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MICROCHANNEL –TECHNOLOGIES

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Abstract

The miniaturization of devices achieves small process volume and hold-up, large specific transport rates and high surface-to-volume ratios. The combination of these features results in extremely short response times considerably simplifying process control, and eases the handling of large heat and mass fluxes thus making the synthesis of dangerous compounds safer with reducing hazardous waste. For chemical technologies, the applications of miniaturized reaction systems or microreactors, is centered on gas and liquid phase reactions covering simple microscale mixing of different fluids volumetric titrations, heterogenous and homogeneous catalysis, catalytic oxidation, pyrolysis, heterocyclic synthesis, photochemical reactions and microfuelcell applications. Due to higher yields and selectivities, the application of environmentally more favorable reaction routes, and the possibility to replace large plants by small plants for distributed production according to actual demand, it is to be expexted that micro-technologies will eventually contribute to their sustainable development.

Keywords: Microreactors; Microchannels; Flow distribution; Heat transfer; Process intensification; Organic synthesis; Flow chemistry; Gas phase reactions; Pyrolysis.

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1. Introduction

In last two decades micro technologies and micro equipment are the objects of great interest in chemical engineering. Small series of high-performance micro-heat exangers, reactors, mixers, extractors, pumps and valves has been already developed and produced.Such equipment have the range of cross-section dimension between 10 µ and 1-3 mm. Microfluids, micro- or microchannel-technologies, as it is called sometimes, essentially accomplishes the miniaturization of conventional process devices and enables the integration of reaction and unit operation elements directly with sensors and actuators. Research in the field of microscale devices has accelerated during the past 10-15 years. Researchers from various fields are intensively analyzing the possibilities offered by miniaturization of equipments to achieve a fundamental change in design philosophy for chemical plants. The smaller characteristic dimensions in microscale devices leads to extremely high surface to volume ratio (S/V), which in turn provides several advantages over conventional-size reactors, mixers and heat transfer equipments, such as

1. higher transport (e.g. heat and mass transfer) rates;
2. safe environment for hazardous or toxic chemicals (due to low amount of chemicals used during process);
3. simplify process control for effective process/materials screening (due to extremely short response time);
4. on-demand or on-site synthesis of critical chemicals such as H_2O_2,ethylene oxide;
5. no strict limit in size reduction or expansion of plant components since any production capacity is achievable by means of parallel operation;
6. development of intergrated chemical analytical platforms as in micrototal analysis systems.

For chemical technologies, the applications of miniaturized reactions systems, or microreactors, is centered on gas and liquid phase reactions covering simple microscale mixing of different fluids to volumetric titrations, heterogeneous and homogeneous catalysis, catalytic oxidation, heterocyclic synthesis, photochemical reactions and microfuel cell applications. Due to higher yields and selectivities, the applications of environmentaly more favorable reactions routes, and the possibility to replace large plants for distributed production according to actual demand, it is to be expected that microtechnologies will eventually contribute to their sustainable development.

Revolutionary advances offered by miniaturized devices for real world applications are demanding a paradigm shift of approach. In many cases, it is interesting to find that reality has overtaken imagination in the research of micro-technologies. The interests of established researches from multidisciplinary backgrounds have led to a broad spectrum of research in the field of microchannel-technologies and, interstingly, how these technologies are opening new pathways and reinventing approaches in chemical technologies, micro-reaction engineering as well as in medical sciences.

The microscale devices should influence the future of the process industry. Therefore the understanding and proper evaluation of the flow and mixing behavior in microscale devices such as microreactors and mixers is critical to their effective design and optimization.The accurate and optimized design of microreactors and mixers heavily relies on flow characteristics (laminar, turbulent and laminar-to-turbulent flow regimes) and pressure drop correlations is still discussed contraversially in the literature; therefore a careful analysis of experimental data reported by various researchers is highly desirable.

The research articles and patents publications published between year 1999 and 2009 on microreactors and mixers have been analyzed in terms of their field of application [1]. Many publication do not include the actual information about microreactors and mixers; they are only mentioned either in the introduction or the main text. The large number of both research articles and patents are assigned to the field of chemistry (physical, analytical, organic and inorganic), biochemistry, nanoscience and nanotechnology, instruments and instrumentations, etc. A number of chemical companies are trying to exploit the advantages of microreactors. It is observed that microreactors and mixer technologies are prominent in fine chemicals, speciality chemicals, pharmaceuticals and consumer products applications. However, microreactors still have challenges for industrial production, which includes the fundamental and basic understanding of hydrodynamics and mixinge process in the microscale devices. For an industrially designed and optimized microscale devices it is required to understand geometrical, flow and mixing parameters.

2. Fluid flow in microchannels

Over the course of the past two decades, many conflicting publications with the results on the validity of classical macro-scale equations for microchannel fluid flow and heat transfer have been given. Among this research are the investigations of the validity of the macro-scale equations number, and the Nusselt number on the microscale. Some authors claim that new phenomena occur in microchannels, while many others report there exist several effects, usually neglected in deriving correlations, which lead to larger discrepancies with observed experimental results in microchannels. Usually several assumptions were made in literature studies when flow and heat transfer were modeled [2] : (i) steady – state fully developed flow; (ii) thermophysical properties of the fluid do not vary with temperature; (iii) simplified boundary conditions (constant wall temperature of constant heat flux); and (iv) the fluid heating due to viscous dissipation can be neglected.

An accurate estimate of the pressure drop and flow bahavior in microscale devices requires precise measurement techniques. In spite of the existence of numerous experimental investigations for flow resistence and transition from laminar-to-turbulent flow in microchannels, there are discrepancies in experimental data with the conventional theories, which results into different arguments. The database [1] is comprised of experimental papers that directly deal with the pressure drop measurements and transition from laminar-to-turbulent flow in microchannels for various cross-sectional geometries (circular, rectangular, triangular, trapezoidal, hexagonal, etc.), flow rates (in terms of Reynolds number, Re) and fluids (gases or liquids). In the case of gas (both compressible and incompressible) flow in microchannel; air, nitrogen, helium, argon, etc. reported while in the case of liquid flows; water, isomers of alcohols silicon oils, R134a, etc. are analyzed. The hydraulic diameter of microchannels investigated by different researchers is varied between 1 and 4010 µm. The experimental friction factor data is compared with conventional theory and it is observed that there is no univocal answer though microchanel dimensions, process fluids and condition considered were similar in different studies. The discrepancy which has been reported by many authors was transition from laminar-to-turbulent flow, even though the surface roughness is ≤ 1%. In some case, even though the microchannel cross-section was not circular, the experimental Poiseuille numbers was compared with the conventional results for micropipes (fRe = 64).

As most microreactors operate at elevated temperatures, it is often the case that temperature differences in microchannels can create a non-uniform flow distribution due to differences in the pressure drop, which is temperature dependent [3]. This situation can be observed even when a proper flow distributor is applied. Therefore the problem of flow distribution is closely related to the temperature distribution in a downstream microreactor or micro-heat-exchanger. On the other hand most heat transfer and pressure drop calculations of microstructured reactors, it is presumed that the inlet flow and temperature distribution across the reactor cross-section are uniform.

3. Intesified superheated processing

By reconsideration of the novel chemistry concept introduced in 2005 [4], meanwhile termed novel process windows [5,6], six major process intensification pathways were identified :

- new chemical transformation;
- routes at much elevated temperature;
- routes at much elevated pressure;
- routes at much increased concentration or even solvent-free;
- process integration and simplification, and
- routes in the explosive of thermal runaway regine.

Here effects by operation at temperatures above the atmospheric boiling point are reported [7]. There are two kind of processing at much elevated temperature. The first involves bringing strongly cooled (cryogenic) chemical processes to ambient temperature or slightly above/below. Here, the intrinsic kinetic potential of these reactions is realeased, which cannot be exploited by conventional technology since mixing masking is inherent (owing to the too long mixing times; in the seconds range). The second and more novel process windows (NPW) relevant issue is to perform organic reactions under much higher temperatures of > 150°C, most favorably in the range from 180 to 250°C, which is significantly above the solvent's boiling point and uses overpressure to maintain a single-phase operation-superheated processing. Here, the reactions rates are accelerated according to the temperature dependence given in the Arrhenius equation. There is a considerable enlargement of the operational regime with regard to temperature and pressure as compared to batch operation and even to the encased harsh processing in microwave chemistry, which nicely demonstrates the potential of and justifies the naming of novel process windows.

Diverse gas-phase reactions have been investigated in micro-reactors, amoung them (partial) oxidation, hydrogenation dehydrogenations, dehydrations , and reforming processes [10]. Particular attention has been drawn to achieve excelent temperature control and to prevent hot-spots. So, for many reactions increases in selectivity were found. Especially, many examples of partial oxidations were described, including processes of utmost industrial importance such as ethylene oxide synthesis. With consecutive processes, as e.g. given for multiple hydrogenations, high selectivity was achieved for species that are thermodynamically not the most stable molecule of all species serially generated such as monoenes yielded by hydrogenation of polyenes. Also increasesin conversion were achieved, e.g. by processing at higher pressure and high temperature, often in the explosive regime. As a consequence, high space-time yields were reported as well. In many cases reactor performance better compared to fixed-bed technology was achieved Process safety was found to be high when using micro-reaction devices. With respect to process optimisation, fast serial screening of processess parameter variation was conducted, at low sample consumption.

The advantages of the microchannel technology seem to be very useful for performing fast and strongly exotermic heterogeneously catalyzed gas phase reactions.The oxidative dehydrogenation of propane was found to be a well suited and sensitive test reaction, which shows many typical features of this class of reactions [8]. Due to their superior heat transfer properties, microstructured reactors are well suited for performing strongly exotermic heterogeneously catalyzed gas phase reactions. In order to utilize the full potential of this reaction technology , a new low-cost manufacturing concept was developed, using a Ni-Ag-Sn solder system for bonding the individual structured steel platelets. Three different methods for depositing a VO_x/ γ-Al_2O_3 material on the micro-channels were investigated with respect to morphology, mechanical stability and catalytic behavior of the obtained coatings. For evaluating the performance of the coatings, the oxidative dehydrogenation of propane servered as a sensitive test reaction. The modules and the catalytic coatings withstood the applied reaction conditions (400-600°C at ambient pressure), which makes them safe and flexible tools for research activities and small scale production processes.

Microchannel chemical reactors are a new type structured reactors. The common feature of such reactors is small single or many parallel channels with submillimeter cross-reaction. The small cross-reaction of microchannels permits one to obtain also a high surface-to-volume ratio and high mass-and-heat transfer rates, which can be 1-2 orders of magnitude higher than those observed for the systems with the fixed catalyst bed. As the result, microchannel reactors can provide nearly isothermal conditions even for extremely exotermic or endotermic reactions. In case the microchannel reactors are directed to use microchannels [9,10]. The microchannel plates for the heterogeneously catalyzed reactions, the catalyst is generally deposited onto the walls of the catalytic partial oxidation of methane reactors are traditionally made of the FeCrAl alloy, the surface of which is covered with a thin catalyst layer using sol-gel methods . Microchannel catalytic reactors have repeatedly proved their high efficiency in the process of partial oxidation of methane (at 650-780°C) as compared to traditional fixed-bed catalytic reactors [11].

Steam reforming of ethanol was studied over $Rh/CeO_2/Al_2O_3$ catalysts in a microchannel reactor. First, the catalyst support was deposited on the metallic substrate by washcoating and then CeO_2 and active metal were sequentially impregnated [12]. The effect of support composition as well as active metal composition on steam reforming of ethanol in microchannel reactor was studied at atmospheric pressure, with an ethanol to water molar ratio 1 : 6, over a temperature range of 400-600°C. The microchannel reactor performance was compared with that packed bed reactor using 2% Rh/20% CeO_2/Al_2O_3 catalyst at identical operating conditions. The activity was similar in both the reactors but the selectivity to desired products were higher in microchannel reactor. The hydrogen yield obtained in the microchannel reactor was high (~ 65 $l.g^{-1}.h^{-1}$) as compared to 60 l hydrogen $g^{-1}.h^{-1}$ in the packed reactor.

The Fischer –Tropsh synthesis is a a well-know catalytic process for the conversion of synthesis gas into liquid fuels. The main product of the process is a mixture of hydrocarbons of variable molecular weight. Different metallic supports (aluminum foams of 40 ppi, honeycomb monolith and micromonolith of 350 and 1180 cpsi, respectively) have been loaded with 20% Co-0,5% Re/γ-Al_2O_3 catalyst by the wash coating method. Layers of different thicknesses have been deposited onto the metallic supports. The catalytic coatings were characterized measuring their textural properties, adhesion and morphology. These structured catalysts have been tested in the Fischer-Tropsch synthesis (FTS) and compared with a microchannel block presenting perpendicular channels for reaction and cooling [13]. The selectivity depends on the type of support used and mainly on the thickness of the layer deposited. The C_5^+ selectivity of the microchannels reactor is higher than that of the structured supports and the powder catalyst.

The most efficient path to syn-gas is the conversion of natural gas via steam methane reforming. Both the steam methane reforming and Fischer-Tropsch benefit from process intensification offered by microchannel technology, resulting in smaller, less costly processing hardware; thus enabling cost effective production of synthetic fuels from smaller facilities, appropriate for stranded and associated gas resources, both on and offshore.The products from FT processes can be upgraded into diesel or synthetic paraffinic kerosene, or simply blended with crude oil for transport to the word market [14]. Compared to conventional tube style reactors, the reaction passages in microchannels FT have orders of magnitude smaller characteristic dimensions, which greatly improve heat and mass transfer. This allows optimal temperature control across the catalyst bed, which minimizes catalyst activity and life, and leads to far higher reactor productivity. Microchannel steam methane reforming offers similar advantages, reducing reactor size by up to 90%. Due to improved volumetric and catalytic productivity, microchannel steam methane reforming and Fischer –Tropsch enables lower capital and operating costs compared to conventional gas-to-liquids (GTL) process. Because conventional GTL technologies are not economically viable at small scale, the current focus is on large, land-based natural fields, such as those in Qatar. Microchannel technology permits economic production at this smaller scale. In addition to steam methane reforming and FT, microchannel processing technology is being applied to the final step of a synthetic fuel process-hydrocracking [14].

4.Steam cracking of hydrocarbons

The advantages of microchannel technology seem to by very useful for performing fast and strongly endotermic homogeneously and heterogeneously catalyzed gas phase reactions. The pyrolysis of hydrocarbons (from crude oil and natural gas) were found to be a well suited and sensitive test reaction, which shows many typical features of this class of reaction. In addition, the pyrolysis of hydrocarbons seems to be produce low molecular olefins oppose to conventional production processes [15]. Although ethylene is very important base chemical, it is primary obtained as a main product from steam cracking and other refinery processes (e.g. fluid catalytic cracking and deep catalytic cracking). However, all of these processes are thermodynamically limited, extremely energy-intensive, and commonly suffer from catalyst deactivation by heavy coking. There, a route that avoids most of these problems appears to be atractive.

The main route to ethylene production is by the thermal cracking of hydrocarbons. This reaction is carried out in tubular coils located in the radiant zone of fired heaters. Steam is added to reduce the partial pressure of the hydrocarbons in the radiant coils. The reactions that result in the transformation of mostly saturated hydrocarbons to olefins are highly endothermic and require reactor temperature in the range of 750 to 900^{o}C depending on the feedstock and design of the reactor coils.

The on-stream availability of thermal cracking reactor is determined by fouling of either the cracking coils or the cracked effluent transferline exchanger (TLEs). Coke is produced as a side product of thermal cracking and deposits on the radiant coil walls and inside the tubes of TLEs. This limits the heat transfer and decreases the pressure drop, thus reducing the olefine selectivity. The run length is normally determined by tube metal temperature in crease of the radiant coil, the outlet temperature of the TLE, or the increased pressure drop.

Coke is believed to be formed by two mechanisms-catalytic and condensation. The metal surface of the cracker coil catalyzes the growth of a filamentary type of coke and contains metal granules. The second type of coke is formed by condensation, polymerization, and/or agglomeration of heavies in the gaseous phase. The precise modeling of coking in commercial cracking coils is a highly complex process, and the mechanism is not fully understood.

The radiant coils are centrifugally cast from 25 Cr/35 Ni or 35 Cr/45 Ni materials for their carburization and creep resistance. These materials have a maximum service temperature of up to 1150^{o}C. The SRT heater design is characterized by a configuration that maximizes the coil surface-to-volume ratio at the coil inlet, where coking, tendeciencies are low. This is done by using small-diameter parallel tubes in the inlet pass or passes. At the outlet, where coking tendencies are high, large-diameter tubes are used. Typical radiant coil dimensions for hig-selectivity furnace are in the range of 40 to 120 mm ID (S/V, surface-to-volume ratio = 1,0 – 0,33 cm^{-1}).

The main question connected with the use of the pyrolysis turbular reactor deals with the deviations from ideality. In the laboratory, it is very difficult to realize ideal plug flow, characterized by a Reynolds number greater than 10^4 and a length/diameter ratio greater than 100. Generally, the Reynolds number is less than 100, internal diameter of the reactor tube is around 5 mm S/V, surface-to-volume ratio = 4 cm^{-1}) and the gas flow is laminar, with a parabolic profile. In the use of a laminar-flow turbular reactor, however, it is customary to assume that (a) entering gas molecules warm up instantaneously to reaction temperature, (b) there is a single residence time, (c) the reactant mixture is quenched instant-aneously at the outlet of the reactor, and (d) there is no pressure drop along the tube [16]. Normally, the pressure drop is negligible in laminar-flow experiments, and measurements of pressures permit ready confirmation of this fact. But it is more difficult to correct the results of deviations from plug flow due to axial nad radial diffusion, and of nonconstant temperature due to imperfect radial heat transfer.

With smaller diameter tubes, surface reactions in pyrolysis units are relatively more important and have hence received greater attention the designers. Recent evidence obtained in both laboratory and industrial units indicates that these surface reactions are more important than was thought. Surface reactions produce the following results [16,17].

1. Pyrolysis coils using smaller diameter tubes have moreover resulted in higher selectivity toward production of olefins and diolefins (1,3-butadiene) because of shorter residence time
2. At least some coke is produced
3. Part of coke is gasified. Apparently all CO and CO_2 produced occur as a result of surface reactions involving steam. For laboratory experiments in Vycor glass tubes, no CO or CO_2 was produced.
4. Carburization reaction weaken stainless steels and are a factor in eventual tube failure
5. Surface roughening and corrosion occur as a result of repeated oxidizing-reducing and sulfiding-desulfiding steps [18]. Coke production at metal surfaces also destroys the integrity of the metal surface .

Extrapolating these laboratory results to the industrial units involved the following problems, among others. Surface-to-volume ratios of the laboratory coil were 4 to 20 times greater than thouse of industrial coils in the 1-in. to 5-in. range. The ratio of surface to mass of reacting gases is inversely proportional to the total pressure of reactant. Because commertial units normally operate at 0,2 to 0,4 MPa in the reaction zone (radiant section), the relative importance of surface reactions would be two to four times less because of the pressure effects as compared to the laboratory units operated at atmospheric pressure. At least seven surface reactions occur during most industrial pyrolyses. In a complex and as yeat not completely understood manner, they all contribute directly or inderectly to coke formation.

Elemental sulfur, hydrogen sulfide, light mercaptans such as methyl or ethyl mercaptan, thiophene, dimetylsulfide, or diethylsulfide are suitable sulfur-containing compounds that react readily with stainless-steel surfaces in ethylene furnaces to produce metal sulfides on surface [16,18]. Reactions with these sulfur-containing gases are complicated and have not been completely clarified. Certainly the gases react with either oxidized or somewhat reduced metal surfaces to produce metal sulfides. Oxidized metal surfaces and H_2S ract to produce metal sulfides on the surface, steam, sulfur dioxide, hydrogen, and sulfur; at least some H_2S decomposes to form sulfur and hydrogen. Sulfur also reacts with the metal surfaces to produce metal sulfides. No information was found in the literature as to the relative rates of formation of the several metal sulfides or as to specific sulfides produced. Sulfiding to a limited extent the inner surface of a coil that has just been decoked and is hence oxidized is often beneficial for subsequent pyrolyses of hydrocarbons. As a result, production of coke, carbon oxides, and hydrogen is significantly reduced while ethylene yields are improved.

However, among a number of challenges , high production costs for microstructured devices have prevented a break through of this innnovative technology in the past. In order to utilize microreaction technology for possible industrial applications, a new flexibile and scalable manufacturing concept for microstructured reactors was developed and optimized [19]. Special attention was paid to the possibilities of affecting radical transformation of hydrocarbons by homogeneous additives and heterogeneous surface of the reactor with the intension of spreading the findings dealing with chemical reactions of free radicals and critical evaluation of the possibilities of their practical application for industrial pyrolysis processes. Many studies have been carried out investigating of reactivity of some organic and inorganic substances which have, in their molecule sulphur, nitrogen, oxygen, phosphorus, and chlorine with orientation to sulphur and its compounds. We studied the initiated pyrolysis from the point of acceleration of radical decomposition of hydrocarbons, selectivity improvement or desired alkenes and a decrease in the course of secondary reactions, the consequence of which is the formation of coke. The reactor wall modifies in many directions the course of radical decomposition of hydrocarbons with the application of heterogeneous reaction stages. The surface treatment (coatings) of the reactor by sulfur substances and oxidizing agents (history of reactor) which precedes pyrolysis itself, is important factor in the pyrolysis of hydrocarbon feedstock, when heterogeneous stages affect the rate of decomposition and coke formation. For the same reason we studied unconventional materials with the aim of contributing knowledge and intensification of industrial processes [18].

Many studies have been carried out investigating different means of catalyst preparation/deposition on microchannels and relevant results have been recently reviewed [20, 21]. However, only few reports combine catalyst deposition with reactor fabrication in a single study, which is a major prerequisite for a coherent manufacturing concept. Especially, methods suitable for mass production of microstructured reactors such as soldering and spray coating technologies are rarely described. Our research activities were not exclusively focused on the thermal decomposition reaction of hydrocarbons. All methods and processes were developed with respect to the general applicability of microstructured reactors to heterogeneously catalyzed gas phase reactions. The results of this study will be published in consecutive papers. In the first paper obtained reactors will be characterized and used for kinetic investigations of the pyrolysis of heptane.

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References

[1] Kumar,V., Parshivoiu, M., Nigam, K.D.P. : Chemical Engineering Science 66 (2011) 1329 – 1373.

[2] Rebrov, E.V., Schouten, J.C., Croon, M.H.J.M. : Chemical Engineering Science 66 (2011) 1374 – 1393.

[3] Chaudhuri, A.., Guha, C., Dutta, T. K. : Chemical Engineering Technology (2007)30, 425 – 430.

[4] Hessel, V.,Lőb, P., Lőwe, H. : Current Organic Chemistry (2005) 9 (8), 765 – 787.

[5] Hessel, V., : Chemical Engineering Technology (2009) 32 (11), 1655 – 1681.

[6] Illg, T., Hessel, V., Lőb, P. : Bioorganic and Medicinal Chemistry (2010) 18 (11), 3627 – 4154.

[7] Hessel, V., Cortese , B., de Croon, M.H.J.M : Chemical Engineering Science (2011) 66, 1426 – 1448.

[8] Schwarz, O., Duong, P.-Q., Schäfer, G., Scomäcker, R. : Chemical Enggeering Journal (2009) 145, 420 –428.

[9] Ehrfeld, W., Hessel, V., Loewe, H. : Microreactors-New Technology for Modern Chemistry, Willey-VCH, Weinheim, 2000.

[10] Kolb, G, Hessel, V.: Review : micro-structured reactors for gas phase reactions,Chem. Eng. J. (2004), 98, 1-38.

[11] Makarshin, L. L.,Andreev, D., Gribovskyi, A.G., Parmon, V. N.: Chemical Engineering Journal (2011), 178, 276-281.

[12] Peela, N. R., Mubayi, A., Kunzru, D.: Chemical Engineering Journal (2001) 167,578-587.

[13] Almeida, L. C., Echave, F. J., Sanz, O., Centeno, M. A, Arzamendi, G., Gandia, L.M., Sousa, E. F., Odriozola, J. A., Montes, M: Chemical Engineering Journal (2011), 157, 536-544.

[14] Lerou, J. J. :9th Novel Gas Conversion Symposium, Book of Abstracts, Lyon-France-30 May-3 June 2010, PL5, p. 27.

[15] Meyers, R. A. : Handbook of petrochemicals production processes, The Mc Graw-Hill Companies, Inc., New York, 2005.

[16] Albright, L. F., Crynes, B.L., Corcoran, W. H. : Pyrolysis : Theory and Industrial Practice, Academic Press, New York, 1983, p. 266; p. 233.

[17] Bajus, M., Veselý, V. : Patent Slovak Republic 175 812, (1974).

[18] Bajus, M. : Sulfur Reports (1989), vol. 9, Part 1, 25-71.

[19] Bajus, M. : Thermal Conversion of Petroleum Hydrocarbons into Petrochemicals, D.Sc Thesis, Slovak University of Technology in Bratislava, Faculty of Chemical and Food technology, Bratislava, Slovak Republic, 1987, pp. 210.

[20] Avila, P., Montes, M., Miro, E. E. : Chem. Eng. J. (2005), 109, 11-36.

[21] Meilla, V. : Appl. Catal.A : Gen. 315, (2006) 1-17.