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.

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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.

[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.

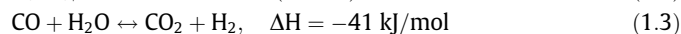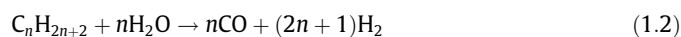## 3. Experimental studies on hydrogen production

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.
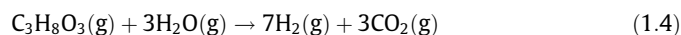
3.1. Steam reforming

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:

$$\text{substrate } (C_nH_mO_p) + \text{steam} \rightarrow \text{carbon oxides} + \text{hydrogen}, \quad \Delta H > 0 \tag{1.1}$$
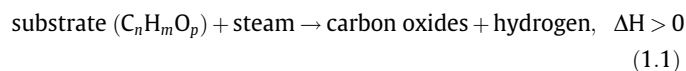
The steam reforming of hydrocarbons has been the preferred method for many decades for industrial scale hydrogen production. Reforming process mainly involves splitting of hydrocarbons in the presence of water and water–gas shift reaction as given below [17]:

$$C_nH_{2n+2} + nH_2O \rightarrow nCO + (2n+1)H_2 \tag{1.2}$$
$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H = -41 \text{ kJ/mol} \tag{1.3}$$

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:

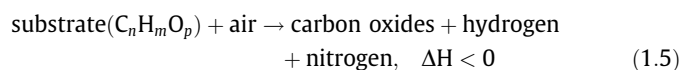$$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO_2(g) \tag{1.4}$$

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/γ-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 co-workers [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.
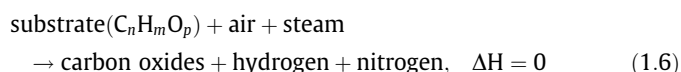
3.3. Autothermal reforming

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

Table 1
Catalysts and operating conditions used for steam reforming of glycerol.

Catalysts	Operating parameters	Remarks
Ir/CeO$_2$, Ni/CeO$_2$, Co/CeO$_2$	Temperature: 400–550 °C; mass of catalyst: 200 mg; particle diameter: 40–60 mesh, C$_3$H$_8$O$_3$:H$_2$O:He = 2:18:80 vol.%; and GHSV = 11,000 mL/g-cat.h	Ir/CeO$_2$ gave the hydrogen selectivity and glycerol conversion of 85% and 100%, respectively, at 400 °C [20]
Y$_2$O$_3$, ZrO$_2$, CeO$_2$, La$_2$O$_3$, SiO$_2$, MgO, and Al$_2$O$_3$ supported Group 8–10 metals.	Temperature 500–600 °C; a steam-to-carbon molar ratio (S/C) = 3.3; and a W/F (contact time) of glycerol of 13.4 g-cat h/mol. Atmospheric pressure	A complete conversion of glycerol was achieved over ruthenium on Y$_2$O$_3$ (Ru/Y$_2$O$_3$) at 600 °C. At similar conditions, hydrogen yield was 82.8%. From the list of the tested catalysts, Ru/Y$_2$O$_3$ was found to be the best [21]
Ni/Al$_2$O$_3$	Temperature 850 °C; a steam-to-carbon ratio (S/C) = 2.1 and 2.6; GHSV = 1400 h^{-1}	The yield of hydrogen was ~23.6 g/100 g of glycerol (77% of stoichiometric yield) at S/C of 2.6. [22]
Pt/Al$_2$O$_3$, Ni/ Al$_2$O$_3$, Pd/ Al$_2$O$_3$, Ru/ Al$_2$O$_3$, Rh/ Al$_2$O$_3$	Feed flow rate = 0.15–0.5 mL/min; temperatures 600–900 °C; steam/carbon molar ratio (S/C) = 1/3–3.0	About 80% of hydrogen selectivity was obtained with Ni/Al$_2$O$_3$, whereas the selectivity was 71% with Rh/CeO$_2$/Al$_2$O$_3$ at a S/C = 3, 900 °C temperature, and feed flow rate of 0.15 mL/min [23].
Ni/MgO, Ni/CeO$_2$, Ni/TiO$_2$	Feed flow rate = 0. 5–0.7 mL/min; temperatures 550–650 °C; steam/carbon molar ratio (S/C) = 2–4; catalyst loading = 0.75–1.5 g (Ni 9.6–12.7 wt.%)	Ni/CeO$_2$ was found to be the best performing catalyst compared to Ni/MgO and Ni/TiO$_2$ under the experimental conditions. Ni/CeO$_2$ gave the maximum hydrogen selectivity of 74.7% at a S/C ratio of 4, temperature of 600 °C, and a feed flow rate of 0.5 mL/min compared to Ni/MgO (38.6%) and Ni/TiO$_2$ (28.3%) under similar conditions [26]
Pt/Al$_2$O$_3$	Temperature 880 °C; 0.12 mol/min glycerol flow per kg catalyst and S/C = 2.5	Hydrogen selectivity of 70% and glycerol conversion to gas 100% [27]
Pt supported on Al$_2$O$_3$, ZrO$_2$, CeO$_2$/ZrO$_2$, MgO/ZrO$_2$, and Carbon.	Temperature = 350 °C; pressure = 1 bar with aqueous glycerol feed solution (30 wt.%) over oxide supported Pt catalysts (1.0 g) or Pt/C catalyst (0.060 g) and a feed flow rate of 0.32 cm^{3}min^{-1}. Pt/C catalyst was tested at various feed rates and temperatures. Other catalysts tested were Pt–Ru and Pt–Re	Pt/C catalysts showed the superior performance. At 400 °C and pressure = 1 bar, 100% glycerol conversion was achieved at feed rate of 0.32 cm^{3}min^{-1} [28]
Pd/Ni/Cu/K supported on γ-Al$_2$O$_3$	Temperature 550–850 °C; and S/C = 3.0	Hydrogen yield was ~42% at 850 °C [29]
Ni/γ-Al$_2$O$_3$ modified with Mg, Ce, La, Zr.	Temperature 600 °C; WHSV = 2.5 h^{-1}; glycerol concentration = 1 wt.%	100% conversion was achieved with all the catalysts. Catalyst promoted with Zr showed the highest H$_2$ selectivity similar to the equilibrium values [25]

the reactor. This process is carried out in the presence of a catalyst. The steam reforming process absorbs the heat generated by the partial oxidation process. The process can be depicted as follows:

$$\text{substrate}(C_nH_mO_p) + \text{air} + \text{steam}$$
$$\rightarrow \text{carbon oxides} + \text{hydrogen} + \text{nitrogen}, \quad \Delta H = 0 \qquad (1.6)$$

Dauenhauer et al. [11] produced H$_2$ via autothermal steam reforming of glycerol over Rh-Ce/Al$_2$O$_3$ catalyst. Their study found that the addition of steam suppressed CO formation and Rh catalysts supported on Ce with γ-Al$_2$O$_3$ washcoat exhibit higher H$_2$ selectivity. The main benefit of the autothermal process is that, ideally, it should not require any energy for reaction to occur whereas steam reforming is highly an endothermic process. Although the autothermal steam reforming process has advantages over conventional steam reforming [11], the amount of hydrogen produced from autothermal reforming would be less (on a thermodynamic basis). Swami and Abraham [29] compared autothermal and conventional steam reforming of glycerol process over γ-Al$_2$O$_3$ supported Pd/Ni/Cu/K catalyst. The operating conditions were 550–850 °C, steam/carbon (S/C) = 3.0 and oxygen/carbon (O/C) = 0.3. Their study showed that the autothermal steam reforming process produced higher amounts of hydrogen, which was in contrast to the previous study [32]. However, higher temperatures favor hydrogen production in both cases. Douette et al. (2007) [33] performed glycerol

reforming for hydrogen production at various ratios of O/C and S/C. Their study showed that 4.4 mol of hydrogen was produced per mole of crude glycerol under similar conditions but coking and catalyst deactivation was of great concern. Table 2 depicts the list of catalysts and operating parameters used for hydrogen production from glycerol.

3.4. Aqueous-phase reforming

The APR process, a relatively new process developed by Dumesic and his co-workers [12] at University of Wisconsin, has opened a new pathway for hydrogen production from alcohols and sugars. This process operates at relatively higher pressures ~60 bar and at low temperatures (~270 °C) in comparison to steam reforming (atmospheric pressure and temperatures higher than 500 °C). The main advantage of this process is that it is a liquid phase process as opposed to all the other available technologies being gas phase processes (except supercritical water) and most biomass based liquids are difficult to vaporize. The process also produces less amount of CO, which is another advantage of the process. At 265 °C and 56 bar, hydrogen selectivity was achieved as 51% over Pt/γ-Al$_2$O$_3$ catalyst [12]. Claus and Lehnert [34] studied the effect of Pt particle size and support type on the APR process with pure and crude glycerol (obtained from biodiesel plant). Hydrogen selectivity was found to be higher with larger particle (3.1 nm)

Table 2
Catalysts and operating conditions used for autothermal reforming of glycerol.

Catalyst	Operating parameters	Remarks
RhCe/γ-Al$_2$O$_3$	Temperature 500–1050 °C; C/O = 0.9–1.6; S/C = 0–4.5	100% glycerol conversion and 79% H$_2$ selectivity was achieved at S/C = 4.5, C/O = 0.9, temperature = 862 °C, GHSV = 10^5 h^{-1} [11]
G-91 EW from Sud-Chemie Inc.	Temperature 770–810 °C; O/C = 0–0.55 and S/C = 2.0–2.4	4.5 mol of hydrogen was produced per mole of glycerol at O = 0.0 and S = 2.2 and temperature = 804 °C [33]
Pd/Ni/Cu/K supported on γ-Al$_2$O$_3$	Temperature 550–850 °C; O/C = 0.3 and S/C = 3.0	Hydrogen yield was ~68% at 850 °C compared to ~42% using steam reforming process under similar conditions [29]

Table 3
Catalysts and operating conditions used for aqueous-phase reforming of glycerol.

Catalyst	Operating parameters	Remarks
$Pt/\gamma-Al_2O_3$	Temperature 225–265 °C; pressure = 29–56 bar; weight hourly specific velocity (WHSV) = 0.008 g of glycerol/g_{cat}h	The hydrogen selectivity was 65% at 225 °C and 29 bar whereas it dropped to 57% at 265 °C and 56 bar. At higher temperature and pressure, CH_4 selectivity increased [12]
Pt supported on Al_2O_3	Temperature = 250 °C; pressure = 20 bar; glycerol concentration 10 wt.%; feed flow rate = 0.5 mL/min and catalyst = 300 mg (Pt loading = 3 wt.%)	The highest glycerol conversion achieved was 57% and the reaction rate of hydrogen was 7.6×10^{-3} mol/min. g_{cat} [34]
$Pt/\gamma-Al_2O_3$	Temperature = 180–220 °C, pressure = 11–25 bar; feed rate = 0.05–0.1 mL/min; glycerol concentration 5–10 wt.%; catalyst weight = 1–2 g; and Pt loading = 0.3–1.2 wt.%	Al_2O_3 supported Pt catalyst with 0.9 wt.% loading showed the best performance compared to 0.3, 0.6 and 1.2 wt.% loading [35]
$Ni/\gamma-Al_2O_3$ modified with Mg, Ce, La, Zr	Temperature 225 °C; pressure = 3 MPa; WHSV = 1.25 h^{-1}; glycerol concentration = 1 wt.%	All the catalysts showed severe deactivation. Initially, glycerol conversion decreased in the following sequence: lanthanum > cerium > zirconium > aluminium [25]

compared to 1.6 nm. Similarly, the mixture of γ- θ- and δ- phases of Al_2O_3 showed the highest selectivity compared to γ-phase and Boehmit. Furthermore, due to the impurities present in the crude glycerol, H_2 selectivity was found to be lower than pharma grade glycerol. Navarro and co-workers [25] had conducted APR over Ni catalysts supported with alumina using various promoters such as, Ce, Mg, Zr and La. Ni catalysts suffered from severe deactivation and the reason was gradual transformation from metallic to oxidized state [25]. The highest glycerol conversion (37%) was achieved with lanthanum promoted catalysts.

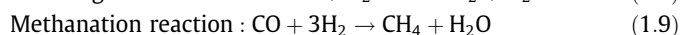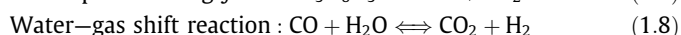Table 3 depicts catalysts and operating conditions used for aqueous-phase reforming of glycerol.

3.5. Supercritical water reforming

Supercritical water is defined as water that is heated and compressed at its critical temperature (374 °C) and pressure (22.1 MPa). Detailed information on applications of supercritical water for energy applications can be found elsewhere [36]. Supercritical water reforming is being performed under the critical temperature and pressure. Recently, Gupta and co-workers [14] reported hydrogen production from glycerol in supercritical water over Ru/Al_2O_3 catalysts. At dilute feed concentration (5 wt.% glyc-

erol in water), 6.5 mol of hydrogen/ mol of glycerol was obtained at a temperature of 800 °C and pressure of 241 bar.

4. Kinetics and reaction mechanism

The steam reforming reaction of glycerol proceeds according to the following equations [21]:

Decomposition of glycerol : $C_3H_8O_3 \overset{H_2O}{\to} 3CO + 4H_2$ (1.7)

Water–gas shift reaction : $CO + H_2O \Longleftrightarrow CO_2 + H_2$ (1.8)

Methanation reaction : $CO + 3H_2 \to CH_4 + H_2O$ (1.9)

The production of hydrogen from glycerol requires C–C bond cleavage [37,38]. Other processes, such as dehydration [39,40] and dehydrogenation [37] with subsequent rearrangement produce several compounds as shown in Fig. 1.

Dumesic and co-workers [41] measured the kinetics of glycerol steam reforming processes over platinum and platinum–rehenium catalysts. Their study reported activation energies of 60–90 kJ/mol for Pt and Pt–Re catalysts and the reaction order of 0.2 for glycerol. Our study found that the activation energy and the reaction order were 103.4 kJ/mol and 0.233, respectively, over Ni/CeO_2 supported catalysts [42]. Gupta and co-workers [14] reported that activation
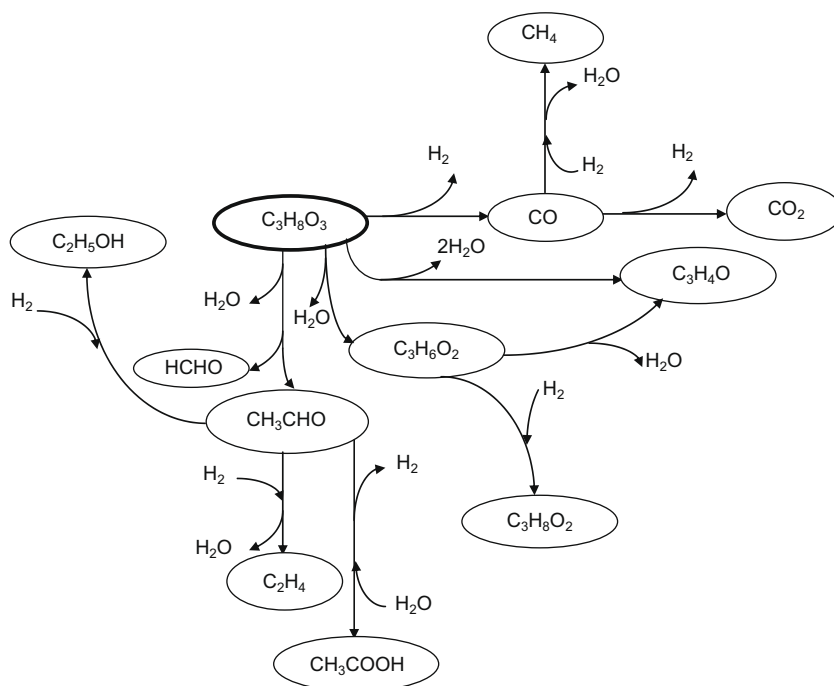

Fig. 1. Reaction pathways during glycerol reforming process.

energy for glycerol reforming was 55.9 kJ/mol in supercritical water reforming over Ru/Al$_2$O$_3$ catalysts.

5. Conclusions and final remarks

Hydrogen can be produced using steam reforming, partial oxidation, autothermal, supercritical water and aqueous-phase reforming processes. Most of the studies were focused on producing hydrogen via steam reforming process using various noble-based metal catalysts. A very few studies are being conducted on supercritical water reforming and partial oxidation. In the case of aqueous-phase reforming process, mainly Pt based catalysts were studied. Although the objective of most of the studies was to produce hydrogen from crude glycerol, a very few studies focused on producing hydrogen from the crude glycerol. Studies on crude glycerol reforming had pointed that the presence of impurities in the crude glycerol caused a catalyst deactivation and impeded the performance of the catalyst. Purification of glycerol produced from the biodiesel production process is still the major hurdle in producing hydrogen. Future studies should focus more on either producing hydrogen using crude glycerol or solving the problems of removing catalysts used in biodiesel production process.

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