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Overview of glycerol reforming for hydrogen production

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ABSTRACT

Hydrogen is used by the chemical industry in numerous processes, and today almost 95% is produced from raw materials based on fossil fuels, such as methane (CH_4). However, catalytic reforming technologies face a number of technical and scientific challenges involving the quality of raw materials, conversion efficiency, and safety issues in the integration of systems of H_2 production, purification and use, among others. Glycerol is a versatile raw material for H_2 production because it is the main by-product of biodiesel production, which a few years ago was consolidated in the world energy matrix and whose production continues to grow in the main consumer markets. Moreover, it has the noteworthy characteristic of decentralized production, which is directly reflected in its easy use. This paper presents a literature review on the reforming technologies applied to glycerol, the advantages of each route, and the main problems involved.

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1. Introduction

Biodiesel was consolidated in the world energy matrix a few years ago and its production continues to grow in the main consumer markets. The European Union is still the largest market, with 12.5 million cubic meters (MCM) produced in 2014, a figure that is predicted to continue up the end of 2015 [1]. The US, another major producer, produced 4.8 MCM in 2014 [2]. In Brazil, biodiesel production in 2014 was 3.1 MCM. In July 2014, the Brazilian government authorized an increase from the previous 5% to 7% in the percentage of biodiesel to be added to diesel for road use, with a projected production of 3.8 MCM by the end of 2015 [3].

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In these markets, biodiesel is produced industrially via transesterification of readily available oil-containing raw materials such as rapeseed in the EU and soybeans in the US and Brazil. The reaction involves mixing the raw material with a short chain alcohol and a catalyst, usually methanol and potassium methoxide, under controlled heating and stirring. At the end of the process, approximately 10 m^3 of glycerol is generated for every 90 m^3 of biodiesel produced [4]. Considering this proportion, more than 2 MCM of glycerol will be obtained in 2015 just from the largest biodiesel producer markets.

In 2013, over 350 thousand tons of glycerol were produced in biodiesel plants in Brazil to meet the domestic demand of 40 thousand tons by the textile, cosmetics and food industries [5,6]. Most of the excess volume was exported, mainly to China, which adds value to the product. In addition, Brazil exported over 230 t of crude glycerol to China in 2014 [7].

Glycerol derived from the biodiesel production process has a dark color and contains variable amounts of soap, catalyst, alcohol (typically methanol), monoglycerides, diglycerides, glycerol oligomers, polymers, water, and unreacted triacylglycerols and biodiesel. This crude glycerol (crude glycerin) contains glycerol concentrations of 40 to 85%, depending on the efficiency of the steps involved in the biodiesel production process. When subjected to a partial purification process involving the addition of mineral acid, the derivatives of fatty acids are removed and the glycerol content increases to 80–85%, and the product contains water, methanol and dissolved salts. Pharmaceutical grade glycerin can be obtained after a distillation process [8–10].

Biodiesel plants normally use crude glycerol to generate energy or to sell, since the cost benefit of purification processes is disadvantageous. An alternative is burning it directly, although the combustion of glycerol is not that simple because it is highly viscous, which greatly hinders the flow, pumping and flame spray process. Its high ignition temperature is also problematic because it reduces the combustion efficiency, resulting in the formation of acrolein, an aldehyde that is highly toxic even at low concentrations. Moreover, the high concentration of residual salts after burning glycerin leads to the formation of deposits and plaque that clog the equipment used in this process. These problems of acrolein formation can be overcome by a preheating step followed by the addition of an auxiliary fuel in burning [11–13].

On the other hand, much of the glycerol that is not used for burning is treated by the dewatering process in a controlled environment for the formation of acrolein as a standard product. When produced, purified and stored, acrolein becomes a product with high added value, since it is an important intermediate for the agricultural and chemical industries. The conventional acrolein production process involves the oxidation of petroleum-based propylene derivatives [14].

Glycerol is also used in pyrolysis and gasification processes that are carried out between 600 and 850 °C, which represent options to partially oxidize the fuel or convert it into another one of higher quality and energy content, such as synthesis gas, which is a mixture of gases (mainly H_2 and CO) formed during these procedures [11].

2. Hydrogen production from biodiesel derived raw glycerol

Currently, almost 95% of global hydrogen production uses raw materials based on fossil fuels, such as CH_4 [15–17]. Given that the global glycerol market currently shows a trend for growth until 2020, an alternative for the large scale use of this product is as raw material for the production of hydrogen and synthesis gas [15,18–20].

The main hydrogen production processes are: water electrolysis [21], and thermochemical [11,16,18,22] and biological processes [23,24]. Among these processes, biological production can be a favorable alternative because it involves less energy expenditure and is carried out at ambient temperature and pressure. When biological reactors are with wastewater, for instance, hydrogen becomes an even more promising alternative energy source [23,24]. The electrolysis of water to produce hydrogen offers advantages such as high purity of the resulting H_2 and absence of waste generated during the process. However, water electrolysis is used only in special cases that require high purity hydrogen, and is not an economically viable alternative source for hydrocarbon substitution. The route most widely used to produce H_2 is the thermochemical process, and CH_4 steam reforming is the most common one [21]. Several hydrogen production technologies using glycerol in the thermochemical route have been studied, but they require power (endothermic reactions) for the conversion of glycerol into synthesis gas. The main processes are steam reforming (SR), autothermal reforming (ATR), supercritical water reforming (SCWR), partial oxidation reforming (POR), liquid phase reforming (LPR) and gasification [11,18,22,25,26].

The hydrogen produced worldwide has many applications. As world faces unprecedented energy challenges, the hydrogen emerges like a promising fuel to move vehicles and to provide power and heat for industries. Despite its employment as energy source, hydrogen can be used as byproduct in chemical industry to obtain cyclohexane, formic acid, hydrochloric acid, polyurethane, methacrylates and also methanol and ammonia that are used to synthetize other important solvents and reagents like formaldehyde, acetic acid, methyl *terc*-butyl ether and urea. Other two process that depend of hydrogen are hydrocracking process carried out in petrochemical refineries and hydrogenation in food industries.

Envisioning a medium term future in which the worldwide use of hydrogen is more widespread and diversified, an important production strategy is decentralization, which will facilitate distribution logistics, reduce costs and increase safety during transportation. In this regard, given that a large proportion of biodiesel plants (glycerol producers) are located in rural regions, hydrogen production from glycerol could become attractive particularly because so many agribusinesses that use hydrogen are established in those very regions. A good example are the agroindustrial plants that operate in the food industry and use hydrogen as feedstock in the production of hydrogenated products such as margarine, hydrogenated fats, etc. Depending on their distance from the hydrogen producers, which are usually located in large cities, the purchase cost of hydrogen for these agroindustrial plants is high. In fact, it should be noted that the cost of hydrogen transportation may account for up to 50% of the price paid by agroindustrial plants. Therefore, the lower cost of hydrogen resulting from shorter transport distances and from the use of glycerol as a renewable raw material can be an advantage for agroindustrial plants located far away from urban centers, thus increasing their competitiveness. The flow chart in Fig. 1 summarizes the raw materials, processes, products and actors involved in the production of hydrogen from glycerol in rural regions.

3. Hydrogen production processes from glycerol

This paper presents an overview of the glycerol reforming processes discussed in recent literature, which include the processes of SR, ATR, LPR, POR, and SCWR [15,25,27,28]. Table 1 describes the main reactions that occur in these processes.

The major constituents of the compounds formed in the thermal decomposition of glycerol are carbon monoxide, hydrogen and