energetic solids, including mechanical deformation, phase transitions, and chemical reactivity triggered by shock or thermal loading. The method was build upon our advances both in generating coarse-grain models under high strains and in developing a variant of DPD that includes chemical reactions.

In the third part, we described the general features and trends of the electrostatic assembly of block polyelectrolytes by performing DPD simulations of the associative behavior of aqueous mixtures of diblock copolymers containing one neutral water-soluble block and one either positively or negatively charged polyelectrolyte block. While the neutral block was readily soluble in water, the hydrophilic vs. hydrophobic nature of the neutral backbone of the polyelectrolyte block and the compatibility of the blocks varied in a broad range. We investigated the role of (i) electrostatics, (ii) solvophobicity of the polyelectrolyte block, (iii) compatibility of the polymer blocks, and also (iv) compatibility of small ions with the polymer blocks.

Supporting projects and Students involved

Projects of Czech Science Foundation and joint projects under collaborative agreement between US ARL. Two PhD thesis had been defended on this topic.

Key References:

Petrus et al., *Langmuir* 26, 3695, 2010. Petrus et al., *Langmuir* 26, 14680, 2010. Posocco et al., *J. Mat. Chem.* 20, 10511, 2010. Lísal et al., *J. Chem. Phys.* 135, 204105, 2011. Sirk et al., *J. Chem. Phys.* 136, 134903, 2012. Posel et al., *Soft Matter* 9, 2936, 2013. Posel et al., *Macromolecules* 47, 2503, 2014. Larentzos et al., *Comp. Phys. Commun.* 185, 1987, 2014. Brennan et al., *J. Phys. Chem. Lett.* 5, 2144, 2014. Šindelka et al., *Macromolecules* 47, 612, 2014. Posel et al., *Mol. Sim.* 40, 1274, 2014. Hart et al., *J. Chem. Phys.* 141, 204902, 2014.

Topic 10: Molecular Simulations of Solid-Liquid Interface

Solid-liquid interfaces play a key role in the adsorption of ions and molecules from liquid solutions onto solid surfaces, be it metal surfaces, metal-oxides or metal-hydroxides, functionalized surfaces formed by substrate and task-designed coatings. Among the various applications one can list sensors detecting molecules adsorbed on the surface, water and soil decontamination (pumping aqueous solutions of particles onto which e.g. heavy metals adsorb), distribution of nutrients in the environment, paint industry, anti-oxidation, self-cleaning and other types of functionalized coatings. The solid-liquid interface is also essential in heterogeneous catalysis, geochemistry, understanding the dissolution of minerals, ores (typically mixture of metal-oxides and metal-hydroxides), clays, etc. There is growing interest in chemical reactions in confinement, which produces conditions unparalleled in bulk simulations and can result in significantly increased reaction yields. Obviously, the solid-liquid interactions between the confining surfaces and the reacting fluid are crucial for the thermodynamics of the confined system. Nano-encapsulation biotechnology is another example of a system where the interactions of aqueous solutions (including organic molecules and biomolecules) with inorganic solid supports play an important role.

Description of results and share of the team

In the publication 2010 we have completed our work on studying the structure in contact with spherical or planar surface studied on the level of both primitive and standard models of water. The course-grained interaction potential for interactions with large spherical particles was derived and applied.

The next papers (2012, 2014) form the key results of Ph.D. student Stanislav Pařez and his supervisor Milan Předota. Equations for determination of distance-dependent viscosity of solutions in contact with planar surface were investigated including interesting case of highly non-ideal water-alcohol mixtures. The results are important for understanding if (and how accurately) the experimental known bulk viscosity data are applicable to the nanoworld. Having resolved this issue, our quest for the understanding of the electric double-layer properties led to our study of the dielectric response of the interface, once again exploring the distance-dependence of studied phenomena. We have identified the sources of differences of dielectric behavior of nearest interfacial layers (density, rotational mobility, hydrogen bonding) as detailed in the publication. We have also observed the over-compensation of external electric field, which is not possible in bulk systems, as it would lead to negative permittivity. The conclusions were also linked to theoretical models of solid-liquid interfaces within the MultiSite Complexations models (MUSIC) in collaboration with M. Machesky from University of Illinois, USA.

Supporting projects and Students involved

Project of the Czech Science Foundation No. 203/08/0094. One Ph.D thesis and one master thesis have been defended on this topic.

Key References:

M. Předota, I. Nezbeda, and S. Pařez:, *Collect. Czech. Chem. Commun.* 75, 527-545 (2010).
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Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Department of Catalysis and Reaction Engineering

2.1. Brief summary

During the inspected period of 2010-2014 the research at the Department of Catalysis and Reaction Engineering was carried out in the priority areas of catalysis, reaction engineering, surface science, materials engineering, chemical and environmental technologies, process development, and other related fields. The main expertise had covered all major aspects of homogenous and heterogeneous catalysis, materials` science with special focus on texture and morphology studies, transport phenomena, environmental processes, mathematical modelling, nanotechnology and biotechnology. It is evident the research activities were very diverse and broad.

The Department profits of its international recognition based on long-term scientific contacts, intensive publication activities, high rate of success in reaching the grant funding, and close links to the Czech and also abroad industry. During the recent years the Department`s profile has significantly changed due to the increased number of PhD students and young researchers. It can be accentuated that the organization structure of the Department is optimized to promote the internal collaboration, to increase chances in fund-raising and to promote the level of scientific education and skills of young researchers and PhD persons. The Department activities can be clearly visible in the numbers of projects which have been solved within last five years; 4 EU projects, 1 NATO project, 8 eight collaborative international projects supported by Ministry of Education, 15 grants supported by Grant agency of the Czech republic, and 1 by Academy of Sciences of the Czech Republic, 8 projects supported by Technology Agency of the Czech Republic including a Centre of Competence focused on Biotechnology and 4 another technology related projects supported by Ministry of industry. It is necessary to emphasize the project numbers had tremendously increased in comparison with the period 2005-2009. Moreover, the Department had also carried out the contract-research for variety of Czech and international companies.

An essential part of the Department is the Centre for Textural Studies (CTS), which was founded in the early 80th in 20th century as the part of the Department of Catalysis and Reaction Engineering. CTS has long-standing experiences with characterization of porous materials and study of transport processes in pores. CTS has a unique position in the field of textural studies in the Czech Republic and it is well-known not only in CR but also in abroad and it serves as an expert in this research field. CTS had been involved in many projects (Horizon, RFCR, CSF, and TACR) and solved research problems for industrial partners based on many bilateral agreements. CTS also provided texture and transport analyses of any materials on contracts. About 80 % of the user community belonged to the external users and 30 % were within the international collaboration.

Obviously, it is not a simple task to characterize briefly the main research achievements at the Department during the inspected period 2010-2014. In summary more than 200 scientific achievements could be tracked in the form of research papers, books and book chapters, patents, industrial approved technologies, and best

available technologies. It must be emphasized that the performed research included also some very fundamental scientific topics, such as principles of molecular templating in the preparation of organized particles, the research of synthesis, thermodynamics, and structural prediction of ionic liquids, and the development of advanced nanostructured photonic electrodes for sensor purposes. In parallel special attention was paid to the environment related processes, mostly focusing on the treatment of water pollution. In this context photochemical oxidation processes with titanium dioxide, with various types of photosensitive phthalocyanines, or with hydrogen peroxide and UVC had been developed from the bench laboratory level up to the half-scale or even up to the industrial full scale. The special focus on the evaluation of production parameters for various types of dyes and pigments must not be also omitted. Some of the special systems were then applied in the industrial development of time sensitive photonic sensors for medical use. It is necessary also stressed a new research area focuses on biotechnology.

2.2. Main research areas

2.2.1. Catalysis

Besides the very many research areas mentioned above, the principle Department's activity is nearly always associated in some way with catalysis and/or reaction engineering, catalysts/materials research, and the design, development and construction of various types of reactors. Obviously the catalyst's and the reactor's design are always intimately linked. No doubts catalysis is a key principle for selective transformations in the industrial-scale manufacture of specialty chemicals, and this part had been one of the major focuses in the department catalytic research during the inspected period. Attention was paid to the parameter of selectivity of a particular hydrogenation catalyst, specifically of the Ru/BINAP complexes, driving the model reactions in the stereo selective course. The stereo selective hydrogenation is the formation of an excess of one stereoisomer over others. Stereo selectivity is subdivided into enantioselectivity and diastereoselectivity according to the formation of enantiomers or diastereomers. In fact, industrial applications of ruthenium as catalyst are limited to only some specific reactions, in which it holds, however, a firm position. Selective hydrogenation of unsaturated aldehydes to unsaturated alcohols is an important step in production various "large scale" fine chemicals. The effectiveness of Ru in such transformations can be enhanced by combining it with other metals, with suitable catalyst modifiers or by using various supports. Geometric effects of adsorbed species, particle size, SMSI (strong metal-support interactions) and some other factors may further increase the selectivity of the reaction toward unsaturated alcohols. A very strong position of the department in the field of selective catalytic reactions over Ru catalysts must be emphasized similarly as the innovative catalysts with high content of Pt developed within EU IMMEDIATE project for application in automotive industry.

There had been already a tradition of the synthetic mesoporous silica-aluminas (MSA). These structures had been systematically studied as supports of Pt, Pd and Pd/Pt catalysts for hydrodesulphurization (HDS). Part of Pd phase accumulated hydrogen in the form of β -Pd hydride, which amounts correlated with HDS.

In the catalysis area there had been also a substantial research work was focused on the development of heterogeneous catalysts for the oxidation of volatile organic compounds. First ceria-zirconia mixed oxide prepared by sol-gel method was used as a support for platinum and gold catalysts. The catalysts were thoroughly characterized and tested in the oxidation of ethanol, toluene, dichloromethane, and

chlorobenzene. It was shown that a compromise between acidity, reducibility, and resistance to poisoning is needed to obtain an efficient catalyst, which has to be tailored for a given pollutant. Besides the work that was done with ceria-zirconia mixed oxide, polymeric electrospun nanofibres were also employed as innovative catalyst supports. Monometallic palladium and platinum catalysts supported on poly(2,6-dimethyl-1,4-phenylene) oxide electrospun mats were prepared, characterized and tested in the complete oxidation of methane. It was shown for the first time that polymeric electrospun nanofibre mats represented an efficient catalyst support for VOC oxidation noble metal catalysts and might have been utilized in the preparation of novel catalysts with very low mass transfer resistance resulting in a low pressure drop. Finally, commercial catalysts for the oxidation of volatile organic compounds were studied as comparative materials during the development of new catalysts.

Another catalytic research dealt with mesoporous silicas such as SBA-15. At first, new technique of synthesis of mesoporous silica with protonated amino groups avoiding microwave treatment of mesophase was developed using a template method. The preparation of supports and catalysts was studied, especially the oxide catalysts on ceramic (alumina, alumina-ceria, cordierite) and metal (aluminum, stainless steel) supports. The prepared catalysts were characterized by various methods and employed in the total oxidation of VOC.

2.2.2. Environmental processes

As already mentioned the activities were also strongly directed towards the photochemical and photocatalytic environmental processes. The research had been devoted to thorough investigation of a series of specially designed methods for decontamination of polluted industrial and waste waters including preparation of active photocatalytic and catalytic materials, design of effective reactors, principal analytical evaluation of reaction products and intermediates and mathematical modelling of the involved physical and chemical processes. Besides the main topics the research involved nanotechnology preparation of uniform and highly active photocatalytic species, preparation and utilization of photosensitive and catalytically active synthetic porphyrines, a rational reactor design with a special focus on the established functionality of the produced catalysts and oxidation species toward decomposition of a wide range of pollutants of water. The fundamental novelty of this research involved the integrated oxidation and / or (photo)catalytic devices housing the highly effective nanostructures or organometallics for selective decontamination of water from particular pollutants. Another task was to describe the involved processes mathematically and to generalize the obtained results. There had been several parallel and consecutive projects during the 2010-2014 aiming for the realization of sophisticated decontamination devices based on photocatalytic and catalytic properties of selectively prepared nanostructures and porphyrinoic organometals in combination with specific physical conditions, and designed in a complex way together with the reactor systems. These integrated devices nearly always revealed enhanced performance in comparison with reported standards by taking advantage of the novel properties and transferring principles resulting e.g. from the application of nanotechnology. Of special interest were photoactive metal oxide nanoparticles, especially TiO_2 -transition-metal oxide and phthalocyanines - macrocyclic porphyrinoic compounds, which revealed unusual molecular stability caused by the ideal conjugation of double bonds and the symmetrically coordinated central atom in the aromatic skeleton, and also, what was in the context of this project important, virtually zero toxicity. Some phthalocyanines are capable to generate an active species upon

visible light absorption. These photo-induced events may occur due to the ability to excite ground-state molecular oxygen ($^3\text{O}_2$) to highly active singlet oxygen ($^1\text{O}_2$), an extremely effective agent for complete oxidation of common pollutants of water including e.g. chlorinated phenols.

Besides the oxidation based technologies an important part of our effort in this field had been spent to the electrocoagulation and to sorption processes. Electrocoagulation is a method that utilizes electrochemical dissolution of electrode and simultaneous creation of small hydroxide particles (coagulants) in solutions. These small particles aggregate to larger particles (flocks) which can be described as highly porous aggregates created from many smaller particles. Flocks comprise oxides, hydroxides and oxohydroxides that have high absorption capacity and their high surface area enable pollutant adsorption. Therefore, electrocoagulation was used for a wide range of pollutants removal.

Sorption methods are applicable for variety of contaminants, e.g. heavy metals as well as phenolic compounds which can be found in waste water generated from petroleum and petrochemical, pharmaceutical, plastic, rubber proofing, similarly as steel and phenol production industries. As sorbents usually active carbons, zeolites or special soils are applied.

The combined thermal desorption and catalytic oxidation for soil decontamination supported by several grants, which was studied not only at laboratory but also at the pilot plant scale, must be also emphasized. The influence of strong oxidant addition on consequent catalytic oxidation or alternatively applied biodegradation of condensates was successfully tested. Numerous unique species attributable to 2-methylnaphthalene oxidation together with products of motor oil oxidation and benzoyl peroxide destruction were identified in condensed vapors, whereas oxidation products of xylene were not detected. The application of benzoyl peroxide significantly accelerated biodegradation of condensates by *Pseudomonas* sp. Moreover, it was confirmed that the presence of partial oxidation products in the condensates did not increase their eco-toxicity.

Another topic focused the study of migration rates of representative contaminants through porous environment of any source of contaminant leakage. The so-called geo-reactors in gaseous and liquid phase were modelled on the basis of practical studies, and on results from many pilot experiments. Effects of pore size, porosity, tortuosity, and reaction conditions on the migration rate were individually evaluated and taken into account. The contamination risk for aquifers and potential leakage of poisonous gases on environment impact were thoroughly discussed and assessed.

2.2.3. Nanotechnology

Attention must be also paid to the department's substantial position as one of the national leading center of the nanotechnology research, achieved during the inspected period of 2010-2014. To emulate at least some of the effectiveness of nature in making functional systems, including those useful for environment protection, it has had developed many different concepts. Currently such attempts are reflected in the steep growth of interest e.g. in nanoscience and nanotechnologies, in utilization of the bio-mimetic approach, in biotechnologies or in a complete re-design of traditional systems. Apparently there has been a significant gap between constantly growing fundamental scientific progress, e.g. in the field of photoactive nanostructures, and practical demands of the environment protection. The new approaches are expected to reveal a strong impact on environmental protection, effective energy storage, green

energy production, etc. Independently of types of new concepts, one of the most important points concerns chemical (or physical) pathways that are capable to provide them. Another point is the incorporation of these concepts into complex functional systems, such as energy generators with high capacity storage units, advanced detoxification and decontamination reactor units, complex solar cells, etc. The corresponding projects focused on generation of multicomponent functional systems with an inherent electrochemical or photocatalytic end-function originating in partial functionalities of the well-defined components. Each of the constituents contributed either with its structure or function or both to fulfil the mission of the target material. The controlled overall functionality required these basic structures to be perfectly predefined, already by means of special physical and chemical methods used for their preparation. In this respect bottom-up nanotechnology approaches involving molecular templates were widely used. Special attention was paid to the self-assembly process for yielding aggregates of various structurally different room temperature ionic liquids (ILs), and/or surfactants. These ILs here used as templating microemulsions in ternary systems with other components were partially synthesized and characterized at the department. Their coexistence with assemblies of ionic surfactants to form multicomponent templating superclusters was also surveyed. This strategy, together with special physical methods mostly based on utilization of active plasma, was understood as the basis for generating functional nanoparticulate constituents of the hierarchical functional structures. Such systems were used as highly useful parts of dye sensitized solar cells, new generation lithium batteries and advanced optical and optoelectrical sensors. The final materials were designed, produced and tested for their expected function with the assistance of advanced computational chemistry methodologies.

2.2.4. Biotechnologies

A systematic solution of utilization of renewable material and energy provided by natural ecosystems based on the application of the chemical engineering principles has been newly started. This research area respects rational concept of sustainable development and besides new scientific knowledge contributes to acquisition of the alternative products with high added value based on the so-called Green chemistry. This new scientific field found platform in the project BIORAF – a competence centre supported by Technology Agency of CR, where ICPF is being coordinator. This project employs the techniques of green chemistry for biomass utilization to the high added-value products and energy sources. By refining, it is possible to obtain food supplements, fodders and fertilizers, new-generation biofuels and energy from the biomass of microbial, plant or animal origin. Sustainable biomass resources, which don't compete with food crops in the use of agricultural land, as microalgae, plants or the waste materials from animal husbandry were utilized.

New technology including proteins hydrolysis of chicken cartilage and feathers carried out at increased temperature and pressure in the presence of carbon dioxide must be emphasized. The resulting aqueous solution of amino acids contained in the same representation as peptides forming collagen and keratin of raw material. This product is perspective for various applications, first, for dampening the composted agricultural waste, next could be useful as nutritional additives to livestock feed and finally as a nutrient supporting growing algae for biotechnology applications. Therefore, cultivation of microalgae in novel high-rate photobioreactors using waste streams as nutrients, novel low-energy cell harvesting techniques and lipids extraction directly from wet biomass coupled with advanced high-yield enzymatic transesterification of

algal oil into biodiesel belongs to another solved task. Another solved issue concerning technology of Jerusalem artichoke treatment to inulin production in the form of powder or fructose or inulin syrup for diabetics and sportsmen mustn't be also omitted.

2.2.5. Mathematical modelling

Neither of the discussed research directions could be, in principle, successfully approached and solved without at least partial involvement of mathematical modelling. The design of hierarchical nanostructures with physical and chemical functionality requires an understanding of the molecular interactions leading to these structures. Computational methods both classical and hybrid quantum methods were used with this purpose. Nowadays many idealized surface structures, templating principles, and some functionalities are reasonably predictable. Feasibility of each preparation and assembly step might be assessed theoretically first with a high degree of precision. It should be emphasized that in case of nanomaterials and superior systems built up of components inspired by Nature the departure from reality is not so significant. This is an exquisite property of artificially made nanostructures and of the compiled artefacts and it can hardly be found anywhere else. The computational models will be used to "design" templates aimed to optimize certain variables, e.g., enhanced diffusion of the molecules in the self-assembled structure may require a specific topology for the network. This work can be very efficiently done with the computational models and will guide experimental efforts in the design of optimal hierarchical structures. Classical methods (Reverse Monte Carlo, Molecular Dynamics) were employed to obtain computational models of self-assembled structures with uses as nanoreactors. The input needed for the model (neutron X-ray diffraction, microscopies, etc.) were provided experimentally. The models were used to characterize the internal architecture of the self-assembled structures. The interactions and microscopic behavior of molecules inside the self-assembled structures can be studied in detail using hybrid quantum-molecular dynamics methods. Full advantage of these technologies was taken to create a database of hierarchical nanostructures targeting different variables, e.g., specific topology, specific molecule-substrate interaction energy. One main outcome of the effort within the computational approaches was the assessment of the feasibility of specific self-assembly steps, the estimation of properties difficult to measure experimentally and the prediction of new materials with specific functionality.

Another interesting computational area covered the application of the methodologies (generalized population analysis and the analysis of domain averaged Fermi holes) for the analysis and elucidation of the structure of molecules with nontrivial bonding pattern. These methodologies attracted the interest of a number of colleagues and experts in the field. The data mostly resulted from the wide international collaboration with these colleagues on the various problems ranging from the analysis of metal-metal and multicenter bonding in multi-nuclear transition metal complexes to the extension of the above methodologies for the description of the bonding in infinite periodical structures (solids).

2.3. International and industrial cooperation

The research teams at the Department of Catalysis and Reaction Engineering extensively cooperated on the international level in the fields relevant to department's activities: catalysis, reactors design, preparation of functional materials, synthesis of uniform nanoparticles, mathematical modelling of nanoparticles, photoprocesses, photonic devices, electrochemical characterization and utilization of new conductive

and semiconductive materials, adsorption properties of various solids, synthetic organometals, utilization of active plasma, analytical environmental chemistry, remediation strategies, risk assessment etc.

The major cooperating institutions were Department of Chemistry, University of Wales in Bangor (electrochemistry), Queen`s College Belfast (ionic liquids), European Institute of Membranes, CNRS and University of Montpellier (templating principles), University of Szeged, Hungary (synthesis of phthalocyanines), University of Oulu, Finland (texture studies), Université Catholique de Louvain, Belgium (catalytic tests of dichloromethane and chlorobenzene oxidation), Institute of Surface Chemistry, NAS of Ukraine, Swedish University of Agricultural Sciences in Uppsala (catalytic research), Institute of Catalysis of Bulgarian Academy of Sciences (VOC oxidation), University of Padua, Italy (ion exchange catalysis), University of Udine, Italy (reactions and catalysis engineering), Istanbul Technical University, Department of Chemistry and Polymer Science and Technology, Turkey (texture and morphology surface properties), The University of Poitiers, Department of chemistry, France (thin semiconductor oxide films preparation and their characterization).

There had been also many important industrial partners and collaborators participating on the technology research. Among others Dekonta (photocatalytic and photooxidation processes, electrocoagulation), Invos (smart optical sensors), Teluria (new dyes), Synthesia (production of pigments), Abbott Laboratories, GmbH (solving of technology problems concerning pancreating production), LASAK (dental replacement), COC Ltd. (optical sensors and phthalocyanines), Elentec and First Elements (electrocoagulation), Rabbit, Brikli, Ecofuel and Agra (biotechnological processes) should be mentioned.

2.4. Concluding remarks

- Deep research commitment clearly evidenced by a number of papers coming from the Department every year, and published in prestigious field journals.
- Involvement of young researchers (from the Czech Republic and abroad) and their participation on a wide range of projects. The rate of success of the PhD persons in completion of their doctoral theses at the Department is more than 80 %. The PhD are mentally accepted as full team members, the positive atmosphere of the Department toward young colleagues is generally recognized.
- Recently optimized structure of the Department toward better internal communication, effective fund raising, wider research scope and education of PhDs and pre-graduated students, Master and Bachelor degrees.
- Close links with many industrial companies from the Czech Republic and abroad together with significant involvement in application research.
- Extensive international cooperation. During the recent years the Czech as well as international industrial and private-sector partners had started to approach the Department frequently seeking for the applied research partnership, collaboration, common project applications, etc. It is a real challenge to the Department members and it is believed this trend will still reveal an increasing tendency in future. It is also noteworthy that quite a few new international partners have appeared in the recent years, not bringing their idea, but willing to take part on cultivation of the ICPF topics and inventions.

Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Department of Multiphase Reactors

Our basic research has been focused on the behavior of multiphase dispersed systems, namely on the transport of mass and momentum. Our goal is to understand the key underlying mechanisms governing their behavior.

In particular, we study gas-liquid, gas-liquid-solid, liquid-solid and gas-solid systems. These basic studies have the following specific applications: aerated and sparged vessels, bubbly flows and bubble layers, foams and foaming, flotation columns, three-phase (bio)reactors and contactors, sedimenting tanks, powders and granular media - flow and rheology.

We apply the multi-scale approach: (i) large scales (e.g. hydrodynamics of bubble columns, flow regimes and stability, mass transfer, beer over-foaming, bubble production and rise in lakes), (ii) small scales (e.g. bubble formation, rise, oscillations, coalescence and breakup, bubble-solids interaction in flotation, bubble motion in non-circular micro-channels), (iii) intermediate scales (bubble-bubble interactions, hydrodynamics of unsteady flow in channel expansions, bubble motion in flat channels).

We use three complementary ways for our investigations: (i) experimental measurements, (ii) theoretical modelling (physically based simplified models) and time series analysis (non-linear dynamics), (iii) numerical simulations (Computational Fluid Dynamics - Fluent, CFX; DEM for granular materials).

For experimental evaluation of the multi-phase flow characteristics, we use the visualization methods (PIV, micro-PIV, hot-film/wire anemometry, high-speed cameras) and electrodiffusion diagnosis (characterization of wall-turbulence, flow recirculation zones or measuring the shear stress on the wall), coupled with the rheology testing of both liquid systems (complex fluids, micro-dispersions) and granular media (flowability, internal friction, cohesion), supplemented with surface tension measurements (static, dynamic) to study interfacial phenomena due to the presence of surfactants. Hydrophones are used for hydro-acoustics essays.

The results achieved in evaluated period could be arranged e.g. in the following way (with collaborations, the activity of the other teams are indicated and specified).

I. Large scales

A simple theoretical model for the bubble column hydrodynamics was formulated through the mass balance of the gas phase with two closures for the hindrance and enhance effects. The model is account for steady states, stability, and unsteady behavior of bubble column.

CFD simulations and experiments of the hydrodynamics in two-phase gas-liquid flow in an internal loop airlift reactor with three different riser tubes were performed. They were aimed at obtaining the global flow characteristics: gas holdup and liquid interstitial velocity in the riser/downcomer. We tested whether the CFD with the standard closures for the interphase forces and turbulence was able to capture the flow features, with constant size bubbles. Also was tested the sensitivity of the simulation results to different closures for the drag and turbulence models. The agreement

between simulations and measurements were good, unless the gas holdup in the downcomer was not too large. Generally, the use of different multiphase models or different codes (Fluent, CFX) gave very similar results. This work was done jointly with the Centre of Biological Engineering, University of Minho, Portugal (experiments with the airlift).

A novel concept was designed for CFD calculation of the fluid age distribution (RTD) within the interior of a flow system or an apparatus with multiphase mixtures. In contrast to the standard RTD approach, the fluid age was considered as the field quantity and the governing equation was formulated for its spatio-temporal distribution within the flow domain. Numerically calculated results (Fluent) were compared with experimental data measured jointly at the Univ. of Minho.

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II. Small scales

Unsteady phenomena in the gas-liquid systems were studied at the micro/meso-scale both numerically and experimentally. Numerical approach was applied to studies of the added mass effects of spherical, ellipsoidal and spherical cap particles in different flow situations, because it is problematic to obtain this information experimentally or analytically. Several geometrical configurations and type of interface (rigid/deformable) were considered, which are physically relevant. The easy-to-use correlations were obtained for the added mass coefficient of e.g. particles near a gas/liquid interface, particle pairs and particle arrays.

Experimental studies were carried out on the bubble formation process on a perforated plate. The particular focus was on the behavior of the gas-liquid interface (meniscus) inside a transparent orifice, to reveal the role the oscillating meniscus plays in coupling between the gas and liquid phases. Further, a parametric study was performed, where the effect of several key operational parameters on the meniscus dynamics was identified (orifice size, plate thickness, gas chamber volume, liquid viscosity), how they alter the bubbling period, the size and uniformity of the produced bubbles.

A joint study with Dept. of Chemistry at the Technical University of Ostrava (Czech) was focused on single wobbling bubble with unsteady shape and rise path. It was experimentally studied in Ostrava in downward conically diverging flow of low and moderate viscous liquids selected using dimensional similarity with bubbles in liquid steel. Bubble shape, position and motion were reconstructed by means of two plane projection obtained by high speed camera from our group. Dimensional analysis was used to formulate a simple correlation of bubble rising velocity separating the effects of viscosity and surface tension and we contributed meaningfully to interpretation of results.

Study of the attachment of bubbles onto a collecting surface plays a critical role in flotation which is utilized for the separation of mineral ores, coal or plastic materials. Our studies motivated by the possibility of separation of plastic particles of different types from mixtures. Here (unlike mineral flotation) we have the interaction between small bubbles and larger particles. These bubble-particle interactions were investigated in a model laboratory system, where the collision dynamics was studied both experimentally and theoretically. The theoretical model was based on detailed

formulation of the forces acting on the bubble with either mobile or immobile surface. The model predictions agreed well with the experimental bubble trajectories and velocities.

The measurement accuracy of a mono-fiber optical probe for gas-liquid flows was studied experimentally in our lab, in collaboration with our partners from LEGI, Grenoble, France who had the know-how on fabricating these optical sensors. Isolated bubbles were issued from the 'bubble generator', rose freely in a still liquid, and were pierced by the optical fiber. The dwell time of the probe tip within the gas phase was obtained from both the optical probe signal and high-speed visualization. This time was compared with the 'ideal value' expected for an undisturbed bubble. The mean dwell time (averaged over piercing locations) was lower than should be, whence the local void fraction indicated by the probe was underestimated. The void fraction error was correlated with a modified Weber number, giving a helpful uncertainty estimate.

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III. Small scales with surfactants

Selective flotation of plastics lead to the study of an idealized situation of a bubble interacting with an immersed horizontal solid surface in presence of non-ionic surfactants. The surfactants significantly affected the bouncing process. The initial bubble velocity was decreased, the bubble deformation after the collision was reduced, and the bubble rebound from the surface was suppressed. The adhesion time varied with increasing the surfactant concentration, depending on the surface material.

The attenuation of the bubble oscillations caused by the surfactants led to other fundamental studies on linear shape oscillations of a spherical bubble or drop in a pure liquid, for which a part of its interface was fixed due to contact with a solid support (orifice rim). This was studied analytically using variational methods in the frame of the irrotational flow. This analysis was also able to determine the response of the fluid particles (bubbles or drops) to movements imposed on their supports, or to variations of their volumes. The analysis leads to the equations of motion with a simple structure, from which the eigenmodes and frequency response to the periodic forcing were determined. The theory was compared with experiments. Good agreement was found for small bubbles, with spherical static shape. Experimental results for larger bubbles and drops deviate from the theory, if a neck is formed. It was shown that this deviation correlates well with the ratio of bubble volume to the maximum volume, when a detachment occurs.

Further, inertial shape oscillations of oil drops rising in water were investigated experimentally in our lab with colleagues from the Institute of Fluid Mechanics, Toulouse, France. The effect of a small surfactant contamination was tested. The drag coefficient was considerably increased compared to that of a clean drop due to Marangoni effect. Thanks to the decomposition of the shape into spherical harmonics, the eigenfrequencies and the damping rates of first four oscillations was measured. Frequencies were not affected by contamination, while damping rates was increased by a considerable amount that depended neither on drop instantaneous velocity nor on diameter. Because previous similar investigation of a drop attached to a capillary

has not revealed such an increase of the damping rates, the coupling between the rising motion and surface contamination was made responsible for this effect. All authors attributed significantly to interpretation of result and final manuscript.

Because surface-active agents strongly modifies properties of gas-liquid interface, we carried out extensive experiments, in which we studied the effect of the common surfactants (terpineol, SDS, CTAB, Triton X-100, Triton X-45) on the shape oscillations of a bubble, which was attached at a tip of a capillary. It was observed that surfactant addition leads to an increase of the oscillation frequency (though surface tension is decreasing), which effect can be attributed to increasing the interfacial elasticity. The decay time of oscillation was strongly decreasing, as a consequence of energy dissipation linked with Marangoni stresses. At a certain critical concentration, frequency decreased abruptly and the decay time passed through a minimum. With further addition of surfactant, frequency decreased, and the decay time slightly lengthened. Above the critical micelle concentration, all these parameters stabilize. Interestingly, the critical concentration, at which frequency drop occurs, depends on the oscillation mode order. This clearly shows that the frequency drop and minimum decay time are not a consequence of some abrupt change of interfacial properties, but are a consequence of some phenomena, which still need to be explained. All above mentioned studies was studied experimentally using unique device (called "bubble generator") developed in our group.

Over-foaming of beer is manifestation of fungal contamination of raw materials used in their production. Fungi produce small, powerful, surface-active hydrophobic proteins which participate in stabilization of small carbon dioxide bubbles in bottled or canned beer. We focused on research in the field physical and chemical basis of over-foaming (dynamics of rapid nucleation, influence of mixture composition). In the frame of this joint research with Dept. of Fermentation Chemistry and Bioengineering, UCT Prague, a novel apparatus for gushing analysis in carbonated beverages was created and utility model was granted for this device.

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IV. Intermediate/Small scales explored with use of electrodiffusion diagnostics

Theoretical development on voltage-step transient problem, useful in Electrodiffusion Diagnostics (ED) of the near-to-wall flow diagnostic, was resolved for microdispersion liquids that manifest non-linear velocity profile ranging from simple shear flow to ideal slip motion. The solution of this problem for probe of arbitrary convex shape within a diffusion-layer approximation was derived and corrected on the edge effects important at low Peclet number, i.e. for the small probes and slow flows, as well as at medium Peclet numbers, using the numerical data about the strip-like probes as well as disk-like probes. Effect of additional resistances (Faradaic resistance at surface of working electrode and Ohmic losses in the bulk of electrolyte solution) was analyzed using the Nernst model of a two-electrode cell.

Because ED method allows measurement of wall shear stress, which was a crucial parameter e.g. for the cleaning of membrane modules used in water filtration, a comprehensive summary of the theory of steady flow, unsteady flow, and transient voltage step experiments was created in collaboration with TU Berlin, Germany and University of Alberta, Canada. Factors influencing the accuracy of the measurements were thoroughly discussed. Furthermore, a new approach to calibrate the system from voltage step experiments was introduced, and practical issues related to its application in flow measurements was discussed for an exemplary signal response to a near-wall flow.

Other important field of ED use, microfluidics, was studied in collaboration with Univ. of Nantes. Flow behavior of the T-shaped and the cross-shaped micromixers with square cross-section was studied through numerical and experimental investigations. Measuring microelectrodes were placed at several wall positions of the cross-shaped micromixer. The electrochemical method was able locally characterize the formation of swirling flows. The high values of wall shear rate, in the impact zone, confirmed the near wall disturbance created by the impingement of the flow and also the appearance of vortices that could enhance fluid mixing.

Into the microfluidic domain belongs also the study of the flow around a flow-disturbing rib in a rectangular microchannel. In cooperation with Aristotle Univ. of Thessaloniki, Greece, we investigated the effect of key design parameters (i.e. the rib height and length as well as the Reynolds number) on the size of the reattachment length of the recirculation zones and the wall shear stress profiles in the vicinity of the rib. The wall shear rate along the channel as well as the velocity field were experimentally determined in our lab, using the ED technique and the μ -PIV method, respectively. The experimental results were then used for validating the CFD code of our Greece colleagues. It was found that the recirculation length in the laminar regime was affected mainly by the Re value and the rib height, whereas in the turbulent regime it was affected strongly by the rib height and slightly also by the rib length. Based on our results two new correlations, which can predict the length of the bottom recirculation zone with reasonable accuracy, are proposed for the design of microdevices.

The backward-facing step flow was investigated experimentally and numerically by CFD (Fluent). Different channel expansion ratios and inlet flow conditions (steady and pulsatile) were applied with the aim to analyze the structure and stability of the flow behind the step. ED technique was used to measure the wall shear rate along the experimental water channel. Direction sensitive sensors detect the near-wall extent of different flow-recirculation regions (primary recirculation and secondary corner, roof, and bottom eddies). Scaling for the reattachment length and roof eddy size was formulated. In the transitional regime the near-wall flow exhibits an unsteady character with a high sensitivity to external low-frequency perturbations. The inlet pulsatile forcing was found to affect strongly the overall flow structure behind the step. Up to 80% reduction of the reattachment length was achieved by applying flow pulsations at frequencies close to that of the global flow instability.

Further, two-phase flow in the form Taylor bubble in inclined rectangular channels was experimentally investigated. Two-segment electrodiffusion probes were used to measure wall shear rate profiles along the passing bubbles. They provided information on reverse flow in a liquid film separating the bubble from the wall, capillary waves appearing at the bubble tail, and near-wall flow fluctuations in the bubble wake. The corresponding bubble shapes and rise velocities were obtained from simultaneous visual observations done by a high-speed camera. In vertical channels, the wall shear

rate trace of a bubble rise was primarily influenced by the channel depth. In inclined channels, the liquid film was unequally distributed above and under the bubble with the maximum reverse flow observed under the bubble at middle inclinations.

Finally, the knowledge of local wall shear rates and its fluctuations is of primordial interest for industrial applications like tangential filtration, membrane reactors and bioreactors containing shear sensitive cells. Wall shear rate and its axial and azimuthal components were evaluated in stable Taylor vortices by using three-segment electrodiffusion probes and single probes flush mounted in the wall of the outer fixed cylinder. The axial distribution of wall shear rate components was obtained by sweeping the vortices along the probes using a slow axial flow. The experimental results were verified by CFD simulations.

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V. Granular matter (solid-liquid mixtures and dry powders systems)

One of the new research directions explored in our group deals with solid-liquid systems and behavior of granular matter. Arching structures created by sedimentation of polydisperse mixtures of non-spherical natural particles was studied experimentally. Families of inter-connected arching patterns in the form of voids or cavities were identified, of highly complex geometry similar to structures found by geologist in nature. It was found that arches in granular matter tend to form when initial mixture contains fractions with large and small grains.

Another experimental work inspired by geological observation was focused on inter-particle collisions in turbulent flows, particularly small conical shells telescoping at sea bed. It was observed that large-scale periodic motion of water reproduced in sloshing tank lead to high amount of irreversible packed shells. On the their hand small-scale irregular stirring motion in turbulent bulk imitated by a shaker caused similar rate of coalescence and break-up of the cones, the key factor for enhancement of telescoping was an increase of content of suspended fine particles. These two topics was studied jointly with the Institute of Geology, CAS, Prague. We participated on experiments, we performed CFD simulations a collaborated on publications.

A fine aqueous suspension of fine powder photocatalytic TiO₂ (today named nanofluids) were prepared and tested for the possible presence of the apparent wall slip effect by means of a novel viscometric technique. All the samples manifest Newtonian behavior with the fluidities almost unaffected by the presence of the dispersed phase.

Beside the presented work, our group acquired a powder rheometer to have suitable method for characterization of dry powder behavior and several studies on granular matter are underway. Also we cooperated via powder rheometry with the Dept. of Catalysis and Reaction Engineering ICPF on applied research projects IonPigment and IonColor granted by Ministry of Industry and Trade.

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Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Department of Analytical and Material Chemistry

The basis of the Department of Analytical and Material Chemistry was created in 2010 by merging of Department of Analytical Chemistry and Department of New Processes in Chemistry and Biotechnology. In 2014 the Department was extended by Laser Chemistry Group. These administrative measures should provide better sharing of research and instrument capacities and also secure closer cooperation within new emerged department.

There are 5 rather independent well established working groups or laboratories, namely: Group of Analytical Chemistry and NMR Spectroscopy, Group of Organic-Organometallic Chemistry, Group of Advanced Materials and Organic Synthesis (GAMOS), Group of Immobilized Biocatalyst and Optical Sensors, and Group of Laser Chemistry.

Analytical Chemistry and NMR Spectroscopy

Group of Analytical Chemistry and NMR Spectroscopy provides analytical support to all department of the Institute. Laboratories are well equipped for the qualitative and quantitative analysis of organic compounds and their mixtures (NMR, LC-NMR, HRMS, LC-MS, GC-MS, HPLC). The majority of organic samples come from the department itself, these results will be cited *vide infra* in the corresponding part. The analyses for the rest of the Institute usually require highly innovative approach of the analytical expert; however, they lead quite seldom to the joint publication. Only the analyses of natural extracts (E.H. Laboratory of Separation Processes, Pavela et al. (2010), Sajfrtová et al. (2014)) and reaction mixtures (Department of Catalysis and Reaction Engineering, Environmental Process Engineering Laboratory, Topka et al. (2011), Šyc et al. (2015)) resulted in joint publications reflecting the significance of analytical contribution. In some cases the analytical approach represents the main content of the articles, e.g. Horník et al. (2013), Žáček et al. (2014).

The NMR spectrometers serve for the routine NMR measurements but also for independent research. Original research is focused on design of pulse sequences in order to precisely determine the value and sign of various spin-spin coupling constants. This data can reveal further details of the electronic structure of studied molecules. Due to the long tradition in organosilicon compounds original studies were focus on determination of $^nJ(^{29}\text{Si}-^{13}\text{C})$ coupling constants; Blechta et al. (2010-2013). Recently, with the support of the synthetic part of the Department, the attention is more directed to polycyclic aromatic compounds and to determination of $^nJ(^{13}\text{C}-^{13}\text{C})$.

The 500 MHz spectrometer can be also coupled to analytical HPLC. This LC-NMR equipment was for a long time the only one in the Czech Republic and therefore frequently sought-after technique. It has been a subject of many collaboration and joint projects outside the Institute. The unstable sulphur compounds were identified, Kubec et al. (2011). Branched oligosilanes in the phenylsilane dehydrocoupling reaction were identified by this technique, Pinkas et al. (2012). Polyphenolic glycosides were

identified in natural plant extracts, Tříška et al. (2013). Some of the LC-NMR analyses were performed for pharmaceutical companies (Zentiva, Contipro). Qualitative analysis by heteronuclear NMR spectroscopy was often a subject of collaboration outside the Institute. The contribution to the results is not that significant in quantity, on the other hand, the contribution to the results was essential. The identification of unexpected substitution product in calixarene chemistry, Slavík et al. (2012), the anion complexation studies of calixarene and thiacalixarene derivatives, Kundrát et al. (2011), Hudeček et al. (2013), the identification of natural compounds in allium, Kubec et al. (2010), in honey, Lachman et al. (2010), the variable temperature study of chelated stannylenes, Padělková et al. (2013), are worth to mention.

Group of Analytical Chemistry is also equipped for the analysis of inorganic compounds and heavy metals (AAS, MP-AES, UV-VIS spectrophotometer). The analysis of catalyst composition is mainly performed for the Department of Catalysis and Reaction Engineering and the analysis of lanthanides and heavy metal contents performed for the Environmental Process Engineering Laboratory.

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Organic and Organometallic Chemistry

A substantial part of the Department is formed by organic and organometallic laboratories. These laboratories went through rigorous reconstruction in 2013 and they can provide dignified and save workplace for contemporary research in the field of organic synthesis. Besides traditional synthesis of new types of carbohydrates, cyclopentadienyl catalysts and carbosilane dendrimers, a new ambitious topic of materials for molecular electronics has emerged within last five years.

Research in carbohydrate laboratory has focused on the synthesis of fluorinated monosaccharides where the special emphasis was given to the preparation of fluorinated amino sugars, Karban et al (2010) and Karban et al (2014). These compounds have potential for example as metabolic inhibitors of glycan biosynthesis or as sugar components of glycopeptide anticancer vaccines. The attention was also devoted to mechanistic aspects of nucleophilic fluorination itself, Karban et al. (2012). More recently, the cooperation with Jiří Pinkas and Martin Lamač (J. Heyrovsky Institute of Physical Chemistry) and Roman Hrstka (Regional Centre of Applied Molecular Oncology Brno) was established with the focus on the field of anticancer carbohydrate-metallocene conjugates. We were engaged in the synthesis of titanocenes and ferrocenes bearing a carbohydrate moiety bonded to the cyclopentadienide ligand with the aim to improve cytotoxic and pharmacological properties of the resulting complexes. Our ferrocene-iminosugar conjugates were

found e.g. more cytotoxic than cisplatin against A2780cis line, Hodík et al. (2014) and Strašák et al. (2014).

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A long-term attention is paid to new types of cyclopentadienyl catalysts. The catalyst structure is modified to facilitate its removal or recovery from reaction mixture. Our group is concentrated to highly fluoruous catalysts that are soluble in fluoruous phase. Such phase form biphasic catalytic systems when mixed with organic phase. The reaction takes place at elevated temperature where both phases (fluoruous and organic) become just one phase. When the reaction is finished and the system is cooled down both phases get separated and the catalyst can be recovered from the fluoruous phase. In 2010 we succeeded in preparation of tetramethyl-(perfluoroalkyl)-cyclopentadienyl rhodium(I) complexes with alkene and diene ligands, Čermák et al. (2010). Partition coefficient measurements, however, revealed rather low fluorophilicity, Čermák et al. (2011). In the search for truly “heavy fluoruous” i.e. highly fluorophilic cyclopentadienyl ligand we synthesized also cyclopentadienes bearing one and two tris(2-perfluoroalkylethyl)silyl substituents. Monocyclopentadienyl titanium complexes were then prepared and their fluorophilicities shown to be much higher, Červenková Šťastná et al. (2010). The disadvantage of ligands of this type is their fluxional behavior hampering their characterization at room temperature. Using variable temperature multinuclear NMR we were able to characterize thoroughly this phenomenon and fully characterize the system, Červenková Šťastná et al. (2010).

Then we introduced and further developed the concept of branching of fluoruous “ponytails” on the silicon atom. Novel cyclopentadienes with $(\text{CH}_2)_n\text{Si}(\text{CH}_2\text{CH}_2\text{R}^f)_3$ substituents ($n = 2, 3$ and $\text{R}^f = \text{perfluoroalkyl}$) were synthesized and later used for preparation of transition metal complexes. This led to the development of the $(\text{CH}_2)_n\text{Si}(\text{CH}_2\text{CH}_2\text{R}^f)_3$ substituent as a general tag for making heavy fluoruous compounds. A broad series of compounds with this substituent was synthesized including general synthons with halo-, alkyne-, and azide-derivatives, N-ligands, and imidazolium-type ionic liquids. Cyclopentadienyl complexes of Co(I), Co(III), Ti(IV) and Zr(IV) with $(\text{CH}_2)_3\text{Si}(\text{CH}_2\text{CH}_2\text{R}^f)_3$ substituent were prepared, Strašák et al. (2014). The cobalt complexes were used for catalysis of cyclotrimerization and cocyclotrimerization reactions of alkynes and nitriles in organic media and in supercritical carbon dioxide. Partition coefficients in a standard system perfluoro (methylcyclohexane)/toluene were measured for all the new compounds. The results showed that the new substituent indeed brings high fluorophilicity to the tagged molecules. A new class of highly fluorophilic (heavy fluoruous) compounds was identified, namely imidazolium-type ionic liquids (submitted, 2015).

Another approach to separate the catalyst from reaction mixture is based on the size of catalyst support. Here we focus on development of carbosilane dendrimer support and subsequent derivatization of dendrimer periphery by metallocenes. At the beginning we studied the synthesis of carbosilane dendrimers in detail. Our characterization by NMR and mass spectrometric techniques led to the first published thorough analysis of their defects, Krupková et al. (2010). Based on this analysis a reliable procedure for construction carbosilane dendrimers up to the third generation was developed. Metallodendrimers of the first and second generation with variations of branching degree and the length of a spacer connecting dendrimer periphery with

titanocene dichloride function were prepared, Strašák et al. (2012). The structures were studied by molecular dynamics calculations confirming hypotheses about the availability of titanocene dichloride sites. The new metallodendrimers were used in catalysis. As the model reaction the allylic coupling reaction was used. The results showed that in our metallodendrimers titanium active sites did not lose activity compared to the parent low-molecular complexes, Strašák et al. (2014).

An attempt was also undertaken to join the research themes fluorine chemistry and dendrimers. The carbosilane dendrimers bearing both fluorine ponytails and transition metal complexes (cyclopentadienyl titanium(III) units) were prepared. However, their properties prevented their use in catalysis, Krupková et al. (2012).

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Advanced Materials and Organic Synthesis

In last five years a new synthetic group (Group of Advanced Materials and Organic Synthesis - GAMOS) has emerged and brought an ambitious topic of novel materials suitable for molecular electronics. The target molecules were polycyclic aromatic hydrocarbons (PAHs), particularly $[n]$ helicenes and their derivatives. The original synthetic approach developed in the group was based on metal catalyzed cyclotrimerization. However this approach could not be applied generally, e.g. the azahelicenes can be hardly produced by this procedure, Storch et al. (2010). Also another synthetic approach based on intramolecular cascade hydroarylation/cycloisomerization was soon abandoned, Storch et al. (2013). In parallel, former microwave photocyclization procedure was revisited and new methods leading to preparation of various substituted helicenes in multigram scale as well as various to other types of PAHs was introduced. Starting stilbene-like precursors undergo intramolecular photocyclization to the corresponding products under UV/Vis irradiation. Efficient synthesis of stilbene-like precursors was also the subject of our research. The invention dealing with the development of methodology and apparatus for production of various $[n]$ helicenes in multigram scale has been patented (Storch et al. Pat. No. 303997/PV 2012 - 245) in cooperation with industrial partner (Lach-Ner Company). Lach-Ner launched a production of racemic helicenes in 2014 and their distribution to customers in the specialty chemicals market (www.lach-ner.com/helicenes/t-400/). Owing to these efforts, helicenes and other similar molecules (e.g. phenacenes) can be integrated into applied research more intensively.

With sufficient quantity of desired compounds in hand we could approach the thorough studies directed towards new materials applicable in optoelectronics, sensors and separation techniques. First step included the detailed screening of 9-bromo[7]helicene reactivity which represented starting molecule in majority of further studies, Žádný et al. (2013). The subsequent study was focused on electrochemical preparation of conjugated thiophene-based polymer systems bearing helicene moiety as a conductive and optically active component. This polymer opens up new possibilities for the development of novel helicene-modified surfaces with applications in material science and electronics, e.g. stationary phases for separations, circularly polarized light detection and circularly polarized electroluminescence devices, Hrbáč et al. (2014). Another study was focused on preparation of substituted imidazolium

cation by [6]helicene backbone in order to improve helicene properties for the surface immobilization and enhancing the solubility in polar solvents. The deposited layer was used for the development of organic molecular semiconductor device and construction of a novel type of fully reversible humidity sensor, Storch et al. 2015.

Recently, a new type of photocyclization was developed for the preparation of fluorinated PAHs, which opens up the way to new electronically polarized molecules potentially applicable in OPV and OFETs. Fluorine atoms are known to lower the HOMO and LUMO energy levels, making electron-injection easier and materials more stable towards oxidation. Furthermore, strongly altered packing of fluorinated materials in the solid state leads to closer arrangement of the molecules and more efficient π -orbital overlap leading to improvements in electron mobility. The inversed electron distribution in perfluorinated PAHs leads to dramatic changes of their chemical reactivity, which can be further exploited in functionalization of [n]phenacene backbone (e.g., nucleophilic aromatic substitution).

Recently, it has been shown that phenolic cyclopentenedione nostotrebin 6 is able to form the functional polymer with permselective properties. The thin film was selective for positively charged species (e.g. dopamine) whereas neutral and negatively charged compounds were not able to pass through the film. This initial finding motivated us for the preparation of other cyclopentenedione derivatives with structural similarity to nostotrebin 6 and ability to form functional films. The main activities in this field were therefore focused on design and preparation of novel cyclopentenediones, via modified Knoevenagel condensation, which are able to undergo electropolymerization process leading to the formation of stable and defect-free polymeric films. We have prepared over 25 new compounds and in cooperation with Palacký University Olomouc we have performed electropolymerization giving poly(cyclopentenedione) films formed on glassy carbon electrode. These novel polymeric films were tested for their permselective properties towards charged species. We have found that modified electrodes by synthetically prepared cyclopentenedione derivatives also exhibit permselectivity for positively charged dopamine, while neutral and negatively charged species (ascorbic acid, NO and NO₂⁻) cannot pass through the layer.

This group can also provide custom synthetic service for other departments of the Institute. This activities are mainly focused on synthesis of various types of ionic liquids for separation processes; Andresová et al. (2014), Lísal et al. (2014).

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Immobilized Biocatalyst and Optical Sensors

The group of Immobilized Biocatalyst and Optical Sensors has its origin in organosilicon chemistry which was one of the main research specializations of the Institute in the past. Group is focused on sol-gel immobilization of microorganisms, their whole cells or just parts (enzymes) as industrial catalysts or sensitive recognition elements of optical sensors. The group does not engineer new biocatalysts, cells or enzymes, but it actively searches for collaborations with research teams, which developed new biocatalysts or organic-inorganic materials. The most important cooperation was established with Centrum of Environmental Biotechnology, University

of Tennessee, Knoxville (CEB). CEB provided genetically engineered cells of *P. Fluorescens* HK44, which were tested as detectors of pollution under real conditions, Trögl et al. (2010).

Bioluminescent bioreporter *P. putida* TVA8 was successfully used as a selective detector of benzene derivatives, Kuncová et al. (2011). The enzyme diamino oxidase was utilized as a recognition component in quantitative optical sensor for detection of biogenic amines, Pospíšková et al. (2013). The properties of immobilized yeast were studied rigorously, Bolyó et al. (2010), Magalhaes et al. (2011). The immobilized lipase enzyme was tested in various types of continuous chemical reactors, packed column, meander and slug flow microreactors, Hetflejš et al. (2011), Čech et al. (2012), Drhová et al. (2014). This approach of production of monoacylglycerides resulted in two Czech patents, Vlček T. et al.: Pat. No. 303842/PV 2012-147, Vlček T. et al.: Pat. No. 25584/PUV 2013-27669.

Currently, the research has been oriented to biocompatible composite materials as the titania hydrogels and the chemically triggered release of a photo-sensitive dyes (porphyrins), Rychtáriková R. et al. (2012). Very recently, the whole-cell optical biosensor for mercury was developed and tested, Solovyev et al. (2015).

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Laser Chemistry

Last working group of the Department is the Laser Chemistry Group which is focused on preparation of various types of nanostructured materials by broad range of deposition techniques (reactive and non-reactive laser ablation, laser CVD, thermal CVD, matrix assisted pulsed laser evaporation, radiofrequency plasma deposition). Materials prepared are characterized in the Group by FTIR, UV/VIS, Raman, EDX and XPS spectroscopy, SEM microscopy and thermogravimetry. The Group also provides these measurements also for the rest of the Institute on collaborative/service basis.

The Group is active in the field of laser-induced chemical reactions and has prepared and identified very rare ambient-pressure unstable nanophases of metals (Ag, Ga, and Fe), Křenek et al. (2010), Murafa et al. (2010), Pokorná et al. (2010), Urbanová et al. (2010), Křenek et al. (2012), Křenek et al. (2013), Urbanová et al. (2014), Gondal et al. (2014) and binary Fe compounds, Pola et al. (2014) as products of laser photolysis and reactive laser ablation of metal in dielectric breakdown of carbonizing precursor. These results indicate that reactive laser ablation carried out under optimized conditions can become a common tool for synthesis of highly unusual stabilized nanosized high-pressure polymorphs and they open door for other researchers to initiate an intense research of physical and chemical properties and applications of these novel unique materials.

Further effort in the evaluated period was concerned on laser photolysis for deposition of nanomagnetic carbonaceous materials, Pola et al. (2010), Urbanová et al. (2012), carbothermal and hydrothermal reduction, and on formation of nanosized titanium monoxide, Jandová et al. (2011, 2013), laser-induced dielectric breakdown in

gases for deposition of nanoalloys and nanocomposites and reactive laser ablative deposition of FeS on copper surface, Pola et al. (2011), Urbanová et al. (2012), and Mg₂Si nanoparticles in amorphous silicone matrix, Galkin et al. (2013). These results have been achieved in collaboration with other institutes of CAS (Institute of Inorganic Chemistry, Institute of Physical Chemistry, and Institute of Physics) and participation of visitors from universities in Plzen, Macedonia and Saudi Arabia. The cooperating institutes contributed mainly by analytical techniques to the obtained results, principal investigation was carried out in the Group.

In cooperation with Basque partners there were published papers on preparation of reduced graphene oxide (rGO)/polymer composites synthesized by *in situ* polymerization. The main challenge was to synthesize stable composite films for their possible application as electrically conductive coatings. The *in situ* prepared composites show decreased aggregation of rGO, uniformly distributed rGO in the polymeric matrix and conductivity depending on preparation conditions and rGO content, Arzac et al. (2014). The composite film was used as a target for laser ablation and the prepared graphene based thin films were studied as substrates for deposition of Ag, Au and Au/Ag alloy nanoparticles for their use in Surface Enhanced Raman Spectroscopy (SERS), Siljanovska Petreska et al. (2014).

A novel hybrid photocatalysts were prepared using a carbon nitride (g-C₃N₄) substrates modified with BiOCl having controllable mass ratios among the g-C₃N₄ and BiOCl. The microstructure, morphology and optical properties of the synthesized photocatalysts were studied using diffraction, microscopy, and spectroscopy techniques. The photoactivity of the g-C₃N₄/BiOCl was evaluated by photodegradation of Rhodamine B from water as a model toxic contaminant. The photodegradation results revealed that the photocatalytic activity of the hybrid photocatalyst exhibits superior activity as compared with pure BiOCl under visible light irradiation, Shi S. et al. (2014). The Group contributed to the preparation and characterization of the photocatalysts. The photocatalytic activity and following quantum chemical calculations were performed solely at Chinese and Saudi universities.

In the Group there was prepared a wide range of various nanostructured objects using standard low pressure CVD. At first, bare Ge nanowires (GeNWs) were prepared by this technique, Dřínek et al. (2010). The growth was achieved without any external metal seeds via auto-catalyzed approach. By this way GeNWs were grown at stainless steel, W, Ta, Fe, Cu, and Ni substrates. Adding a tetramethyl-disilazane precursor to the standard used hexamethyldigermane (HMDG), GeNWs covered by Si/O/C material were fabricated, Dřínek et al. (2010), Krabáč et al. (2012). By subsequent annealing to 900 °C germanium was evaporated out of the tube and Si/O/C nanotubes were left over.

The Cu/Ge and Cu/Si/Ge nanoplatelets (NPs), Klementová et al. (2013), Křenek et al. (2011) were prepared by pyrolysis of HMDG and mixture HMDG/ ethylsilane at 500 °C. Copper was revealed to diffuse from a copper substrate and NPs with thickness from 50 to 200 nm grew. Cu/Si/Ge NPs possessed an incommensurately modulated structure, Palatinus et al. (2011). The NPs have high aspect ratio; dimensions (length, width) are tens of microns. When tetraethyllead (TEL) was added to HMDG, Cu/Ge NPs arose. However their structure was different from those grown from only HMDG. Swapping TEL for tetramethyltin, Cu/Ge NPs were grown again and tin was not found in the NP structure. In some NPs a structure derived from a Cu/Si/Sn alloy was detected; in this case it seems that NPs epitaxial growth was initiated over those Cu/Si/Sn spots.

Resonant infrared matrix assisted laser pulsed evaporation (RIR MAPLE) technique was performed for preparation of carbon rich Si/C films, Dřínek et al. (2014). The main problem of diamond-like and Si/C films with high content of carbon persist in graphitic residues and sp^2 carbon fraction. Very mild laser evaporation of dendritic precursor with allyl groups on its periphery resulted only in polymerization and formation of Si/C films free of sp^2 content. UV absorption edge of the films starts approximately at 230 nm. These results have been achieved solely in the Group and became a basis for a broad cooperation between the Group and the Institute of Physics CAS.

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Research Report of the team in the period 2010–2014

Institute	Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Scientific team	Environmental Process Engineering Laboratory

Research in Environmental Process Engineering Laboratory (EPEL) has been focused on modern technologies for sustainable power generation and various aspects of environmental protection, remediation, pollution abatement and waste recycling and utilization. Other research activities have been directed towards applications of the electrodeless discharge lamps in photochemistry and photocatalysis in microwave fields and applications of such technique in organic synthesis. Valuable applications of selective microwave heating were exploited in recycling of the waste plastics, repairs of the asphalt roads, drying of the detergents, soil in-situ and ex-situ decontamination, etc.

Laboratory was established by unification of several research groups dealing with combustion/gasification research, hydrometallurgy, waste recycling and research of microwave chemistry and heating effects. The main activities of EPEL with various aspects of protection of the environment, and applications of new techniques for such purpose, can be assessed in four directions as follows:

- Clean combustion and co-combustion technologies with reduction of pollutants (SO_x , NO_x , N_2O , persistent organic pollutants, heavy metals) and CO_2 .
- Gasification and co-gasification technologies with deep gas cleaning for advanced applications (fuel cells, catalytic processes) and development of small and medium gasifiers with integral production of fuel gas for gas engines.
- Waste related research aiming at recovery of valuable materials, metals, non-metallic elements and energy (recycling and recovery of plastics, recovery of critical elements, e.g. rare earth elements (REE) from electronic and electrical waste, urban mining).
- Research (chemistry, catalysis and synergetic treatment) and applications of microwave based technologies (mainly for environmental utilization).

Topic 1

Clean combustion and co-combustion technologies with reduction of pollutants and CO_2

Research in combustion processes turns the attention worldwide on reduction of CO_2 emissions, separation of clean, concentrated CO_2 streams, co-processing of biomass and waste with coal, on efficient, low emission combustion of biomass, sewage sludge, municipal and industrial solid waste. Nowadays, processes like chemical looping combustion and oxy-fuel combustion with production of concentrated CO_2 gaseous streams are intensively studied.

Fluidized bed (FB) and grate combustion of biomass in small and medium scale plants call for development of efficient problem-free combustion process (without ash/char particle agglomeration, with suppressing of fouling and corrosion of heat exchangers in production of steam) and with low emissions of dust, acid gases (SO_2 ,

HCl), NO_x and other pollutants like heavy metals, dioxins etc. Incineration of organic and mixed (e.g. MSW) waste is proven method for recovery of energy from non-recyclable and difficultly separable mixed waste materials. Incineration technologies, abatement of emissions (particularly NO_x, HCl, heavy metals, dioxins), development of multi-filters and overall accompanying eco-effects are still important issues in waste and biomass related combustion research and development.

EPEL addressed in combustion processes related research mainly three subjects: oxy-fuel fluidized bed combustion with impacts on emissions, unburnt carbon and ash quality, fluidized bed combustion of sewage sludge with minimization of emissions (mainly NO_x, N₂O, HCl, heavy metals and dioxins) by primary measures, application of FB for incineration of contaminated materials and combustion with measures for minimization of emissions of heavy metals. The research was supported by several research projects mostly oriented to applied research, e.g. Brownfields - Source of Renewable Energy (2011-2014, supported by TACR), Waste-to-Energy Competence Center (2014-2018, supported by TACR), Waste as raw material and energy source (2008-2011, supported by MEYS), Fluidization and decontamination of organic-polluted solids in a fluid-bed reactor (2007-2011, supported by GA AS) etc.

In development of biomass combustion technologies with efficient gas cleaning the attention was turned on research and development of wet precipitator for solution of safe capture and removal of red-hot dust particles mainly in combustion of straw and herbaceous biomass. Development of new three stage flue-gas cleaning technology is based on dry and wet/dry lime/limestone technology and final dry filter cleaning with injected active carbon particles to remove heavy metals (mercury, Zn, Pb), PCDD/PCDF, etc. The research was supported by two projects from TACR.

As the most important results of the research and development in the frame of Topic 1 can be noted for example: the determination of new emission factors for organic and major pollutants from domestic heating appliances; proposal and experimental verification of treatment cycle for contaminated biomass from phytoextraction, development of insulated capsule for monitoring of conditions on MSWI grates (cooperation with JRC, Institute for Energy, Petten) the construction of experimental fluidized bed reactor for process optimization, newly developed wet electrostatic precipitator etc.

The results connected with the above topic are for example:

Hartman M. et al.: *Ind. Eng. Chem. Res.* 49(6), 2672-2680 (2010); Martinec J. et al.: *Appl. Therm. Eng.* 30(8-9), 1022-1028 (2010); Horák J. et al.: *Chem. Listy* 105(11), 851-855 (2011); Šyc M. et al.: *Envir. Sci. Technol.* 45(21), 9427-9434 (2011); Šyc M. et al.: *Biomass Bioenerg.* 37, 106-113 (2012); Elsasser T. et al.: *Chemie Ingenieur Technik* 85(12), 1-7 (2013); Hartman M. et al.: *Chem. Pap.* 67(2), 164-172 (2013); Hartman M. et al.: *Ind. Eng. Chem. Res.* 53(49), 19145-19158 (2014); Trkal L. et al.: *Bioresour. Technol.* 171, 442-451 (2014); Hartman M. et al.: *Chem. Listy* 105(7), 546-552 (2011); Pohořelý M. Pat. No. 26697 /PUV-28341.

Topic 2

Research and Development in Gasification and Co-gasification Technologies

Transformation of solid fuels into gaseous fuels enables, after proper gas cleaning, application of gas engines with internal combustion for efficient power generation. Deep, intensive gas cleaning is required for advanced utilization of fuel gas in fuel cells, and in catalytic processes (for production of synthetic liquid fuels (gasoline, diesel oil, dimethyl-ether, etc.) and chemicals. Research in cleaning of producer gas from gasification processes is diversified into high selectivity and perfection of wet cleaning processes, research of new membrane based methods of separation of

gaseous impurities and on solid sorbents for medium and high operating temperature. Together with this effort, the attention is worldwide concentrated also on separation and utilization of CO₂ in gasification processes, on simple, efficient, low emission gasification/co-gasification of biomass and organic waste. Development of smaller and medium scale innovative biomass gasifiers for co-generation units with simple, reliable and cheap gas cleaning for gas engines is in the center of applied research in European and other countries at present.

EPEL concentrated attention in basic research on fluidized bed gasification of different coals, co-gasification of coals with biomass (wood) and plastics. Two international EU grants from RFCS supported this research. Not only solid fuels but also binary and ternary slurry fuels have been gasified. Possibilities of production of cleaner producer gas (low concentrations of tar, H₂S, HCl, etc.) by primary measures, in-bed catalyst application and by secondary gas cleaning methods were studied. Gasification of the sewage sludge, the contaminated waste wood and the herbaceous biomass with measurements of impacts on gas composition were investigated.

Dry cleaning of producer gas at higher temperatures (de-HCl, desulfurization, de-HF) was studied both theoretically (attainable chemical equilibria) and experimentally in a fixed bed reactor in the frame of two successive bilateral projects with NSC and INER Taiwan.

In development of small and medium scale efficient gasifiers for various biomass fuels our attention was focused on innovative construction, stage processes, innovative construction enabling operation without grate and on attaining cleaner gas (low tar content) by pre-treatment of woody biomass, two stage process (pyrolysis / gasification), excellent utilization of process heat and application of medium / high temperature filters. The research was supported by contracts with private small companies and by TACR projects.

Co-processing of biomass with mineral oils for production of hydrogen by gasification (partial oxidation) was studied in the frame of Ministry of Industry project. According to operating conditions hydrogen or methane as valuable products could be produced.

The results are connected with the following publications and patents:

Šyc M., et al.: *Energy and Fuels* 25(5), 2284–2291 (2011); Hartman M. et al.: *Chem. Listy* 106(9), 844-846 (2012); Svoboda K., et al.: *Fuel Process. Technol.* 95(1), 16-26 (2012); Šulc J., et al.: *Waste Management* 32(4), 692-700 (2012); Hartman M., et al.: *Chem. Pap.* 67(2), 164-172 (2013); Hanika J., et al.: *Chem. Eng. J.* 176-177(1), 286-290 (2011); Veselý V., et al.: *Journal of Energy and Power Engineering* 7(10), 1940-1945 (2013); Hartman M., et al.: *Ind. Eng. Chem. Res.* 53(49), 19145-19158 (2014); Jeremiáš M., et al.: *Fuel* 117(Part B), 917-925 (2014); Pohořelý M., et al.: *Fuel* 117(Part A), 198-205 (2014).

Czech Patents:

Svoboda K., et al.: *Method and Apparatus/Equipment for Gasification of Adapted Biomass*. Pat. No. 303367/PV2011-404. Applied: 11.07.01, Patented: 12.07.09.; Pohořelý M., et al.: *The Facility for the Fluidized-Bed Gasification of Solid Fuels*. Pat. No. 304060/PV 2012-516. Applied: 12.07.27, Patented: 13.07.31.; Tlustoš P., et al.: *Equipment for the Preparation of Pyrolysis Coke*. Pat. No. 26846/PUV 2014-29083. Applied: 14.01.14, Patented: 14.04.24; Lederer J., et al.: *Process for Hydrogen Production by Partial Oxidation of High Boiling Hydrocarbon Mixtures and Biomass, and Apparatus for Processing*. Pat. No. 303392/PV 2010-653. Applied: 10.09.02, Patented: 12.08.29.

Topic 3

Waste separation, recycling and recovery related research and development

Nowadays, with increasing consumption of various raw materials and formation of huge amount of various waste materials in production sectors, business sector, municipalities, water cleaning, hospitals, etc. simultaneously economic, environmental and social pressures on waste separation, recycling, recovery and re-utilization sharply increase. Separation of basic sorts of recyclable waste (plastics, paper, metals, glass etc.) is prerequisite for application of further technologies for production of secondary products based on them. Plastic waste can be further separated on fractions rich in PET content, PE content etc., which facilitates recycling technologies. Increasing amount of electronic and electric appliances based waste streams (PC's, monitors, mobile phones, batteries, printed boards, home-appliances, fluorescent lamps LED diodes containing waste, waste el-motors, etc.) containing increasing amount of critical elements (Ga, REE, In, Y, etc.) require research and development of ecologically friendly and efficient reclaiming and recovery processes tailored for such mixed, special waste (i.e. separation of Cu, Sn, precious metals, gallium, REE, etc.).

The mixed waste materials (e.g. municipal solid waste, MSW) present another significant stream of waste materials, which enables recovery of energy by means of incineration and recovery of valuable metals (mainly iron, aluminum, copper and zinc) from bottom ash and fly ash. Because the MSW incineration facilities are often placed within municipal dense populated area, and because of considerable variability of such waste, the requirements (emission limits) on flue gas cleaning process and applied cleaning technologies are high. Sewage sludge from water cleaning facilities, its management, handling and reliable, ecologically friendly liquidation with reclaiming of valuable components (some metals, phosphorus etc.), is still a great challenge today.

EPEL has focused in last 5 years on development of technologies for polyethylene terephthalate (PET) chemical recycling based on polymer-molecular unlock, raw material chemical recycling and on development of revolutionary method using microwaves for facilitation of PET chemical depolymerization to the monomers (terephthalic acid and ethylene glycol). One of the great advantages of this method is avoiding sorting process before processing (i.e. no need of preliminary removal of PE lids, PE and paper labels from PET bottles, etc.). The technology was successfully patented. Company Noen, which initiated the cooperation on PET recycling, decided to cooperate with Polish company NRT Polska. The patent was sold (on basis of purchase contract), after verification of the technology, for 5 mil. CZK and after finishing erection of plants for the technology the company will start production of the monomers in Poland. The microwave depolymerization technology attracts attention of known international companies (Coca Cola, Pepsi Cola, Nestlé). The research was supported by Ministry of Industry (MIT) and by private company Noen.

Waste of electrical and electronic equipment (WEEE) treatment, recycling and recovery of valuable elements is currently one of the most important challenges in waste management as well. Recovery of metals from WEEE by acid leaching methods and enhancement of the process by microwave irradiation was investigated and recovery of Al, Zn and Pb was significantly improved in the frame of bilateral collaborative project with Slovakia (TU Košice). The method for precious and special metals recovery (e.g. Eu, Y) from electric and electro-technical wastes by means of liquid-liquid extraction was developed in cooperation with Safina a.s. Special attention was paid to reprocessing of phosphors from spent TV screens and PC monitors and to recovery of permanent magnets from used PC hard discs. Complex recycling of compact fluorescent lamps (PFLs) solved in EPEL enables sorting on glass, metals and luminophores, separation of mercury from luminophores and either reclaiming of Hg or

conversion of mercury to a stable chemical form (HgS) suitable for deposition. Separation technology based on leaching and extraction was developed for separation of yttrium and europium from luminophores (in cooperation with Laboratory of separation processes of ICPF). Pilot plant unit was constructed in cooperation with Kwa-Zulu Natal University, Durban, RSA. The recycling method and technology was patented. The technology development was supported by project from TAČR.

Lately in EPEL a big project on waste to energy related processes focused particularly on complex dry gas cleaning and recovery of valuable bottom ash components started (Waste-to-energy Competence Center, supported by TAČR). In the frame of the project the possibilities of application of 4-D filters for simultaneous removal of dust, acidic gases, NO_x and dioxins are assessed and they will be studied experimentally and optimized. Suitable methods for mercury removal from flue gas are evaluated and will be further investigated. The main target of WtE Center consortium partners is the development of small-scale MSW incineration facility.

The most important results of the research and development in the frame of Topic 3 – waste recycling and recovery are methods for microwave depolymerization of waste PET, complex recycling method for treatment of compact fluorescent lamps and method for precious and special metals recovery (e.g. Eu, Y) from electrical and electro-technical wastes by means of liquid-liquid extraction.

The results are connected with the following publications and patents:

Znamenáčková I. et al.: *Chem. Listy* 105(5), 625-628 (2011); Keppert M., et al.: *Waste Manage Res.* 30(10), 1041-1048 (2012); Šyc M. et al.: *Biomass Bioenerg.* 37, 106-113 (2012); Elsasser T. et al.: *Chemie Ingenieur Technik* 85(12), 1-7 (2013); Hartman M. et al.: *Ind. Eng. Chem. Res.* 52(31), 10619-10626 (2013); Hartman M. et al.: *Ind. Eng. Chem. Res.* 53(49), 19145-19158 (2014); Hájek M. and Sobek J.: *Pat. No.* 301761/PV 2009-5; Hájek M. et al.: *Pat. No.* EP2176327 PCT/EP/2008/058917; Gruber V. et al.: *Pat. No.* 302854/PV 2010-928; Hájek M. et al.: *Pat. No.* CN101688015/2008 80002443.4; Kruliš Z. et al.: *Pat. No.* EP2183311; Veselý V. et al.: *Pat. No.* EP2061744 PCT/CZ2007/000086.

Topic 4

Research and development of applications of microwave based technologies

Microwave energy absorption in a material (matter) depends on dielectric properties of media, operating conditions, structure/texture and geometry. Microwave heating is extremely efficient in the selective heating of materials. Compared with conventional heating techniques, microwave heating offers: higher heating rates; no direct contact between the heating source and the heated material; selective heating of some definite parts may be achieved; controlled heating in drying processes; reduced equipment size and amount of waste, desorption processes, mineral processing, soil remediation, waste treatment, recycling, selective carbon heating, etc.

Microwaves (MW) are applicable in photochemistry, photocatalysis and in changes of reaction kinetics/selectivity in chemical systems. Coupled activation of photochemical reactions by using of two different types of radiation, MW and UV/Vis, is covered by the Microwave Photochemistry. The energy of MW radiation is considerably lower than that of UV/Vis radiation, thus insufficient to disrupt the bonds of common organic molecules. So, essentially, UV/Vis is responsible for a photochemical change, and MW radiation subsequently affects the course of the subsequent reaction. Electrodeless discharge lamps generate effectively UV/Vis when they are placed into a microwave field. Such technique can be used in organic chemistry and in environmental chemistry for destruction of organic pollutants (The

research was supported by TAČR – project Preparation of helicene based chiral stationary phase for HPLC, and MIT CR – project Technology of the oxidative photocyclization leading to helicenes).

The basic and applied research is focusing on the effect of microwave radiation on the course of *cis-trans* photoisomerization and photocyclization of stilbenes and o-terphenyls leading to phenanthrene, triphenylene, phenacene, and helicene derivatives, or to their hetero analogues (two publications and patent).

In the sphere of environmental applications of microwave based technologies the team developed a new ex-situ decontamination technology (together with company Dekonta a.s.). Project Thermo-desorption (supported by TAČR) resulted in a patent, the proven, certified technology and two proved methodologies for the new technology.

In 2010 cooperation began with company Nanocar a.s. (now Futtec) leading to development of prototype of microwave-based mobile equipment for repair of depressions, holes and ruptures of asphalt roads. During the cooperation 3 kinds of prototypes of such equipment were developed and tested under real conditions for road repair. The last prototype (FT3) was finished, tested and finally given as basis for preparation of design, certification and production. In the frame of the cooperation the developed method and equipment for asphalt road repairs was patented and selling of the license is expected at present (revenues about 1.2 mil. CZK).

In 2012 cooperation started in development of microwave method of detergent drying with company Chempharm Engineering s.r.o. and company Enaspol a.s. This cooperation gained about 150 th. CZK, led to new Czech patents and new equipment (type Nautamix) in estimated value around 600 th. CZK. The project of detergent drying continues and prospects are for erection of equipment for production capacity around 3000 tons/year. Further application of microwave techniques involves surface thermal decontamination, and improvements in production of paper bags/sachets with good isolation, antibacterial and hydrophobic properties. The technology for PET depolymerization was mentioned in the waste related chapter.

The results of research of microwave assisted synthesis and photocatalytic processes are connected with the following publications:

Církva V., et al.: *Photocatalysis on Titania-coated Electrodeless Discharge Lamps*. 76 pp., Nova Science Publisher, New York 2010; Církva V., et al.: *J. Chem. Technol. Biotechnol.* 85(2), 185-191 (2010); Čermák J.K., et al.: *Lett. Org. Chem.* 10(2), 126-130 (2013); Církva V., et al.: *Curr. Org. Chem.* 15(2), 248-264 (2011); Kmentová H., et al.: *J. Chem. Technol. Biotechnol.* 88(6), 1109-1113 (2013); Čermák J.K., Církva V.: *Tetrahedron Letters* 55(30), 4185-4188 (2014).

Helicene related articles and patent:

Žádný J., et al.: *Exploration of 9-bromo[7]Helicene Reactivity*. *Tetrahedron* 69(30), 6213-6218 (2013); Hrbáč J., et al.: *Immobilization of Helicene onto Carbon Substrates through Electropolymerization of [7]Helicenyl-thiophene*. *RSC Adv.* 4(86), 46102-46105 (2014); Storch J., et al.: *Method and Apparatus for Production of [6]Helicenes*. Pat. No. 303997/PV 2012 - 245. Applied: 12.04.11, Patented: 13.06.26.

The applications of microwave in environmental technologies – articles:

Kaštánek P., et al.: *J. Environ. Eng.-ASCE* 136(3), 295-300 (2010); Hájek M., et al.: *Restaurator* 31(1), 1-7 (2011); Mašín P., et al.: *Fresenius Environ. Bull.* 22(7A), 2017-2021 (2013); Hájek M.: *Microwave Recycling of Waste PET Bottles*, *Chemagazín* 24(4), 8-9 (2014); Hájek M.: *Microwave Recycling of Waste PET Bottles*. *Odpady* 24(6), 25-26 (2014).

Patents:

Hájek M., et al.: *Method for the Chemical Depolymerization of Waste Polyethylene Terephthalate*. Pat. No. EP2176327 PCT/EP/2008/058917. Applied: 08.07.09, Patented: 10.11.10.; Kruliš Z., et al.: *Method for Recycling of Waste Polyurethan Foams*. Pat. No.

301686/PV 2007-576. Applied: 07.08.23, Patented: 10.04.14.; Hájek M., et al.: Method for the Chemical Depolymerization of Waste Polyethylene Terephthalate. Pat. No. CN101688015 /200880002443.4. Applied: 10.01.12, Patented: 12.09.19.; Hájek M., et al.: Method of Decontamination of Solids. Pat. No. 304205/PV 2012-269. Applied: 12.04.19, Patented: 13.11.20.; Hájek M., Sobek J.: Method of Reparation of Damaged Roads. Pat. No. 304810/PV 2013 - 705. Applied: 13.09.17, Patented: 14.09.24.; Hájek M., et al., Method of Drying of Surfactants. Pat. No. 304481 /PV 2013-439. Applied: 13.06.11, Patented: 14.04.09.; Hendrych J., et al.: Binder Mixture for Stabilization and Solidification of Liquid Waste and the Stabilization Product and Solidification Product. Pat. No. 26651/UV 2013-28265. Applied: 13.07.29, Patented: 14.03.24.; Kruliš Z., et al.: Method of Recycling Waste Polyurethane Foams. Pat. No. EP2183311. Applied: 10.05.12, Patented: 14.12.03.; Sobek J., et al.: Equipment for Decontamination of Solids. Pat. No. 26360/UV 2013-28260. Applied: 12.07.29, Patented: 14.01.20.; Sobek J., et al.: The Processing of Algae for Obtaining Oil Resulting. Pat. No. 304392/PV 2013-323. Applied: 13.04.30, Patented: 14.02.26.