Conversion of Glycerol to Propanediol and Acrolein by Heterogeneous Catalysis

ELISABETA RALUCA BOZGA[1], VALENTIN PLESU[2], GRIGORE BOZGA[2*], COSTIN SORIN BILDEA[2], ELENA ZAHARIA[2]

[1]National Institute for Economic Researches, Economics Industry and Services Center, 13 Calea 13 Septembrie, 050711, Bucharest, Romania

[2] Politehnica University, Chemistry Engineering Department, 313 Spl. Independentei, 060042, Bucharest, Romania

Consequence of an important increase in world biodiesel production, in the last decade the level of glycerol offered on the market exceeded the consumption rate. Beside its classical utilizations, particularly in pharmaceutical and food industries, glycerol emerges as an important renewable chemical that can be transformed into medium tonnage chemical products, replacing petroleum based intermediates. An important category of processes for glycerol conversion into value added chemicals are based on heterogeneous catalysis. This paper reviews the main research works investigating the glycerol transformation into two chemical products of industrial importance: propanediols and acrolein. Even if, on short term, these researches do not have an obvious economical impact, they certainly present an important potential for the future, when new feedstocks and processes will have to replace actual petroleum based products and technologies.

Keywords: hydrogenolysis, dehydration, propanediols, acrolein, solid catalysts

Glyerol is the simplest trihydric alcohol which has IUPAC name of propane-1,2,3-triol known also commercially as glycerin, 1,2,3-propanetriol, 1,2,3-trihydroxypropane, or glycyl alcohol. This substance is present in large quantities in nature, in the vegetal oils and animal fats, under the form of esters with different fatty acids, usually called 'triglycerides'. By its chemical structure and physical properties, the glycerol is one of the most versatile and valuable organic compounds. It is edible, virtually nontoxic for living organisms, easily biodegradable and obtainable from renewable sources. It also presents some physical properties that make it particularly interesting in common practical applications: high hygroscopicity, miscibility with the water, low volatility (normal boiling point 290°C), high viscosity, low freezing point.

Industrially, glycerol is produced by fats and oils saponification, hydrolysis, or transesterification. During the World Wars I and II, glycerol was also produced by fermentation or hydrogenolysis of carbohydrates, but these routes are not currently utilized industrially. During the last period of time, important amounts of glycerol were obtained as a byproduct of "biodiesel" production by vegetable oils and fats transesterification. From this process, glycerol results in a ratio of approximately 1:9 with respect to biodiesel product. In the biodiesel production, crude solutions containing typically 50-60% glycerol are separated from the transesterification mixture by gravity. These solutions contain, besides the alcohol used as transesterification reagent (usually methanol), the catalyst used in the transesterification, soaps and different salts. They are treated with an inorganic acid (hydrochloric or sulfuric acids) and separated from the formed free fatty acids by gravity, neutralized with caustic soda and further distilled for removing methanol and water. The result is the so called 'raw glycerol' which contains 80-85 % glycerol. Further glycerol purification from these solutions is rather difficult, and usually involves several separation steps including vacuum distillation at pressures as low as 10^{-5} bar and 120°C [1], refining on ion exchange resins, extraction, adsorption over silica, membrane separation etc. [2-4]. Nowadays, as a consequence of the important increase of world biodiesel production, the crude glycerol production attained over one million tones per year [5]. The spectrum of glycerol utilizations also developed continuously, so that presently it has over 1500 known end uses [6]. The increased glycerol offer on the market triggered efforts to find new valorization technologies, particularly by its conversion into medium tonnage chemicals, replacing petroleum derivatives. An important category of processes for glycerol conversion into commodity chemicals are based on the heterogeneous catalysis (hydrogenolysis, dehydration, etherification, esterification, oxidation, reforming etc.). General data concerning these processes are given by Pagliari and Rossi [7]. The aim of this work is to review the recent published research works concerning the catalytically conversion of glycerol into two important medium tonnage chemical intermediates: propane-diol isomers and acrolein respectively. The review is focused on data concerning the catalysts, working conditions and reported process performances. The best reported results are systematized in Table 1.

Glycerol hydrogenolysis to 1,2-propanediol and 1,3-propanediol

The two isomers of the propanediol, i.e. 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD) represent products of high commercial value. The conversion of glycerol to these products is performed typically by hydrogenolysis, with gaseous hydrogen in the presence of a solid catalyst. Of the two propanediol isomers, glycerol hydrogenolysis leads preponderantly to the 1,2-PD isomer, called also propylene glycol. This is presently produced from propylene via propylene-oxide and is used for the manufacture of polyester resins, pharmaceuticals, liquid detergents, cosmetics, paints, antifreeze, flavors etc. The other isomer, 1,3-PD, is even more valuable, being an important monomer used to fabricate polyester fibbers, films and coatings. For example, it is used for the manufacture of polyester SORONA® (DuPont) or CORTERRA® (Shell). The

* *email: g_bozga@chim.upb.ro*

economic importance of the two propanediols and the accessibility of glycerol led to a high interest in development of efficient glycerol hydrogenolysis processes. A large number of scientific papers and patents were published, particularly in the last two decades, describing the performances of different hydrogenolysis catalysts and technologies.

The catalytic process of glycerol hydrogenolysis was investigated both in liquid phase (in batch and continuous setups) and vapour phase (normally in continuous setups). Due to better access of the two reagents to the catalyst surface sites, the kinetics of the vapor phase transformation is significantly higher than in liquid phase. Generally, in the continuous processes a lower reaction time is necessary for a given conversion (0.5 -1.5 h as compared with 5- 12 h for batch ones). This is explained by the contribution of vapour phase reaction in partially wetted catalyst particles and could also be the consequence of a better hydrogen transfer towards the catalyst particles.

Good catalytic activity for glycerol hydrogenolysis has been reported for metal based catalysts, including noble metals (Rh, Ru, Pt, Pd) or transition metals, mainly Cu, Ni, Co, Cr and Zn, supported on porous materials (usually active carbon, SiO_2 or Al_2O_3). The process is performed either with pure glycerol or with glycerol solutions, usually in water, but also in other solvents (alcohols, sulfolane etc). Besides the propanediol as main product, several byproducts are also generated in glycerol hydrogenolysis, among which the most important are hydroxiacetone (acetol), 2-propanol, ethylene glycol and methanol.

The general accepted mechanisms for glycerol hydrogenolysis involve a first step dehydration to an intermediary product, catalyzed by acidic or basic catalyst sites, followed by intermediary product hydrogenation catalyzed by metallic sites (fig. 1).

Glycerol hydrogenolysis on copper based catalysts

One of the first studies of glycerol hydrogenolysis was published by [8]. The authors obtained 1,2-PD from glycerol of 98% purity (250 °C, 35 bar), in presence of copper-chromium-barium oxide catalyst, which proved in next studies to be among the most efficient catalysts for this process.

Comparative catalyst screening tests for glycerol hydrogenolysis were carried out by [9] on different metals, the best performances being obtained on Raney Cu catalyst. Working with diluted aqueous solutions of glycerol, at 240 °C and 30 bar hydrogen pressure, they obtained a glycerol conversion of 86% with an 1,2-PD selectivity of 66%. Better results on the same catalyst were reported by [10] (table 1). Dasari et al. [11] also investigated comparatively the glycerol hydrogenolysis process on several metallic catalysts: Ru/C, Ru/alumina, Pd/C, Pt/C, Raney nickel, Raney copper, Cu, copper chromite, Ni/C and Ni/silica-alumina. Among these, the best performances were obtained on the copper chromite catalyst. This finding was further confirmed by other authors. It was evidenced also a very good activity and selectivity of cupper chromite catalyst (table 1) [12]. The authors compared also the promoting effects of Al, Zn and Ba on the copper chromite catalyst, pointing out a higher improvement effect of Ba. This is explained by the enhanced acidity, which catalyzes the first step of dehydration of glycerol to acetol and by the increase of Cu-Cr catalyst stability in the presence of Ba [13]. Another improvement is due to BaCrO4 phase, which stabilizes the crystallite size of Cu at a lower value (69 nm), compared to the case of bare Cu–Cr catalyst (150 nm). The same authors also present an interesting comparison between the performances of batch and continuous hydrogenolysis processes [12].

Another study on the performances of Cu/γ-Al_2O_3 catalyst for glycerol hydrogenolysis to 1,2 – PD was published [14]. The Cu/Al_2O_3 catalyst with the optimized amount of Cu (~15 wt%) showed a selectivity to propanediols of about 96.8% with a glycerol conversion of about 49.6% (batch experiments at 220°C, 15 bar H_2 pressure, reaction time 10 h, Cu/glycerol molar ratio 3:100). Mane et al. [15] report hydrogenolysis data obtained on a Cu:Al nano-sized catalyst, in batch system. The reported best results indicate a glycerol conversion of 75 % and a selectivity in 1,2-PD around 87 %.

The effect of residual sodium originating from catalyst synthesis, on the CuO/SiO_2 catalysts prepared by precipitation-gel method was [16] investigated. The tests showed that the residual sodium had a negative effect on the properties of the catalyst. However, small amounts of sodium proved to be beneficial for CuO/SiO_2 catalyst, favouring both catalytic activity and good stability. The authors report 1,2- PD selectivity of 94.6 % at glycerol conversion 41.1 %, obtained in batch experiments with 40.0 g aqueous solution 80 wt% glycerol, 2.0 g of reduced catalyst, total pressure 90 bar, 453 K, 12 h reaction time, initial *p*H=12.

The role of specific metal surface area in glycerol hydrogenolysis on different copper catalysts finding a linear relationship between the specific copper surface area and the catalytic activity was studied [17]. The best results were obtained carrying out vapour phase hydrogenolysis of glycerol over a Cu/SiO_2 catalyst: 1,2-PD selectivity 87 % at total glycerol conversion (continuous fixed bed reactor;

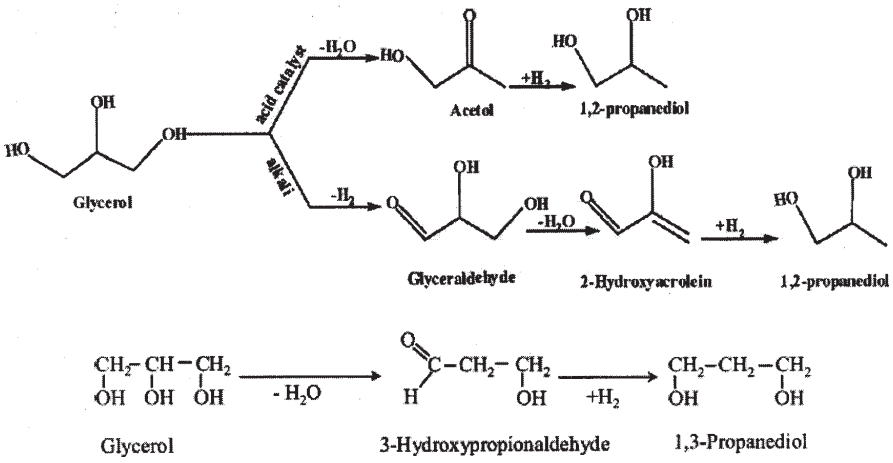


Fig. 1 General reaction schemes for glycerol hydrogenolysis

5 mL/h 40 wt % aqueous glycerol solution, 1 g catalyst, 255 °C, 15 bar, 300 mL/min H_2).

In [18] it was performed glycerol hydrogenolysis over CuO/MgO catalysts at 180 °C and 30 bar H_2 pressure. The conversion of glycerol and the selectivity of 1,2-PD over Cu (15 wt%)/MgO reached 72.0% and 97.6%, respectively (reaction conditions: 8.0 mL aqueous solution of 75 wt.% glycerol, 1.0 g of reduced catalyst, batch reaction time 20 h). An increase of glycerol conversion to 82.0% was achieved by adding small amounts of NaOH in the reaction mixture. A more selective catalyst was prepared and tested in glycerol hydrogenolysis by the same research group [19], by dispersing copper on a hydrotalcite solid base ($Cu_{0.4}Mg_{5.6}Al_2O_{8.6}$). Working batch-wise with 8.0 mL aqueous solution of glycerol 75 wt%, 1.0 g of catalyst, at 30 bar, 20 h reaction time, and 180 °C, the authors detected a glycerol conversion of 80 % with a 98.2 % selectivity toward 1,2-PD. A total glycerol conversion was reported by doubling the reaction time, without a significant loss in 1,2- PD selectivity.

A screening of the activity in glycerol hydrogenolysis for several metal oxides mixtures, derived from the corresponding hydrotalcite structures, was reported by [20]. The Mg/Al, Zn/Al, Ni/Mg/Al, Ni/Co/Mg/Al, and Cu/Zn/Al mixed-metal oxide catalysts were prepared from their related hydrotalcite precursors. The maximum yield of glycerol conversion to 1,2-PD was obtained in the case of Cu/Zn/Al catalyst. For a catalyst concentration of 5% (w/w), hydrogen pressure 14 bar, aqueous solution 80% glycerol, a glycerol conversion of 52 % with 93-94 % selectivity to 1,2-PD were obtained in batch experiments over 24 h of reaction. It is worth to note also that the authors tested successfully this catalyst with both purified and demethanolized crude glycerol (83 wt% glycerol).

Interesting catalytic properties for the glycerol hydrogenolysis were evidenced for different Cu-Zn mixtures in the studies published by [21-27]. The best results obtained on this catalyst appear to be those reported by Huang L. et al. and Franke and Stankowiak (table 1).

Performances of Ni/Al_2O_3–CuCr mixtures as hydrogenolysis catalyst were tested by [28] in batch experiments. The authors report selectivities in 1,2-PD over 90 % for a glycerol conversion of 45 %, working at 200 °C and 17 bar, 20 h reaction time.

As already mentioned, the experimental observations revealed that, on acid sites, the glycerol hydrogenolysis process occurs through the glycerol dehydration into hydroxyacetone (acetol), followed by the acetol hydrogenation into 1,2-PD. Thermodynamically, the endothermic dehydration step is favored by relatively high reaction temperatures, whereas the exothermic hydrogenation step is favored by low temperatures and high hydrogen concentration. These properties suggested developing two-step hydrogenolysis processes, where glycerol is firstly dehydrated into acetol at relatively high temperatures and, in a second step, the acetol is further hydrogenated into 1,2-PD at lower temperatures. Such a two-step technology was proposed by [29] on copper chromite catalyst. High acetol selectivity levels (> 90% for glycerol conversions over 90 %) were achieved in a semi-batch reactive distillation setup. Further improvements to the same process were reported by [30]. Akiyama et al. [31] developed a similar two-step process for glycerol conversion to 1,2-PD at ambient H_2 pressure, over copper metal catalyst. The first dehydration step was performed at temperatures around 200°C, whereas the second step of acetol hydrogenation at 120 °C. Under these conditions, the authors reported an 1,2-PD yield of 96.9 %, at total glycerol conversion (continuous fixed bed reactor, 8.7 g catalyst Cu/Al_2O_3 (55 wt%CuO-45 % Al_2O_3), feed rate of 30 wt.% glycerol solution, 1.8 mL/h; 360 mL/min H_2, H_2:glycerol molar ratio = 141). Dividing the reaction time into a dehydration period (under nitrogen, 1 bar) and a hydrogenation period (under a hydrogen pressure of 60 bar) was also investigated [32].

It should be noted that acetol is also an important intermediate in various organic syntheses. Sato et al. [33] studied the vapour phase glycerol dehydration to acetol, on copper based catalysts. Alumina-supported copper showed the highest catalytic activity with an acetol selectivity over 90 % for total glycerol conversion, at ambient pressure of nitrogen and 250 °C (1.5 g Cu/alumina catalyst with 60 mol% Cu ;1.8 mL/h of 30 wt.% glycerol aqueous solution, 25 mL/min N_2). There were also reported interesting results regarding the glycerol dehydration to acetol on a CeO_2-ZrO_2 binary oxide and Na-doped CeO_2 respectively [34, 35].

Glycerol hydrogenolysis on Ni and Co catalysts

A hydrogenolysis process using Nickel Raney catalyst leading to 1,2-PD yields around 70 % at low pressures was proposed [36]. In [37] it was used Ni supported on NaX zeolite as catalyst for hydrogenolysis (25 wt% glycerol aqueous solution). The conversion of glycerol reached 86.6% after 10 h reaction time, with 80.4% selectivity to 1,2-PD and 14.2% to ethylene glycol, under 60 bar H_2 pressure at 200°C.

In [38] it was prepared a hydrogenolysis catalyst by KBH_4 treating of the carbothermal reduced Ni/activated carbon. By KBH_4 treating, the surface carbonyl groups were reduced to phenolic groups, which considerably increased the catalyst acidity. The as-prepared catalyst gave 43.3% conversion of glycerol and 76.1% selectivity for 1,2-PG at 200°C under 50 bar H_2 after 6 h, and 63.2% conversion with 77.4% selectivity for 1,2-PG after 24 h. The same research group [39] found that the addition of cerium at Ni/activated carbon catalyst induces a remarkable promoting effect on the catalytic performance compared with other metals including copper, tin, zinc, aluminum, iron and cobalt. For example, 90.4% of glycerol conversion and 65.7 % 1,2-PD selectivity could be achieved at 473 K under 50 bar of H_2 with 6 h (150 ml of glycerol aqueous solution 25 wt.% and 6.95 g of Ni–Ce/AC catalyst.).

In [40] were prepared and demonstrated catalytic properties in glycerol hydrogenolysis for a complex containing Nickel Raney bonded on a macrocyclic structure of Fe-Co with organic ligands. A good selectivity to 1,2-PD but rather low glycerol conversion (< 50 %) were reported. Guo X. et al. [41] tested the bi-functional Co/MgO catalyst in the hydrogenolysis of glycerol to 1, 2-PD. Generally, the activity and selectivity were inferior to reported results for other tested catalysts (44.8 % glycerol conversion and 42.2 % 1,2 - PD selectivity in batch experiments at 473K, 20 bar H_2, 40 g aqueous solution of 10 wt.% glycerol, 0.2 g catalyst; 9 h reaction time). Highly efficient hydrogenolysis processes were also patented on a mixture of Co, Cu and Mo oxides as catalyst [42] and using Ni-Rh/active carbon catalyst (table 1) [43].

Glycerol hydrogenolysis on noble metals catalysts

Furikado et al. [44] compared the activities of Rh, Ru, Pt and Pd, supported on active carbon, SiO_2, Al_2O_3. Rh/SiO_2 exhibited higher activity and higher selectivity, as compared to other tested catalyst systems. Special designed experiments reported by the same authors concern the reaction mechanism and the reactivities of

the 1,2-PD and 1,3-PD in the reaction mixture. 1,3-PD has a higher reactivity in hydrogenolysis and transforms easily in 1-propanol. In addition, the authors found that the conversion can be increased in the presence of the ion exchange resin Amberlyst, due to acceleration of the glycerol dehydration to acetol, consequence of resin high acidity. Studies focused on the acidic resins effects on the activity of Ru/C catalyst were also published [45-48], and [32]. Shinmi et al. [49] showed that addition of Re, Mo or W to Rh/SiO_2 enhances the catalytic activity of the glycerol hydrogenolysis using water as a solvent. The modification with Re gave the highest conversion and yield of 1,3-PD. The $Rh\text{-}ReO_x/SiO_2$ (Re/Rh = 0.5) exhibited 22 times higher glycerol conversion and 37 times higher 1,3-PD yield than Rh/SiO_2 (batch experiments with 20 mL glycerol aqueous solution 20 wt% glycerol, reaction temperature 393 K, reaction time 5 h, initial H_2 pressure 80 bar, 150 mg catalyst, resulting 80 % glycerol conversion, selectivity toward 1,2 – PD ~40 % and selectivity toward 1,3 – PD ~15 %). The promoting effect of Re on the catalytic performances of Ru catalysts was also pointed out [50, 51].

Commercial carbon-supported monometallic Ru and Pt or bimetallic Pt-Ru and Au-Ru catalysts performances in glycerol hydrogenolysis were compared in [52,53]. In [54] it was investigated the catalytic activity of Ru supported on $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (CsTPA), a rather strong solid acid. It has been found that this is an active bifunctional catalyst for the hydrogenolysis of glycerol, providing 1,2-PD with 96 % selectivity at 21% conversion at relatively mild conditions (150 °C and 5 bar). In a similar study, Balaraju et al. [55] carried out glycerol hydrogenolysis to propanediols over 5 wt% Ru/C catalysts using different solid acids as co-catalysts. Solid acids such as niobia (Nb_2O_5), 12-tungstophosphoric acid (TPA) supported on zirconia (ZrO_2), cesium salt of TPA and cesium salt of TPA supported on zirconia were used. The order of conversion of glycerol for the solid acid catalysts were as follows: Nb_2O_5 > TPA/ZrO_2 > CsTPA > CsTPA/ZrO_2. It was found that when Nb_2O_5 is used as solid acid, both the conversion of glycerol and the selectivity towards 1,2-PD are higher, as compared to other acid catalysts. Working batch-wise with an aqueous solution of 20 wt% glycerol on Ru/C- Nb_2O_5 catalyst, reaction temperature of 180 °C, H_2 pressure of 60 bar, reaction time of 8 h, a glycerol conversion of 62.8 % and 1,2 – PD selectivity of 66.5 % were reported, simultaneously with an ethylene glycol selectivity of 21.2 %. Further investigations of Ru/TiO_2 catalyst in similar working conditions were reported by the same authors [56]. It is worth to note that the catalyst proved to be active even when crude glycerol and glycerol with alkali salts were used. Also, it was claimed that the catalyst showed similar conversion values and selectivities upon reuse without loss of any activity and selectivity. Nevertheless, the catalyst performances are close but not superior to those reported by authors for Ru/C- Nb_2O_5 catalyst. Conclusions of other investigations regarding the influence of preparation conditions and nature of support for Ru catalysts were published [57]. Vasiliadou et al. [58] also tested Ru-based catalysts for glycerol hydrogenolysis to 1,2-PD, highlighting the role of acid sites concentration on the catalyst performances.

Glycerol hydrogenolysis using Pt supported on amorphous silico alumina (ASA) as catalyst was studied [59]. The results show that ASA acid sites are responsible for glycerol dehydration to acetol, while Pt metal sites catalyze acetol hydrogenation to 1,2-PD. However, the amount of acetol formed and reacted was higher with Pt/ASA than with single ASA, suggesting that Pt sites are also involved in glycerol dehydration to acetol. Experiments with Pt/ASA performed in absence of molecular hydrogen revealed that glycerol hydrogenolysis took also place, due to the H_2 available from the aqueous phase reforming of glycerol. Nevertheless, low selectivity to 1,2-PD and 1,3-PD were achieved, as compared to other published results. Roy et al. [60] studied the glycerol hydrogenolysis in aqueous solutions to 1,2-PD, catalyzed by a mixture of 5 wt.% Ru/Al_2O_3 and 5 wt.% Pt/Al_2O_3 catalysts, without externally added hydrogen. Using a 1:1 (wt) mixture of the Ru and Pt catalysts, at 493 K, 14 bar and 6 h batch runs, a glycerol conversion of 50.1 % and a 1,2-PD selectivity of 47.2 % were obtained, superior to the results obtainable over the individual catalysts. Yuan et al. [61] performed batch glycerol hydrogenolysis tests on a Pt/hydrotalcite catalyst, in alkaline aqueous solutions. Even if in acid medium the reported performances of Pt catalyst are modest, in alkaline solution the authors obtained a glycerol conversion of 92 % with a 93 % selectivity to 1,2- PD (table 1). This study is interesting from practical point of view, as raw glycerol solution derived from biodiesel process is alkaline, due to its content in transesterification catalyst.

Another category of works focused on the increase of glycerol hydrogenolysis yield in 1,3-PD, but the results are yet modest. A method for the synthesis of 1,3-PD by hydrogenolysis, on a catalyst containing Rh/SiO_2 and H_2WO_4 was reported [27]. The result is a 4% yield in 1,3-PD at 200 °C and 80 bar. Che [62] developed a process for glycerol hydrogenolysis in 1-methyl-pyrrolidinone under 320 bar with syngas at 200°C, using as catalyst a homogeneous rhodium complex ($Rh(CO)_2$(acetyl-acetonate)) and H_2WO_4. By this process, 1,3-PD and 1,2-PD were produced with 21 % and 23 % yield, respectively. Drent and Jager [63] patented a catalyst system including Pd complex and methane sulfonic acid in water-sulfolane solvent. At 60 bar, a reaction time of 10 h, with syngas (H_2/CO= 2:1) and 140 °C, selectivities to 1,3-PD of 30.8 % and 21.8% to 1,2-PD were obtained. In other study, Kurosaka et al. [64] reported yields of 24.2 % in 1,3-PD and 12,5 % in 1,2-PD respectively, performing glycerol hydrogenolysis over $Pt/WO_3/ZrO_2$ in 1,3-dimethyl-2-imidazolidinone at 170 °C and 80 bar, for a 18 h reaction time. The researchers also demonstrated that glycerol can be directly converted to 1,3-PD , using Cu/SiO_2 and $H_4SiW_{12}O_{40}$ catalyst in vapour-phase conditions (table 1) [65].

Gong et al. [66, 67] investigated the glycerol hydrogenolysis to 1,3-PD on $Pt/WO_3/TiO_2$ catalyst and the influence of support and solvent on process performance. The authors found that protic solvents such as ethanol and water favored the formation of 1,3-PD from glycerol. Also, SiO_2-supported $Pt/WO_3/TiO_2$ catalysts were more active and selective than the $Pt/WO_3/TiO_2$ catalyst for glycerol hydrogenolysis to 1,3-PD in a slurry batch reactor. XRD patterns and TEM images showed that the presence of TiO_2 species in the catalyst favored the dispersion of platinum. The weak Bronsted acid sites formed by addition of WO_3 to the catalyst were concluded to play a key role in selective formation of 1,3-PD. The authors reported selectivity levels of 50.5 % toward 1,3-PD and 9.2 % to 1,2 –PD at a glycerol conversion of 15.3 %, in experiments with 10 wt.% glycerol aqueous solution (40 ml) and H_2 pressure of 55 bar, temperature 453 K, reaction time of 12 h and catalyst loading of 2 mL. When the reaction time was extended to 24 h, a higher glycerol conversion (33.9 %) with a slightly decreased selectivity of 1,3-PD (41.3%) was obtained, suggesting the occurrence of 1,3-PD hydrogenolysis. Nakagawa et al. [68] studied direct hydrogenolysis of glycerol to 1,3-PD in an aqueous media,

over rhenium-oxide-modified iridium nanoparticles supported on silica. The yield of 1,3-PD reached 38 % at 81% conversion of glycerol (batch experiments, catalyst 150 mg and 31 mmol Ir, glycerol 4 g, water 16 g, sulfuric acid (H^+/Ir = 1) and 80 bar H_2 at 393 K for 36 h). A more complex multi-step process for glycerol transformation to 1,3-PD, involving protection of lateral hydroxyl groups by acetalization was proposed [70]. Transformation of glycerol to 1,3- PD by biochemical routes, was also reported [69]. Nevertheless, the productivity of this process is still limited, due to its slow kinetics and low product concentration.

Due to the mechanism complexity, the kinetics of the glycerol hydrogenolysis is rather poorly known, being investigated in a small number of published studies. Lahr and Shanks [71] investigated the kinetics of the process in liquid phase, in presence of 5 wt % Ru/C catalyst, using aqueous solutions 10 wt % glycerol. The authors developed a Langmuir-Hinshelwood type kinetic model based on a simplified reaction scheme, involving 1,2-PD and ethylene glycol as intermediate products. These are further transformed in secondary products. An extension of this work, including studies of temperature and *p*H influence on the process kinetics, was published by the same authors [72]. In addition, the effect of sulphur presence on the Ru/C catalyst activity and selectivity was experimentally investigated at different loadings. Another kinetic study was published recently [73]. The catalyst used in the glycerol hydrogenolysis study contained 2.5 wt % Co, 0.5 wt % Pd, and 2.4 wt % Re supported on activated carbon. Experiments on a continuous reactor in trickle flow regime were performed using an aqueous solution containing 40 wt % glycerol in the presence of NaOH, at 453- 475°C, 33 – 133 bar and H_2: glycerol molar ratio of 5:1. The proposed model describes only the overall glycerol conversion kinetics and is deduced considering as controlling step the surface reaction between adsorbed glycerol and non-adsorbed hydrogen (Eley- Rideal scheme). It was proposed a more detailed kinetic model based on a six reactions hydrogenolysis scheme [40]. This kinetic model was fitted to data obtained using as catalyst Raney Ni complexed with a macrocyclic structure of Fe-Co with organic ligands. A ten reactions model accounting for the formation of liquid and gaseous secondary products was published [74] for glycerol hydrogenolysis catalyzed by a bimetallic Ru-Re catalyst. Even if the liquid reaction mixture is expected to feature important non-ideal behaviour, due to the lack of reliable data for the calculation of component activities, all these studies use reaction rate expressions in molar concentrations.

Conclusions

Among the two isomers of propanediol, 1,2- PD is the most easily available by glycerol hydrogenolysis. The published research studies demonstrate the possibility to transform glycerol into 1,2-PD with relatively high yields. In the process of glycerol transformation to 1,2-PD, supported Ru, Pt and Cu catalysts, single or combined with other metals proved to be the best performing. Among the prepared and tested catalysts, considering both the transformation performances and the price, the supported copper catalysts, simple or combined with other metals, conditioned following different recipes, appear as being the most efficient. Very good conversions and selectivities to 1,2-PD are reported, both in batch and continuous operation, these being favored by hydrogen pressure and glycerol dilution. From productivity point of view, the continuous operation appears to be more interesting, permitting relatively high glycerol conversion and selectivity values at shorter reaction times. The disadvantages are the relatively high hydrogen excess and the presence of solvent, which involve costly separation and recycling steps. Considering the glycerol hydrogenolysis mechanism and thermodynamics, a continuous two steps process was proposed, consisting in a higher temperature dehydration to acetol and a lower temperature hydrogenation of acetol to 1,2-PD.

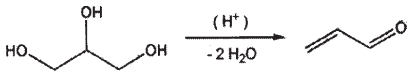
Recent published studies demonstrated also the possibility of direct glycerol transformation to 1,3-PD in the presence of solid catalysts, but the reported yields are still low (~ 26 %). However, the research in this direction are in progress and probably soon, better catalysts and processes for 1,3-PD synthesis will be developed.

Research and design efforts are focused on developing commercial plants to transform glycerol to propanediol. A conceptual design scheme for a hydrogenolysis process plant was analyzed by Bildea et al. [75]. Several companies (Dow, Huntsman, Ashland, Senergychem, Cargill and others), already announced plans to build new commercial scale plants to convert biodiesel-derived glycerin into propanediol [76].

Glycerol transformation into acrolein

Glycerol can be transformed by direct dehydration to acrolein, an important chemical used as intermediate in the manufacture of acrylic acid and its esters, methionine, monomer for acrylic resins, herbicides etc. Currently, acrolein production is based on the oxidation of propylene in a multi- step process involving utilization of chlorine, a corrosive reagent. This inconvenient as well as the continuous increase of propylene price, make the production of acrolein from the renewable glycerol a commercially and environmentally attractive route.

Glycerol dehydration to acrolein is catalyzed by acidic catalysts and occurs following the scheme:



The dehydration reaction is usually accompanied by side reactions leading to by-products. Among these, the most important are the acetol, propanaldehyde, acetaldehyde, acetone, adducts of acrolein with glycerol, glycerol polycondensation products, cyclic glycerol ethers, etc., but also phenol and polyaromatic compounds, which induce catalyst deactivation by coking. To prevent the accumulation of coke on the catalyst, in some studies small amounts of oxygen are added in the feed in order to oxidize the heavy products.

Hoyt and Manninen [77] patented a process using diatomaceous earths impregnated with phosphoric acid salts as catalyst. Working in vapor-liquid conditions they reported an acrolein yield of 72.3 %. In other patents Dubois et al. [78, 79] proposed a continuous process in vapor phase based on phosphoric acid salts as catalyst, providing acrolein yields higher than 75%. Neher et al. [80] recommend, for the glycerol dehydration catalysts, synthetic siliceous materials (mordenite, montmorillonite, acidic zeolites), alumina (Al_2O_3) or titanium oxide (TiO_2) coated with mono-, di- or triacidic inorganic acids, oxides or mixed oxides such as g- alumina, the mixed oxide ZnO-Al_2O_3, or alternatively heteropolyacids. Working with a continuous setup in vapour phase, on a catalyst prepared by coating Al_2O_3 with H_3PO_4 (the so called solid phosphoric acid) and aqueous solution containing 20 % glycerol at

300 °C, total conversion with an acrolein yield of 70.5% are reported. Approximately 10% of 1-hydroxyacetone, related to the glycerol, is obtained as a significant secondary product. The catalyst exhibits no loss in activity after 60 h of operation. In liquid- phase glycerol dehydration tests on H-ZSM5 zeolite, the researchers obtained a glycerol conversion of 16 % and an acrolein selectivity of 75 % at 70 bar, 250 °C and a LHSV of 2 h^{-1}. The catalysts exhibited no loss in activity after 50 h of operation.

Chai et al. [81] investigated the effect of the catalyst acidity and basicity on the dehydration of glycerol to acrolein in vapour phase. The most selective catalysts for the production of acrolein by gas-phase glycerol dehydration are those having the highest acid strength in the range of Hammett acidity function: -8.2 < Ho <-3.0. This category includes the catalyst with composition 15 wt% WO_3/ZrO_2, which exhibited an acrolein selectivity of 65 % at total glycerol conversion (315 °C, aqueous solution of 36.2 wt% glycerol, 1 bar, GHSV by glycerol of 80 h^{-1}). The catalysts having much stronger acid sites (Ho < -8.2) produce a lower acrolein selectivity (40–50 mol %) due to more severe catalyst coking. In an additional paper, the same authors [82] report data obtained by glycerol dehydration using Nb_2O_5 as catalyst. The Nb_2O_5 catalyst performance is significantly influenced by its calcination temperature, due to the changes induced in surface acidity and crystallization. The catalyst calcined at 400 °C was found to have the highest fraction of acid sites with the strength in the optimum interval (-8.2 < Ho <-3.0) and exhibited the highest activity and acrolein selectivity (up to 51 % for glycerol conversions over 80 % in the working conditions already mentioned, given in the first mentioned paper). In a third paper published by the same group [83] a catalyst containing 12-tungstophosphoric acid (HPW) on a high surface area ZrO_2 support was prepared and tested. The vapour phase dehydration reaction of glycerol was carried out in a continuous fixed bed reactor, at 315°C under atmospheric pressure, using an aqueous solution containing 36.2 wt% glycerol, at a high weight hourly space velocity (WHSV) of 400 h^{-1} by glycerol. On a catalyst with 10 wt % HPW loading, the authors report a glycerol conversion of 79 % with selectivities to acrolein 69%, hydroxylacetone 14 % and acetaldehyde 4 %.

Tsukuda et al. [84] tested comparatively the activities in the dehydration of glycerol to acrolein for several supported acids. H_3PO_4, H_3BO_3 and three kinds of heteropoly-acids (HPA): phosphotungstic acid (PW), silicotungstic acid (SiW), and phosphomolybdic (PMo) were deposed on supports of Al_2O_3 , TiO_2, ZrO_2 ,SiO_2–Al_2O_3 and SiO_2 with mean pore diameter of 3, 6, and 10 nm. Among the combinations of acid components and supports tested, the best performance was identified for the SiW/SiO_2 catalyst with pore diameter of 10 nm (table 1). A similar study was published [85], several heteropoly-acids on different supports being tested on a continuous fixed bed reactor. The best results were obtained on silicotungstic acid (20 wt%) supported by aluminosilicate (75% selectivity for acrolein at complete conversion at 275°C, contact time 0.2 s, feed 10 wt % glycerol in water). The catalyst proved also a good stability. After 300 h on-stream, it still provided a conversion above 70%, without significant change in acrolein selectivity.

Ning et al. [86] investigated the glycerol dehydration catalyzed by silicotungstic acid supported on activated carbon. By using a continuous reactor operated at 330 °C, feed water/glycerol molar ratio of 46:1, atmospheric pressure, LHSV = 3.8 h^{-1}, on a catalyst with 10 wt% HSiW loading, they report a 92.6 % glycerol conversion and 75.1% acrolein selectivity, reaching an acrolein productivity of 68.5 mmol/(g·h). The dehydration of glycerol to acrolein on WO_3/ZrO_2 solid heterogeneous catalysts, in a continuous flow fixed bed reactor was investigated [87]. Working with 20 wt% aqueous glycerol solution in the presence of WO_3 (19 wt %)/ ZrO_2 catalyst at atmospheric pressure, 280 °C, LHSV of 3 h^{-1}, in the presence of 2.5 mL/min oxygen, a maximum of 75% acrolein selectivity was obtained at 100 % conversion of glycerol. The experimental observations pointed out that acrolein selectivity correlates positively with the existence of the weak acidic sites on the WO_3/ZrO_2 catalyst.

In [88] it is studied the vapor phase glycerol dehydration on vanadium phosphate oxides (VPO) in the presence of molecular oxygen. Among three VPO formulae they tested, the hemihydrate ($VOHPO_4 \cdot 0.5H_2O$) showed the best catalytic performance, giving total glycerol conversion with selectivities to acrolein of 66% and to acetaldehyde of 14 % (LHSV=2,5 h^{-1}; 300 °C, 1 bar, molar ratios N_2:O_2:H_2O:glycerol, approximately 40.8:9.1:20.5:1). Also, no coke formation was detected on the catalyst, when the reaction is conducted in the presence of oxygen.

Liu et al. [89] tested the catalytic activity for vapour phase glycerol dehydration of several metal-doped mesoporous aluminophosphates. The best performances were obtained on meso-LaCuCrAlPO (table 1). Other researchers [90] synthesized acrolein by glycerol dehydration in gas phase, catalyzed by sulfated zirconia, in the presence of O_2 and He. The best selectivity to acrolein, 42%, at 49% glycerol conversion was obtained under atmospheric pressure and a temperature around 330 °C.

Jia et al. [91] investigated thoroughly the catalytic performance of nanocrystalline HZSM-5 catalysts with different Si/Al molar ratios in the gas phase dehydration of aqueous glycerol. Compared with bulk HZSM-5, the small-sized catalyst exhibits a higher catalytic activity in glycerol dehydration. The catalytic dehydration of glycerol over the HZSM-5 catalyst was firstly performed with 35 wt% aqueous glycerol at 320 °C and atmospheric pressure. Using a HZSM-5 with Si/Al molar ratio around 65, at space velocities (GHSV) of glycerol between 155 h^{-1} -719 h^{-1} the authors reported glycerol conversions between 100 % and 83 % and selectivities to acrolein between 60 and 65 %. Other byproducts identified were acetaldehyde, propanol, and allyl alcohol. A measured decrease of glycerol conversion after an on-stream time of 24 h, by 17 %, demonstrates that the catalyst deactivates to some extent.

Alhanash et al. [92] prepared and proved the catalytic activity in glycerol dehydration for caesium 12-tungstophosphate (CsPW) and CsPW doped with Pd (table 1). The activity, however, decreases significantly with the time on stream due to the catalyst coking. The authors found that, by doping CsPW with palladium and co-feeding hydrogen, the catalyst stability to deactivation improved, while maintaining a high selectivity to acrolein. The catalyst 0.5 % Pd/CsPW, after 5 h time on stream, gives 96 % acrolein selectivity for 79% glycerol conversion. It provides an acrolein production rate of 23 mmol h^{-1} g_{cat}^{-1}, a value significantly superior to specific rates reported in the literature for similar catalysts (5– 11 mmol h^{-1} g_{cat}^{-1}).

Suprun et al. [93] proposed a new technique for fast catalyst screening, based on thermogravimetric (TG) setup, coupled with temperature-programmed desorption (TPD) and online MS analysis. By using this technique, they comparatively investigated the activity in glycerol dehydration for a class of alumophosphates having the general formula $MO_xAl_2O_3PO_4$ (where M stands for a transitional metal: V, Fe, Cr, Cu, Ce, Mn, Mo and W). The

Catalyst	Working conditions	Process performance	Reference
a) Glycerol hydrogenolysis to propanediol			
(1) Raney Cu with 68% Cu, (2) Raney Cr–Cu with 2.6% Cr and 66% Cu	190–210 °C; 14–28 bar; aqueous solution 80% glycerol flow rate 0.025–0.175 mL/min; H_2 flow rate 50–500 mL/min; Fixed bed reactor, 14 mL catalyst;	C_{GLO} 72- 100 %; S_{12PD} :67- 94 %	Schmidt et al., [10]
Copper- chromite promoted with Barium	453-513 °C; 20-60 bar; solvent 2-propanol; glycerol feed concentration; 20-60 % (wt) ; 18 to 54 mL/h; H2 flow rate 10-30 NL/h; Fixed bed tubular reactor 23 g of catalyst;	C_{GLO} 65%; S_{12PD}: over 90 %	Rode et al. [12]
$CuO – ZnO/Al_2O_3$	Continuous fixed bed reactor; 100 mL of catalyst; 150 bar ; 230-265 °C; Reactor feed: 1,1 to 1,5 l/h aqueous solution 30 % glycerol H_2/Glycerine molar ratio=4:1	C_{GLO}: 94- 99 %; S_{12PD}: 78- 89%	Casale and Gomez [21]
$Cu/ZnO/Al_2O_3$	Fixed-bed tubular reactor; WHSV = 0.08 h 1, temperature 190 °C; pressure 6.4 bar; undiluted glycerol; H_2/glycerol molar ratio = 140:1;	C_{GLO} 96,2 % ; S_{12PD} 92,2 %	Huang L. et al. [24]
CuO (30-35% by wt) and ZnO.	Autoclave reactor; 3750 g glycerine of 99,5 % purity and 150 g catalyst; pressure 50 bar; temperature 200 °C; reaction time 12 h.	C_{GLO} - 100%; S_{12PD} :over 96 %	Franke and Stankowiak [26]
Cu/Al_2O_3	Fixed-bed reactor with temperature gradient (200 °C entry section →120 °C exit); WHSV – 0.2 h^{-1}; pressure 1 bar; aqueous solution 30 wt% glycerol; H_2/glycerol molar ratio = 141: 1;	C_{GLO} 100 % S_{12PD} 96,9%	Akiyama et al. [31]
68% CoO, 17% CuO, 6% MnO_2; 4% H3PO4; 5% MoO_3;	Continuous fixed bed reactor; 21,9 kg of catalyst; 295 bar ; 210-220 °C; Reactor feed: 35 l/h=22 m^3/m^2 h aqueous solution 86.5% glycerol (Liquid WHSV= 1,9 h^{-1});Gas feed 2.5 m^3/h (H_2/Glycerine molar ratio=0.280);		Schuster and Eggersdorfer [42]
a) Ni-Rh/Carbon ; b) Sud-Chemie HC-1 catalyst	Feed solution contains 20-80 wt% glycerol (purified or crude); WHSV= 1,8 h^{-1}; H2/glycerol ratio– max 10/1; P=65- 135 bar; T– 180 -250 °C	C_{GLO} up to 99 %; S_{12PD} up to 99 %	Bloom [43]
Pt/hydrotalcite (alkaline medium)	220 °C ; 30 bar; 0.5 g catalyst/ 20.0 mL aq. solution of glycerol (0.2 g glycerol/ mL), reaction time 20 h; initial pH = 12	C_{GLO} 92%; S_{12PD} 93 %	Yuan et al. [61]
Cu/SiO2 and $H_4SiW_{12}O_{40}$	Tubular fixed bed reactor; 210 °C; 5.4 bar; H2/glycerol molar ratio – 140:1; WHSV– 0,1 h^{-1}; undiluted glycerol;	C_{GLO} 83,4% ; S_{12PD} 32.1% ; S_{12PD} 22.2 %	Huang et al. [65]
b) Glycerol dehydration to acrolein			
Silicotungstic acid/SiO_2	Fixed bed reactor; 275 °C and 1 bar; 10 wt.% aqueous glycerol solution; liquid space velocity of 5.7 $mL/g_{cat}/h$, in a flow of 30 mL/min He	C_{GLO}- 98 %; S_{AC}–86 %;	Tsukuda et al. [84]
meso-LaCuCrAlPO	Fixed bed reactor; 340 °C and 1 bar; 2,5 mL/h glycerol; 0.2 g catalyst	C_{GLO}- 99 %; S_{AC}-80 %; Sel. to acetol 10 %;	Liu et al. [89]
caesium 12-tungstophosphate (CsPW)	Aqueous solution 10 wt% glycerol; glycerol WHSV 2.8 h^{-1}, 275 °C and 1 bar;	C_{GLO}- 100 %; S_{AC}-98 %;	Alhanash et al. [92]

C_{GLO}- glycerol conversion; S_{12PD} and S_{13PD} - selectivity to 1,2-PD and 1,3-PD respectively; S_{AC}- selectivity to acrolein.

Table 1
THE MAIN PUBLISHED STUDIES OF GLYCEROL HYDROGENOLYSIS AND DEHYDRATION

comparative tests carried out by the authors revealed that the most active among the catalysts tested is $WO_xAl_2O_3PO_4$. These results correlate well with the results of conventional catalytic tests in a fixed bed reactor. By feeding a fixed bed reactor with a 5 % glycerol aqueous solution, at 265 °C, 1 bar and a glycerol WHSV of 75 h^{-1}, the authors obtained (on $WO_xAl_2O_3PO_4$ catalyst) a 98 % glycerol conversion and selectivities of 66 % to acrolein and 14 % to acetol. It is also to be mentioned the interesting performances reported for glycerol dehydration processes under homogeneous supercritical conditions [94, 95].

To simultaneously solve the problems of glycerol dehydration and catalyst deactivation/regeneration, it was recently investigated the dehydration of glycerol on zeolite-based catalyst in a moving bed reactor similar to a FCC reactor [96]. This reaction system allows a continuous regeneration of the catalyst and a better gas-solid heat and mass transfer than those of fixed-bed reactors. High acrolein yield (55–61%) was obtained at 350 °C with a HZSM-5-based catalyst (Si/Al = 100). The process is also described in [97].

Published reports and patents indicate process development activities oriented to perform glycerol conversion to acrolein at an industrial scale. The first commercial facility for producing acrolein from glycerol was announced by Arkema at Beaumont, Texas [7].

One of the main derivatives of acrolein is the acrylic acid. Several recently published studies describe processes for synthesis of acrylic acid from glycerol. Generally, two-step technologies are proposed, a first step dehydrating glycerol to acrolein, followed by the second step of acrolein oxidation. No separations are necessary between the two process steps, the only treatment of the first step effluent being a change of temperature. Diluted aqueous glycerol solutions are usually used in this process, in order to limit the occurrence of undesired reactions between acrylic acid or acrolein and glycerol. Shima and Takahashi [98] patented such a process, where the dehydration is performed on a catalyst A, prepared by impregnating α-alumina with phosphoric acid and silica, whereas the oxidation step on a catalyst B, consisting of a mixture of Mo, V, W and Cu oxides supported on α-alumina. The two catalysts were tested in continuous fixed bed reactors, both as separated

beds or a unique bed, with mixed catalysts (mechanically mixed or composites mixtures realized in the process of preparation). The tests were carried out in vapor phase, with aqueous solutions having glycerol concentrations between 2 and 10 wt %, in presence of oxygen, obtaining acrylic acid yields up to 65%. The best performance was obtained using the two catalysts as two separate fixed beds, operated at different temperatures (292°C the dehydration and 270°C the oxidation).

Dubois et al. [99] patented a similar two-step process based on a tungsten oxide on zirconia dehydration catalyst and a multi-metal oxide (W, Sr, V, Cu, Mo) oxidation catalyst supported by an inert. Acrylic acid yields up to 73.7% are reported, working with the two catalysts in separate fixed beds, with 20 % glycerol aqueous solutions and molecular oxygen at 280°C. In a subsequent patent, Dubois [100] describes a process of glycerol dehydro-oxydation to acrylic acid carried out in a membrane reactor. This is built of two layers of catalyst, one transforming the glycerol into acrolein and the other oxidizing the acrolein to acrylic acid. The advantages reside in a limitation of acrylic acid degradation and a better energy management, by coupling the endothermic dehydration step with the exothermic oxidation one in the same apparatus.

Another interesting valorization of glycerol is its conversion into acrylonitrile. However, few results are published until now in this domain. Guerrero-Pérez and Banares [101] describe a one-step process for glycerol transformation, in the presence of ammonia, into acrylonitrile. Glycerol conversions of 82.6% with a selectivity to acrylonitrile of 58.3% are reported on a VSbNb/Al based catalysts.

Conclusion

The glycerol conversion to acrolein is a process that is usually performed in vapour phase on solid acid catalysts. Good process yields were obtained on supported heteropoly-acids, particularly tungstic acid, tungsto-phosphoric acid and their derivatives. Also, practically interesting results were obtained on cheaper zeolite class of catalysts. An important drawback of this process is the catalyst deactivation, predominantly by coking. Therefore, a technical solution for commercial implementation was proposed, similarly to FCC units, by using circulating catalyst reactors.

Acknowledgements: The authors gratefully acknowledge the financial support provided by Romanian National Programme PNII grants no. 1545/IDEI, no. 71053/2007 and no. 22138/PARTENERIATE.

References

1.YONG, K C., OOI T. L., DZULKEFLY, K., YUNUS, W. W. M. Z., HAZIMAH, A. H, Journal of Oil Palm Research ,**13**, (2), 2001, p. 39
2.VLAD, E., BILDEA, C.S., PLESU, V., MARTON, G., BOZGA, G., Revista de Chimie, **61** (6) , 2010**,** p. 595.
3.CHIU, C. W., DASARI, M. A., WILLAM, R. SUTTERLIN, W. R., SUPPES, G. J., Ind. Eng. Chem. Res., **45,** (2), 2006, p.791
4.ABBOTT, A. P., CULLIS, P. M., GIBSON, M. J., HARRIS, R. C., RAVEN, E., Green Chemistry, **9,** 2007, p. 868.
5.RAHMAT, N., ABDULLAH, A. Z., MOHAMED, A. R., Renewable and Sustainable Energy Reviews, **14**, 2010, p. 987.
6.*** Glycerine: an overview, The Soap and Detergent Association (SDA), 1990; http://www.aciscience.org/docs/Glycerine-an_overview.pdf
7.PAGLIARI, M., ROSSI, M., The future of Glycerol. New Uses of a Versatile Raw Material, RSC Publ., Cambridge, 2008.
8.CONNOR, R., ADKINS, H., J. Am. Chem. Soc., **54**, 1932, p. 4678.
9.MONTASSIER, C., GIRAUD, D., BARBIER, J., Stud. Surf. Sci. Catal., **41,** 1988, p.165.
10.SCHMIDT, R. S., SETRAK, K., TANIELYAN, S. K., MARIN, N., ALVEZ, G., AUGUSTINE, R. L., Topics in Catalysis, **53**, 2010, p. 1214.
11.DASARI, M. A., KIATSIMKUL, P. P., SUTTERLIN, W., SUPPES, G. J., Applied Catalysis A: General, **281**, 2005, p. 225.
12.RODE, C. V., GHALWADKAR, A. A., MANE, R. B., HENGNE, A. M., JADKAR, S. T. BIRADAR, N. S., Organic Process Research & Development **14,** 2010, p. 1385.
13.MANE, R.B., GHALWADKAR, A.A., HENGNE, A.M., SURYAWANSHI, Y.R., RODE, C.V., Catalysis Today, in press (2010), doi:10.1016/j.cattod.2010.10.032.
14.GUO, L., ZHOU, J., MAO, J., GUO, X., ZHANG, S., Applied Catalysis A: General **367**, 2009, p. 93.
15.MANE, R. B., HENGNE, A. M., GHALWADKAR, A. A., VIJAYANAND, S., MOHITE, P. H., POTDAR, H. S., RODE, C. V., Catalysis Letters, **135,** 2010, p. 141.
16.HUANG, Z., CUI, F., KANG, H., CHEN, J., XIA, C., Applied Catalysis A: General **366**, 2009, p. 288.
17.BIENHOLZ, A., HOFMANN, H., CLAUS, P., Applied Catalysis A: General **391**, 2011, p. 153.
18.YUAN, Z., WANG, J., WANG, L., XIE, W., CHEN, P., HOU, Z., ZHENG, X., Bioresource Technology, **101,** 2010, p. 7088.
19.YUAN, Z., WANG, L., WANG, J., XIA, S., CHEN, P., HOU, Z., ZHENG, X., Applied Catalysis B: Environmental, **101,** 2011., p. 431.
20.MEHER, L. C., GOPINATH, R., NAIK, S. N., DALAI, A. K., Ind. Eng. Chem. Res., **48,** 2009, p. 1840.
21.CASALE, B., GOMEZ, A. M., U. S. Patent, 5,214,219, 1993
22.WANG, S., LIU, H., Catalysis Letters, **117**, (1–2), August 2007, p. 62.
23.BALARAJU, M., REKHA, V., PRASAD, P.S., PRASAD, R.B.N., LINGAIAH, N., Catalysis Letters, **126**, 2008, p. 119.
24.HUANG, L., ZHU, Y. L.,ZHENG, H. Y., LI, Y. W., ZENG, Z. Y., Journal of Chemical Technology and Biotechnology, **83**, 2008, p. 1670.
25.HENKELMANN, J., BECKER, M., BÜRKLE, J., WAHL, P., THEIS, G., MAURER, S., U. S. Patent Application 20090216050, 2009.
26.FRANKE, O., STANKOWIAK, A., U. S. Patent Application 201000361175, 2010.
27.CHAMINAND, J., DJAKOVITCH, L., GALLEZOT, P., MARION, P., PINEL, C.,ROSIER, C. , Green Chemistry , **6**, 2004, p. 359.
28.MARINOIU, A., IONITA, G., GASPAR, C. L., COBZARU, C., MARINESCU, D., TEODORESCU, C. OPREA, S., Reaction Kinetics, Mechanisms and Catalysis, **99,** 2010, p. 111.
29.CHIU, C. W., DASARI, M. A., SUPPES, G. J., SUTTERLIN, W. R., AIChE Journal, **52**, (10), 2006, p. 3543.
30.CHIU, C. W., TEKEEI, A., SUTTERLIN, W. R., RONCO, J. M., SUPPES, G. J., AIChE Journal, **54,** 2008, p. 2456.
31.AKIYAMA, M., SATO, S., TAKAHASHI, R., INUI, K., YOKOTA, M., Applied Catalysis A: General, **371**, 2009, p. 60.
32.BOLADO, S., TREVI O, R. E., GARCÍA-CUBERO, M. T., GONZÁLEZ-BENITO, G., Catalysis Communications, **12**, 2010, p. 122.
33.SATO, S., AKIYAMA, M., TAKAHASHI, R., HARA, T., INUI, K., YOKOTA, M., Applied Catalysis A: General, **347**, 2008, p. 186.
34.VASCONCELOS, S. J., LIMA, C.L., FILHO, J.M., OLIVEIRA, A.C., BARROS, E.B., DE SOUSA, F.F., ROCHA, M.G.C., BARGIELA, P., OLIVEIRA, A.C., Chemical Engineering Journal, 2010, in press, doi:10.1016/j.cej.2011.01.053.
35.KINAGE, A. K., UPARE, P. P., KASINATHAN, P., HWANG, Y. K., CHANG, J. S., Catalysis Communications, **11**, 2010, p.620.
36.PEROSA, A., TUNDO, P., Ind. Eng. Chem. Res., **44,** 2005, p. 8535.
37.ZHAO, J., WEIQIANG YU W., CHEN, C., MIAO H., MA H., XU J., Catalysis Letters, **134,** 2010, p. 184.
38.YU, W., XU, J., MA, H., CHEN, C., ZHAO, J., MIAO, H., SONG, Q., Catalysis Communications, **11,** 2010, p.493.
39.YU, W., ZHAO, J., MA, H., MIAO, H., SONG, Q., XU, J., Applied Catalysis A: General, **383,** 2010, p.73.
40.ANAND, K. A., ANISIA, K. S., AGARWAL, A. K., KUMAR, A., The Canadadian J. of Chem. Engineering, **88,** 2010, p. 208.
41.GUO, X., LI, Y., SHI, R., LIU, Q., ZHAN, E., SHEN, W., Applied Catalysis A: General, **371,** 2009, p. 108
42.SCHUSTER, L., EGGERSDORFER, M., U. S. Patent 5,616,817, 1997.

43.BLOOM, P., U. S. Patent Application 20080228014, 2008
44.FURIKADO, I., MIYAZAWA, T., KOSO, S., SHIMAO, A., KUNIMORI, K., TOMISHIGE, K., Green Chemistry, **9,** 2007, p.. 582
45.KUSUNOKI, Y., MIYAZAWA, T., KUNIMORI, K., TOMISHIGE, K., Catalysis Communications, **6**, 2005, p. 645
46.MIYAZAWA, T., KUSUNOKI, Y., KUNIMORI, K., TOMISHIGE, K., Journal of Catalysis, **240**, 2006, p. 213
47.MIYAZAWA, T., KOSO, S., KUNIMORI, K., TOMISHIGE, K., Applied Catalysis A: General, **318,** 2007, p. 244
48.MIYAZAWA, T., KOSO, S., KUNIMORI, K., TOMISHIGE, K., Applied Catalysis A: General, **329,** 2007, p. 30
49.SHINMI, Y., KOSO, S., KUBOTA, T., NAKAGAWA, Y., TOMISHIGE, K., Applied Catalysis B: Environmental, **94**, 2010, p. 318
50.MA, L., HE, D., LI, Z., Catalysis Communications, **9**, 2008, p. 2489.
51.MA, L., HE, D., Catalysis Today, **149**, 2010, p.148
52.MARIS, E. P., DAVIS, R. J., Journal of Catalysis, **249**, 2007, p. 328
53.MARIS, E. P, KETCHIE, W. C., MURAYAMA, M., DAVIS, R. J., Journal of Catalysis, **251**, 2007, p. 281
54.ALHANASH, A., KOZHEVNIKOVA, E. F., KOZHEVNIKOV, I. V., Catalysis Letters, **120**, 2008, p. 307.
55.BALARAJU, M., REKHA, V., PRASAD, P.S., PRABHAVATHI DEVI, B.L.A., PRASAD, R.B.N., LINGAIAH, N., Applied Catalysis A: General, **354**, 2009, p. 82
56.BALARAJU, M., REKHA, V., PRABHAVATHI DEVI, B.L.A., PRASAD, R.B.N., SAI PRASAD, P.S., LINGAIAH, N., Applied Catalysis A: General, **384**, 2010, p.107.
57.FENG, J., FU, H., WANG, J., LI, R., CHEN, H., LI, X., Catalysis Communications, **9**, 2008, p.1458.
58.VASILIADOU E.S., HERACLEOUS E., VASALOS I.A., LEMONIDOU, A.A., Applied Catalysis B: Environmental, **92**, 2009, p. 90.
59.GANDARIAS, I., ARIAS, P.L., REQUIES, J., GÜEMEZ, M.B., FIERRO, J.L.G., Applied Catalysis B: Environmental, **97**, 2010, p. 248.
60.ROY, D., SUBRAMANIAM, B., CHAUDHARI, R.V., Catalysis Today,**156**, 2010, p.31.
61.YUAN, Z., WU, P., GAO, J., LU, X., HOU, Z., ZHENG, X., Catalysis Letters, **130,** 2009, p. 261.
62.CHE T. M., U. S. Patent, 4 642 394, February 1987.
63.DRENT, E., JAGER, W., US Patent 6,080,898, 2000.
64.KUROSAKA, T., MARUYAMA, H., NARIBAYASHI, I., SASAKI, Y., Catalysis Communications, **9**, 2008, p. 1360.
65.HUANG, L., ZHU, Y., ZHENG, H., DING, G., LI, Y., Catalysis Letters, **131,** 2009, p. 312.
66.GONG, L., LÜ, Y., DING, Y., LIN, R., LI, J., DONG, W., WANG, T., CHEN, W., Chinese Journal of Catalysis, **30,** (12), 2009, p.1189.
67.GONG, L., LU, Y., DING, Y., LIN, R., LI, J., DONG, W., WANG, T., CHEN, W., Applied Catalysis A: General, **390**, 2010, p. 119.
68.NAKAGAWA, Y., SHINMI, Y., KOSO, S., TOMISHIGE, K., Journal of Catalysis, **272**, 2010, p. 191.
69.ZHANG, G., MA, B., XU, X., LI, C., WANG, L., Biochemical Engineering Journal, **37**, 2007, p. 256.
70.WANG, K., HAWLEY, M. C., DEATHOS, S. J., Ind. Eng. Chem. Res., **42,** 2003, p. 2913.
71.LAHR, D. G., SHANKS, B. H., Ind. Eng. Chem. Res., **42,** 2003, p. 5467.
72.LAHR, D. G., SHANKS, B. H., Journal of Catalysis, **232**, 2005, p. 386.
73.XI, Y., HOLLADAY, J. E., FRYE, J. G., OBERG, A. A., JACKSON, J. E., MILLER, D. J., Organic Process Research & Development, **14,** 2010, p. 1304
74.TORRES, A., ROY, D., SUBRAMANIAM, B., CHAUDHARI, R. V., Ind. Eng. Chem. Res., **49,** 2010, p. 10826.
75.BILDEA, C. S., ZAHARIA, E., BOZGA, G., SOARE, G., in Pierucci S. and Buzzi Ferraris G. (Editors), 20th Eur. Symp. on Computer Aided Process Eng. –ESCAPE 20, **28,** 2010, p. 1973.
76.SHELLEY, S., Chemical Engineering Progress, August 1, 2007
77.HOYT, H. E., MANNINEN T. H., U. S. Patent 2,558,520, 1951.
78.DUBOIS, J. L., DUQUENNE, C., HOLDERICH, W., KERVENNAL, J., Patent FR2882053 2006
79.DUBOIS, J. L., DUQUENNE, C., HOLDERICH, W., Patent WO2006087083, 2006
80.NEHER, A., HAAS, T., ARNTZ, D., KLENK, H., GIRKE, W., U. S. Patent 5,387,720 1995
81.CHAI, S. H., WANG, H. P., LIANG, Y., XU, B. Q., Green Chemistry, **9,** 2007, p. 1130
82.CHAI, S. H., WANG, H. P., LIANG, Y., XU, B. Q., Journal of Catalysis, **250**, 2007, p. 342
83.CHAI, S. H., WANG, H. P., LIANG, Y., XU, B. Q., Applied Catalysis A: General **353**, 2009, p. 213.
84.TSUKUDA, E., SATO, S., TAKAHASHI, R., SODESAWA, T., Catalysis Communications, **8,** 2007, p. 1349.**OMM**
85.ATIA, H, ARMBRUSTER, U, MARTIN, A., Journal of Catalysis, **258,** 2008, p.71.
86.NING, L., DING, Y., CHEN, W., GONG, L, LIN, R., LÜ, Y. XIN, Q., Chinese Journal of Catalysis, **29**, (3), 2008, p. 212.
87.ULGEN, A., HOELDERICH, W., Catalysis Letters, **131,** 2009, p. 122.
88.WANG, F., DUBOIS, J. L., UEDA, W., Journal of Catalysis, **268,** 2009, p.260.
89.LIU, S. Y, ZHOU, C.-J., LIU, Q., LIU, G.-C., HUANG, C.-J., CHAO, Z.-S., ChemSusChem, **1,** 2008, p. 575.
90.CAVANI, F., GUIDETTI, S., MARINELLI, L., PICCININI, M., GHEDINI, E., SIGNORETTO M., Applied Catalysis B: Environmental, **100**, 2010, p.197.
91.JIA, C. J, LIU, Y., SCHMIDT, W., LU, A. H., SCHÜTH, F., Journal of Catalysis, **269**, 2010, p. 71.
92.ALHANASH, A., KOZHEVNIKOVA, E. F., KOZHEVNIKOV, I. V., Applied Catalysis A: General, **378**, 2010, p. 11.
93.SUPRUN, W., LUTECKI, M., PAPP, H., Chemical Engineering and Technology, **34,** 2011, p. 134.
94.OTT, L., BICKER, M., VOGEL, H., Green Chemistry, **8,** 2006, p. 214.
95.WATANABE, M., IIDA, T., AIZAWA, Y., AIDA, T. M., INOMATA, H., Bioresource Technology, **98**, 2007, p. 1285.
96.CORMA, A., HUBER, G.W., SAUVANAUD, L., O'CONNOR, P., Journal of Catalysis, **257**, 2008, p. 163.
97.O'CONNOR, P., CORMA, C. A. HUBER, G., SAVANAUD, L. A., WO/2008/052993, 2008.
98.SHIMA, M., TAKAHASHI T., EP1710227 B1, 2006.
99.DUBOIS, J. L., DUQUENNE, C., HÖLDERICH, W., WO/2006/114506, 2006.
100.DUBOIS, J. L., WO/2008/ 007002, 2008.
101.GUERRERO-PÉREZ, M. O., BA ARES, M.A., Chem Sus Chem, **1,** 2008, p.511

Manuscript received: 19.11.2010