



Crude glycerol as a raw material for the liquid phase oxidation reaction



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ABSTRACT

In the present work, crude and partially purified glycerol fractions received from large biodiesel production plant were used as a raw material in the catalytic partial oxidation process. Before using, each fraction was carefully characterized in order to identify and quantify the major contaminants. Depending on the purification degree, the weight concentration of glycerol in the different fractions varied from 40.3% to 98.2%, the methanol content did not exceed 29.1%, mineral salts (determined as ash) varied from 0.03% to 6.6%, while the residual organic matter (non-glycerol and non-methanol, named here MONG-NM) was between 0.7% and 22.1%. The reaction of glycerol oxidation was carried out in the liquid phase over a commercial 1 wt.% Pt/Al₂O₃ catalyst. The effect of each identified impurity type was independently studied, both in the presence and absence of base in the reaction mixture. The results indicated that MONG-NM is the most problematic compound, as it strongly hinders the reaction. As the post-reaction analysis of spent catalyst (Elemental Analysis and XPS) showed practically negligible leaching of platinum and lack of important changes in its oxidation state, the most probable explanation for observed decrease in glycerol conversion is blocking of glycerol access to the catalyst active sites by adsorbed heavy-weight components of MONG-NM. An attempt of regeneration and reusing of spent catalyst proved that such poisoning can be reversed by simple washing of catalyst with organic solvent able to dissolve hydrophobic fatty acid derivatives. The mineral salts also have a detrimental effect on the glycerol oxidation process, but much tinier than that of MONG-NM. In contrast, the presence of methanol in the feed promoted the process reactivity, which was attributed to improved oxygen solubility in the methanol–water solutions (at least in the analysed range of methanol concentrations ≤ 5 wt.%).

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1. Introduction

From many years, the European Union is strongly promoting the production and use of biofuels by the Member States and developing countries. According to the Renewable Energy Directive 2009/28/EC [1], 20% share of renewable energy sources in final energy consumption is required by 2020, including a target

of 10% of energy content (calorific value) for liquid biofuels in transport. Consequently, the annual production of biodiesel in Europe in 2011 was about 9 million tons, with an estimated capacity close to 24 million tons [2]. Taking into account that such production generates simultaneously 10 wt.% of crude glycerol (the so-called 'glycerine pitch' or 'glycerol glut') [3–5], it can be easily estimated that almost 1 million tons of crude glycerol are produced each year in Europe together with another 1 million tons in the rest of the World [6]. Such an important production has environmental and economic implications on both biodiesel production and on the global glycerol market. All these elements, constitute a driving force for intensive investigations on possible glycerol valorization routes. This trend is perfectly reflected by the growing number of scientific papers annually published in the field (in 2013 it was almost 5000 scientific publications, what was the double of

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number recorded in 2003 [7]). On the other hand, there is an evident lack of scientific studies using real crude fractions directly issued from biodiesel production units (10% of all publications in 2013 [7]). The majority of papers concerns application of crude glycerol for direct, non-chemical purposes [8–14], and in biotechnology, where it can be used as a nutrient medium [8,15–18] or raw material subjected to microbial fermentation, enzymatic processes or anaerobic digestion [6,8,19–30]. These works are quite successful and relatively well documented, but their industrial use does not represent a volume that could absorb the glut of glycerine produced by biodiesel units. In contrast, while potentially feeding the market with new applications, the transformation of crude glycerol by chemical routes is still an area that needs an extensive investigation effort. The main difficulty of such technologies is that the impurities present in glycerine might most probably directly influence the reaction route (by competition with glycerol or poison the active sites of the catalysts. However, no systematic study in this field can be found in the literature. Usually, no data [31,32] or only minimum of information about crude glycerol composition can be found in the majority of the papers concerning chemical transformation of crude glycerol to value-added chemicals [33–38]. However, sometimes partially purified glycerol fractions are used in the investigations (glycerol concentration above 80–90 wt.%) [39–42]. As a matter of fact, the articles, where the effect of the possible impurities (mainly the effect of mineral salts or methanol) on the process efficiency is investigated, are very rare [43–46], while the literature dealing with low quality crude glycerol used as a raw material for the liquid phase partial oxidation is extremely scarce.

From our best knowledge, only two papers [38,42] discuss about the use of crude glycerol as a raw material for the liquid phase partial oxidation, while this reaction, if well controlled, can yield products with prices from 20 to 4000 higher than that of pure, anhydrous, glycerol (Fig. 1). Thus, using a crude glycerol fraction from biodiesel production, with minimal market value, can make such an oxidation process even more profitable.

The first of the two aforementioned papers, by Kondamudi et al. [38], describes crude glycerol catalytic photo oxidation over a titanium disilicide catalyst (TiSi_2) at 65 °C under atmospheric pressure using a 300 W solar simulator as a light source. The authors obtained almost 64% of conversion after 6 h (and even 97.6% after 12 h) with 100% selectivity to glyceric acid. However, no information was given on the composition of the used crude material (except about its high basicity, with a pH = 11–14). In the second paper, by Gil et al. [42], partially purified crude glycerol samples (minimum purity 95.5%, 96.4% and 97.1%) were oxidized at 60 °C under 5 bar of O_2 over carbonaceous materials-supported gold catalysts, using a 0.3 M glycerol solution and molar ratios of NaOH/glycerol and glycerol/Au of 2 and 3500, respectively. The conversion over the most active catalyst was below 50% after 10 h with two glycerol samples (“crude” and “evaporated” samples with purities of 95.5% and 96.4%, respectively), while using a neutralized fraction (97.1% purity) gave results comparable to those obtained with commercial anhydrous glycerol.

So far, no systematic investigation of the impurities effect on the glycerol conversion and catalysts activity was published in literature. From that reason, the selection of the catalyst for current study was made on the basis of general data on pure glycerol oxidation process and results of preliminary tests. Most of the catalysts commonly used in this process were reviewed in our previous article [47], indicating the metal particle size diameter (preferably below 10 nm with optimum value about 6 nm for Pt-based materials [48]), type of the support (usually various carbons [48–53]) and initial pH of the mixture as the most important parameters, together with evident role of the reaction temperature, governing the catalysts activity and selectivity. It is generally admitted that the glycerol oxidation occurs in acidic or basic pH conditions when

using platinum or palladium, while the activity of gold is almost exclusively limited to basic media [47]. From one side, an operating at low initial pH results in the important decrease of the reaction rates: from 110 $\text{mol h}^{-1} \text{mol}^{-1}$ at pH 11 to 40 $\text{mol h}^{-1} \text{mol}^{-1}$ at pH 6 according to work of Gallezot et al. [50] using 1%Pt/C catalysts, and from 375 to 107 $\text{mmol h}^{-1} \text{mmol}^{-1}$ by changing initial pH from 7 to 2 over 5%Pt/C according to work of Garcia et al. [53]. From the second side, an increase in initial pH from a slightly acidic or neutral one to a basic one results in a change in the glycerol oxidation pathway and leads to different products [47,53,54]. As it is shown on simplified Scheme 1 (based on the literature and our own experiences), glyceraldehyde and dihydroxyacetone are mainly formed in the absence of a base in the reaction mixture, and at higher pH they are easily subsequently transformed to various derivatives via Cannizzaro reaction and C–C bond cleavage [55]. At a high pH, depending on the initial base to glycerol molar ratio, glycerol is mainly oxidized to $\text{C}_{\leq 3}$ carboxylic acids, remaining in the non-acidified reaction mixture as salts, i.e., sodium or potassium glycerate, tartronate, glycolate, oxalate and formate. Of course this scheme does not include the possible mechanism routes mentioned in the literature, however such schemes are characterized by very high complexity and are presented elsewhere [47,55].

Generally, there is lack of literature information about the behaviour of potential crude glycerol impurities at various pH. In order to feel this gap we decided to compare the results at both variants of the oxidation process, i.e., in the presence and absence of base in the reaction mixture. Thus, in this work, we selected an alumina-supported platinum catalyst for testing with crude glycerol fractions, as this system enabled obtaining the highest conversion rates (from preliminary studies with pure glycerol) both in the presence and the absence of base in the reaction mixture. Consequently, we determined the composition of several crude glycerol samples with different grades of purification, and tested them in the liquid phase oxidation process. Moreover, in order to decouple the effect of each impurity, the results of oxidation of pure glycerol solutions contaminated on purpose with methanol, mineral salt and mixture of fatty acid derivatives are presented.

2. Experimental

2.1. Catalysts

Commercial 1 wt.% Pt/ Al_2O_3 purchased from Aldrich (batch MKBG9524) was crushed in a mortar to obtain powder, which was further sieved to get a 50–125 μm fraction before using without any additional pre-treatment.

The catalysts spent after selected glycerol oxidation tests, were recovered by filtration, washed with 200 cm^3 of distilled water and dried 24 h at 105 °C prior to the analysis and reusing.

Regeneration of the catalysts recuperated after oxidation of glycerol contaminated with MONG-NM was performed by a simple washing with 50 cm^3 of ethyl ether (Aldrich) followed by a rinsing with 200 cm^3 of distilled water. The solids were then dried 24 h at 105 °C prior reusing.

2.2. Catalyst characterization

The specific surface area (BET method) and pores distribution (BJH method) were measured by the nitrogen adsorption technique using TriStar II 3020 apparatus from Micromeritics.

XRD spectroscopy was performed at ambient temperature with D8 Advanced apparatus from Bruker AXS instrument. The diffractogram was compared with the JCPDS reference cards: 00-010-045 for gamma-alumina and 00-001-1311 for Pt (metal).

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