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Challenges and strategies for optimization of glycerol steam reforming process

Joel M. Silva, M.A. Soria*, Luis M. Madeira*

LEPABE, Department of Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias s/n, 4200-465 Porto, Portugal

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ABSTRACT

The steam reforming of the main biodiesel by-product, glycerol, has been catching up the interest of the scientific community in the last years. The use of glycerol for hydrogen production is an advantageous option not only because glycerol is renewable but also because its use would lead to the decrease of the price of biodiesel, thus making it more competitive. Consequently, the use of biodiesel at large scale would significantly reduce CO_2 emissions comparatively to fossil fuels. Moreover, hydrogen itself is seen as a very attractive clean fuel for transportation purposes. Therefore, the industrialization of the glycerol steam reforming (GSR) process would have a tremendous global environmental impact. In the last years, intensive research regarding GSR thermodynamics, catalysts, reaction mechanisms and kinetics, and innovative reactor configurations (sorption enhanced reactors (SERs) and membrane reactors (MRs)) has been done, aiming for improving the process effectiveness. In this review, the main challenges and strategies adopted for optimization of GSR process are addressed, namely the GSR thermodynamic aspects, the last developments on catalysis and kinetics, as well as the last advances on GSR performed in SERs and MRs.

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Abbreviations: CTAB, cetyltrimethyl ammonium bromide; CVD, chemical vapor deposition; EP, electroless plating; GHSV, gas hourly space velocity; GSR, glycerol steam reforming; IUPAC, international union of pure and applied chemistry; MR, membrane reactor; PEMFC, polymer electrolyte membrane fuel cell; PSA, pressure swing adsorption; PSS, porous stainless steel; SEGSR, sorption-enhanced glycerol steam reforming; SER, sorption-enhanced reactor; SRM, steam reforming of methane; TR, traditional reactor; WGFR, water/glycerol feed ratio (molar); WGS, water–gas shift; WHSV, weight hourly space velocity; YSZ, yttria-stabilized zirconia

* Corresponding authors. Tel.: +351 225081519.
E-mail addresses: masoria@fe.up.pt (M.A. Soria), mmadeira@fe.up.pt (L.M. Madeira).

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1. Introduction

Biodiesel is a promising alternative energy source because it is a renewable fuel and reduces greatly CO_2 emissions compared to fossil fuels (Fig. 1). The production of biodiesel is most commonly done through transesterification with methanol of triglycerides extracted from sunflower oils, soybean and rapeseed (Fig. 2). This process produces glycerol as the main by-product (100 kg of glycerol/ton of biodiesel) [1,2]. Moreover, the annual worldwide production of biodiesel has been in an increasing trend lately, as can be seen in Fig. 3 [3]. However, biodiesel is not competitive in terms of price yet [4]. One way of lowering the production cost of biodiesel would be to use its main by-product, glycerol, to produce H_2 (or syngas) via steam reforming, for example, thus providing an extra value to such a waste.

Hydrogen is a clean energy source with numerous uses and its demand is expected to greatly increase in the future, mainly due to the technological advancements in the fuel cell industry. Nowadays, nearly 48% of the worldwide produced hydrogen is generated through the steam reforming of methane (SRM), while the reforming of naphtha/oil contributes with 30%, the coal gasification with 18% and electrolysis with only 3.9% [5]. The SRM, in particular, consists of CH_4 reacting with H_2O to yield syngas at high temperatures (700–1100 °C) [4]. Stoichiometrically, 3 mol of H_2 can be obtained per mole of methane through SRM, while 7 mol of H_2 can be extracted from 1 mol of glycerol through glycerol steam reforming (GSR), as presented in Eq. (1).

$$C_3H_8O_3 + 3H_2O \leftrightarrow 7H_2 + 3CO_2 (\Delta H_r^{298\ K} = 128\ \mathrm{kJ\ mol^{-1}}) \tag{1}$$

Furthermore, while for SRM a fuel (CH_4) is consumed to produce another fuel, the same thing does not happen for GSR. Therefore, the use of glycerol instead of methane would be advantageous [4]. Even though steam reforming is the main target of focus in this review, there are other methods to convert glycerol into H_2:

- Auto-thermal reforming [6–8].
- Partial oxidation gasification [9–11].
- Aqueous-phase reforming [12–14].
- Supercritical water reforming [15–17].

The reason why GSR was chosen as focus of study instead of any of the other processes is mainly due to the fact that the steam reforming process is widely used in industry and it would not require many changes in the system if the feedstock was changed from natural gas or naphtha to glycerol [4].

The GSR process, like any other process, has some challenges that need to be overcome in order to accomplish its effective commercialization. Some of the main challenges are:

- The GSR is an endothermic reaction, thus requiring high temperatures and inherently high operating costs. Furthermore, more resistant reactors would be needed and so higher capital costs would be involved.
- The GSR process has side reactions, which affect both production and purity of H_2. The main side reactions represented by Eqs. (2–4) lead to methane formation either by reaction of carbon monoxide and hydrogen or reaction of carbon dioxide and hydrogen or through hydrogenolysis of glycerol, respectively.

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O\ (\Delta H_r^{298\ K} = -165\ \mathrm{kJ\ mol^{-1}} \tag{2}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O\ (\Delta H_r^{298\ K} = -165\ \mathrm{kJ\ mol^{-1}}) \tag{3}$$

$$C_3H_8O_3 + 2H_2 \leftrightarrow 2CH_4 + CO + 2H_2O\ (\Delta H_r^{298\ K} = -160\ \mathrm{kJ\ mol^{-1}}) \tag{4}$$

- Although 7 mol of hydrogen should theoretically be produced per each mole of glycerol that reacts, many authors have observed upper H_2 yield limits lower than 7 [18–23].
- The GSR is a thermodynamically-limited reaction (Eq. (1)), being inherently the conversion detrimentally affected in certain conditions, particularly at lower temperatures [24].
- The formation of coke is also an issue since it deactivates the catalyst, thus affecting H_2 yield and purity and long term operation.
- Besides producing hydrogen the GSR reaction also produces carbon dioxide, whose release is target of environmental concern and restricted by legislation.

With the aim of addressing these problems, new catalysts have been developed and different purification methods have been studied. Moreover, new reactor configurations combining the GSR reaction and hydrogen or carbon dioxide selective removal have also been target of intense research, due to their potential to solve some of the limitations previously mentioned. In this review some