

## Environmental Process Engineering Laboratory

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## Fields of research

- Electrodeless discharge lamps for photochemistry and photocatalysis in microwave field
- Simultaneous cooling at microwave heating - a new method in heterogeneous catalysis
- Effect of microwaves on selective leaching of Pb, Zn and Al from the electronics waste
- Fluidization and decontamination of organic-polluted solids in a fluid-bed reactor
- Fluidized bed incineration of dry sewage sludge from the waste water treatment plant
- Advanced processes for gasification, gas cleaning and hydrogen production
- Persistent organic pollutants and heavy metals from small sources

## Applied research

- Fluidized bed combustion and gasification
- Moving bed gasification of wood and waste wood
- Development and verification of thermal desorption technology using microwaves
- Brownfields - source of renewable energy
- Waste and sewage sludge combustion and co-combustion
- Simultaneous microwave drying and disinfection of flooded books
- Hydrogen production via synthetic gas by biomass/oil partial oxidation
- Method for obtaining extracts containing europium and yttrium and method for recovery of spent phosphors from compact fluorescent lamps

## Research projects

### Photochemistry and photocatalysis in the microwave field - overview

(V. Církva, [cirkva@icpf.cas.cz](mailto:cirkva@icpf.cas.cz); supported by ICPF)

The coupled activation of photochemical and photocatalytic reactions by using of two different types of radiation, microwave and UV/Vis, is covered by the new discipline called microwave photochemistry and photocatalysis. Such a connection might have a synergic effect on reaction efficiencies or, at least, enhance them by summing up the individual effects.

The objective of this discipline is frequently, but not necessarily, connected to the electrodeless discharge lamp (EDL) as a novel light source which generates efficiently UV/Vis radiation when placed into a microwave field. This review article is focused on the general principles of microwave photochemistry and photocatalysis, i.e. generation of UV/Vis discharge in EDL (theory of the microwave discharges, construction of EDL, preparation of the thin titania films on EDL, spectral characteristics of EDL, and performance of EDL). Likewise, the various microwave photochemical and photocatalytic reactor types (batch with external or internal light source, flow-through with external light source, annular flow-through with internal EDL, and cylindrical flow-through surrounded with EDL) with different arrangement of the lamps are described. The concept of microwave photochemistry and photocatalysis as an important issue in synthetic chemistry and material science is presented in several tables. [Refs. 1, 12]



Experimental set-up for microwave photochemistry and photocatalysis

**Simultaneous cooling at microwave heating - a new method in heterogeneous catalysis**

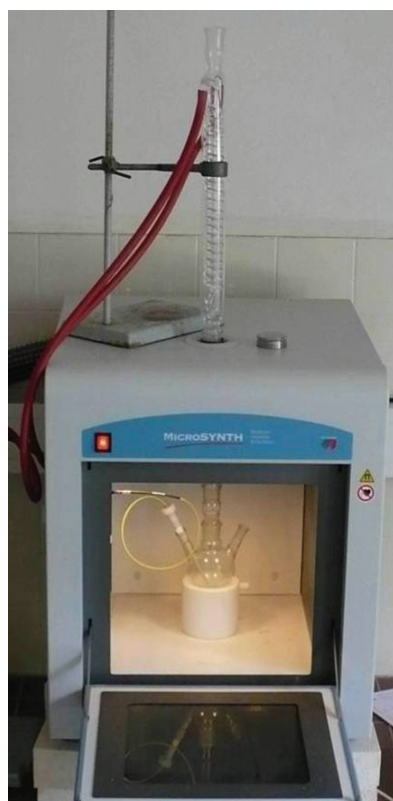
(M. Hájek, [hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz); supported by GACR, grant No. 104/08/0416)

The research has been focused on application in heterogeneously catalyzed reactions in liquid phase. It has been observed that selectivity of catalytic reaction can be significantly improved. These important findings evoked continuation to study this effect in more detail, what is the subject of this project. Scope and limitation of this method including possibility of potential applications has been studied on model reactions with non-polar (non-absorbing) reactants (alkylation of aromatics by cycloalkenes) in the presence of strong acidic (strong absorbing) solid catalysts. [Ref. 18]

**Effect of microwave energy on selective leaching of Pb, Zn and Al from the electronics waste with high Cu contents**

(M. Hájek, J. Sobek, [hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz), [sobek@icpf.cas.cz](mailto:sobek@icpf.cas.cz); joint project with Institute of Geotechnics of the SAS, Košice, Slovakia; supported by SAS, projects No. APVV-51-035505 and VEGA 02/0087/08)

The project deals with the use of conventional and microwave-assisted leaching of copper, aluminium, zinc and lead from electronics scrap using 2 M HCl. The method has been investigated to improve the yields of extracted metals and to reduce the processing time. The leaching was carried out at the boil of the acid. The experiments were performed in a modified microwave oven, applying a full factorial design involving the acid concentration, the liquid/solid ratio and irradiation time. The impact factors and their interactions affecting the metal yields were different. The maximum recovery of Al, Zn, Pb was up to 90 % at 30-min leaching. The dissolution of Cu was negligible. The yields of Pb and Al were dependent on temperature, time and the method of leaching. The yields were 91 % after 60 min of microwave heating at 60 °C, and 83 % in the case of conventional heating. At 80 °C virtually all Pb went into solution after 60-min microwave leaching, while the yield of the conventional leaching was only 60 %. [Ref. 11]



**Microwave synthesis labstation  
MicroSYNTH  
(Milestone srl, Italy)**

### Fluidization and decontamination of organic-polluted solids in a fluid-bed reactor

(M. Hartman, [hartman@icpf.cas.cz](mailto:hartman@icpf.cas.cz); supported by GA ASCR, grant No. IAA400720701)

An ideally mixed flow model is developed for the high-temperature oxidation of toxic carbon monoxide into inert carbon dioxide occurring in an afterburner chamber. The extent of the oxidation reaction in oxygen – and water vapor – bearing flue gas is explored as a function of the relative throughput, the gas density, and the global rate of reaction. Steady-state experimental measurements of the CO, O<sub>2</sub>, CO<sub>2</sub>, and water vapor concentrations were conducted in a pilot-plant refractory afterburner fitted with a natural gas burner. The global burnout reaction is assumed to be first order in carbon monoxide and one-half order with respect to oxygen and water vapor. The numerical solutions of the model equations outline the possibilities and limitations for the performance of a well-mixed afterburner chamber (reactor) under realistic operating conditions. [Ref. 4]

### Fluidized-bed incineration of dry sewage sludge from the waste water treatment plant in Brno-Modřice

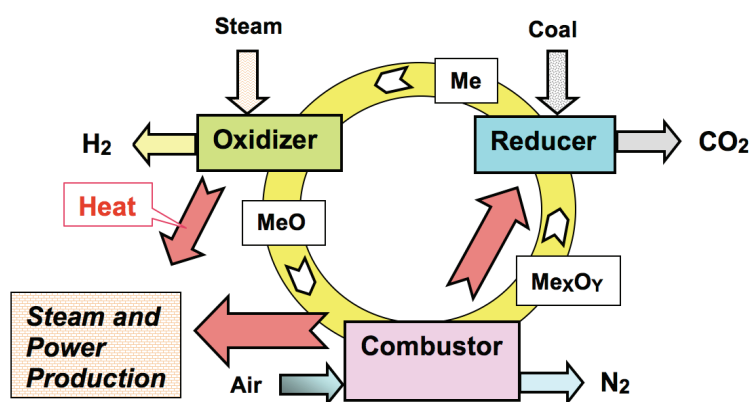
(M. Pohořelý, [pohorely@icpf.cas.cz](mailto:pohorely@icpf.cas.cz); contract with Brno University of Technology)

Contract devoted to experimental tests in the field of emission generation in sewage sludge incineration. Primarily, the experiment aimed at evaluating the influence of limestone addition to sludge incineration on the generation and removal of acidic components (hydrogen halides, sulfur dioxide). Additionally, further gaseous emissions as well as heavy metals were explored. The results were evaluated on the basis of current legislation.

### Advanced processes for gasification, gas cleaning and hydrogen production - PPP bilateral Czech-Taiwanese research project

(K. Svoboda, [svoboda@icpf.cas.cz](mailto:svoboda@icpf.cas.cz); research co-operation between ICPF and Institute of Nuclear Energy Research, Longtan, Taoyuan County, Taiwan, project No. NSC 100-2911-I-042A-501)

The bilateral research project is aimed at development of advanced fluidized bed gasification process with efficient gas cleaning and research of advanced processes for chemical looping technologies for hydrogen production. Barrier filters with fixed/moving bed of granular materials and dry methods for removal of sulfur and chlorine compounds are studied and further developed. Also effects of staging of gasification media and effects of fluidized bed particulate materials on gasification, tar destruction and limitation of sulfur compounds emissions are among subjects of bilateral research.



Simplified scheme of Coal Direct Chemical Looping process for hydrogen production and CO<sub>2</sub> separation (Me = metal, e.g. Fe)

### **Emission factors of POPs and heavy metals from small sources**

(M. Šyc, [syc@icpf.cas.cz](mailto:syc@icpf.cas.cz); joint project with Energy Research Center VŠB-TU Ostrava, Institute of Public Health in Ostrava; supported by Ministry of the Environment of the CR, project No. SP/1a2/116/07)

Domestic heating appliances are significant source of air pollution. The project reports on the first complex data set of emission factors (EFs) of selected pollutants from combustion of five fuel types (lignite, bituminous coal, spruce, beech, and maize) in six different domestic heating appliances of various combustion designs. The effect of fuel as well as the effect of boiler type was studied. Numerous EFs were measured, including the EFs of particulate matter (PM), carbon monoxide (CO), polyaromatic hydrocarbons (PAH), hexachlorobenzene (HxCBz), polychlorinated dibenzo-p-dioxins and furans (PCDD/F), etc. The obtained data set can be used for unambiguous recommendation of suitable heating appliances and fuels leading to minimization of environmental pollution. [Refs. 5, 7, 9, 16]

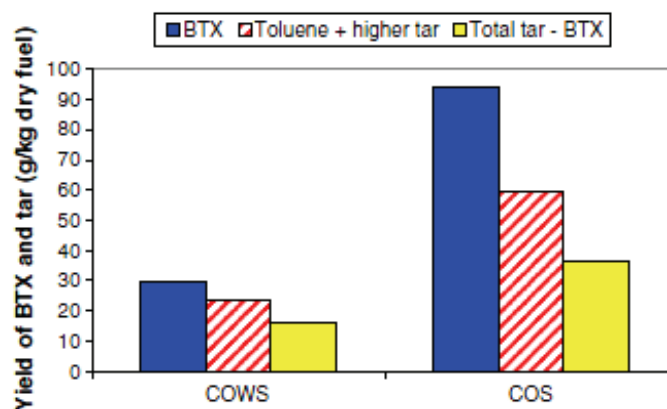


**Czech village in winter season (photo by Jiří Horák)**

### **Advanced concepts and process schemes for CO<sub>2</sub> free fluidized and entrained bed co-gasification of coals**

(K. Svoboda, [svoboda@icpf.cas.cz](mailto:svoboda@icpf.cas.cz); joint research project with CNR (Italy), LNEG (Portugal), CIEMAT (Spain), TUV (Austria), ICL (United Kingdom), ELCOGAS (Spain), UNISA (Italy); supported by MEYS and RFCS, grant No. RFCR-CT-2010-00009 and 7C11009)

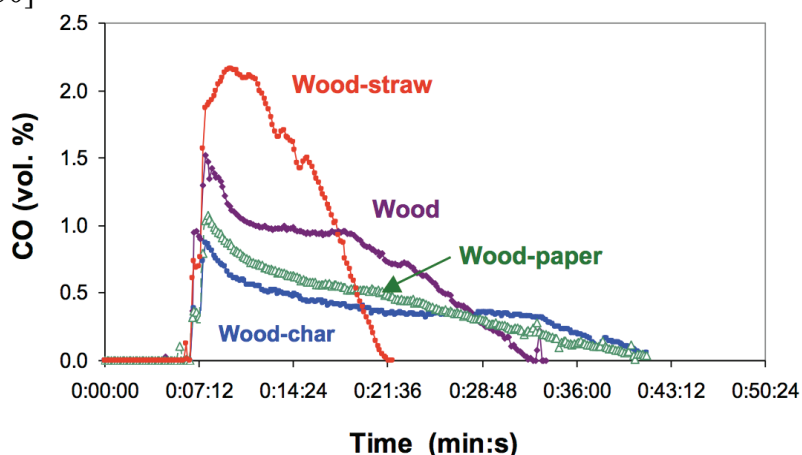
The project aims at integrating gasification schemes for the co-gasification of coal, biomass and waste with processes for CO<sub>2</sub> separation and capture. Fluidized bed and entrained flow gasification processes are considered thanks to their flexibility and effectiveness for carrying out thermal conversion of different feedstock and for matching different requirements of producer gas end-users and for effective CO<sub>2</sub> separation. Fuel feeding in a form of solid particles, mixtures of solid particles and various slurries (suspensions of solid fuel particles) and different fluidized bed particulate materials (sand, dolomite, olivine) are compared in terms of their effects in fluidized bed gasification. Effects of both, primary measures (involved in overall conditions of a given gasification process) and secondary (downstream) measures on syngas properties (particularly composition, purity and heating value) and possible applications are studied. [Refs. 27, 28, 29, 30]



**Comparison of BTX and tar yield from FB gasification of Polish coal based ternary slurry COWS (ER=0.19, CO<sub>2</sub>/dry fuel mass ratio=2.39, H<sub>2</sub>O/C molar ratio=0.7) at 850 °C and Polish coal based COS (ER=0.20, CO<sub>2</sub>/dry fuel mass ratio=2.43)**

### **Moving bed gasification of biomass and biomass pellets and producer gas cleaning** (K. Svoboda, [svoboda@icpf.cas.cz](mailto:svoboda@icpf.cas.cz); contract with UJEP)

Contract dealing with experimental support for development of a new type of moving bed gasifier (up-draft, co-current), production and testing of various biomass pellets for such gasification, experimental research of suitable conception for producer gas cleaning (mainly dry, adsorption based methods) and effects of air staging on tar concentration in produced gas. [Refs. 19, 30]



**Comparison of CO<sub>2</sub> gasification rates of the four kinds of pellets in terms of measured CO concentrations in outlet gas**

### **Development and verification of thermal desorption technology using microwave radiation**

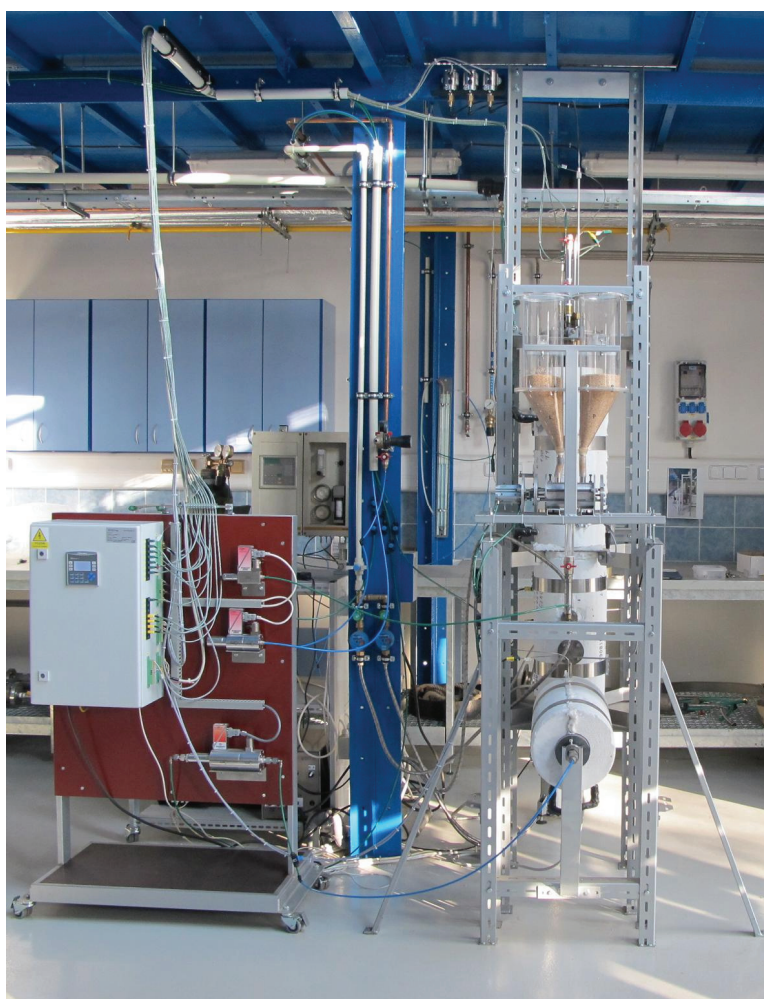
(M. Hájek, J. Sobek, [hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz), [sobek@icpf.cas.cz](mailto:sobek@icpf.cas.cz); joint project with ICT and Dekonta, a.s; supported by TACR, projects No. TA01020383)

The main goal of the project is development and verification of thermal treatment method utilizing microwave radiation for heating up contaminated material in a primary treatment unit. An originally designed pilot-scale treatment unit will be assembled. Operation efficiency of the unit will be verified by treatment of wide range of contaminated soil and solid waste samples. By development of this innovative technology, the applicant will strengthen his market position and improve his competitiveness in the field of remediation services and hazardous waste treatment activities. [Refs. 6, 23]

**Brownfields - Source of renewable energy (BROZEN)**

(M. Punčochář, M. Šyc, [punc@icpf.cas.cz](mailto:punc@icpf.cas.cz); [syc@icpf.cas.cz](mailto:syc@icpf.cas.cz); joint project with EVECO Brno Ltd., CULS Prague; supported by TACR, project No. 01020366)

The phytoextraction ability of some fast growing plant species leads to the idea of connecting biomass production with soil remediation of contaminated industrial zones and regions. This biomass will contain significant amount of heavy metals and its energetic utilization has to be considered carefully to minimize negative environmental impacts. Therefore, behavior of selected heavy metals was observed during fluidized bed gasification and combustion of contaminated biomass (willows, poplars, flax). This knowledge is essential for further utilization of all products of gasification and for the fulfillment of emission limits during combustion. [Refs. 10, 31, 32]

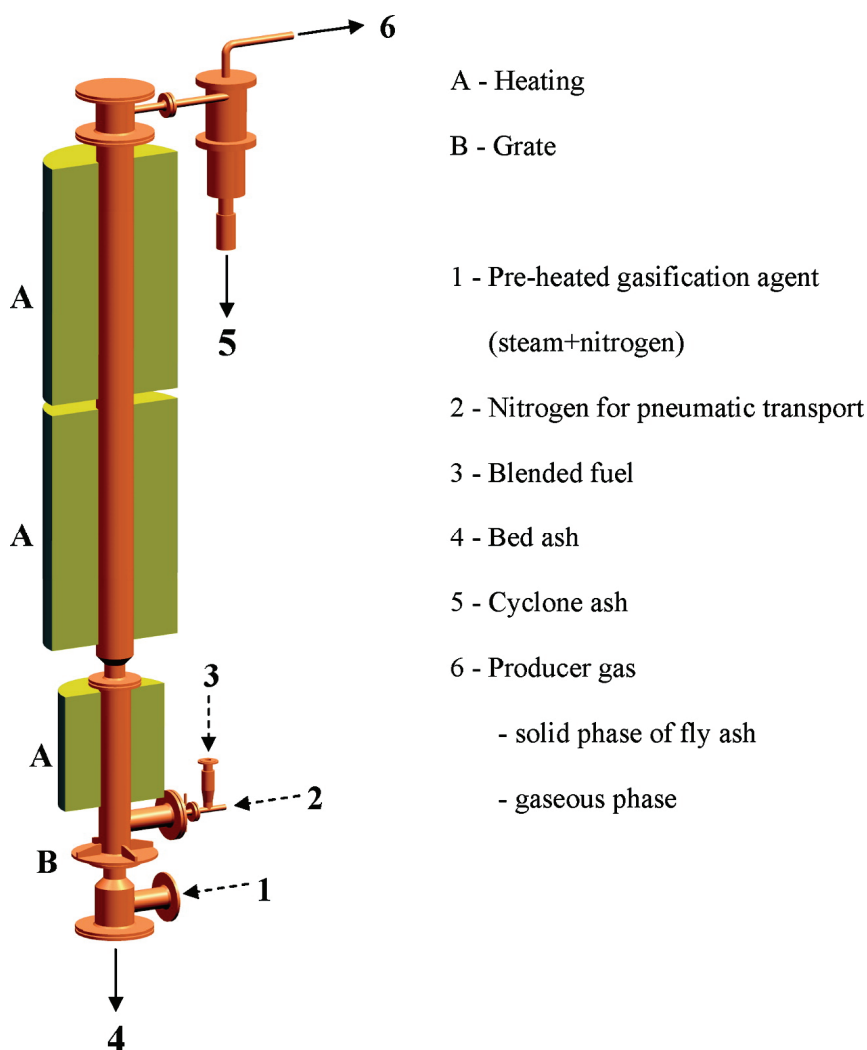


**Fluidized bed reactor**

**Waste as raw material and energy source (WARMES)**

(M. Punčochář, [punc@icpf.cas.cz](mailto:punc@icpf.cas.cz); joint project with Brno University of Technology, EVECO Brno Ltd.; supported by MEYS, project No. 2B08048)

The project is concerned with research and application of modern approaches leading to the higher efficiency in using different classes of wastes in energy and recycling processes. Attention is paid especially to the processes of thermal processing of wastes with the aim of maximal use of produced energy with minimization of released harmful substances. Project involves both experiments and computer simulations. [Refs. 10, 14, 15, 20, 25]



Scheme of fluidized bed reactor

### Simultaneous microwave drying and disinfection of flooded books

(M. Hájek, [hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz); joint project with ICT and National Archives of the CR; supported by ASCR, grant No. AV0Z40720504)

An advanced microwave drying technology has been developed using a microwave continuous dryer combined with an air cooling unit and a simultaneous disinfection process. This new technology uses microwave absorption filters made from special porous ceramics which act as both absorbent and transparent material for microwaves. Ceramic slabs reduce the intensity of the microwave radiation to such an extent that overheating and hot-spot formation as well as red-heating of metallic objects and other kinds of damage is prevented. Almost all books and documents were dried without any damage to printing in metallic inks, colored reproductions, metallic objects and other components sensitive to microwaves. The treatment also destroyed moulds and their spores by use of UV electrodeless lamps, which rendered additional disinfection unnecessary. [Ref. 2]





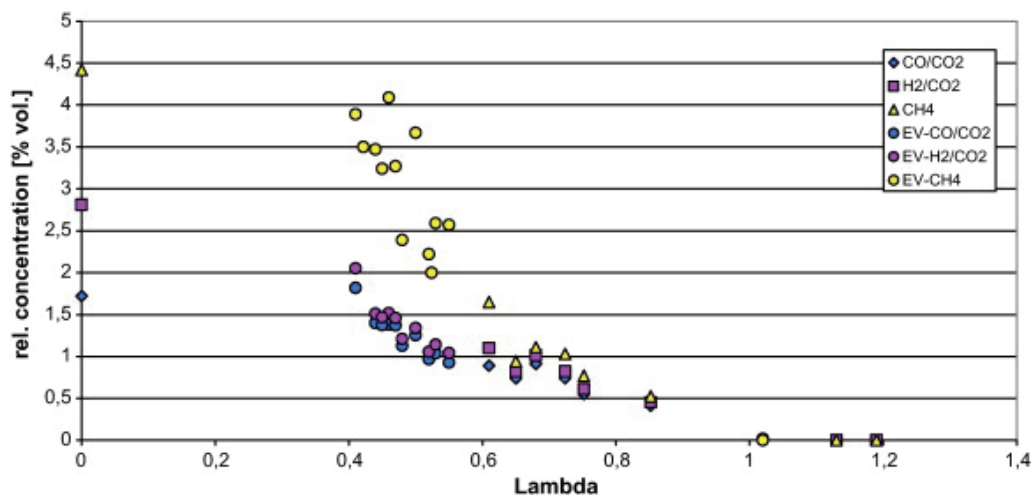
**Continuous microwave drying equipment**

### **Hydrogen production via synthetic gas by biomass/oil partial oxidation**

(V. Veselý, J. Hanika, [vesely@icpf.cas.cz](mailto:vesely@icpf.cas.cz), [hanika@icpf.cas.cz](mailto:hanika@icpf.cas.cz); joint project with VÚAnCh, a.s., Ústí n. Labem and ICT Prague; supported by MIT, grant No. MPO 2A-2TP1/024)

Common research efforts of ICPF, Institute of Inorganic Chemistry Ústí n/L and ICT Prague were focused on comparison of pilot plant partial oxidation of meal rape and hydrocarbon oil mixture with process simulation using equilibrium reactor model by process simulator Aspen Plus which resulted in a good agreement. The application of representative compounds method for simulation of such complex mixture was found as a useful tool for optimal process conditions prediction. Based on this procedure the ratio feed to both oxygen and steam were proposed for prediction of good experimental parameters for good process yield of hydrogen. The advantage of co-gasification of bio-waste and hydrocarbon oil mixture using suspension of 10 wt% meal rape in the feed can be observed in higher hydrogen production in cca 2.5 % rel. and lower oxygen and steam process demand in cca 5 % rel. It was stated that key parameter lambda (or analogously oxygen to feed ratio) controlling the partial oxidation process in optimal regime should be in the interval 0.6–0.8, i.e. under reaction conditions.

Partial oxidation regime can be characterized by similar lambda parameter used e.g. in characterization of car engine regime. Lambda is the dimensionless ratio of actual quantities of oxygen into the reactor should amount to, in theory, the quantity of oxygen required for combustion of carbon in the fuel to CO<sub>2</sub> and hydrogen to water. Where fuel (biomass) contains oxygen, then this oxygen is considered a reactive and reduces the theoretical quantity of oxygen. If the fuel contains moisture, its oxygen does not count. The effect of small content of nitrogen and sulfur in the feed on oxygen demand was neglected. Regime of partial oxidation of the complex feed strongly influenced the product composition. Figure illustrates the effect of lambda parameter on different product components ratio in the product stream. This is experimental evidence of necessity to operate the process under the reduction conditions for lambda value interval 0.6–0.8. In case of more reduction regime the dominant production of methane was observed. [Refs. 3, 33-36]



**Product composition versus gasification regime. Temperature 1200 °C; experiments with pure oil and (EV) with 8% meal rape content in hydrocarbon oil, resp.**

### **Method for obtaining extracts containing europium and yttrium and method for recovery of spent phosphors from compact fluorescent lamps**

(V. Gruber, [gruber@icpf.cas.cz](mailto:gruber@icpf.cas.cz); supported by ICPF)

In the present invention, there is disclosed a method for obtaining extracts containing Eu and Y from raw material comprising acid inorganic aqueous spent liquors of luminophore concentrate when recycling color kinescopes and monitors wherein the method is based on countercurrent continuous extraction with subsequently elutriation of extract with a diluted mineral acid from acid aqueous spent liquors containing inorganic acid and water, using an extraction agent consisting of bis-(2-ethylhexyl)phosphoric acid and liquid aliphatic hydrocarbons wherein the method of the present invention is characterized in that obtained mixture is extracted in a extraction countercurrent column with two separating terminal sections and two inlets of aqueous phase and one inlet of organic phase. [Refs. 13, 17]

### **International co-operations**

Central Mechanical Engineering Research Institute, Durgapur, India: Waste gasification

Institute for Energy and Transport, Joint Research Centre of EC, Petten, the Netherlands:

Atmospheric and pressurized fluidized bed combustion/gasification technologies; Waste incineration/gasification

University of KwaZulu-Natal, Durban, Republic of South Africa: Gaseous and particulate emissions

The Vienna University of Technology, Austria: Fluidized bed biomass gasification

Imperial College, London, United Kingdom: Pressurized FB gasification, combination with SOFC

The Combustion Research Institute, National Research Council, Napoli, Italy: In-bed catalytical processes for fluidized bed gasification and tar reduction

Institute of Nuclear Energy Research, Atomic Energy Council, Taiwan: Development of fluidized bed gasification with efficient gas cleaning, chemical looping production of hydrogen

Laboratório Nacional de Energia e Geologia, Portugal: Syngas cleaning, removal of tar, sulfur and nitrogen compounds

## Visits Abroad

P. Kameníková: Hawaii Natural Energy Institute, University of Hawaii, USA (2 months)

## Teaching

- V. Církva: ICT, Faculty of Chemical Technology, postgraduate course “Microwave Chemistry”
- V. Církva: ICT, Faculty of Chemical Technology, postgraduate course “Photochemistry”
- M. Pohořelý: ICT, Faculty of Environmental Technology, courses “Alternative Energy Sources I”, “Chemical Calculations”, “Laboratory of Fuel Analysis”, and “Laboratory of Fuels”
- M. Punčochář: Czech University of Life Sciences Prague, course “Renewable and alternative sources of energy”
- K. Svoboda: UJEP Ústí nad Labem, Faculty of Environment, courses “Decontamination and Bio-remediation Technologies” and “Energetics (Power generation) and Protection of the Environment”

## Publications

### Original papers

- [1] Církva V., Relich S.: Microwave Photochemistry and Photocatalysis. Part 1: Principles and Overview. *Curr. Org. Chem.* 15(2), 248-264 (2011).
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- [9] Šyc M., Horák J., Hopan F., Krpec K., Tomšej T., Ocelka T., Pekárek V.: Effect of Fuels and Domestic Heating Appliance Types on Emission Factors of Selected Organic Pollutants. *Environ. Sci. Technol.* 45(21), 9427-9434 (2011).

- [10] Šyc M., Pohořelý M., Jeremiáš M., Vosecký M., Kameníková P., Skoblia S., Svoboda K., Punčochář M.: Behavior of Heavy Metals in Steam Fluidized Bed Gasification of Contaminated Biomass. *Energy and Fuels* 25(5), 2284–2291 (2011).
- [11] Znamenáčková I., Lovás M., Hájek M., Sobek J.: Vplyv mikrovlnnej energie na selektívne lúhovanie Pb, Zn a Al z elektronického odpadu s vysokým obsahom Cu. (Slov) The Effect of Microwave Energy on Selective Leaching of Pb, Zn and Al from the Electronics Waste with High Cu Contents. *Chem. Listy* 105(5), 625-628 (2011).

### Review papers

- [12] Církva V., Relich S.: Microwave Photochemistry. Applications in Organic Synthesis. *Mini-Reviews in Organic Chemistry* 8(3), 282-293 (2011).

### Patents

- [13] Gruber V., Rousková M., Heyberger A., Staf M.: Způsob získávání extraktů s obsahem europia a yttria. (Czech) Method for Reclaiming of Organic Extracts Containing Europium and Yttrium Ions. Pat. No. CZ302854/PV 2010-928. Applied: 10.12.14, Patented: 11.12.14.
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- [17] Gruber V.: Způsob přepracování odpadních luminoforů z kompaktních fluorescenčních lamp. (Czech) Method for Recovery of Spent Phosphors from Compact Fluorescent Lamps (CFLs) . Pat. No. PV 2011-298. Applied: 11.05.18.
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- [21] Čapek L., Smoláková L., Prieceľ P., Kutálek P., Hájek M., Bulánek R., Kubičková I., Matějová L.: Analysis of Basic Sites at Solid-Base Catalysts. 4<sup>th</sup> International Symposium Advanced Micro- and Mesoporous Materials 2011, Book of Abstracts, p. 110, Riviera Resort, Bulgaria, 6-9 September 2011.
- [22] Čapek P., Veselý V., Kolafa J., Hejtmánek V., Brabec L.: Simulace transportu hmoty v replikách pórovitých látek pro účely odhadu jejich efektivních transportních vlastností. (Czech) Mass Transport Simulation in Replicas of Porous Material: Effective Transport Properties Estimation. 58. Konference

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- [23] Kašťánek F., Sobek J., Kašťánek P., Šolcová O., Hájek M.: Dehalogenation of Polyhalogenated Compounds Dissolved in Organic Solvents with the Help of AOPs in a Two-Phase Solvent-Water System under the Influence of Ultrasound. 12<sup>th</sup> International Conference on Environmental Science and Technology CEST 2011, Proceedings, p. 114, Dodecanese, Rhodes Island, Greece, 8-10 September 2011.
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