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Hydrogen production from glycerol: An update

Sushil Adhikari [a,*], Sandun D. Fernando [b], Agus Haryanto [c,1]

[a] Department of Biosystems Engineering, Auburn University, Auburn, AL 36849, USA
[b] Department of Biological and Agricultural Engineering. Texas A&M University, College Station, TX, USA
[c] Department of Agricultural and Biological Engineering, Mississippi State University, Mississippi State, MS, USA

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ABSTRACT

The production of alternative fuels such as biodiesel and ethanol has increased over the last few years. Such fuels are vital for the reduction of energy dependence on foreign countries and to protect the environmental damage associated with the use of fossil fuels. Due to the increased production of biodiesel, a glut of crude glycerol has resulted in the market and the price has plummeted over the past few years. Therefore, it is imperative to find alternative uses for glycerol. A variety of chemicals and fuels including hydrogen can be produced from glycerol. Hydrogen is produced by using several processes, such as steam reforming, autothermal reforming, aqueous-phase reforming and supercritical water reforming. This paper reviews different generation methods, catalysts and operating conditions used to produce hydrogen using glycerol as a substrate. Most of the studies were focused on hydrogen production via steam reforming process and still less work has been done on producing hydrogen from crude glycerol.

1. Introduction

Alternative energy resources are becoming increasingly important because of dwindling petroleum reserves and mounting environmental concerns that are associated with fossil fuel utilization. Consequently, alternative bio-based fuels are emerging as the long-term solution. Biofuels have become surrogate to fossil-based fuels because they are renewable and theoretically, carbon dioxide (CO_2) neutral. Over the last few years, the demand and production of biodiesel has increased tremendously. With the production of biodiesel, glycerol is being produced as a byproduct and several efforts are being made to utilize excess glycerol and produce value-added products. Glycerol is a highly versatile product and since 1945, 1583 different uses for glycerol have been documented [1]. Almost two third of the industrial uses of glycerol are in food and beverage (23%), personal care (24%), oral care (16%) and tobacco (12%). Our previous study concluded that glycerol and its derivatives can possibly be blended with gasoline [2]. Etherification of glycerol with either alcohols or alkenes may produce branched oxygen containing components, which could have suitable properties for use as a fuel or solvent [3]. Glycerol can be used to produce a variety of chemicals and fuels including hydrogen [4–6].

Demand for hydrogen (H_2), the simplest and most abundant element, is growing due to the technological advancements in fuel cell industry [7]. At present, almost 95% of the world's hydrogen is being produced from fossil fuel based feedstocks [8]. Renewable resources based technologies for hydrogen production are attractive options for the future due to carbon neutral nature of these technologies with lesser effects to the environment. We have seen a great interest in utilizing glycerol for hydrogen production over the last few years. Hydrogen can be produced from glycerol via steam reforming [9], (partial oxidation) gasification [10], autothermal reforming [11], aqueous-phase reforming (APR) [12,13], and supercritical water reforming [14] processes. In this paper, we attempt to review hydrogen production methods using glycerol. Most of the studies on hydrogen production were focused on thermochemical routes and therefore, we limit this discussion only on thermochemical processes.

2. Thermodynamic studies on hydrogen production

Thermodynamic studies are very important because they provide information on conditions that are conducive for hydrogen production. Such studies are also helpful in defining the operating parameters that will inhibit carbon formation. It is very important to avoid the conditions that are favorable for carbon formation because coking deteriorates catalyst activity. Adhikari et al. [15] had performed a thermodynamic analysis of steam reforming of glycerol for hydrogen production. Their study found that the best conditions for producing hydrogen is at a temperature >627 °C, atmospheric pressure, and a molar ratio of water/glycerol of 9:1. Under these conditions methane production is minimized, and the carbon formation is thermodynamically inhibited. Luo et al.

* Corresponding author. Tel.: +1 334 844 3543.
E-mail address: sushil.adhikari@auburn.edu (S. Adhikari).
[1] Present address: Agricultural Engineering Department, University of Lampung, Jl. Sumantri Brojonegoro No. 1, Bandar Lampung 35145, Indonesia.

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[16] performed a thermodynamic study on the APR process. Their study found that carbon monoxide (CO) content was primarily dependent on temperature whereas H_2 and CO_2 were mainly dependent on pressure and temperature. Higher reaction temperatures favor higher hydrogen production while increasing CO concentration. With addition of oxygen during the APR process, H_2 content was mainly influenced by oxygen/glycerol molar ratio whereas CO was affected by temperature. The effect of pressure was not discussed in the paper. On the other hand, CH_4 production is increased at lower temperatures. Under the supercritical water reforming [14], hydrogen production increases as temperature is increased and decreases as the feed concentration is increased. According to the authors, the effect of pressure was negligible in the supercritical region.

3. Experimental studies on hydrogen production

Conversion of fuels to hydrogen has been carried out by several techniques, such as steam reforming (SR), partial oxidation (PO), autothermal reforming (ATR), aqueous-phase reforming (APR) and supercritical water (SCW) reforming. In this section, each process and operating conditions used for hydrogen production from glycerol will be discussed.

3.1. Steam reforming

The steam reforming is the most commonly used method for producing hydrogen in the chemical industry. In this process, the substrate is reacted with steam in the presence of a catalyst to produce hydrogen, carbon dioxide, and carbon monoxide. The steam reforming process is highly endothermic. In general, the process can be depicted as follows:

$$\text{substrate } (C_nH_mO_p) + \text{steam} \rightarrow \text{carbon oxides} + \text{hydrogen}, \quad \Delta H > 0 \tag{1.1}$$

The steam reforming of hydrocarbons has been the preferred method for many decades for industrial scale hydrogen production. Reforming process mainly involves splitting of hydrocarbons in the presence of water and water–gas shift reaction as given below [17]:

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \tag{1.2}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H = -41 \text{ kJ/mol} \tag{1.3}$$

The first step Eq. (1.2) is highly endothermic, taking more heat than it evolves from water–gas shift reaction. Therefore, overall steam reforming is an endothermic process. Thermodynamically, steam reforming process favors high temperatures and low pressures; whereas, water–gas shift reaction is inhibited by high temperatures and unaffected by pressure. Excess steam favors the reforming reaction and the steam/carbon ratio of 3.5–4.5 is common in practice, especially in the case of methane steam reforming [17]. Extensive studies have been carried out on the steam reforming reaction to produce hydrogen from ethanol, a bio-based feedstock, and two review papers [18,19] are available including one from our group [19]. A few studies have been conducted on hydrogen production from glycerol via steam reforming process. The overall reaction of hydrogen production by steam reforming of glycerol ($C_3H_8O_3$) could be depicted as follows:

$$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO_2(g) \tag{1.4}$$

Zhang et al. [20] performed glycerol steam reforming process over ceria-supported metal catalysts. They reported that the Ir/CeO_2 catalyst resulted in a complete glycerol conversion at 400 °C; whereas, the complete conversion over Co/CeO_2 and Ni/CeO_2 catalysts occurred at 425 and 450 °C, respectively. Hirai et al. [21] reported that steam reforming of glycerol on Ru/Y_2O_3 catalyst exhibited H_2 selectivity of ~90% and complete conversion at 600 °C. Czernik et al. [22] used commercial Ni-based reforming catalyst for H_2 production from glycerol. Adhikari et al. [23] tested several noble metal based catalysts and their study found that Ni/Al_2O_3 and $Rh/CeO_2/Al_2O_3$ were the best performing catalysts in terms of H_2 selectivity and glycerol conversion under the experimental conditions investigated. Furthermore, it was found that with the increase in water/glycerol molar ratio (WGMR), H_2 selectivity and glycerol conversion increased. About 80% of H_2 selectivity was obtained with Ni/Al_2O_3, whereas the selectivity was 71% with $Rh/CeO_2/Al_2O_3$ at 9:1 WGMR, 900 °C temperature, and a feed flow rate (FFR) of 0.15 mL/min (15,300 GHSV-gas hourly space velocity). Another study by Adhikari et al. [24] found that Ni/CeO_2 was the best performing catalyst compared to Ni/MgO and Ni/TiO_2 under the experimental conditions investigated. Ni/CeO_2 gave the maximum H_2 selectivity of 74.7% at a WGMR of 12:1, temperature of 600 °C, and an FFR of 0.5 mL/min compared to Ni/MgO (38.6%) and Ni/TiO_2 (28.3%) under similar conditions. Navarro and co-workers [25] had performed steam reforming of glycerol over Ni catalysts supported with alumina using various promoters such as, Ce, Mg, Zr and La. Their study concluded that the use of Mg, Zr, Ce and La increases the hydrogen selectivity. Higher activities of those catalysts were attributed to higher Ni concentration, higher stability and higher capacity to activate steam. A complete glycerol conversion was achieved at temperature of 600 °C, weight hourly space velocity (WHSV) 2.5 h^{-1} and atmospheric pressure. Table 1 depicts a list of catalysts and operating parameters used for steam reforming of glycerol for hydrogen production.

3.2. Partial oxidation

In the partial oxidation process, a substrate is reacted with oxygen at sub-stoichiometric ratios. The oxidation reaction results in heat generation and high temperature. The objective of reforming in the presence of the air is to balance the energy required for the process by oxidizing some of the substrate. If excess air is added, all the substrate will be oxidized and produce mainly carbon dioxide and water. The process can be shown as follows:

$$\text{substrate}(C_nH_mO_p) + \text{air} \rightarrow \text{carbon oxides} + \text{hydrogen} + \text{nitrogen}, \quad \Delta H < 0 \tag{1.5}$$

This process may be conducted with or without catalysts [30]. Gasification is an analogous example for the partial oxidation process. Dauenhauer et al. [11] had performed glycerol oxidation at various temperatures and C/O ratios over $Pt/\gamma\text{-}Al_2O_3$. The complete combustion of glycerol occurs at C/O = 0.43. The hydrogen selectivity increased as the C/O increased from 1.0 and became flat and started decreasing as C/O increased further. The reduction of H_2 selectivity at higher C/O (less oxygen) is mainly due to reduction in temperature which results in lower glycerol conversion. At C/O ratio of 1.2, temperature = 1055 °C, complete glycerol conversion was achieved and the H_2 selectivity was 56%. [11] Dalai and his coworkers [31] performed steam gasification of crude and pure glycerol at 800 °C at various steam to glycerol ratio with and without catalyst. Their study concluded that H_2 and total gas production was higher from crude glycerol than those from pure glycerol. That was probably due to the presence of potassium in the crude glycerol which tends to favor the gasification process. However, the authors did not explicitly discuss catalyst deactivation with crude glycerol compared to that of pure glycerol.

3.3. Autothermal reforming

Autothermal process combines the effect of partial oxidation and steam reforming by feeding fuel, air, and water together into