



Production of gaseous and liquid chemicals by aqueous phase reforming of crude glycerol: Influence of operating conditions on the process



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ARTICLE INFO

Article history:

Received 29 September 2015

Accepted 25 November 2015

Available online 24 December 2015

Keywords:

Crude glycerol
Aqueous phase reforming
Value-added liquids
Gas production
Renewable hydrogen

ABSTRACT

The present work studies the influence of the temperature (200–240 °C), pressure (38–50 bar), glycerol concentration (10–50 wt.%) and mass of catalyst/ glycerol mass flow rate ratio ($W/m_{\text{glycerol}} = 10\text{--}40$ g catalyst min/g glycerol) during the aqueous phase reforming (APR) of a glycerol solution obtained from the production of biodiesel. The operating conditions exerted a statistically significant influence on the reforming results. Specifically, the global glycerol conversion and the carbon converted into gas and liquid products varied as follows: 4–100%, 1–80% and 16–93%, respectively. The gas phase was made up of H_2 (8–55 vol.%), CO_2 (34–66 vol.%), CO (0–4 vol.%) and CH_4 (6–45 vol.%). The liquid phase consisted of a mixture of alcohols (monohydric: methanol and ethanol; and polyhydric: 1,2-propanediol, 1,2-ethanediol, 2,3-butanediol), aldehydes (acetaldehyde), ketones (C3-ketones: acetone and 2-propanone-1-hydroxy; C4-ketones: 2-butanone-3-hydroxy and 2-butanone-1-hydroxy; and cyclic ketones), carboxylic acids (acetic and propionic acids) and esters (1,2,3-propanetriol-monoacetate), together with unreacted glycerol and water. The relative amount (free of water and un-reacted glycerol) of these compounds in the liquid phase was as follows: monohydric alcohols: 4–47%, polyhydric-alcohols: 14–68%, aldehydes: 0–5%, C3-ketones: 2–33%, C4-ketones: 0–10%, ciclo-ketones: 0–6%, carboxylic acids: 2–43%, and esters: 0–46%. This process turned out to be highly customisable for the valorisation of crude glycerol for the production of either gaseous or liquid products. Gas production is favoured at a low pressure (39 bar), high temperature (238 °C), high W/m_{glycerol} ratio (38 g catalyst min/g glycerol) and employing a 15 wt.% glycerol solution. A high pressure (45 bar), medium temperature (216 °C), medium W/m_{glycerol} ratio (22 g catalyst min/g glycerol) and the feeding of a 16 wt.% glycerol solution favours the production of liquid products.

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1. Introduction

Worldwide biodiesel production is increasing intensely as a result of widespread environmental concerns and firmer regulations for fuels. This biofuel is commonly produced by the transesterification of triglycerides using an alcohol in the presence of a catalyst. Unfortunately, despite the environmental benefits of biodiesel, its production originates glycerol as a by-product: 1 kg of crude glycerol is yielded with the production of 10 kg of biodiesel. This scenario could create a surplus of crude glycerol unable to be absorbed by its current market, which may cause economic and environmental problems, hampering the development of the biodiesel industry [1].

Given this background, two main options are usually considered to deal with this biodiesel-derived glycerol. The first consists

of its purification for further use in other industries such as the food, cosmetics and pharmaceutical sectors [1,2]. The second option consists of upgrading the crude glycerol employing different valorisation routes. These include gasification, steam reforming, aqueous phase reforming and supercritical reforming, among others [3,4], allowing the production of different value-added chemicals and/or energy, and thus improving biodiesel economy and sustainability [5,6].

The glycerol discharged from biodiesel production plants consists not only of glycerol but also of many other chemicals [1], which can significantly reduce the yields and efficiencies of the valorisation processes. Therefore, an intermediate option that includes a first purification of the crude glycerol up to an appropriate level for use in the subsequent valorisation processes should be addressed. This pre-treatment helps to reduce troublesome impurities such as fatty acid methyl esters (FAMES) and soaps. A cost-effective purification method consists of the physical separation of the FAMES and the elimination of the soaps by an

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initial acidification, normally with acetic, sulphuric or phosphoric acid, and a subsequent liquid–liquid extraction with a polar solvent [1]. This pre-treatment using acetic acid provides a glycerol solution with 85–90% purity, which still contains some of the acid used in the neutralization, part of the catalyst employed in the biodiesel production (usually KOH or NaOH) as well as the alcohol used during the transesterification reaction and/or in the purification step.

A promising strategy to obtain value-added chemicals from this biodiesel derived glycerol is aqueous phase reforming (APR). APR is a catalytic process carried out at quite low temperatures and moderate pressures, allowing the production of different chemicals (gases and liquids) from an organic feedstock. During the APR of glycerol, various liquid–gas–solid chemical reactions take place. These include cracking and reforming reactions to generate hydrogen, dehydrogenation of alcohols/hydrogenation of carbonyls, deoxygenation and hydrogenolysis as well as cyclisation reactions. The gas phase consists of a gas with a high H₂ content, the liquid phase being a complex mixture of different organic compounds in water. These include alcohols, ketones, acids, esters, paraffins, aldehydes and other oxygenated hydrocarbons with different compositions depending on the operating conditions of the process and the nature of the feed [6–9]. The versatility of this valorisation process allows the customised conversion of glycerol into chemicals of a different nature to suit the necessities of the market, thus converting this process into a very promising tailor-made route for the treatment and valorisation of the glycerol obtained from the biodiesel industry.

Works dealing with the aqueous phase reforming of crude glycerol are extremely scarce [7,9–11] 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 reagent-grade glycerol. The catalysts used in the process are noble metals based on Pt [11–16], Ni [11,12,16–20], Pt–Ni, Cu, Co or Ru [9,12,16,18,21] supported on different oxides such as Al₂O₃, ZrO₂, MgO, SiO₂, CeO₂, or carbon [7,22] and modified, in some cases, with promoters such as La, Ce, Mg and Zr.

The influence of the operating variables on the process has been studied in some works. Özgür et al. [14] studied the effect of the temperature (160–280 °C), flow rate (0.05–0.5 mL/min), pressure (0–75 atm) and glycerol concentration (5–85 wt.%). The optimum temperature for hydrogen production was 230 °C and the maximum gas production rate was found using feed flow rates of 0.1 mL/min. In addition, they reported that the hydrogen concentration in the gas increased with decreasing the glycerol concentration of the feed. Wawrzetz et al. [23] reported the effect of the glycerol concentration (10–30 wt.%) and pressure (26–45 bar) at 498 K. Reaction rates increased with the increase in the glycerol concentration. The pressure was found to have a significant effect on the liquid product distribution without affecting the global conversion of the process.

Roy et al. [21] investigated the effect of the initial pressure (0–41 bar of N₂) at 493 K using a 9.2 wt.% glycerol solution in a batch reactor, initially fed with 3 g of glycerol and 0.125 g of catalyst, for 6 h. An increase in the initial pressure up to 14 bar of N₂ augmented the glycerol conversion from 43.2% to 50.2%, while a further increase up to 41 bar decreased the glycerol conversion. The product distribution was not greatly affected by the pressure. An increase in temperature from 473 to 523 K at 14 bar of N₂ raised the glycerol conversion from 20.6% to 82.6%, reduced the proportion of ethylene glycol and increased the concentration of ethanol in the liquid.

Manfro et al. [19] used a batch reactor to study the effect of the glycerol concentration (1–10 wt.%), temperature (523–543 K) and its corresponding pressure (37–52 atm). The highest glycerol conversion (30%) was achieved at 543 K using a 1 wt.% glycerol

solution. An increase in the glycerol concentration decreased the glycerol conversion and H₂ formation. A rise in the temperature and pressure increased the glycerol conversion and decreased the proportion of H₂ in the gas. Luo et al. [24] reported the effect of the temperature (180–220 °C) and its corresponding pressure (1.14–2.5 MPa), glycerol concentration (5–10 wt.%) and liquid hourly space velocity (1.56–3.12 h⁻¹) in a flow reactor. An increase in temperature (and its corresponding pressure) facilitated the reforming process and increased the hydrogen yield. The carbon conversion to gas and the H₂ yield decreased with augmenting the glycerol concentration. Decreasing the hourly space velocity resulted in a higher hydrogen yield, hydrogen selectivity and carbon conversion to gas.

Seretis and Tsiacaras [25,26] studied the effect of the reaction time (30–240 min), temperature (200–240 °C), glycerol concentration (1–10 wt.%) and catalyst weight using a Ni/SiO₂–Al₂O₃ catalyst (0.5–10 g) [25] and a Pt/Al₂O₃ catalyst (0.5–2.5 g) [26]. The glycerol conversion increased with increasing the reaction time and temperature. The H₂ production was maximised with the use of short reaction times and low glycerol concentrations. An increase in the amount of catalyst increased the C–C cleavage, favouring the formation of ethylene glycol, ethanol and methane. When using the Ni/SiO₂–Al₂O₃ catalyst, the highest conversions to gaseous and liquid products were 74% and 36%, respectively, while for the Pt/Al₂O₃ catalyst they were 41% and 39%, respectively.

The large number of operating variables significantly influencing the process increases its intrinsic complexity. Some interactions between some of the operating variables can occur so that the effects of some variables may depend on others, resulting in different consequences for the process. These interactions have never been considered in the parametric studies reported in the literature, and they could be responsible for some of the contradictory results reported. In addition, the effect of the operating conditions on the production and selectivity to the different liquid products is not yet well understood; therefore, an in-depth study is needed for gaining a better understanding of this process.

Given this background, this work addresses the effect of the temperature (200–240 °C), pressure (38–50 bar), glycerol concentration (10–50 wt.%) and W/m_{glycerol} ratio (10–40 g catalyst min/g glycerol) on the aqueous phase reforming process of biodiesel-derived glycerol using a Ni-based catalyst. Optimal values for the production of gas and liquid products were also sought for their selective production.

2. Material and methods

2.1. Crude glycerol

The crude glycerol used for this work was obtained from the transesterification of sunflower oil with methanol, employing potassium hydroxide as a catalyst. The characterisation results of the crude glycerol, including the Total Organic Carbon (TOC), density, viscosity, pH and chemical composition, are listed in Table 1. The chemical composition was calculated by means of a Gas Chromatography–Mass Spectrometry analysis, Karl Fischer titration and ash content. The GC–MS analysis of the glycerol also revealed the presence of a small proportion of some FAMES (linoleic, palmitic, oleic and stearic). The properties of this crude glycerol are consistent with those reported in other works in the literature [27–29].

The crude glycerol was neutralised with acetic acid using a final pH of 6. Acetic acid was selected for the glycerol purification as its presence in the refined glycerol solution can contribute to H₂ formation, without deactivating the catalysts used in APR as occurs when using H₂SO₄ due to the presence of S. In addition, the work

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