

# Environmental Process Engineering Laboratory

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(UNTIL 31 MAY 2012)

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(SINCE 1 JUNE 2012)

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OLEKSIY KHRAMKOV

## Fields of research

- Microwaves in photochemistry and photocatalysis
- Advanced processes for gasification, gas cleaning and hydrogen production
- Development of process for disposal of plastic waste using plasma pyrolysis technology
- Persistent organic pollutants and heavy metals emissions and behavior
- Urban mining - metals recovery from waste ashes
- Fluidized bed gasification of solid, liquid and slurry feedstock
- Medium and high temperature gas cleaning (particularly removal of HCl and H<sub>2</sub>S from producer gas)

## Applied research

- Grateless moving bed gasification of wood and waste wood
- Brownfields - Source of renewable energy (BROZEN)
- Development and verification of thermal desorption technology using microwaves
- Method for the chemical depolymerization of waste polyethylene terephthalate
- Complex recycling of compact fluorescent lamps (CFLs) and removal of toxic mercury
- Process for preparing hydrogen by partial oxidation of high-boiling hydrocarbon mixtures and biomass
- Wet precipitators PM for medium-power boilers burning renewable biomass
- Fluidized bed combustion and gasification
- Sewage sludge combustion and co-combustion
- Optimization of waste-to-energy plant and air pollution control devices

## Research projects

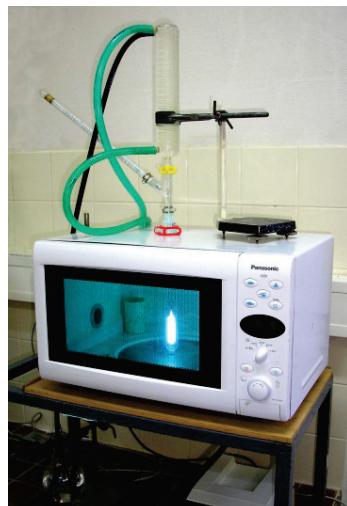
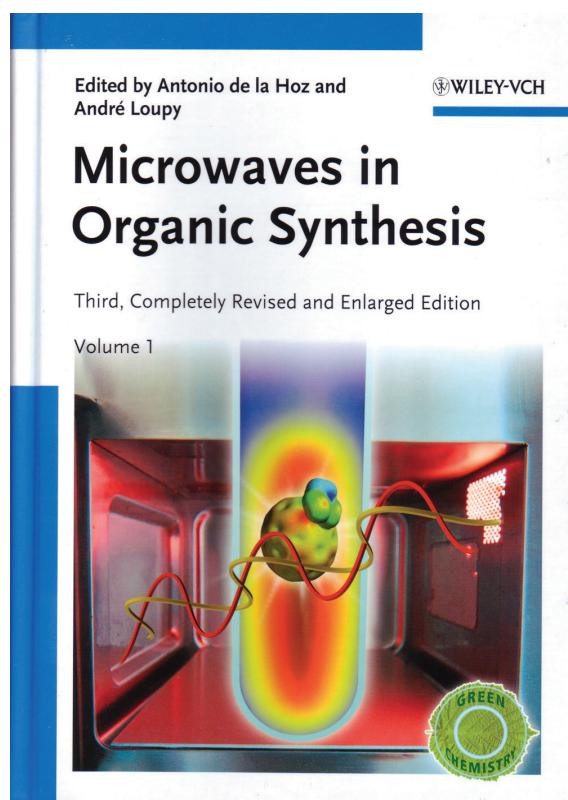
### Microwaves in photochemistry and photocatalysis - overview

(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 chapter in book is focused on the general principles of microwave photochemistry and photocatalysis, i.e. generation of UV/Vis discharge in EDLs (theory of the microwave discharges, construction of microwave-powered EDLs, preparation of the thin titania films on EDLs, spectral characteristics of the EDLs, and performance of the EDLs). 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 have been described.

We have discussed how the concept of microwaves in photochemistry and photocatalysis is already an important issue in synthetic chemistry and material science. Although still in the beginning, detailed analysis of past and present literature confirms explicitly the usefulness of this method of chemical activation. The application of EDL simplifies the technical procedure, especially in the field of organic photochemical and photocatalytic synthesis, environmental chemistry, or analysis. [Refs. 12, 18]

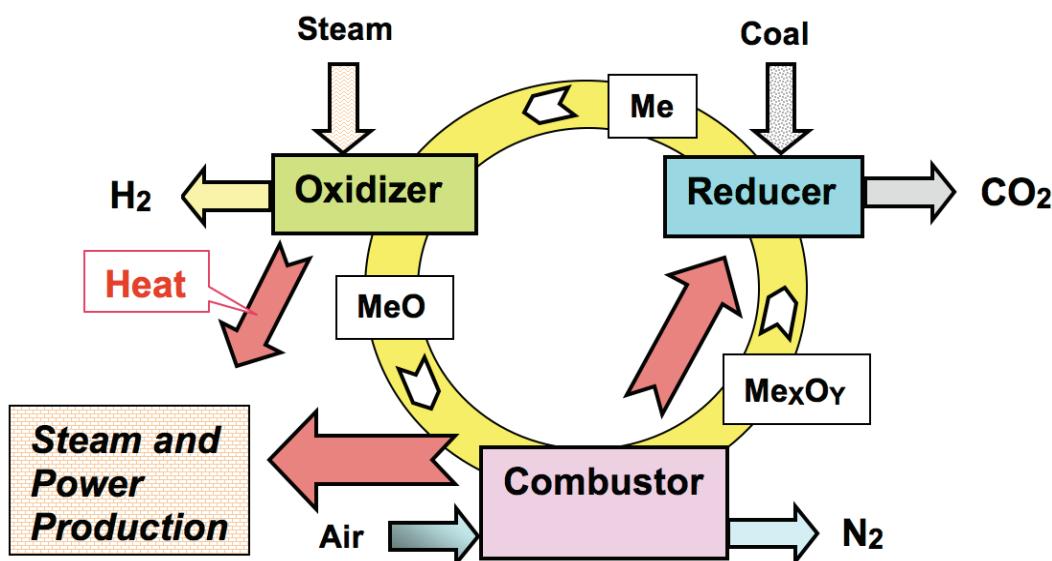


**Book cover and experimental set-up for microwave photochemical reactions**

## **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 processes 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 medium/high temperature methods for deep 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. The target of the overall research and development is efficient combination of fluidized bed gasification with deep producer gas cleaning for long-term fuelling of solid oxide fuel cells (SOFC) and production of hydrogen and CO<sub>2</sub> rich streams by chemical looping processes. [Refs. 1, 2, 16]



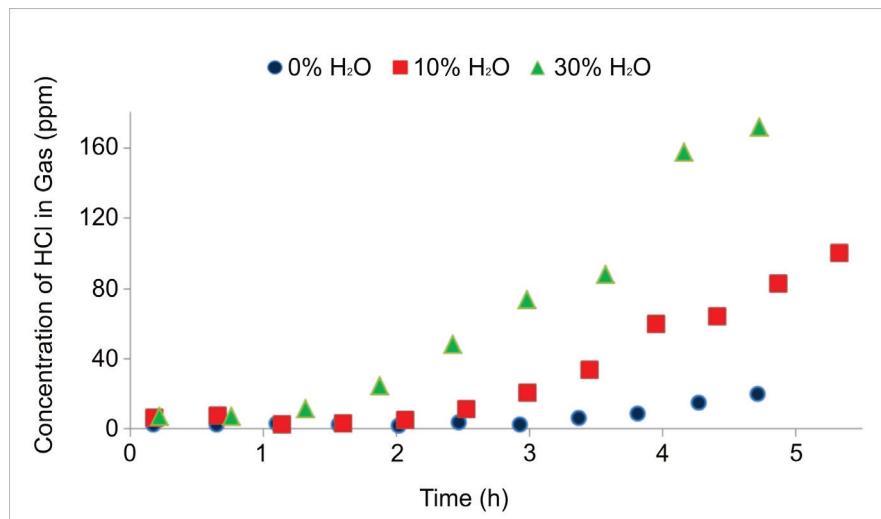
**Simplified scheme of Coal Direct Chemical Looping process for hydrogen production and CO<sub>2</sub> separation (Me = metal, e.g. Fe)**

## **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, project No. RFR-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 as well as effects of partial substitution of steam by CO<sub>2</sub> in gasification medium on gasification characteristics and producer gas properties. [Refs. 6, 8, 11, 15]



**Outlet concentrations of HCl - dependence on time and water vapor concentration in gas, sorption on KHCO<sub>3</sub>-alumina based sorbent (Reaction conditions: c(HCl) = 559±36 ppm-v; GHSV = 3385±215 h<sup>-1</sup>), temperature = 500°C**

### Development of process for disposal of plastic waste using plasma pyrolysis technology and option for energy recovery

(M. Punčochář, [puncochar@icpf.cas.cz](mailto:puncochar@icpf.cas.cz); joint research project with Central Mechanical Engineering Research Institute (CMERI), Durgapur, India; supported by Joint Research Project under ASCR and Council of Scientific and Industrial Research (CSIR), India)

Plasma pyrolysis is an innovative technology for transforming high calorific plastic waste into a valuable synthesis gas (syngas) by means of thermal plasma. The process developed is a drastic non-incineration thermal process, which uses extremely high temperature in an oxygen-starved environment to completely decompose input plastic waste into syngas, composed of very simple molecules: CO, H<sub>2</sub> and small amount of higher hydrocarbons. A 20 kg/h capacity plasma arc pyrolyser for treatment of plastic waste as well as energy recovery options from waste plastic has been indigenously designed, developed, installed and studied its performance at the CMERI, Durgapur. After pyrolysis of plastic waste in the plasma arc reactor, generated hot gases (syngas) are quenched through water scrubbing to avoid recombination reactions of gaseous molecules; this inhibits the formation of toxic gases. Syngas composition has been characterized by Gas chromatograph; residue/ash collected at the bottom of the pyrolyser has been analyzed on Neutron Activation Analyzer (NAA). Research results indicated that the developed plasma pyrolyser might be a useful way of plastic waste treatment for energy recovery. [Ref. 7]



**Experimental setup of plastic waste plasma arc pyrolyser**

### **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 grateless 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 or wet, absorption based methods) and effects of air staging and maximum gas temperature attained on tar concentration in produced gas. [Refs. 9, 17]

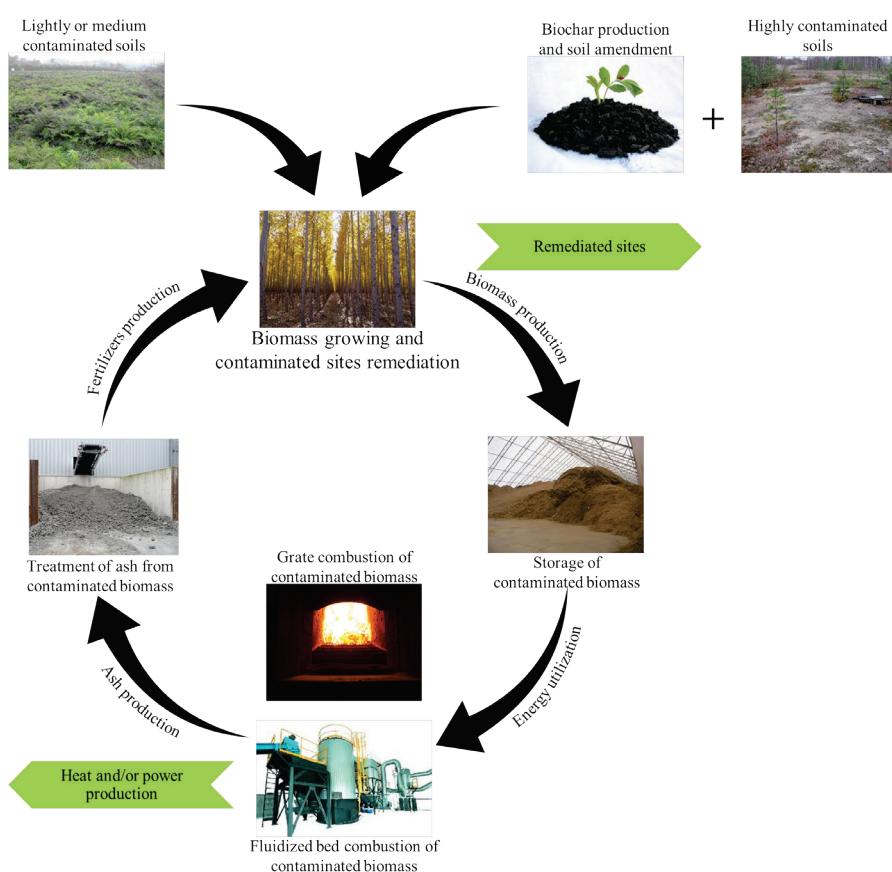


**Grateless moving bed gasifiers**

## Brownfields - Source of renewable energy (BROZEN)

(M. Šyc, [syc@icpf.cas.cz](mailto:syc@icpf.cas.cz); joint project with EVECO Brno s.r.o., 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 on 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, the behavior of selected heavy metals was observed during thermal treatment of contaminated biomass. Moreover, a detailed analysis of trace and nutrient elements distribution and chemical speciation in ashes was performed. The potential of the application of these ashes and methods of treatment for heavy metals removal was evaluated. This knowledge is essential for further utilization of all products of gasification and for the fulfillment of emission limits during combustion. The concept of contaminated biomass growing and utilization was proposed. [Ref. 10]



## The concept of contaminated biomass growing and utilization

### 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, project 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.

This work is focused on a pilot scale experiments of the microwave thermal desorption technology of persistent organic pollutants (POPs). Obtained results showed, that evaporization and co-transport with water vapor are main processes observed by thermal desorption. Consequently, these pollutants can be effectively removed from the solid matrix by the desorption temperature lower than boiling point of monitored contaminants. The decomposition of naturally occurring organic substances in soils was not significant during this low-temperature process (up to 240°C). On the other hand the removal efficiency for some groups of contaminants (polyaromatic hydrocarbons (PAHs) and some congeners of polychlorinated biphenyls (PCB)) was significantly lower. All contaminants were removed very effectively during temperature of batch 400°C, only efficiency of PAHs removal was just 75%. Stirring of the batch by thermal process will represent important step for rising of POPs desorption efficiency, but it could not be performed in this tests. [Refs. 5, 19]

### **Method for the chemical depolymerization of waste polyethylene terephthalate**

(M. Hájek, J. Sobek, [hajek@icpf.cas.cz](mailto:hajek@icpf.cas.cz), [sobek@icpf.cas.cz](mailto:sobek@icpf.cas.cz); supported by NOEN, s.r.o.)

A method for the chemical depolymerization of waste polyethylene terephthalate by application of microwave radiation and solvolysis in the presence of a catalyst comprising the first stage where the waste polyethylene terephthalate is mixed up with an microwaves absorbing activator, the mixture is melted by its exposing to a microwave radiation on a frequency from 915 to 2450 MHz and with a power output from 0.1 to 0.5 kW per kg of a charge, at a temperature from 230 to 330°C, under atmospheric pressure and the second stage, where the molten mixture is subjected to solvolysis, including acidic or basic hydrolysis, alcoholysis or glycolysis in the presence of a catalyst under continuing microwave radiation and atmospheric pressure yielding terephthalic acid, salts or esters thereof, and ethylene glycol. [Ref. 13]



**Purified terephthalic acid**

**Complex recycling of compact fluorescent lamps (CFLs) and removal of toxic mercury contained in input material**

(V. Gruber, A. Heyberger, [gruber@icpf.cas.cz](mailto:gruber@icpf.cas.cz), [heyberger@icpf.cas.cz](mailto:heyberger@icpf.cas.cz); joint project with Recyklace Ekovuk, a.s., supported by TACR, project No. TA02021290)

Project is solving the complex recycling method of compact fluorescent lamps (CFLs) with mercury content: from controlled destruction over the part sorting on glass, metal and luminophore, separation of mercury from luminophore and mercury conversion to chemical stable form suitable for deposition or repeated utilization, up to isolation of precious components (yttrium and europium) and their repeated utilization at fabrication of lighting devices.



**Apparatus for recovery of rare metals**

**Process for preparing hydrogen by partial oxidation of high-boiling hydrocarbon mixtures and biomass and apparatus for making the same**

(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, project No. MPO 2A-2TP1/024)

The present invention relates to a process for preparing hydrogen by partial oxidation of high-boiling hydrocarbon mixtures and biomass wherein the invented preparation process is characterized in that biomass with moisture level of 10 % at the most is treated to a particle size in the range of 0.1 to 0.3 mm. Subsequently, so treated biomass is then mixed in a high-boiling hydrocarbon mixture. The biomass and the high-boiling hydrocarbon mixture ratio ranges within 4:100 to 12:100. Finally, an oxygen-steam mixture is added. The reaction mixture reacts within a reactor at a temperature ranging from 1200 to 1400°C, at a pressure in the range of 3 to 4 MPa and with a dwell of 7 to 20 s to obtain hydrogen and synthesis gases. In the invention, there is further described an apparatus for making the above-indicated preparation process. [Ref. 14]



**Afterburning furnace for incineration of the hydrogen**

### **Research and development of wet precipitators PM for medium-power boilers burning renewable biomass**

(J. Hanika, V. Veselý, [hanika@icpf.cas.cz](mailto:hanika@icpf.cas.cz), [vesely@icpf.cas.cz](mailto:vesely@icpf.cas.cz); joint project with TENZA, a.s., Brno and VSB-TU Ostrava; supported by TACR, project No. TA02020369)

Project is developed the new technology for separating solid particles from flowing mass of air, especially for middle-burning source of renewable biomass resources and the technology present in the form of a utility model and a prototype of representative size. The size of the prototype was chosen to allow transfer of results of experimental research and development in commercial use after project completion.



**Wet separator for flying ash**

## 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 (12 months)

## Visitors

M. Čárský, University of Kwazulu-Natal, Durban, Republic of South Africa  
Y. Kansha, University of Tokyo, Japan

## 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, postgraduate course "Energetic  
Using of Biomass" and 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] Hartman M., Svoboda K., Pohořelý M., Šyc M.: Otěr minerálních katalyzátorů ve fluidním zplyňovacím reaktoru. (Czech) Attrition of a Mineral Catalyst in a Fluidized Bed Gasification Reactor. *Chem. Listy* 106(9), 844-846 (2012).
- [2] Hartman M., Trnka O., Svoboda K., Pohořelý M.: Úletové rychlosti částic vápencového kalcinátu z fluidní vrstvy. (Czech) Entrainment Velocities of Calcined Limestone Particles from Fluidized Bed. *Chem. Listy* 106(4), 303-306 (2012).
- [3] Kárászová M., Vejražka J., Veselý V., Friess K., Randová A., Hejtmánek V., Brabec L., Izák P.: A Water-Swollen Thin Film Composite Membrane for Effective Upgrading of Raw Biogass by Methane. *Sep. Purif. Technol.* 89, 212-216 (2012).
- [4] Keppert M., Pavlík Z., Tydlitát V., Chyba V., Švarcová S., Šyc M., Černý R.: Properties of Municipal Solid Waste Incineration Ashes with Respect to Their Separation Temperature. *Waste Manage Res.* 30(10), 1041-1048 (2012).
- [5] Mašín P., Hendrych J., Kroužek J., Kochánková L., Sobek J.: Čtvrtprovozní ověření mikrovlnné termické desorpce s reálně kontaminovanými materiály. (Czech) Verifying thermal desorption with microwave heating for real contaminated materials in a pilot scale experiments. *Acta Environmentalica Universitatis Comenianae* (Bratislava) 20(Suppl. 1), 78-83 (2012).
- [6] Pohořelý M., Svoboda K., Jeremiáš M., Skoblia S., Kameníková P., Beňo Z., Šyc M., Punčochář M., Hartman M., Durda T., Krček M., Tošnarová M.: Spolu-zplyňování uhlí a dřevní biomasy ve fluidní vrstvě. (Czech) Co-Gasification of Brown Coal and Woody Biomass in the Fluidized-Bed. *Paliva* 4(4), 128-140 (2012).
- [7] Punčochář M., Ruj B., Chatterj P.K.: Development of Process for Disposal of Plastic Waste Using Plasma Pyrolysis Technology and Option for Energy Recovery. *Procedia Eng.* 42(SI), 420-430 (2012).
- [8] Svoboda K., Pohořelý M., Jeremiáš M., Kameníková P., Hartman M., Skoblia S., Šyc M.: Fluidized Bed Gasification of Coal-Oil and Coal-Water-Oil Slurries by Oxygen–Steam and Oxygen-CO<sub>2</sub> Mixtures. *Fuel Process. Technol.* 95(1), 16-26 (2012).
- [9] Šulc J., Štojdl J., Richter M., Popelka J., Svoboda K., Smetana J., Vacek J., Skoblia S., Buryan P.: Biomass Waste Gasification-Can Be the Two Stage Process Suitable for Tar Reduction and Power Generation? *Waste Management* 32(4), 692-700 (2012).
- [10] Šyc M., Pohořelý M., Kameníková P., Habart J., Svoboda K., Punčochář M.: Willow Trees from Heavy Metals Phytoextraction as Energy Crops. *Biomass Bioenerg.* 37, 106-113 (2012).

### Review papers

- [11] Pohořelý M., Jeremiáš M., Kameníková P., Skoblia S., Svoboda K., Punčochář M.: Zplyňování biomasy. (Czech) Biomass Gasification. *Chem. Listy* 106(4), 264-274 (2012).

### Chapters in books

- [12] Církva V.: Chapter 14: Microwaves in Photochemistry and Photocatalysis. In: *Microwaves in Organic Synthesis*, 3<sup>rd</sup> Ed. (de la Hoz, A. - Loupy, A., Ed.), pp. 563-605, Wiley-VCH Verlag, Weinheim 2012.

### Patents

- [13] Hájek M., Sobek J., Brustman J., Veselý V., Drahoš J.: Method for the Chemical Depolymerization of Waste Polyethylene Terephthalate. Pat. No. CN101688015/200880002443.4. Applied: 10.01.12, patented: 12.09.19.

- [14] Lederer J., Kovač D., Veselý V., Hanika J., Nečesaný F.: Způsob výroby vodíku parciální oxidací vysokovroucích uhlovodíkových směsí a biomasy, a zařízení k provádění způsobu. (Czech) Process for Hydrogen Production by Partial Oxidation of High Boiling Hydrocarbon Mixtures and Biomass, and Apparatus for Processing. Pat. No. CZ303392/PV 2010-653. Applied: 10.09.02, patented: 12.08.29.
- [15] Pohořelý M., Kameníková P., Svoboda K., Skoblia S., Jeremiáš M., Šyc M., Punčochář M., Hartman M.: Zařízení pro fluidní zplyňování tuhých paliv. (Czech) The Facility for the Fluidized-Bed Gasification of Solid Fuels. Pat. No. CZ24582/PUV 2012-26461. Applied: 12.07.27, patented: 12.11.19.
- [16] Punčochář M., Skoblia S., Kameníková P.: Způsob stanovení celkového obsahu dehtu v plynu produkovaném zplyňováním paliva. (Czech) Method of Total Tar Content Determination in Gasifier Gas. Pat. No. CZ303491/PV 2008-780. Applied: 08.12.08, patented: 12.09.10.
- [17] Svoboda K., Smetana J., Štojdl J., Šulc J., Vacek J.: Způsob zplyňování upravené biomasy a zařízení k jeho provádění. (Czech) Method and Apparatus/Equipment for Gasification of Adapted Biomass. Pat. No. CZ303367/PV 2011-404. Applied: 11.07.01, patented: 12.07.09.
- [18] Storch J., Církva V., Bernard M., Vokál J.: Způsob výroby [6]helicenů fotocyklizací a zařízení k jeho provádění. (Czech) Method and Apparatus for Production of [6]Helicenes. Pat. No. PV 2012 - 245. Applied: 12.04.11.
- [19] Hájek M., Sobek J., Mašín P., Hendrych J., Kroužek J., Kubal M., Kukačka J.: Způsob dekontaminace tuhých materiálů. (Czech) Method of Decontamination of Solid Wastes. Pat. No. PV 2012-269. Applied: 12.04.19.