

## Influence of glycerol purity on its liquid phase oxidation over Au/TiO<sub>2</sub>

E. Skrzyńska,<sup>a)</sup> M. Capron,<sup>b, c)</sup> F. Dumeignil<sup>b, c, d)</sup>\*

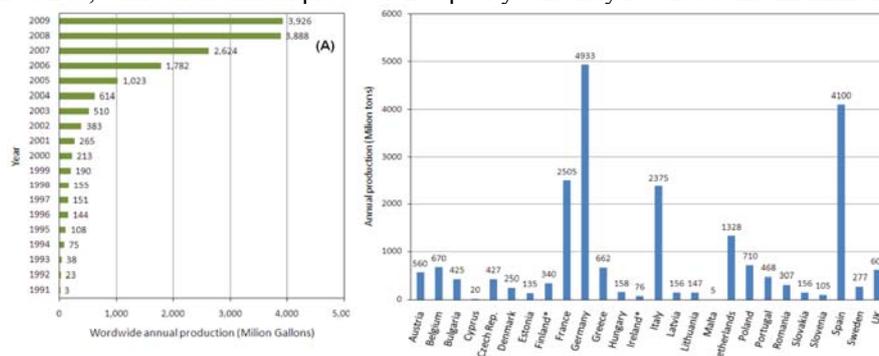
<sup>a)</sup>Cracow University of Technology, ul. Warszawska 24, 31-155 Kraków, Poland; <sup>b)</sup>CNRS UMR8181, Unité de Catalyse et Chimie du Solide, UCCS, F-59655 Villeneuve d'Ascq, France. <sup>c)</sup>Univ. Lille Nord de France, F-59000, Lille, France;

<sup>d)</sup>Institut Universitaire de France, Maison des Universités, 10 Boulevard Saint-Michel, 75005 Paris, France

\*Corresponding Author, e-mail: [franck.dumeignil@univ-lille1.fr](mailto:franck.dumeignil@univ-lille1.fr), telephone: +33(0)320434538

### Introduction

The European Union directives 2003/30/EC and 2003/96/EC promote the use of fuels from renewable sources for transport. In 2010, the mandatory share of them in the market was about 5.75 %, while by the end of 2013 it should rise up to 7.1 %. Except bio-alcohols, the most important liquid biofuel is biodiesel, also known as FAME (fatty acid methyl esters) or FAEE (fatty acid ethyl esters). It is a complex mixture of fatty acid esters, mostly obtained by vegetable oils transesterification or waste oils two steps esterification/transesterification process [1]. Also, some kinds of algae can be used as an oil source, but despite a huge worldwide interest, this has not yet yielded to commercialization. From the statistics published by EPI (Earth Policy Institute), the annually worldwide production of biodiesel in 2009 reached almost 3900 million gallons [2] and shows dynamic progress (Fig.1A). It is worth to underline that, from many years, the European Union is incontestably the global leader in biodiesel production [3]. In July 2010, the number of existing biodiesel facilities in Europe was as high as 245, while their annual production capacity currently reaches some 22 million tons (Fig.1B) [4].



**Figure 1:** Changes of worldwide annual production of biodiesel (A) and annual production capacity in Europe [3, 4].

Taking into account, that about 10 kg of crude glycerol fraction is by-produced for every 100 kg of fuel, we can imagine how a huge amount of this component is generated annually. Although pure glycerol has a lot of applications (food, cosmetics, pharmaceuticals...), the usage of low-quality glycerol from biodiesel production in most of these sectors is avoided. Thus, an advantageous outlet for this overproduction would be to use it as a feedstock for the production of more valuable compounds. Among all the solutions proposed in the literature [1,5], one of the most interesting ways for glycerol valorization is its oxidation in the liquid phase. This reaction leads to compounds such as: dihydroxyacetone (DHA), glyceraldehyde (GLYHYDE), glyceric acid (GLYA), glycolic acid (GLYCA), hydroxypyruvic acid (HPYA), mesoxalic acid (MOXALA), oxalic acid (OXALA) and tartronic acid (TARAC). It should be underlined that most of the aforementioned products have wide applications and are useful intermediates for the synthesis of fine chemicals. Moreover, their market price is about 100-1000 times larger than that of pure glycerol. For example, the price of technical grade glycerol is about 3.5 EUR/kg and crude glycerol issued from biodiesel production is about 0.5 €/kg; on the other hand, the price for 1 kg of OXALA, DHA and GLYCA is about 57, 274 and 400 € respectively, and derivatives such as GLYHYDE and TARAC costs from 31 to 108 € per 1 g, while the price of 1 g of HPYA is up to 14.000 € (prices of commercial products from Sigma-Aldrich). Such extremely high prices are mainly caused by current production methods, including low-yield enzymatic or not-ecological homogenous catalytic processes.

From this point of view, using a mild liquid oxidation process with air as an oxidant on recyclable catalysts should lower the overall production costs and bring benefits to the environment. The big challenge associated with these catalytic oxidation reactions is to control and orientate the reaction pathway to the desired products, as well as to avoid a strong deactivation of catalysts, which is a cause of serious concern for process development.

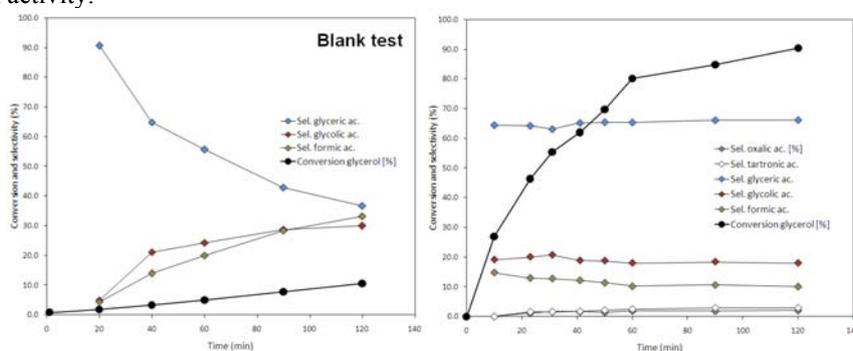
### Experimental

The experiments were carried out in a 300 mL semi-batch stainless steel reactor equipped with a gas-induced turbine, 4 baffles, a thermocouple, a thermo-regulated oxygen supply system and pH electrode. In every experiment the glycerol/water mixture (200 mL) was heated to desired temperature, than the system was pressurized under continuous stirring (1500 rpm) and the reaction began when the catalyst with calculated amount of sodium hydroxide was flushed into the reactor. The temperature, pH and O<sub>2</sub> pressure were monitored continuously, while the reaction mixture was periodically sampled and analyzed with Agilent 1200 HPLC equipped with Rezex ROA-Organic Acid H<sup>+</sup> column (300 × 7.8 mm) and reflective index detector (RID). The solution of H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>CN in deionized water was used as

the eluent with a flow of 0.48 ml/min. Before the analysis the samples were diluted and acidified with the mobile phase, whereas the identification and quantification of the obtained products was done by comparison with calibration curves. A commercial 1 wt% Au/TiO<sub>2</sub> (WGC) with  $S_{BET} = 45.85 \text{ m}^2/\text{g}$  and  $0.35 \text{ cm}^3/\text{g}$  of pore volume was used as a catalyst.

## Results and Discussion

The great influence of some reaction parameters on the glycerol conversion and selectivity to desired products is a commonly known fact and many research papers in the field can be found in the literature: For gold supported catalysts, most of the experiments are carried out using NaOH/glycerol molar ratio from 1 to 4, the temperature being selected between 40 and 90 °C in slightly pressurized oxygen (up to 10 bars) [5]. Similar conditions were chosen for our experiments and, as it can be seen, in figure 2, the gold supported onto titanium oxide shows very high activity in the process, as the glycerol conversion reaches 90 % after 2 h of experiment. The main reaction product is glyceric acid with almost a constant selectivity of 65 %, while the glycolic and formic acids are minor components with selectivity up to 20 and 14 %, respectively. Comparable results can be found in the literature. However, all the experimental data refer to high grade purity glycerol used as a source. There is an absolute lack of data in the case of using glycerol from real biodiesel production, and also no result in the absence of a catalyst can be found. As it can be seen in figure 2, high amount of base in the reaction medium (using stainless steel reactor) induces small conversion of glycerol to the aforementioned three main products. So, the influence of impurities present in technical or crude glycerol fraction should also be investigated. Another aspect, important from the industrial point of view, is reusing the catalyst without considerable loss in activity.



**Figure 2:** Comparison of conversion and selectivity for glycerol oxidation without and with Au/TiO<sub>2</sub> catalyst. Reaction conditions: 60 °C, 5 bar, NaOH/glycerol = 4 (molar ratio), glycerol/Au = 3500 (molar ratio), highly pure glycerol.

Thus, in this work we will compare the results of pure glycerol (Sigma-Aldrich) oxidation in the liquid phase using commercial Au/TiO<sub>2</sub> catalyst (figure 2) with the results of processes using technical grade glycerol from one of the biggest Polish biodiesel producer (Trzebinia S.A.) and crude glycerol fraction obtained by classical two-step transesterification of rapeseed oil.

## Conclusions

It is well known fact, that the right choice of the reaction conditions, particularly the pH, type of active metal used in the catalyst, and even the type of reactor determines the process selectivity [5]. Despite a high interest of the scientific community in this reaction, there is a lack of data using low purity glycerol as a starting material. In this work, the results of oxidation process using pure glycerol are completed with the experiments using technical grade glycerol and crude fraction from biodiesel production. Also, the possibility of reusing the catalysts is investigated, as these aspects are crucial if one wants to meet industrial expectations.

## Acknowledgements

The authors would like to thank the CE for financial support through the contract number MIRG-CT-2007-046383 and European Union through the European Social Fund within „Cracow University of Technology development program - top quality teaching for the prospective Polish engineers; University of the 21st century” project (contract no.UDA-POKL.04.01.01-00-029/10-00).

## References

1. M. Pagliaro and M. Rossi, *The Future of Glycerol*, 2nd edn (RSC Green Chemistry Book Series), 2010.
2. Statistics published by EPI, available at website: [www.earth-policy.org/datacenter/xls/book\\_pb4\\_ch4-5\\_34.xls](http://www.earth-policy.org/datacenter/xls/book_pb4_ch4-5_34.xls)
3. Carriquiry M., *Iowa Ag Review*, 13:2 (Spring 2007) 8-9, [http://www.card.iastate.edu/iowa\\_ag\\_review/spring\\_07/IAR.pdf](http://www.card.iastate.edu/iowa_ag_review/spring_07/IAR.pdf)
4. Annual statistics published by European Biodiesel Board, available at website: [http://www.ebb-eu.org/EBBpressreleases/EBB%20press%20release%202009%20prod%202010\\_capacity%20FINAL.pdf](http://www.ebb-eu.org/EBBpressreleases/EBB%20press%20release%202009%20prod%202010_capacity%20FINAL.pdf)
5. B. Katryniok, H. Kimura, E. Skrzyńska, J-S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul and F. Dumeignil, *Green Chem.*, DOI:10.1039/C1GC15320J

