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## Glycerol, the Co-Product of Biodiesel: One Key for the Future Bio-Refinery

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### 1. Introduction

The uncertainty of supply and prices of oil and the difficulty to establishing a sustainable model of economic and environmental development are weaknesses in the economies that depend entirely on fossil fuels, as in the most industrialized countries. In addition, the chemical industry uses about 15% of total oil consumption, 10% as raw material and 5% as fuel, being this industry still largely based on non-renewable raw materials, whose use does not control. Accordingly, from 1990 has been increasing interest in finding alternative sources of raw materials, emerging as obvious one the biomass, because it is an abundant, sustainable, and renewable energy-primary resource that can provide transport fuel, organic chemicals, and materials currently produced by fossil sources [Fulton, 2004]. In the past few years, research and technological projects related to the use of biomass as raw material to produce energy and industrial products are receiving support in countries like U.S.A., Germany, and Canada [Archambault, 2004; Werpy and Petersen, 2004; Oertel, 2007].

The use of biomass as raw material implies its transformation into chemicals and materials of commercial interest. It means moving from a petroleum-based economy to a biomass-based one; some potential advantages associated with this transition are: exploiting of unused productive capacity in agriculture and forest industry, developing new materials not available from petrochemical sources, revitalizing rural economies through local production and processing of renewable raw material sources, a more balanced development between urban and rural areas, economically sustainable development and environmental sustainability easier to achieve by using renewable raw materials, a decrease in net CO<sub>2</sub> emissions to the atmosphere, and a reduced outside dependence on both energy and raw material sources. In this context and by similarity with the refinery, which is the base industrial unit of petro-economy, emerges the concept of "Biorefinery", which is the production facility in which biomass is transformed into energy and bioproducts.

Bio-compounds, those ones produced from renewable sources, have a growing importance among the transport fuels. The EU imposed a 2% content of biocompounds into transport fuels by the end of 2005, increasing to 5.75% by the end of 2010 [EU Directive 2001/0265]. Transesterification of vegetable oils with methanol produces biodiesel, which is a mixture of methyl esters of fatty acid [Ali et al., 1995; Peterson et al., 1996; Vicente and Martínez, 2004]. This process generates glycerol as by-product, approximately 10 wt.% of total product. In this context, Province of Santa Fe in Argentine produces more than 2,500,000 tons of

biodiesel per year; consequently, 250,000 tons of glycerol are available. Glycerol is a chemical compound widely used in medicines, cosmetics, and sweetening agents, but its world demand is limited. In recent years, a significant increment in biodiesel production is generating an increased supply of glycerol, causing a progressive decline in its price; it encourages to research applications that allow synthesize chemicals with added value, and develop novel processes that utilize glycerol. It is highly desirable to improve the economics of biodiesel production process. Moreover, the conversion of glycerol has benefits because it comes from renewable raw materials, enabling a sustainable environmental development.

Glycerol has three hydrophilic alcoholic hydroxyl groups and it is an intermediate in the synthesis of a large number of compounds used in industry [Corma et al., 2007]. Some products and the corresponding reactions are: propyleneglycol and 1,3-propanediol by hydrogenolysis; acetol and acrolein by dehydration; dihydroxyacetone, and glyceric and hydroxyacetic acids by oxidation; glycidol by epoxidation; glycerol carbonate by transesterification; mono- and diglycerides by selective etherification; and polyglycerol by polymerization. Another possible use of glycerol is as substrate to produce bio-hydrogen, proposed as the next-generation renewable fuel. All these uses allow considering the glycerol as a key-compound in the environment of future biorefinery.

The objective of chapter is to review reactions of glycerol such as hydrogenolysis, oxidation, and steam reforming, also including own results.

## 2. Glycerol reactions

### 2.1 Hydrogenolysis: Glycerol to propanediols

#### 2.1.1 Characteristics, processes, catalysts, reaction conditions, and mechanisms

The hydrogenolysis of glycerol is presented as an alternative to the problem of its growing by increasing the production of biodiesel, allowing that reaction to obtain compounds with added value, such as 1,2-propanediol (1,2-PD) and 1,3-propanediol (1,3-PD). By considering the 1,2-PD, also known as propyleneglycol, in 2007, it was announced the introduction of propyleneglycol derived from renewable resources in the context of sustainable chemical technology search. 1,2-PD is a chemical with a variety of applications such as a solvent for the production of unsaturated polyester resins, medicines, cosmetics, and food, being also used as antifreeze and deicing fluid [Corma et al., 2007]. 1,3-PD can have the same applications as ethylene glycol, 1,2-PD, 1,3-butanediol, and 1,4-butanediol [Maervoet et al., 2011], and it is used as a solvent, for the production of adhesives, laminates, and paints, and in coolant formulations [Sauer et al., 2008]. However, a particular interest is its use as monomer in polycondensation reactions to produce polyesters, polyethers, and polyurethanes; 1,3-PD is copolymerized with acid to produce polytrimethylene-terephthalate (PTT) polymers, which are recognized for their excellent elastic properties, and marketed by Shell Chemical Company and DuPont with the commercial name Corterra™ and Sorona®, respectively [Biebl et al., 1999; Kurian, 2005]. The largest commercial synthesis of 1,3-PD is made by DuPont and Shell; the first hydrating acrolein to 3-hydroxypropanal followed by hydrogenation to form 1,3-PD, while the latter produces 1,3-PD by hydroformylation of ethylene oxide followed by hydrogenation [Saxena et al., 2009]. The problems in these processes are the high pressure applied in the hydroformylation and hydrogenation steps together with the high temperature, the use of expensive catalysts, and the release of toxic intermediate compounds [Saxena et al., 2009].

Propanediols can be produced by alternative routes such as the selective dehydroxylation of glycerol through either chemical hydrogenolysis or biocatalytic reduction [Zheng et al., 2008]. The selective conversion to propyleneglycol by hydrogenolysis in liquid phase has been reported using catalysts such as Raney Ni, Ru/C, Pt/C, Ni/C, and copper chromite, reaching this last material the largest production. Table 1 presents catalysts, operating conditions, and catalytic behavior to hydrogenolysis of glycerol, including results of patents and open literature on supported catalysts containing Ru, Cu, Pt, Ni, Co, Rh, and Re. Catalytic performance during hydrogenolysis on supported metal catalysts followed the order  $\text{Cu} \approx \text{Ni} \approx \text{Ru} > \text{Pt} > \text{Pd}$  [Roy et al., 2010]. Supported catalysts of the Group VIII metal (especially Ru/C) combined with a strong solid acid (Amberlyst 15, 70), were active in hydrogenolysis [Kusunoki et al., 2005; Miyazawa et al., 2006-2007a-2007b]. Using an ion-exchange resin combined with a Ru/C supported catalyst, the first material produce acetol, an intermediate product, being the second one responsible to the conversion of acetol into propyleneglycol [Miyazawa et al. 2006]. Feng et al. [2008] investigated the effect of supports ( $\text{TiO}_2$ ,  $\text{SiO}_2$ , NaY,  $\gamma\text{-Al}_2\text{O}_3$ , and activated carbon) in Ru catalysts, stating the type of support can influence the metal particle size and the reaction pathways. Lahr and Shanks [2005] investigated the effect of addition of sulfur on Ru/C in the hydrogenolysis at high pH and found that higher loads of sulfur increase the selectivity to 1,2-PD, without modifying the selectivity to ethyleneglycol. Maris et al. [2007] reported that Pt-Ru/C was more stable while Au-Ru/C was altered by the harsh operating conditions. Ma et al. [2008-2009-2010] studied the promoting effect of Re on Ru catalysts on several supports ( $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ , C, and ZSM5). Balaraju et al. [2009] reported  $\text{Nb}_2\text{O}_5$  and TPA/ $\text{ZrO}_2$  (TPA: 12-phosphotungstic acid) having moderate acid sites as the most active co-catalysts combined with Ru/C, while the amount of acidity in the acid solid influences its catalytic activity. They also studied the effect of preparation conditions of Ru/ $\text{TiO}_2$  on the behavior during the hydrogenolysis of glycerol [Balaraju et al., 2010]. Roy et al. [2010] used a mixture of Ru/ $\text{Al}_2\text{O}_3$  and Pt/ $\text{Al}_2\text{O}_3$  catalysts to produce 1,2-PD from glycerol without added external  $\text{H}_2$ . Vasiliadou et al. [2009] reported the effect of both support and Ru precursor, obtaining a linear relationship between the total acidity of catalyst and the activity in hydrogenolysis. Unfortunately, Ru catalysts promote an excessive breakage of C-C bonds decreasing the selectivity to 1,2-PD. Copper catalysts having a poor activity in the rupture of C-C bonds and a high efficiency for the hydrogenating/dehydrogenating of C-O bonds, have been proposed as an alternative [Huang et al., 2009]. Commercial copper chromite [Dasari et al., 2005; Chiu et al., 2006-2008] and also prepared by impregnation and co-precipitation [Liang et al., 2009; Kim et al., 2010a-2010b], have been reported as efficient catalysts to produce 1,2-PD by hydrogenolysis. Cu/ $\text{ZnO}$  [Wang and Liu, 2007; Balaraju et al., 2008], Cu/ $\text{ZnO}/\text{Al}_2\text{O}_3$  [Meher et al., 2009; Zhou et al., 2010], Cu/ $\text{Al}_2\text{O}_3$  [Guo et al., 2009; Akiyama et al., 2009; Mane et al., 2010], Cu/ $\text{SiO}_2$  [Huang et al., 2008-2009; Huang et al., 2009], and Cu/ $\text{MgO}$  [Yuan et al., 2010] were also suitable catalysts for hydrogenolysis, while Cu supported on zeolites such as HY, 13X, H-ZSM5, and H $\beta$  did not produce 1,2-PD from glycerol [Guo et al., 2009]. By considering 1,3-PD, a selective hydroxylation involving three steps, acetalization, tosylation, and detosylation was reported as a synthesis way [Wang et al., 2003]. Kurosaka et al. [2008] also reported the selective hydrogenolysis of glycerol to 1,3-PD on Pt/ $\text{WO}_3/\text{ZrO}_2$ , using 1,3-dimethyl-2-imidazolidinone (DMI) as a solvent; using the same catalyst, Gong et al. [2009] studied the effect of both protic and aprotic solvents such as sulfolane, DMI, ethanol, and water. Other catalysts employed to produce propanediols by the hydrogenolysis of glycerol are Pt/ $\text{WO}_3/\text{TiO}_2/\text{SiO}_2$  [Gong et al., 2010], Pt/amorphous silica-alumina [Gandarias et al., 2010], and Pt on MgO, HLT (hydrotalcite), and  $\text{Al}_2\text{O}_3$  [Yuan et al., 2009].

<i>Catalyst</i>	<i>P</i> (MPa)	<i>T</i> (°C)	<i>Time</i> (h)	<i>X</i> (%)	<i>S<sub>1,2</sub></i> (%)	<i>S<sub>1,3</sub></i> (%)	<i>Reference</i>
Rh(CO) <sub>2</sub>	31.7	200	24	n.a.	3.8 <sup>a</sup>	3.5 <sup>a</sup>	Che and Westiefeld, 1987
CuO/ZnO	10.0	270	2	99.9	80.8	-	Casale and Gomez, 1993
CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	15.0	230	n.a.	93.2	94.0	-	Casale and Gomez, 1993
Ru/C	13.0	240	2	100	75.2	-	Casale and Gomez, 1994
Co/Cu/Mn/P/Mo	25.0	250	6	100	91.2	-	Schuster and Eggersdorfer, 1997
Co/Cu/Mn/P/Mo <sup>b</sup>	29.5	210	n.a.	100	92.0 <sup>c</sup>	-	Schuster and Eggersdorfer, 1997
Pd-BCPE	6.0	140	10	n.a.	21.8	30.8	Drent and Jager, 2000
Base of Cu <sup>b</sup>	2.0	195	n.a.	99.5	96.5	n.a.	Tuck and Tilley, 2008
CuO/ZnO	3.0	200	12	100	97.7	-	Franke and Stankowiak, 2010
Pt/C	3.0	160-200	3	9.0-22.0	17.0-9.0	41.0	Susuki et al., 2010a
Pt-W/Al <sub>2</sub> O <sub>3</sub>	3.0-5.5	160	3	20.0-23.0	4.0	67.0	Susuki et al., 2010a
Cu/SiO <sub>2</sub> <sup>b</sup>	2.0-20	210-230	36	94.0-93.0	94.0-98.0	-	Susuki et al., 2010b
CuO/ZnO/MnO <sub>2</sub>	8.0	200	12	100	97.5 <sup>c</sup>	-	Stankowiak and Franke, 2011
Ru/Al <sub>2</sub> O <sub>3</sub> + Pt/Al <sub>2</sub> O <sub>3</sub>	1.4 <sup>d</sup> -4.1	220	6	50.2-62.8	47.2-31.9	-	Roy et al., 2010
Ru/C	8.0	180	10	6.3	17.9	0.5	Kusunoki et al., 2005
Ru/C+Amberlyst 15	8.0	180	10	15.0	53.4	1.6	Kusunoki et al., 2005
Ru/TiO <sub>2</sub>	3.0	170	12	66.3	47.7	-	Feng et al., 2008
Pt-Ru/C	4.0	200	5	42.0-100	24.0-18.0	-	Maris et al., 2007
Ru/Al <sub>2</sub> O <sub>3</sub>	8.0	160	8	18.7	34.5	3.4	Ma et al., 2008
Ru/Al <sub>2</sub> O <sub>3</sub> +Re <sub>2</sub> (CO) <sub>10</sub>	8.0	160	8	53.4	50.1	6.4	Ma et al., 2008
Ru/ZrO <sub>2</sub>	8.0	160	8	25.4	31.9	1.8	Ma and He, 2009
Re-Ru/ZrO <sub>2</sub>	8.0	160	8	56.9	47.2	5.5	Ma and He, 2009
Ru/SiO <sub>2</sub>	8.0	160	8	16.8	39.0	6.4	Ma and He, 2010
Re-Ru/SiO <sub>2</sub>	8.0	160	8	51.0	49.1	8.3	Ma and He, 2010
Ru/C + TPA/ZrO <sub>2</sub>	6.0	180	8	44.0	64.3	-	Balaraju et al., 2009
Ru/CsPW	0.5	150	10	21.0	95.8	-	Alhanash et al., 2008
Rh/CsPW	0.5	180	10	6.3	65.4	7.1	Alhanash et al., 2008
Copper chromite	1.4	200	24	54.8	85.0	-	Dasari et al., 2005
Cu/Cr <sup>e</sup>	4.2	210	10	51.0	97.1	-	Liang et al., 2009
Cu/Cr	8.0	220	12	80.0	86.0	-	Kim et al., 2010
Cu/ZnO	4.2	200	12	10.4-33.9	27.9-77.5	-	Wang and Liu, 2007
Cu/ZnO	2.0	200	16	37.0	92.0	-	Balaraju et al., 2008
Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	4.0	220	n.a.	81.5	93.4	-	Zhou et al., 2010
Cu/Al <sub>2</sub> O <sub>3</sub>	3.6	200	10	34.6	93.9	-	Guo et al., 2009
Cu/Al <sub>2</sub> O <sub>3</sub> <sup>b</sup>	0.0	200	2-5	100	78.2	-	Akiyama et al., 2009
Cu/SiO <sub>2</sub> -P	9.0	200	12	73.4	94.3	-	Huang et al., 2008
Cu/SiO <sub>2</sub> -P <sup>b</sup>	6.0	180	200	83.0	96.0	-	Huang et al., 2008



Cu-STA/SiO <sub>2</sub> <sup>b</sup>	0.5	210	n.a.	83.4	22.2	32.1	Huang, et al., 2009
Cu/SBA-15 <sup>b</sup>	4.0	250	6-7	96.0	92.4	-	Zheng et al., 2010
Cu/MgO	3.0	180	20	72.0-82.0	97.6-95.8	-	Yuan et al., 2010
Raney Cu	1.4	200	n.a.	100	91.0	<0.1	Schmidt et al., 2010
Pt/WO <sub>3</sub> /ZrO <sub>2</sub>	8.0	170	18	85.8	14.6	28.2	Kurosaka et al., 2008
Pt/WO <sub>3</sub> /ZrO <sub>2</sub>	5.5	170	12	24.7-45.6	13.6-18.9	5.3-29.3	Gong et al., 2009
Pt/WO <sub>3</sub> /TiO <sub>2</sub> /SiO <sub>2</sub>	5.5	180	12	15.3	9.2	50.5	Gong et al., 2010
Pt/MgO	3.0	220	20	50.0	81.2	1.6	Yuan et al., 2009
Pt/HLT	3.0	220	20	92.1	93.0	-	Yuan et al., 2009
Pt/Al <sub>2</sub> O <sub>3</sub>	3.0	220	20	39.0	81.2	1.5	Yuan et al., 2009
Raney Ni	1.0	190	20	47.0-63.0	68.0-81.0	-	Perosa et al., 2005
Ni/SiO <sub>2</sub>	6.0	200	10	56.9	44.4	-	Zhao et al., 2010
Ni/NaA	6.0	200	10	65.3	46.8	-	Zhao et al., 2010
Ni/NaX	6.0	200	10	94.5	72.1	-	Zhao et al., 2010
Ni/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	6.0	200	10	97.1	44.2	-	Zhao et al., 2010
Ni/C	5.0	200	6	43.3	76.1	-	Yu et al., 2010a
Ni-Ce/C	5.0	200	6	90.4	65.7	-	Yu et al., 2010b
Co/MgO	2.0	200	9	44.8	42.2	-	Guo et al., 2009
Raney Co	3.0	200	4	97.0	45.4	-	Korolev et al., 2010
Rh/SiO <sub>2</sub>	8.0	120	5	3.3	38.5	8.5	Shinmi et al., 2010
Rh-ReO <sub>x</sub> /SiO <sub>2</sub>	8.0	120	5	66.7	40.0	14.4	Shinmi et al., 2010
Ir-ReO <sub>x</sub> /SiO <sub>2</sub>	8.0	120	24	62.8	10.0	49.0	Nakagawa et al., 2010

BCPE: 1,2-bis(1,5-cyclooclylenofosfine)ethane; n.a.: non available; a): grams of PD produced from 20 g of glycerol; b): experience in gas phase; c): %wt. of products different to water; d) pressure of nitrogen; e) prepared using carbon as template.

Table 1. Catalysts, operating conditions, and catalytic behavior during the hydrogenolysis of glycerol, expressed as conversion of glycerol ( $X$ ) and selectivity to 1,2-PD ( $S_{1,2}$ ) and 1,3-PD ( $S_{1,3}$ ), including the corresponding reference.

Different mechanisms have been proposed to understand the hydrogenolysis of glycerol. Dasari et al. [2005] detected acetol (monohydroxyacetone) between the reaction products, therefore proposing that glycerol is dehydrated to acetol which is hydrogenated to 1,2-PD. The reversible dehydrogenation of glycerol to glyceraldehyde followed by dehydration and/or retroaldolization of glyceraldehyde to 2-hydroxyacrolein and/or glycolaldehyde, and finally both precursors of glycols hydrogenated to 1,2-PD and ethylene glycol, was proposed, while the dehydration of glycerol to 3-hydroxypropionaldehyde, the latter being hydrogenated to 1,3-PD was suggested by Miyazawa et al. [2006].

### 2.1.2 Results and discussion of hydrogenolysis in both liquid and gas phase

In order to value glycerol, the hydrogenolysis reaction to obtain propanediols and/or acetol was studied in both liquid and gas phases, using commercial and prepared catalysts. Commercial materials were: copper chromite (43% CuO and 39% Cr<sub>2</sub>O<sub>3</sub>, specific surface area 49 m<sup>2</sup> g<sup>-1</sup> and pore volume of 0.21 cm<sup>3</sup> g<sup>-1</sup>) and copper chromite stabilized with Ba (38% Cu, 31% Cr, 6% Ba, specific surface 30 m<sup>2</sup> g<sup>-1</sup>). Prepared catalysts were impregnated following the incipient-wetness technique; base materials for impregnation were Zr(OH)<sub>4</sub> (Sigma-Aldrich), ZrO<sub>2</sub> (from Zr(OH)<sub>4</sub>, by calcining at 420°C), ferrierite zeolite in both ammonium

and potassium forms (TOSOH), and 13X (Fluka), while precursors of W, Pt, Cu, and Ni were ammonium metatungstate, tetraamineplatinunchloride, cupric acetate, and nickel nitrate hexahydrate, respectively. Catalysts were identified as Pt/WO<sub>3</sub>/ZrO<sub>2</sub>, Pt/WO<sub>3</sub>/Zr(OH)<sub>4</sub>, Cu/K-Fer, Cu/H-Fer, and Ni/13X, respectively. The metal loadings were 2% platinum, 16% tungsten, 2.2% Cu, and 10% Ni. Reactant used was 99.5% pro-analysis anhydrous glycerin. Experiences in liquid phase were performed in a stainless steel reactor of 200 ml capacity, operated in a discontinuous form, loading 60 ml of glycerol and the finely divided catalyst, purged with nitrogen, reaching to operating temperature, and finally bubbling hydrogen in the liquid at 18 bar. Reagent and reaction products were analyzed by gas chromatography using a megabore DB-20 column and a FID. The gas phase experiments were performed in a tubular quartz down-flow fixed-bed reactor; the system has a vaporizer and a condenser previous and after the reactor, respectively. Reaction was monitored by chromatography, the flow of gases and non-condensates were analyzed on-line using a sampling valve to inject sample into a megabore GS-Alumina (J&W) column; the condensed fraction during reaction was analyzed at the end of it, as by the liquid phase experiences. Catalysts were characterized by temperature-programmed reduction (TPR), ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD), X-ray diffraction (XRD), and FTIR.

XRD patterns of catalysts prepared from Zr(OH)<sub>4</sub> and ZrO<sub>2</sub> show that Zr(OH)<sub>4</sub> was initially amorphous; only the tetragonal (T) crystalline structure of zirconia is formed after calcining at 500°C, while both T and M (monoclinic) structures appeared after calcining at 700°C. The addition of Pt on the W-impregnated material produced an interaction with the W species affecting an adequate definition of the 3 peaks of tetragonal phase of WO<sub>3</sub>. According to IR characterization, the 3400 cm<sup>-1</sup> band decreased due to the loss of hydroxyl groups by effect of calcining of Zr(OH)<sub>4</sub>, which produces dehydration of material, formation of crystalline phases, and their subsequent stabilization. TPR profiles of materials prepared from Zr(OH)<sub>4</sub> and ZrO<sub>2</sub> were qualitatively similar: the addition of Pt after impregnating W favored the reduction of these species, appearing species that reduce at low temperature (300 and 400°C) and shifting to lower temperature the reduction of ones which reduced at 700°C; the sample with only one calcination displayed a well-defined reduction peak at 130°C assigned to Pt, while the preparation with two calcinations the Pt species were more difficult to reduce and did not have a well-defined peak. Finally, the NH<sub>3</sub>-TPD profiles showed that the addition of Pt changes the amount of acid sites and produces a shift of the desorption peak maximum.

Catalytic behavior of Pt/WO<sub>3</sub>/ZrO<sub>2</sub> and Pt/WO<sub>3</sub>/Zr(OH)<sub>4</sub> was evaluated in the liquid phase hydrogenolysis. Operating conditions were selected to reach a low conversion of glycerol to analyze the selectivity to 1,2-PD and 1,3-PD. Table 2 shows selectivity to propanediols and the ratio between both them for catalysts having either only one final calcination or two calcinations, a first one after the W impregnation and the second one after Pt impregnation. It is remarkable that all samples allow forming 1,3-PD, at ratios higher or similar to 1,2-PD. Catalysts with two calcinations improved the selectivity to propanediols and reached a larger proportion of 1,3-PD. Different ratios allow to consider the effect of preparation of catalysts on their catalytic behavior which can be associated to the interaction of platinum and tungsten, the modification of active sites or the formation of new ones. It has been previously reported for this catalytic system [Vaudagna et al., 1997]. The production of 1,3-PD by hydrogenolysis of glycerol on Pt/WO<sub>3</sub>-ZrO<sub>2</sub> was previously reported at higher pressures, 5.5 and 8.0 MPa, higher weight ratio of catalyst/glycerol, and in the presence of organic solvents [Kurosaka et al., 2008; Gong et al., 2009].

Parameter	Pt/WO <sub>3</sub> /Zr(OH) <sub>4</sub> <sup>1</sup>	Pt/WO <sub>3</sub> /Zr(OH) <sub>4</sub> <sup>2</sup>	Pt/WO <sub>3</sub> /ZrO <sub>2</sub> <sup>1</sup>	Pt/WO <sub>3</sub> /ZrO <sub>2</sub> <sup>2</sup>
S <sub>PD</sub> (%)	26.2	29.7	24.4	30.3
R <sub>1,3-PD/1,2-PD</sub>	1.05	1.56	0.79	1.86

Reaction conditions: 200°C, 1.8 MPa, 40 g of glycerol, 1 g of catalyst, 8 h-on-stream.

(1): Samples submitted to only final calcination; (2): Samples with two calcinations.

Table 2. Selectivity to propanediols (S<sub>PD</sub>) and ratio between 1,3-PD and 1,2-PD (R<sub>1,3-PD/1,2-PD</sub>) for the hydrogenolysis of glycerol in liquid phase on Pt/WO<sub>3</sub>/Zr(OH)<sub>4</sub> and Pt/WO<sub>3</sub>/ZrO<sub>2</sub>.

XRD patterns of ferrierite showed peaks of the orthorhombic crystalline structure of zeolite, while Cu/K-Fer and Cu/H-Fer also presented two bands at  $2\theta = 43.4^\circ$  and  $51.3^\circ$  assigned to Cu<sup>0</sup> species [Guo et al., 2009]; the absence of diffraction peaks corresponding to CuO would allow to consider that copper species were completely reduced in the analyzed samples [Wang and Liu, 2007]. Impregnating nickel species on 13X did not modify the crystalline structure of 13X, appearing a peak at  $44^\circ$  assigned to metallic nickel species [Yu et al., 2010]. Considering TPR profiles, K-Fer and H-Fer did not consume hydrogen, while Cu/K-Fer has a small shoulder at 220°C, the main reduction peak at 260°C, and a small one which finished at 500°C; it indicates the presence of three species of copper. Cu/H-Fer only displayed the main reduction peak with a maximum at 260°C. Zeolite 13X showed a slight consumption of hydrogen between 650 and 750°C, while Ni/13X presented the main peak centered at 435°C and a second one mounted on the tail of the main peak; it allows to infer the existence of two nickel species. Considering NH<sub>3</sub>-TPD profiles, H-Fer showed two bands with maxima at 330°C and 500°C; the addition of platinum increased acidity and shifted the maximum from 330 to 400°C. K-Fer showed a single band with maximum at 400°C, being acidity lower than H-Fer; Cu/K-Fer presented a similar profile that K-Fer. Cu/H-Fer has a similar acidity than H-Fer, being it higher than the Cu/K-Fer one. Zeolite 13X showed a broad band with maximum at 500°C; the addition of nickel decreased the acidity of the base material.

Catalytic behavior of materials was measured in the hydrogenolysis of glycerol in gas phase at 200°C and atmospheric pressure. Table 3 shows glycerol conversion and selectivities to acetol and propyleneglycol using Cu/H-Fer, Cu/K-Fer, Ni/13X, and copper chromite with and without barium. Cu/H-Fer was more active than Cu/K-Fer (conversion 22 and 13%, respectively), but Cu/K-Fer was more selective to acetol and 1,2-PD. Ni/13X was very active, 79.9% conversion, but few selective to acetol and 1,2-PD; methane was the only product detected in the gas stream while ethyleneglycol was the major one in the condensed fraction. Copper chromite stabilized with barium was the most active catalyst, reaching 83.0% conversion while both copper chromite samples were the most efficient in selectivity to acetol and 1,2-PD. Sample without barium is the most selective to acetol (67.8%), while the one with barium improved significantly the selectivity to 1,2-PD, up to 29.7%.

Catalyst	Cu/H-Fer	Cu/K-Fer	Ni/13X	Cu/Cr <sub>2</sub> O <sub>3</sub>	Ba-Cu/Cr <sub>2</sub> O <sub>3</sub>
X (%)	22.2	13.0	79.9	24.5	83.0
S <sub>a</sub> (%)	4.0	37.1	2.0	67.8	43.3
S <sub>1,2</sub> (%)	0.7	3.7	0.9	12.2	29.7

Reaction conditions: 200°C, atmospheric pressure, 1 ml h<sup>-1</sup> of 20% w/v glycerol solution, 70 ml min<sup>-1</sup> H<sub>2</sub> stream, 200 mg of catalyst, and 3 h-on-stream.

Table 3. Conversion of glycerol (X) and selectivity to acetol (S<sub>a</sub>) and 1,2-PD (S<sub>1,2</sub>) during the hydrogenolysis of glycerol in gas phase on prepared and commercial samples.



## 2.2 Selective oxidation: Glycerol to dihydroxyacetone (DHA)

### 2.2.1 Characteristics, processes, reaction conditions, and catalysts

The oxidation of glycerol is an alternative to the problem of its growing availability allowing obtain compounds with added value. The oxidation reaction at atmospheric conditions needs adding either stoichiometric acids such as chromic acid or compounds as potassium permanganate, but it generates large amounts of undesirable products; it makes difficult the sustainability of the process which is practically unfeasible [Carrettin et al., 2003]. Primary products of oxidation of glycerol are glyceraldehyde, glyceric acid, tartronic acid and dihydroxyacetone; tartronic acid can be oxidized to glycolic, glyoxylic, oxalic, and mesoxalic acids, while the latter one can be obtained by oxidation of hydroxypyruvic acid, which is obtained by oxidation of DHA [Demirel-Gülen et al., 2005]. The main products have not been yet developed due to low selectivities and yields reached with the existing processes, which operate with low concentration solutions of glycerol [Corma et al., 2007]. Glyceric acid, used in medicine as metabolites in the glycolysis cycle and a precursor in the synthesis of amino acids, is mostly produced by a fermentation process [Kenji et al., 1989; Teruyuki and Yoshinori, 1989; Takehiro et al., 1993]. Hydroxypyruvic acid is obtained by oxidation of glycerol or sugars using mineral acids and it is the precursor of serine aminoacid [Corma et al., 2007]. Tartronic acid is widely used as a precursor of major products such as oxalic acid [Fordham et al., 1995]. Considering the oxidation of glycerol in liquid phase by heterogeneous catalysis, the nature of metal and the pH of medium affect the reaction selectivity. Kimura et al. [1993] demonstrated that the catalytic oxidation process using platinum (Pt) supported on carbon (C) was more efficient than the conventional fermentation; the DHA selectivity decreased drastically in a basic medium (pH 8) and was less than 10% in an acid pH (pH 2-3), increasing the selectivity to DHA to 80% by incorporating bismuth (Bi) to Pt/C. Abbadi and van Bekkum [1996] studied the oxidation of glycerol and DHA on catalysts of Bi-Pt/C at 65°C, reaching 95% conversion of glycerol and 93% selectivity to glyceric acid at pH 5-6; under acidic conditions, DHA, hydroxypyruvic acid, and oxalic acid were the main products, while at pH 8 glyceric acid was obtained and the production of DHA dropped drastically. García et al. [1995] favored the oxidation of primary or secondary hydroxyl group by controlling reaction conditions, the nature of metal and the pH of medium; glycerol conversion was 90% with 70% glyceric acid and 8% DHA using Pd/C, while the production of DHA was 37% with 75% conversion on Bi-Pt/C at pH 2. Using gold catalysts supported on carbon, the selectivity to glyceric acid decreased markedly when gold nanoparticles with average diameter of 6 nm are well dispersed on the surface, while the selectivity increased to 92-95% with nanoparticles larger than 20 nm, indicating the importance of preparation method on performance in the oxidation reaction of glycerol [Porta and Prati, 2004]. Monometallic catalysts such as Pt/C, Pd/C, and Au/C are able to produce glyceric acid [Porta and Prati, 2004; Bianchi et al., 2005], while bimetallic ones as Au-Pd/C and Au-Pt/C produce tartronic acid and glyceraldehyde, respectively [Bianchi et al., 2005].

DHA is a monosaccharide included into the group of ketoses, particularly in the triose one. Its chemical formula is  $C_3H_6O_3$  and has no chiral center, making it the only one that has no optical activity and is not toxic. DHA is naturally found in plants such as sugar cane and beet, produced by the fermentation of glycerol. DHA in its pure form presents in two ways, as a monomer or dimer, predominantly the latter. In aqueous solution, DHA is found as monomer, which can gradually tautomerize to glyceraldehyde. The equilibrium between both compounds depends largely on pH; DHA is favored in an acidic medium (greater

stability at pH 3) while glyceraldehyde in an alkaline one [Yaylayan et al., 1999; Zhua et al., 2003]. DHA is a chemical used in the cosmetic industry to make artificial tans; people with sensitive skin should limit exposure to sun due to the consequences that may ensue. A natural tan carries the risk of getting skin cancer due to the activation and deactivation of multiple cellular signals, so there is a growing demand for artificial tans. DHA is the active ingredient in those bronzers, varying its concentration between 2 and 5% [Brown, 2001]. Due to its potential capacity of tanning, DHA is also used for the treatment of vitiligo, an autoimmune disease that affects the melanocytes (cells related to the coloration of skin). The method of treatment is very well used and accepted [Fesq et al., 2001]. DHA also finds an important application in the chemical industry as reagent of great versatility for the production of compounds like lactic acid, hydroxypyruvic acid or 1,2-PD [Corma et al., 2007; Hekmat et al., 2003; Bicker et al., 2005]. DHA is obtained through a microbiological process producing it by incomplete oxidation of glycerol by means of the glycerol-dehydrogenase enzyme [Young et al., 1980; Gupta et al., 2001].

### 2.2.2 Results and discussion using impregnated catalysts

An optimal catalyst should present a good glycerol conversion with high selectivity to DHA; this section presents the oxidation of glycerol, using both commercial and prepared catalysts. Commercial materials were copper chromite (43% of CuO and 39% of Cr<sub>2</sub>O<sub>3</sub>, 49 m<sup>2</sup>/g specific surface and 0.21 cm<sup>3</sup>/g pore volume) and Raney nickel (PRICAT 9910, Johnson Matthey). Supported catalysts were prepared by impregnation by the incipient-wetness technique; commercial samples of coal (CARBONAC GA-160) and potassium ferrierite (17.8 SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio) were used as starting materials, while tetraammineplatinum-chloride hydrate and nickel nitrate hexahydrate were Pt and Ni precursors, respectively. Solutions with the desirable concentration were prepared. The impregnated materials were maintained at room temperature for 4 h, and then dried overnight in an oven at 110°C. Samples were calcined in a continuous air flow at 500°C; then, they were reduced in a hydrogen flow at 500°C. Catalysts were identified as Pt/C, Pt/K-Fer, and Ni/K-Fer. Catalysts were characterized by TPR, NH<sub>3</sub>-TPD, XRD, and FTIR. The catalytic behavior during the oxidation reaction was measured in a system with a glass reactor that allows the semicontinuous operation; the reactor has an entrance by feeding the airflow which bubbles in the liquid and an exit that derives the unreacted airflow and any volatile product produced by reaction. A continuous stirring is made with a magnetic plate that also allows reach the selected temperature. Reaction conditions were: atmospheric pressure, 60°C, 30 ml of 20% glycerol solution, 300 mg of catalyst, pH 3, and 900 cm<sup>3</sup> min<sup>-1</sup> air flow. The reactant and reaction products were analyzed by gas chromatography, using a 25 m long, 0.33 mm i.d. DB-20 column and a FID. The reaction of glycerol oxidation produces some acids which are not detected by FID; then, the method of the internal standard (1-butanol) to quantify glycerol and DHA and determine conversion and selectivity to DHA, was used.

Figure 1 displays TPR profiles corresponding to both Pt/K-Fer and the support. K-Fer does not show any consumption of hydrogen, while a well-defined peak centered at 120°C appears in the Pt/K-Fer profile, being this peak assigned to the reduction of Pt species.

Figure 2 shows the catalytic behavior during the oxidation of glycerol on different catalysts. Copper chromite, Raney nickel, Ni/K-Fer, and Bi/K-Fer did not present activity for that oxidation reaction under the studied conditions. Pt/C showed activity and oxidized glycerol (34.9% conversion) but without producing DHA. It agrees with previous results indicating this catalyst as selective to glyceric acid [Kimura and Tsuto, 1993]. The best performance in

the selective oxidation to DHA was obtained with Pt/K-Fer, increasing glycerol conversion up to 48.3% and reaching 40.5% selectivity to DHA. In the presence of the same metal sites (Pt), changing the support (C or K-Fer) favored the oxidation of either primary or secondary hydroxyl group. It was reported the addition of a second metal as Bi on Pt impregnated on C promotes the selective oxidation of glycerol to DHA, being it associated to the changing on the environment of the active site [Kimura and Tsuto, 1993]. The goal of Pt/K-Fer is that allows obtain DHA with only platinum sites; it could be related to a selectivity of form presented by the ferrierite zeolite, being capable to favor the formation of DHA.

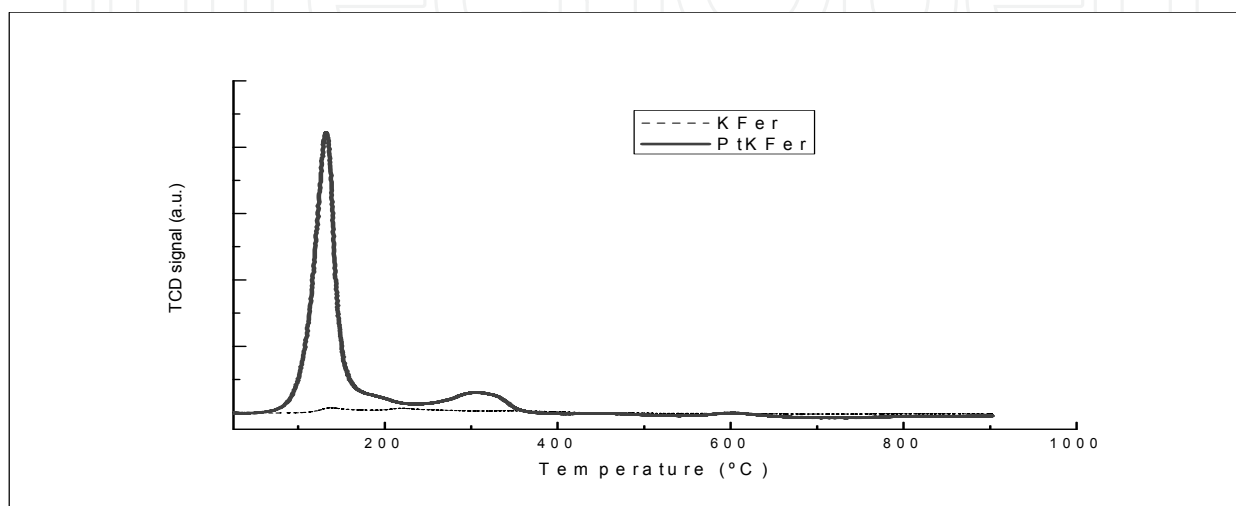


Fig. 1. TPR profiles corresponding to K-Fer zeolite and Pt/K-Fer catalyst.

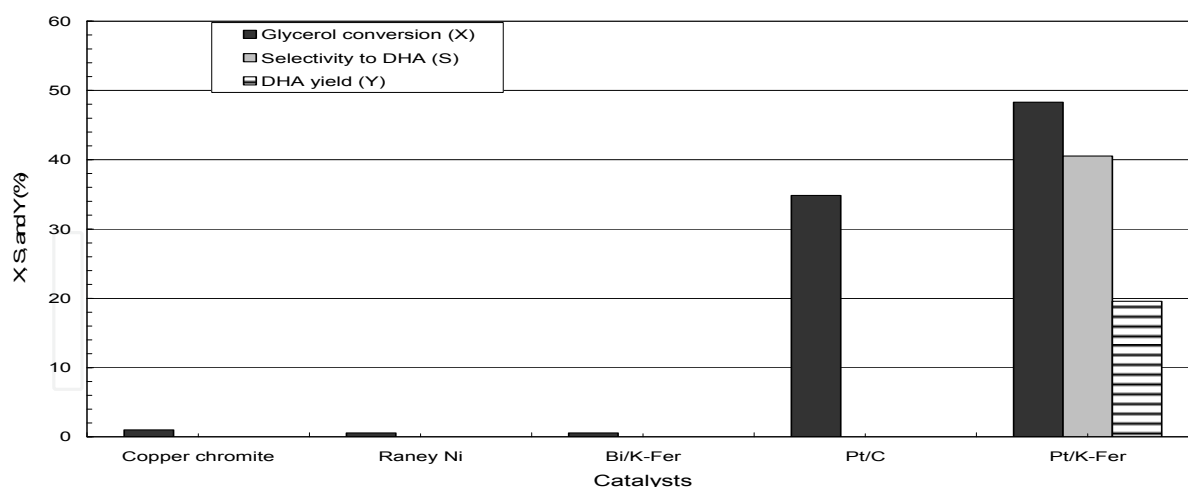
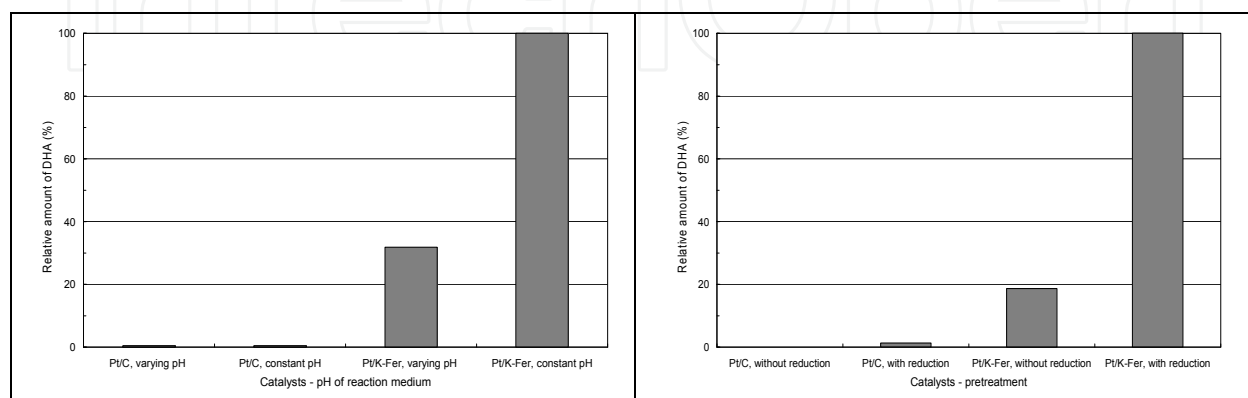


Fig. 2. Conversion of glycerol (X), selectivity to DHA (S), and DHA yield (Y) from the oxidation reaction of glycerol using commercial and prepared catalysts.

Reaction conditions: 300 mg of catalyst, 30 ml of 20% glycerol solution, 60 °C, atmospheric pressure, 900 cm<sup>3</sup> min<sup>-1</sup> air stream, pH 3 and 6 hour-on-stream.

Figure 3 shows the effect of pH of reaction medium on the amount of DHA during the glycerol oxidation on platinum containing catalysts. Pt/C did not practically show activity in the DHA production independently of variable or constant pH. Pt/K-Fer was active to

produce DHA, reaching 9.8 and 31.8% of DHA when reaction takes place at variable and constant pH, respectively. At variable pH, the catalytic performance improved at pH close to 3. Figure 4 displays the effect of pre-reduction step of platinum containing catalysts on their performance during the glycerol oxidation. Pt/C without reduction was inactive to produce DHA, while reduced showed an incipient activity. Pt/K-Fer was active reaching 6.1% of DHA when reaction takes place on catalysts without pre-reduction and increasing to 32.8% for pre-reduced material. The presence of sites in the metallic form improved DHA production, and the pretreatment of catalysts significantly influenced their behavior.



(\*): 100% assigned to the maximum value reached.

(\*): 100% assigned to the maximum value reached.

Fig. 3. Relative concentration of DHA\* in the reaction medium with different catalysts, at 60°C and pH varying or constant.

Fig. 4. Relative concentration of DHA\* in the reaction medium for catalysts with and without reduction, at 60°C and pH 3.

## 2.3 Steam reforming: Bio-hydrogen from glycerol

### 2.3.1 Processes and thermodynamic data

In the last few years, the potential of renewable hydrogen as a clean energy vector has been increasing attention from the business, scientific, and political worlds. Moreover, technical advances in fuel cell industry are increasing the hydrogen demand, the most simplest and abundant element. Currently, hydrogen is mainly obtained from feeding based on fossil fuels, making it necessary to find renewable sources of raw materials to produce it. Consequently, there has been a growing interest in environmentally clean renewable sources for hydrogen production. In this context, new technologies have been developed for glycerol reforming. A complete review related to the processes capable to convert glycerol into hydrogen, including steam reforming, partial oxidation, autothermal reforming, aqueous-phase reforming, and supercritical water reforming, was carried out by Adhikari et al. [2009]. By considering the steam reforming of glycerol to produce hydrogen, it is a highly endothermic process which involves complex reactions, and several by-products are formed during transformation. The yield of hydrogen varies significantly according to the operating conditions, and the process is thermodynamically favored by high temperatures, low pressures, and an excess of steam. Adhikari et al. [2007a] performed a thermodynamic equilibrium study of that steam-reforming in the 600-1000 K, 1-5 atm, and 1:1-9:1 water:glycerol feed ratio ranges, resulting temperature higher than 900 K, atmospheric pressure, and 9:1 water:glycerol molar ratio as the best conditions for producing hydrogen with minimum methane production. By thermodynamic studies in the 550-1200 K, 1-50 atm,



and 1:1-12:1 water:glycerol molar ratio ranges, Wang et al. [2008] reported temperatures between 925 and 975 K and 9-12 water:glycerol ratios at atmospheric pressure as optimal conditions for hydrogen production, whereas higher temperatures and lower reactant ratios at 20-50 atm were suitable for the production of synthesis gas. Rossi et al. [2009] reported the increase of hydrogen production by increasing water:glycerol feed ratio or temperature. Chen et al. [2009] analyzed the adsorption-enhanced steam reforming of glycerol, stating that the use of a CO<sub>2</sub> adsorbent enhanced from 6 to 7 moles of hydrogen produced per mole of glycerol, while the most favorable temperature for steam reforming in the presence of a CO<sub>2</sub> adsorbent was 800-850 K, being about 100 K lower than that for reforming without CO<sub>2</sub> adsorption. Dou et al. [2010] evaluated the steam reforming of both pure glycerol and crude by-product of a biodiesel production plant at atmospheric pressure, with and without in situ CO<sub>2</sub> sorption, between 400 and 700°C; both crude glycerol and steam conversions and the hydrogen purity reached 100, 11, and 68%, respectively at 600°C.

### 2.3.2 Catalysts, reaction conditions, and deactivation processes

By considering catalytic conversion of glycerol to hydrogen, the gas phase reforming has now increased interest due to its operational characteristics and efficiency of reaction. Hirai et al. [2005] reported the production of hydrogen by steam-reforming of glycerol using ruthenium catalyst, being the main reaction product synthesis gas; this syngas can be converted into methanol which is used for methyl esterification of vegetable oils, then, 100% biomass-based bio-diesel fuel could be obtained. Among the catalysts studied, Ru/Y<sub>2</sub>O<sub>3</sub> gave the best performance; at 500°C, the hydrogen yield increased as the ruthenium loading increased up to 3 wt.%, while a further increment in loading to 5 wt.% did not affect the behavior. Zhang et al. [2007] reported the hydrogen production by reforming of ethanol and glycerol over ceria-supported Ir, Co, and Ni catalysts, studying both nature of the active metals and reaction pathways; Ir/CeO<sub>2</sub> showed a quite promising catalytic performance with 100% glycerol conversion and hydrogen selectivity higher than 85% at 400°C. Adhikari et al. [2007b] evaluated the performance of a Ni/MgO catalyst during the steam reforming process and compared it to the thermodynamic data. Adhikari et al. [2008a] also studied the hydrogen production using Ni/CeO<sub>2</sub>, Ni/MgO, and Ni/TiO<sub>2</sub> catalysts. Ni/CeO<sub>2</sub> displayed the best catalytic performance at 600°C, 12:1 water:glycerol molar ratio, and 0.5 mL/min feed flow rate, reaching the maximum hydrogen selectivity (74.7%) compared to Ni/MgO and Ni/TiO<sub>2</sub> which showed 38.6 and 25.3%, respectively. Nevertheless, the maximum hydrogen yield was obtained at 650°C with Ni/MgO, corresponding to 4 mol of H<sub>2</sub> out of 7 mol of stoichiometric maximum [Adhikari et al., 2008b]. Cui et al. [2009] evaluated the steam reforming of glycerol on non-substituted and partially Ce substituted La<sub>1-x</sub>Ce<sub>x</sub>NiO<sub>3</sub> mixed oxides; Ni species were easily reduced in the La<sub>0.3</sub>Ce<sub>0.7</sub>NiO<sub>3</sub>, being this catalyst highly active with conversions approaching to the equilibrium at temperatures between 500 and 700°C, and forming the smallest amount of carbonaceous deposits. It confirmed the efficient operation and high stability of the non-noble, inexpensive catalyst of La<sub>0.3</sub>Ce<sub>0.7</sub>NiO<sub>3</sub>. Slinn et al. [2008] studied the steam reforming of combined glycerol and water by-product streams of a biodiesel plant on a platinum alumina catalyst, reaching a high gas yield (almost 100%) with 70% selectivity (dry basis) at high temperatures; the optimum conditions were 860°C, 0.12 mol/min glycerol flow per kg of catalyst, and 2.5 steam/carbon ratio. Kunkes et al. [2009] reported an integrated catalytic approach for the production of hydrogen by glycerol reforming coupled with the water-gas shift reaction. This process uses two catalyst beds that

can be tuned to yield hydrogen (and CO<sub>2</sub>) or synthesis gas at 573 K and atmospheric pressure; the first bed is a carbon-supported bimetallic platinum-based catalyst to achieve conversion of glycerol to H<sub>2</sub>/CO mixture, followed by a second bed of 1%Pt/CeO<sub>2</sub>/ZrO<sub>2</sub> which is effective for the water-gas shift reaction. This integrated system displayed 100% carbon conversion of concentrated glycerol solutions into CO<sub>2</sub> and CO, with a 80% hydrogen yield of the ideally amount from the stoichiometric conversion of glycerol to H<sub>2</sub> and CO followed by equilibrated water-gas shift with the water present in the feed.

The steam reforming of glycerol has been also studied using other Ni-impregnated catalysts. Adhikari et al. [2007c] prepared fourteen catalysts by incipient wetness impregnating on ceramic foam monoliths (92% Al<sub>2</sub>O<sub>3</sub> and 8% SiO<sub>2</sub>), measuring glycerol conversion and selectivity to hydrogen in the 600-900°C range; Ni/Al<sub>2</sub>O<sub>3</sub> and Rh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> reached the best conversion and selectivity, respectively. By increasing water:glycerol molar ratio, both glycerol conversion and hydrogen selectivity increased; at 900°C, 9:1 water:glycerol molar ratio, and 0.15 ml/min feed flow rate, the hydrogen selectivity was 80 and 71% using Ni/Al<sub>2</sub>O<sub>3</sub> and Rh/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, respectively. By increasing metal loading, conversion increased but hydrogen selectivity did not significantly change. Valliyappan et al. [2008] evaluated a commercial Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the range of steam to glycerol weight ratio of 0:100-50:50 to produce either hydrogen or syngas; pure glycerol was completely converted to gas containing 92 mol% syngas at 50:50 steam:glycerol ratio. At 800°C and 25:75 ratio, a maximum 68.4 mol% hydrogen, and syn gas production of 89.5 mol%, were obtained. Iriondo et al. [2008] compared both aqueous phase and steam reforming of glycerol over alumina-supported nickel catalysts modified with Ce, Mg, Zr, and La; different catalyst functionalities were necessary to carry out aqueous-phase and steam reforming of glycerol. For the aqueous phase process, the addition of Ce, La, and Zr to Ni/Al<sub>2</sub>O<sub>3</sub> improved conversion, although all samples showed an important deactivation associated to the oxidation of active metallic Ni during reaction. In the steam reforming process, Ce, La, Mg, and Zr on Ni based catalysts promoted the hydrogen selectivity; differences in activity were explained in terms of enhancement in: surface nickel concentration (Mg), capacity to activate steam (Zr), and stability of nickel phases under reaction conditions (Ce and La). Iriondo et al. [2009] also studied the performance of monometallic (Ni and Pt) and bimetallic (Pt-Ni) catalysts and the effect of lanthana modified alumina support during the glycerol steam reforming; the lanthana addition improved catalytic activity of Ni catalysts, reaching the best selectivity to hydrogen with an intermediate content of lanthana. Buffoni et al. [2009] prepared and characterized nickel catalysts supported on commercial Al<sub>2</sub>O<sub>3</sub> with and without addition of ZrO<sub>2</sub> and CeO<sub>2</sub>, and measured their catalytic behavior during the steam reforming at atmospheric pressure and 450-600°C. Profeti et al. [2009] studied the steam reforming of ethanol and glycerol on Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts modified with noble metals (Pt, Ir, Pd, and Ru); the presence of CeO<sub>2</sub> dispersed on alumina prevented the formation of inactive nickel aluminate. The highest catalytic performance for the glycerol reforming was obtained with Ni-Pt catalyst, producing the highest H<sub>2</sub> yield and low amounts of CO. Sánchez et al. [2010] using a Ni-alumina catalyst for the steam reforming of glycerol at 600-700°C, atmospheric pressure, and 16:1 water:glycerol molar ratio, obtained 96.8% conversion after 4 hours-on-stream at 600°C, and increasing to 99.4% at 700°C. Dou et al. [2009] produced hydrogen by sorption-enhanced steam reforming of glycerol at atmospheric pressure and 400-700°C on a commercial Ni-based catalyst and a dolomite sorbent for the reforming reaction and in situ CO<sub>2</sub> removal, respectively; hydrogen productivity was increased by increasing temperature and methane became negligible above 500°C. The

optimal temperature was 500°C, at which the CO<sub>2</sub> breakthrough time is the longest and the H<sub>2</sub> purity is the highest. Chiodo et al. [2010] investigated features of Rh and Ni supported catalysts in the steam reforming to produce syn-gas to feed a high-temperature fuel cell system; Rh/Al<sub>2</sub>O<sub>3</sub> resulted more active and stable than Ni supported catalysts. Operating conditions during the steam reforming of glycerol affect stability of Ni-supported catalysts, causing deactivation. Carbon deposition on the catalyst surface will result several undesirable reactions and products affecting the purity of the reforming products. Carbon occurrence may arise due to the decomposition of CO or CH<sub>4</sub> or the reaction of CO<sub>2</sub> or CO with H<sub>2</sub> [Adhikari et al., 2007c]; carbon formation is thermodynamically inhibited at temperature higher than 900 K, atmospheric pressure, and 9:1 water:glycerol molar ratio [Adhikari et al., 2007b]. At water:glycerol molar ratios lower than 3:1, the insufficient steam supply favored the methane decomposition forming solid carbon, decreasing the hydrogen production, and also causing catalyst deactivation [Rossi et al., 2009]. By considering thermodynamic analyses of adsorption-enhanced steam reforming of glycerol, Chen et al. [2009] analyzed the effects of reaction parameters on the carbon formation, concluding the use of a CO<sub>2</sub> adsorbent can suppress the carbon-formation reaction and substantially reduce the lower limit of the water:glycerol feed ratio. Slinn et al. [2008] reported a minimal degradation of a platinum-alumina catalyst after several days of continuous operating under the optimum conditions for glycerol reforming, only 0.4% of feed was deposited. Luo et al. [2008] stated the hydrogen production on a supported-Pt catalyst is accompanied by side reactions which form carbonaceous entities on the surface causing catalyst activity drop. Buffoni et al. [2009] prepared and characterized nickel catalysts supported on commercial Al<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> modified by addition of ZrO<sub>2</sub> and CeO<sub>2</sub>, being Ni/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> the most stable system; it was associated to the Ce effect in inhibition of secondary dehydration reactions that form unsaturated hydrocarbons which are coke precursors and generate a fast catalyst deactivation. Profeti et al. [2009] using Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts modified with noble metals (Pt, Ir, Pd, and Ru) explained the presence of them decreased the reduction temperatures of NiO species interacting with the support and stabilized the Ni sites in the reduced state along the reforming reaction, increasing conversion and decreasing coke formation. Finally, Chiodo et al. [2010] stated that independently of metal (Rh and Ni) impregnated and temperature in the steam reforming, reaction is affected by coke formation mainly promoted by the presence of olefins formed by glycerol thermal decomposition. By thermodynamic reasons the hydrogen production should be favored at high temperature, but operating at higher than 923 K promotes the formation of encapsulated carbon which negatively reflects on catalyst stability. Few information and non-systematic analysis of deactivation processes during the hydrogen production from glycerol are available.

### 2.3.3 Results and discussion with Ni-impregnated on alumina

An optimal catalyst should present a good glycerol conversion with high selectivity to hydrogen, maintaining it with time. This section presents the steam reforming of glycerol, using catalysts of Ni impregnated on alumina prepared by the incipient-wetness technique. The starting material was a commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, previously calcined at 550°C, using nickel nitrate hexahydrate as the nickel precursor. Solutions with adequate concentrations were prepared to obtain 2.6, 5.8, and 9.9 wt.% nickel loading on the solid. Samples were identified as Ni(*x*)/Al<sub>2</sub>O<sub>3</sub>, being “*x*” the corresponding nickel loading. Catalysts were characterized by TPR, NH<sub>3</sub>-TPD, XRD, and FTIR. The catalytic behavior during the steam reforming was

measured in a continuous down-flow fixed-bed quartz tubular reactor; catalysts were calcined in-situ, cooled, reduced in a  $H_2$  stream at 300 or 500°C, and finally heated up to the reaction temperature in a  $N_2$  stream. Feed was a glycerol aqueous solution ( $0.17 \text{ ml min}^{-1}$ ), co-feeding a  $N_2$  stream. The catalytic performance was measured at atmospheric pressure, 600-700°C, 3.4-10.0 WHSV,  $20\text{-}60 \text{ ml min}^{-1}$   $N_2$  flow rate, and 16:1-6:1 water:glycerol molar ratio. Reactant and reaction products were analyzed by gas chromatography; gases and non-condensable products were on-line analyzed detecting  $H_2$ , carbon oxides, and methane in a column filled with Molecular Sieve 13X 80/100 mesh (CRS), using either  $N_2$  or helium as carrier and a TCD, while methane and other light products in a GS-Alumina Megabore column. Samples condensed during reaction were off-line analyzed in a DB-20 Megabore column. Hydrogen production and selectivity to carbon oxides and to methane were calculated from TCD data and using a standard sample containing CO,  $CH_4$ ,  $CO_2$ ,  $N_2$ , and  $H_2$ . More details about preparation, characterization, catalytic evaluation, and analysis were previously reported [Sánchez et al., 2010].

TPR results of catalysts with 5 and 15% Ni impregnated on alumina showed three different Ni species: free or superficial NiO (reduction temperature below 400°C), NiO bonded to  $Al_2O_3$  (reduction temperature between 400 and 690°C), and NiO incorporated into the  $Al_2O_3$  framework and forming  $NiAl_2O_4$  (reduction temperature above 700°C) [Rynkowski et al., 1993; Zhu et al., 2008]. The reduction temperature of Ni species varied between 575 and 660°C by calcining between 300 and 550°C [Rynkowski et al., 1993].  $Al_2O_3$  impregnated with 4 wt.% Ni showed low and high proportion of  $NiAl_2O_4$  species after calcining at 400 or 650°C, respectively; this behavior was related to the diffusion of Ni ions into the  $Al_2O_3$  network [Scheffer et al., 1989]. Furthermore, by decreasing the metal loading, the reduction of Ni species needed higher temperature because of a larger metal-support interaction [Brito and Laine, 1993]. This increment in reduction temperature was understood considering a low Ni loading on the support generates a greater proportion of unreduced Ni species which are better stabilized in the  $\gamma\text{-}Al_2O_3$  vacant sites [Uemura et al., 1986]. In the 2.6-9.9% Ni loading range, the main species was NiO, being  $NiAl_2O_4$  only in a low proportion, possibly due to the calcining temperature used, while  $Ni(2.6)/Al_2O_3$  did not display the free or superficial NiO species; the high reduction temperature of Ni species on  $Al_2O_3$  indicates a difficult reduction of them [Sánchez et al., 2010].  $NH_3$ -TPD results with  $Al_2O_3$  showed a broad band with maximum centered around 340-350°C. [Soled et al., 1988]. The strength of acid sites has been classified as weak, medium, and high according to the desorption temperature below 250°C, between 250 and 400°C, and higher than 400°C, respectively [Auroux et al., 2001; Iengo et al., 1998]. Using  $Ni/Al_2O_3$ , the maximum of desorption band was observed at 300°C, and acid sites were mostly considered Lewis acid sites with medium and weak strength [Hardiman, 2007]. By increasing the Ni loading in the 2.6-9.9% range, total acidity increases without significant changes in the acid strength profiles. Similar XRD patterns to  $Al_2O_3$  support and  $Ni/Al_2O_3$  catalysts indicated the presence of the  $\gamma\text{-}Al_2O_3$  phase [Zhu et al., 2008].  $Ni/Al_2O_3$  has a slight increase in intensity respect to the support, verifying the formation of nickel-aluminate spinel type structure ( $NiAl_2O_4$ ) at  $37^\circ$  [Zhu et al., 2008]. However,  $\gamma\text{-}Al_2O_3$  has a pseudo-spinel structure and their structural network parameters are very similar to those of  $NiAl_2O_4$  species [Lo Jacono et al., 1971]. By calcining  $Ni/Al_2O_3$  at 600°C, the pattern displayed large peaks at 37 and  $44.8^\circ$  due to the presence of  $NiAl_2O_4$ , while NiO species (peak at  $43.2^\circ$ ) were observed to a lesser extent [Auroux, et al., 2001]. After calcining at 300°C, peaks at 43 and  $65^\circ$ , corresponding to crystalline NiO, are only visible on materials with loadings higher than 7.3% w/w Ni; smaller Ni loads only



produced the corresponding profile to support, with defined peaks at 37, 45 and 67° [Mattos et al., 2004]. For catalyst prepared with 2.6-9.9% Ni loadings, calcination temperature may hinder the detection of  $\text{NiAl}_2\text{O}_4$  and NiO species by XRD. FTIR spectra corresponding to Ni/ $\text{Al}_2\text{O}_3$  assigned the 3500  $\text{cm}^{-1}$  broad band to the interaction between OH groups and/or chemisorbed water on the support with the alumina free hydroxyls through hydrogen bonding [Stoilova et al., 2002]. The 3780  $\text{cm}^{-1}$  band has been also related to the presence of OH groups [Knözinger and Ratnasamy, 1978]. By comparing  $\gamma\text{-Al}_2\text{O}_3$  and Ni/ $\text{Al}_2\text{O}_3$  in the high-frequency region, the surface metal oxide species reduced the intensity of the main band; it was related to a decrease in the hydration degree of support surface [Kapteijn et al., 1994]. In the low-frequency region, studies using NO adsorption attributed bands near 1800  $\text{cm}^{-1}$  to nitrite species bounded to reduced Ni ions, bands between 1340 and 1460  $\text{cm}^{-1}$  to linearly bounded nitrite groups, and bands between 1620 and 1640  $\text{cm}^{-1}$  at bounded nitrate species [Centi et al., 1995]. However, bands at 1620 and 1470-1480  $\text{cm}^{-1}$  were also previously identified and assigned to the support [Turek et al., 1992]. On catalysts containing 2.6-9.9% Ni loadings, the increase of Ni loading decreases the hydration degree of support surface, while the intensity of the low-frequency band only decreases at the highest Ni loading, possibly related to the large amount of metal Ni species.

Figures 5 and 6 show glycerol conversion and hydrogen yield, respectively, for catalysts with different Ni loadings and reaction conditions. Using Ni(5.8)/ $\text{Al}_2\text{O}_3$ , conversion was larger by increasing reaction temperature from 600 to 700°C; this behavior was more pronounced at 8 h-on-stream. Independent of operating time, in the ranges of WHSV, water:glycerol molar ratios, nitrogen flow rate, Ni loadings, and reduction temperature, conversion was practically complete. The hydrogen yield was referred to the performance at 700°C, 5.1 WHSV, 40  $\text{ml min}^{-1}$   $\text{N}_2$  flow rate, and 16:1 water:glycerol molar ratio. The lower the WHSV or  $\text{N}_2$  flow rate, the higher the hydrogen yield. Hydrogen production improved by decreasing the water:glycerol molar ratio to 6:1 or reducing catalyst at 500°C. Changing the Ni loading, hydrogen yield did not significantly modify. Ni/ $\text{Al}_2\text{O}_3$  having 2.6, 5.8, and 9.9% Ni loadings showed high both conversion and hydrogen yield, being temperature the reaction parameter with the most important effect over the catalytic performance. Evaluating Rh, Pt, Pd, Ir, Ru, Ni, Ce, Rh/ $\text{CeO}_2$ , Pt/ $\text{CeO}_2$ , Pd/ $\text{CeO}_2$ , Ir/ $\text{CeO}_2$ , Ru/ $\text{CeO}_2$ , Ni/ $\text{CeO}_2$  impregnated on a mixed  $\text{Al}_2\text{O}_3\text{-SiO}_2$  support, Ni reached the best catalytic performance with 94% glycerol conversion and 80% selectivity to hydrogen at 900°C, feeding 0.15  $\text{ml min}^{-1}$  and 9:1 water:glycerol molar ratio [Adhikari et al., 2007c]. By thermodynamic data, optimum conditions for hydrogen production were temperatures between 650 and 700°C, water:glycerin ratios of 9-12, and atmospheric pressure [Wang et al., 2008]. Using a commercial Ni/ $\text{Al}_2\text{O}_3$  catalyst, maximum hydrogen production was obtained at 800°C [Valliyappan et al., 2008]. Then, the good stability observed can be explained considering the catalytic conditions employed, mainly the high water:glycerol molar ratio which improves stability. Neither glycerol conversion nor hydrogen production can be directly related to the Ni loading; there is a minimum loading above which addition of Ni does not improve the catalytic behavior. It agrees with previous results of steam reforming of glycerol on Ru/ $\text{Y}_2\text{O}_3$ , which reported an optimal loading of 3% Ru [Hirai et al., 2005]; the increase in metal loading on Ni/ $\text{Al}_2\text{O}_3$  and Rh/ $\text{CeO}_2/\text{Al}_2\text{O}_3$  increased conversion while hydrogen selectivity remained relatively unaffected, reaching the best performance with 3.5 wt% loading [Adhikari et al., 2007c]. Seeking to determine the active site, Ni(9.9)/ $\text{Al}_2\text{O}_3$  has a significantly larger amount of NiO-bonded to  $\text{Al}_2\text{O}_3$  sites than on Ni(5.8)/ $\text{Al}_2\text{O}_3$ , displaying both materials similar catalytic behavior; then, that higher proportion does not

increase conversion and/or hydrogen yield. Furthermore, Ni(2.8)/Al<sub>2</sub>O<sub>3</sub> was an active material and it did not present the free or superficial NiO sites; then, these sites are not required for the glycerol reforming reaction.

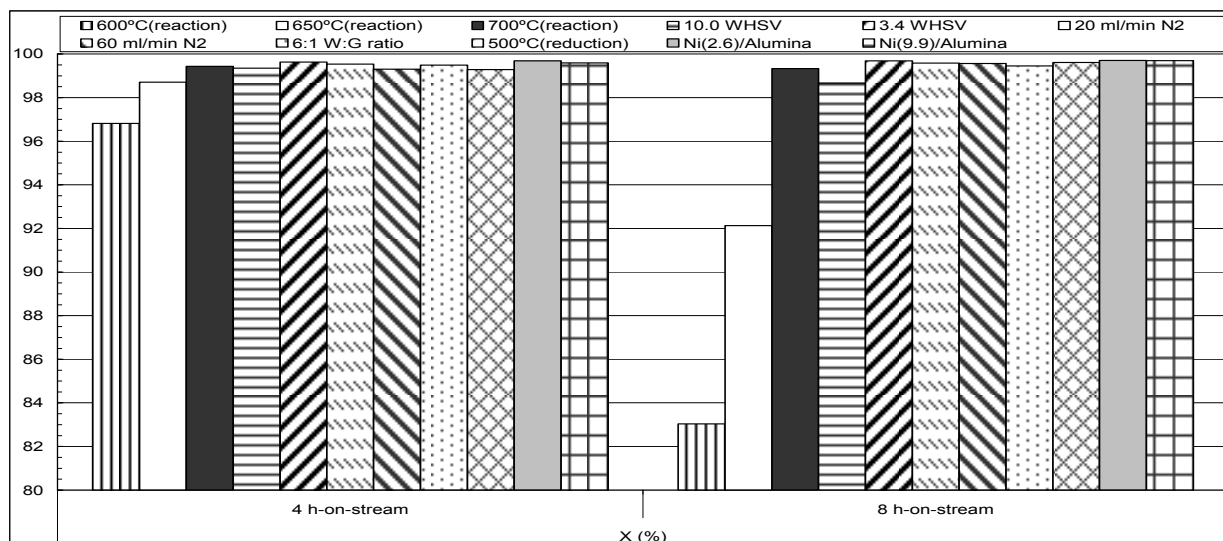


Fig. 5. Glycerol conversion (X) during the steam reforming of glycerol on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts under different pretreatment and operating conditions, at two times. *Unmodified reaction conditions: atmospheric pressure, and 0.17 ml min<sup>-1</sup> glycerol aqueous solution flow rate.*

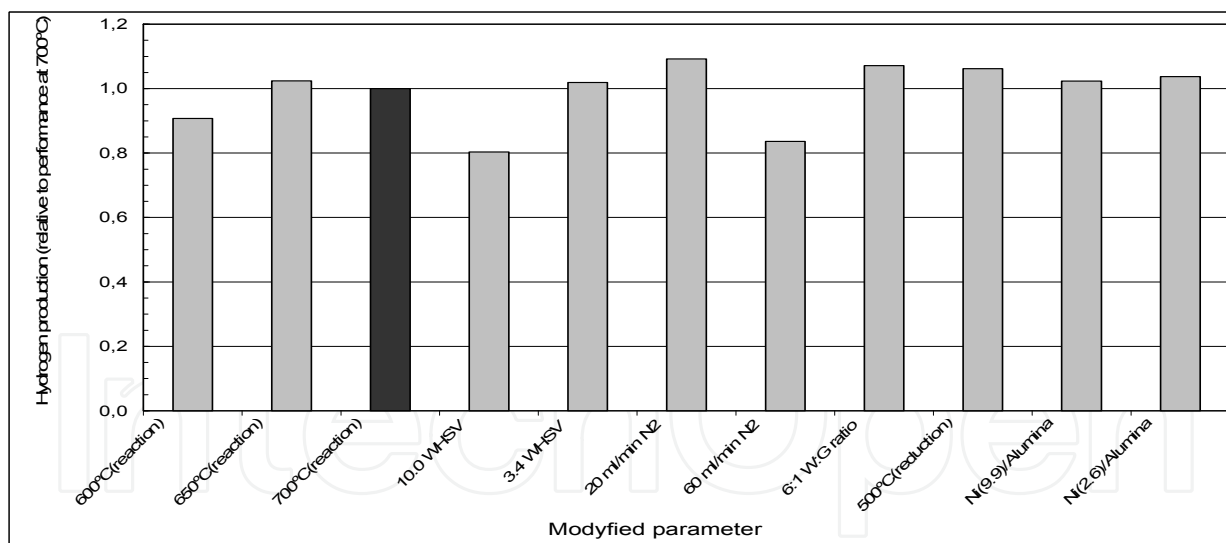


Fig. 6. Hydrogen yield (Y) during the steam reforming of glycerol on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts under the pretreatment and operating conditions detailed in Fig.5. *Unmodified reaction conditions: atmospheric pressure, 0.17 ml min<sup>-1</sup> glycerol aqueous solution flow rate, and 4 hours-on-stream.*

Figure 7 shows by-product distribution in the non-condensed and gaseous stream detected by FID after 4 hours-on-stream for different catalysts and conditions. The main by-product was methane, followed by ethene, ethane, propene, isobutane, propane, and other ones in small proportions. Methane decreased by increasing WHSV, decreasing the water:glycerol

molar ratio to 6:1 or increasing the Ni loading to 9.9%; the effect is more pronounced at 8 h. Distribution pattern only changed at  $10.0 \text{ h}^{-1}$ , being ethene the main by-product (47.1% at 4 h and 55.8% at 8 h) followed by methane (37.1% at 4 h and 27.2% at 8 h). This behavior could be associated with catalyst deactivation by carbonaceous deposit formation. Previous results reported Ni impregnated catalysts undergo a rapid deactivation [Wen et al., 2008]. Figure 8 displays the composition of non-condensed and gaseous stream analyzed on-line by TCD, as a function of time, during the steam reforming on Ni(5.8)/Al<sub>2</sub>O<sub>3</sub> at 700°C, atmospheric pressure, 5.1 WHSV, 40 ml min<sup>-1</sup> nitrogen flow, 16:1 water:glycerol molar ratio, and 0.17 ml min<sup>-1</sup> glycerol aqueous solution flow rate. Products were hydrogen, carbon monoxide, and methane, varying their proportion along 1-6 operating cycles; a similar qualitative behavior was observed during each cycle: hydrogen decreasing whereas carbon monoxide and methane increased. The starting level of each cycle depends on the regenerating conditions. Hydrogen was higher than 60 mol% in all time range, reaching 93.8% as the highest value; carbon monoxide varied between 3.6 and 26.7%, and methane between 2.6 and 12.4%. Both carbon monoxide formation and methanation reactions can be controlled by selecting adequate pretreatment and operating conditions. Undesirable side reactions such as dimerization-oligomerization, thermal decomposition, cracking, disproportion, and hydrogen transfer promote carbon deposition which leading to blockage of catalyst pores with the corresponding loss of activity [Slinn et al., 2008]. At temperature higher than 720 K, glycerol is subjected to pyrolysis phenomena and it drastically decomposes before to reach the catalyst surface; olefins formed by that glycerol thermal decomposition promotes coke formation affecting the steam reforming process [Chiodo et al., 2010]. The highest stability of Ni/CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> has been related to a Ce effect which suppresses secondary dehydration reactions forming unsaturated hydrocarbons that are coke precursors generating fast catalyst deactivation [Buffoni et al., 2009]. By the same catalytic system, the addition of noble metal (Pt, Ir, Pd, and Ru) stabilized the Ni sites in the reduced state along the reforming reaction, increasing glycerol conversion and decreasing the coke formation [Profeti et al., 2009]. Small amounts of ethene and propene were detected between the reaction products (see Fig. 7); then, it could be associated to deactivation process.

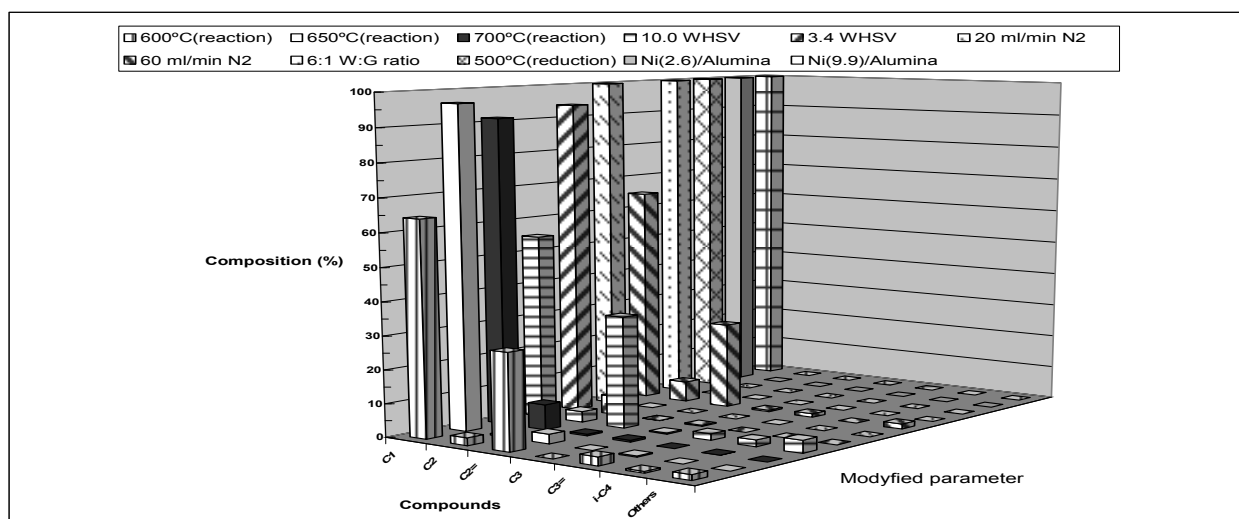


Fig. 7. By-product distribution corresponding to the gaseous fraction during the steam reforming of glycerol on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts under the pretreatment and operating conditions detailed in Fig. 5. *Unmodified reaction conditions: atmospheric pressure, 0.17 ml min<sup>-1</sup> glycerol aqueous solution flow rate, and 4 hours-on-stream.*

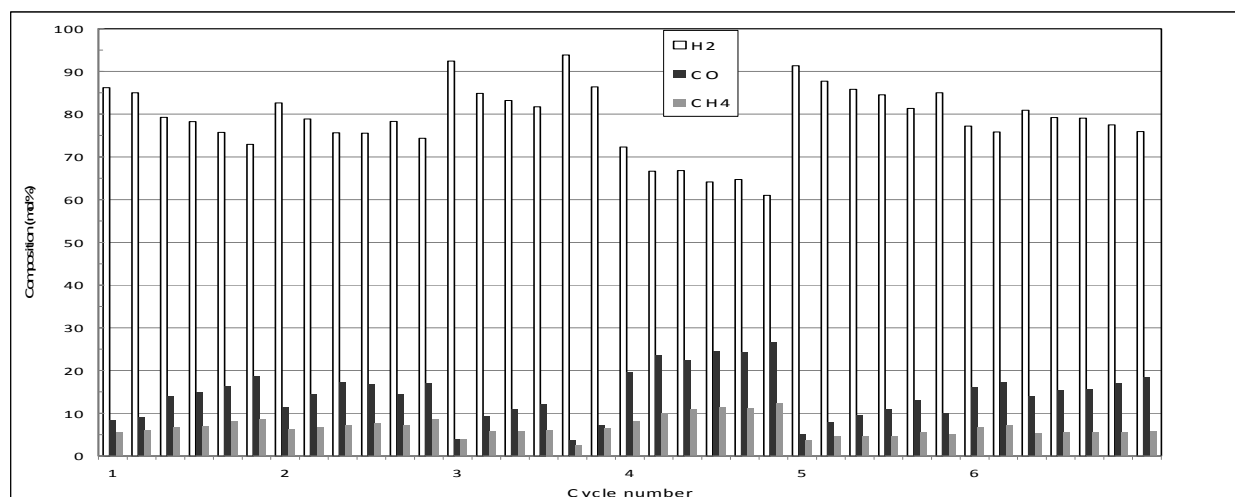


Fig. 8. Composition of the non-condensed and gaseous stream during the steam reforming of glycerol on Ni(5.8)/Al<sub>2</sub>O<sub>3</sub> catalyst as a function of the time-on-stream for several cycles of reaction-regeneration. Reaction conditions: 700°C, atmospheric pressure, 5.1 WHSV, 40 ml min<sup>-1</sup> nitrogen flow, 16:1 water:glycerol molar ratio, and 0.17 ml min<sup>-1</sup> glycerol aqueous solution flow rate.

### 3. Conclusion

The production of biodiesel generates glycerol as by-product. The conversion of glycerol in added-value compounds has benefits because it comes from renewable raw materials, enabling a sustainable environmental development, and also allows improve the economics of biodiesel process. Glycerol is intermediate in the synthesis of some compounds used in industry, such as propyleneglycol, 1,3-propanediol, and ethyleneglycol by hydrogenolysis; acetol and acrolein by dehydration; dihydroxyacetone, glyceric acid, and hydroxyacetic acid by oxidation; glycidol by epoxidation; glycerol carbonate by transesterification; mono- and diglycerides by selective etherification; polyglycerol by polymerization; and bio-hydrogen by steam reforming, partial oxidation, autothermal reforming, aqueous-phase reforming, and supercritical water reforming. All these uses allow considering glycerol as an important key-compound in the environment of future biorefinery. By considering the hydrogenolysis of glycerol, the production of propyleneglycol was reported on several supported catalysts, resulting attractive the improvement in selectivity by using zeolites as base materials, while the production of 1,3-propanediol took place on Pt/WO<sub>3</sub>/ZrO<sub>2</sub>, being important a complete study of the effect of preparation technique of this material over its catalytic performance; moreover, a comparison between both liquid and gaseous phase hydrogenolysis is needed. The selective oxidation of glycerol to dihydroxyacetone has been reached on a monometallic catalyst, Pt impregnated on potassium ferrierite, reaching both conversion and selectivity similar to the ones obtained with active bimetallic materials; the pH of reaction medium played an important role over the selectivity, while the structure of zeolite favored the DHA formation. Finally, the steam reforming of glycerol to produce hydrogen was conducted on Ni impregnated on alumina catalysts, which presented Ni species on the surface difficult to reduce and mainly as NiO, reaching high conversions and selectivity for conditions studied and being carbon monoxide the main by-product followed by methane; catalyst deactivation took place during reaction but regenerating is possible restoring the catalytic performance.



#### 4. Acknowledgment

The author acknowledges the financial support of U.N.L. and CONICET. Finally, the author is also acknowledged to InTech by the possibility to edit this chapter.

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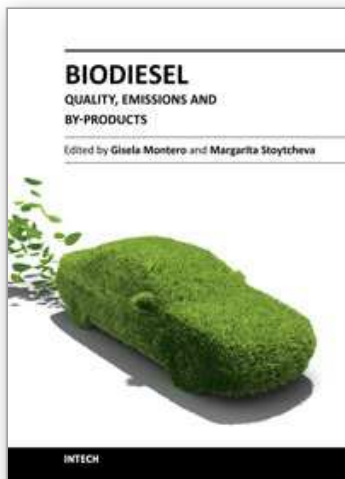
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## **Biodiesel- Quality, Emissions and By-Products**

Edited by Dr. Gisela Montero

ISBN 978-953-307-784-0

Hard cover, 380 pages

**Publisher** InTech

**Published online** 16, November, 2011

**Published in print edition** November, 2011

This book entitled "Biodiesel: Quality, Emissions and By-products" covers topics related to biodiesel quality, performance of combustion engines that use biodiesel and the emissions they generate. New routes to determinate biodiesel properties are proposed and the process how the raw material source, impurities and production practices can affect the quality of the biodiesel is analyzed. In relation to the utilization of biofuel, the performance of combustion engines fuelled by biodiesel and biodiesels blends are evaluated. The applications of glycerol, a byproduct of the biodiesel production process as a feedstock for biotechnological processes, and a key compound of the biorefinery of the future is also emphasized.

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Raúl A. Comelli (2011). Glycerol, the Co-Product of Biodiesel: One Key for the Future Bio-Refinery, Biodiesel- Quality, Emissions and By-Products, Dr. Gisela Montero (Ed.), ISBN: 978-953-307-784-0, InTech, Available from: <http://www.intechopen.com/books/biodiesel-quality-emissions-and-by-products/glycerol-the-co-product-of-biodiesel-one-key-for-the-future-bio-refinery>

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