



# Effect of biodiesel-derived impurities (acetic acid, methanol and potassium hydroxide) on the aqueous phase reforming of glycerol



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## HIGHLIGHTS

- Full analysis of individual/binary/ternary CH<sub>3</sub>OH–CH<sub>3</sub>COOH–KOH mixtures on glycerol APR.
- The pH and the K<sup>+</sup>/H<sup>+</sup> and K<sup>+</sup>/OH<sup>-</sup> ratios of the solution influence glycerol APR.
- Acidic conditions promote Ni and La leaching, causing catalyst deactivation.
- KOH promotes H<sub>2</sub> production from glycerol via base-catalysed reactions.
- Optimum for glycerol APR: low amounts of CH<sub>3</sub>OH & CH<sub>3</sub>COOH and a high amount of KOH.

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## ABSTRACT

This work analyses the influence of three biodiesel-derived impurities (CH<sub>3</sub>OH, CH<sub>3</sub>COOH and KOH) on the aqueous phase reforming of glycerol at 220 °C and 44 bar using a Ni–La/Al<sub>2</sub>O<sub>3</sub> catalyst. The experiments were planned according to a factorial 2<sup>k</sup> design and analysed by means of an analysis of variance (ANOVA) test to identify the effect of each impurity and all possible binary and ternary combinations. The presence of CH<sub>3</sub>OH decreased the glycerol conversion, while CH<sub>3</sub>COOH and KOH decreased and increased the gas production, respectively. Catalyst deactivation took place under acidic conditions due to the loss of part of the active phase of the catalyst through leaching. The gas phase was made up of H<sub>2</sub>, CO<sub>2</sub>, CO and CH<sub>4</sub>. KOH exerted the greatest influence on the gas composition, increasing H<sub>2</sub> production due to the greater gas production and the lower H<sub>2</sub> consumption in the hydrogenation reactions. The liquid phase was made up of aldehydes, monohydric and polyhydric alcohols, C3 and C4 ketones and esters. CH<sub>3</sub>OH increased the proportion of monohydric alcohols, while CH<sub>3</sub>COOH promoted dehydration reactions, leading to an increase in the relative amount of C3-ketones.

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## 1. Introduction

Renewable biomass sources are currently of considerable interest because they provide an interesting route for the production of chemicals and energy [1,2]. Among the various biomass feedstocks, glycerol is an attractive resource due to its widespread availability as a by-product formed in biodiesel production (1 kg of crude glycerol is yielded with the production of 10 kg of biodiesel). Glycerol obtained in biodiesel manufacturing has become a cheap resource for which new valorisation routes need to be developed. In addition, the recent rapid growth of the biodiesel industry could create a surplus of glycerol unable to be absorbed by its current market, which may cause economic and environmental problems. This would hamper the development of the biodiesel industry [3].

A promising strategy for the valorisation of this biodiesel-derived glycerol is aqueous phase reforming (APR). APR is a catalytic process carried out at quite low temperatures and moderate pressures, producing different chemicals (gases and liquids) from an organic feedstock. The gas phase consists of a gas with a high H<sub>2</sub> content while the liquid phase is a complex mixture of different organic compounds such as alcohols, ketones, acids, esters, paraffins, aldehydes and other oxygenated compounds in water. The yields and compositions of the gas and liquid phases depend on the operating conditions of the process, the catalyst type and the nature of the feed [4–7].

Works dealing with the aqueous phase reforming of crude glycerol are extremely scarce [4,7–9] and the vast majority of the publications in the literature are focused on understanding the effect of the catalyst type and the operating conditions during the APR of pure glycerol. The catalysts used in the process are noble metals based on Pt [9–14], Ni [9,10,14–18], Pt–Ni, Cu, Co or Ru

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[7,10,14,16,19] supported on different oxides such as  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{SiO}_2$ ,  $\text{CeO}_2$ , or carbon [4,20] and modified, in some cases, with promoters such as La, Ce, Mg and Zr. The influence of the operating variables (temperature, pressure, glycerol concentration, flow rate, catalyst loading and hourly space velocity) on the process has been studied using reagent grade glycerol in both batch and flow reactors [12,17,19,21,22].

The studies reported to date provide valuable information on the APR process for pure glycerol, but the impurities accompanying the crude glycerol obtained from the biodiesel industry are expected to significantly reduce the yield and efficiencies of the APR process and to deactivate the catalysts. Crude glycerol consists not only of glycerol but also of many other chemicals such as methanol, soap, catalyst, salts and non-glycerol organic matter [3]. Therefore, it is very important to understand how the presence of the most common biodiesel-derived impurities affects the process for the development of this valorisation route.

The comparisons between the results obtained with crude and reagent grade glycerol when subjected to the same valorisation process have shown that the efficiencies of the processes depend on the glycerol used. These results have been compared for valorisation processes including steam reforming, supercritical water reforming and aqueous phase reforming. For steam reforming, Slinn et al. [23] found that the conversions and yields with crude glycerol were 70% of those obtained with pure glycerol, Dou et al. [24] reported that crude glycerol conversions were slightly higher than those of pure glycerol under the same reaction conditions, and Valliyappan et al. [25] indicated that the production of hydrogen and the yield to gas from crude glycerol were higher than those from pure glycerol. Remón et al. [26] analysed the effect of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$  during glycerol steam reforming in a fluidised bed reactor. It was found that the three compounds had a significant impact on product distribution (gas, liquid and solid) in carbon basis; the composition of the gas being little affected.  $\text{CH}_3\text{OH}$  alone did not alter the results obtained with pure glycerol. In contrast,  $\text{CH}_3\text{COOH}$  and  $\text{KOH}$  decreased the initial production of gases, especially for  $\text{KOH}$ . However, the progressive accumulation of  $\text{KOH}$  inside the reactor exerted a positive catalytic effect on the gasification of this char, augmenting the gas production over time. For supercritical water reforming, it was reported that the use of crude glycerol led to higher catalyst deactivation than that obtained with pure glycerol [27].

To the best of the authors' knowledge, there are only three studies currently available on aqueous phase reforming of crude glycerol, and only two of them analyse the effect of some biodiesel-derived impurities on the process. Lehnert and Claus [9] reported the aqueous phase reforming of pure and crude glycerol using different Pt-based catalysts at 250 °C and 20 bar Argon. They found a lower  $\text{H}_2$  selectivity and a higher catalyst deactivation with crude glycerol due to the presence of  $\text{NaCl}$  salts in the solution. King et al. [4] studied the aqueous phase reforming of a 10 wt.% glycerol solution containing  $\text{KOH}$  using different Pt and Re catalysts supported on carbon. The addition of 0.1 wt.% of  $\text{KOH}$  to the solution until reaching a pH of 12 increased both the glycerol conversion and the  $\text{H}_2$  production. It was reported that the pH of the solution exerted a great influence on the selectivity of the process. Boga et al. [8] studied the aqueous phase reforming of glycerol and crude glycerol, establishing a comparison between both feedstocks and analysing the effect of some of the impurities commonly found in crude glycerol. The crude glycerol solution was made up of 6.85 wt.% glycerol, 1.62 wt.% soaps, 1.55 wt.% methanol and 0.07 wt.% esters. The use of this crude glycerol solution resulted in a dramatic drop in APR activity compared to the corresponding 6.85 wt.% pure glycerol solution. The results obtained with different synthetic mixtures revealed that Na salts of fatty acids had a much more pronounced negative influence than  $\text{NaOH}$

and greatly inhibited  $\text{H}_2$  formation. Stearic acid, long chain aliphatics and olefins were shown to be formed and to be involved in the deactivation of the catalyst.

This scenario suggests that the cost-effective reduction of some of the troublesome impurities present in crude glycerol, such as fatty acid methyl esters, (FAMES) and soaps, before the valorisation of this feedstock might be beneficial for increasing the yields and efficiencies of glycerol valorisation processes. This cost-effective strategy consists of the separation of the FAMES and the elimination of the soaps present in the solution by an initial acidification, normally with acetic, sulphuric or phosphoric acid [3,28], and a subsequent liquid–liquid extraction with a polar solvent. The work of Manosak et al. [3] provides an in-depth study of this purification method.

Given this background, the objective of this work is to study the effect on the APR process of the presence of three common biodiesel-derived glycerol impurities that may be present in the glycerol obtained from the biodiesel industry (crude and/or refined glycerol): acetic acid, potassium hydroxide and methanol. Acetic acid is an organic acid that can be used in glycerol neutralisation without poisoning the catalysts that are habitually used in APR, as occurs when using  $\text{H}_2\text{SO}_4$  due to the presence of S, and that can contribute to  $\text{H}_2$  formation. Potassium hydroxide is commonly employed as a homogeneous catalyst in biodiesel production. Methanol is an alcohol generally used in biodiesel production as well as during the glycerol purification step [29]. Specifically, this work provides information about the effect of the presence in a glycerol/water solution of the three impurities considered alone and all the binary and ternary combinations. This strategy not only allows a comparison to be made between pure and crude glycerol, but also leads to an understanding of the individual and synergetic effects on the process of the presence of these impurities in crude glycerol.

The effect of the presence of these impurities has been investigated in a flow reactor at 220 °C and 44 bar using a Ni–La/ $\text{Al}_2\text{O}_3$  catalyst, analysing how and to what extent the glycerol conversion, the product distribution in carbon basis (carbon converted to gas and liquid products) and the compositions of the gas and liquid phases are affected by the presence of these impurities. Given that the combined effect of the presence in crude glycerol of methanol, acetic acid and potassium hydroxide has never been studied before, and considering the limited number of studies dealing with crude glycerol, this work represents a novel investigation for gaining a better understanding of the aqueous phase reforming of crude glycerol.

## 2. Experimental

### 2.1. Experimental system

The experiments were carried out in a small bench scale continuous unit for 3 h employing a Ni–La/ $\text{Al}_2\text{O}_3$  catalyst. The catalyst was prepared by coprecipitation, having 28% (relative atomic percentage) of Ni expressed as  $\text{Ni}/(\text{Ni} + \text{Al} + \text{La})$ , an atomic La/Al ratio of 0.035 and a BET surface area of 187  $\text{m}^2/\text{g}$ . The experimental rig used in the experiments was a microactivity unit designed and built by PID (Process Integral Development Eng & Tech, Spain). It consists of a stainless steel tubular reactor with an inner diameter of 9 mm, heated up by means of an electric furnace [30]. The system pressure is reached with the aid of a micrometric valve that automatically adapts its position with the help of a rotor. A pressure gauge, located at the exit of the reactor, measures the pressure of the reaction section. A PDI control system is used to keep the reactor pressure constant during the experiments. The aqueous solutions of glycerol are fed into the reactor by means of a high

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