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A thermodynamic analysis of hydrogen production by steam reforming of glycerol

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Abstract

Steam reforming of glycerol for hydrogen production involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream affecting final purity of the hydrogen produced. Furthermore, the yield of the hydrogen depends on several process variables, such as system pressure, temperature, and ratio of reactants. The first step to understanding the effects of the aforementioned variables is a complete thermodynamic analysis. In this study, a thermodynamic equilibrium analysis has been performed for the steam reforming process of glycerol over the following variable ranges: pressure 1–5 atm, temperature 600–1000 K, and water-to-glycerol feed ratio 1:1–9:1. The equilibrium concentrations of different compounds were calculated by the method of direct minimization of the Gibbs free energy. The study revealed that the best conditions for producing hydrogen is at a temperature > 900 K, atmospheric pressure, and a molar ratio of water to glycerol of 9:1. Under these conditions methane production is minimized, and the carbon formation is thermodynamically inhibited.
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1. Introduction

After the energy crisis in the 1970s, considerable attention was focused on the development of alternate energy resources. Currently, biomass has received much interest as an alternate energy source because it is renewable and, theoretically, carbon dioxide (CO_2) neutral. Moreover, the use of biodiesel and its production are expected to grow in the future. With increased production of biodiesel, a glut of glycerol ($C_3H_8O_3$) is expected in the world market, and therefore it is essential to find useful applications for glycerol. Currently, glycerol is used in many applications including personal care, food, oral care, tobacco, polymer and pharmaceutical applications. However, explosive growth of biodiesel industry has created a glut in glycerol that has demeaned the market value of this commodity.

Therefore, finding alternative uses for glycerol is important. One such possibility is using glycerol as a source of producing hydrogen. To date only a few studies have been attempted on glycerol reforming for hydrogen production. Dumesic and co-workers [1–3] produced hydrogen from biomass-derived oxygenated hydrocarbons including glycerol in an aqueous phase reforming (APR) process. Czernik and co-workers [4] have produced hydrogen via steam reforming of crude glycerol using a commercial nickel based naphtha reforming catalyst (C11-NK). Recently, Suzuki and co-workers [5] have reported the performance of noble metal based catalyst for glycerol reforming. A catalyst is needed for the steam reformation of glycerol and the knowledge of the conditions promoting carbon formation is essential. Carbon deposition on the surface of the catalyst will result several undesirable reactions and products affecting the purity of the reformation products. Formation of carbon will cause loss of effective surface area, lower the heat transfer rate from catalyst to gas, and plug of the void space within the


Nomenclature

a_{li}	number of gram atoms of element l in a mole of species i	N	total number of moles of all species in the gas mixture
b_l	total number of gram atoms of element l in the reaction mixture	P	pressure
		R	gas constant
G	Gibbs free energy	T	temperature
K	total number of chemical species in the reaction mixture	y_i	mole fraction of species i
		ΔG_i^0	standard Gibbs free energy of formation of species i
M	total number of atomic elements		
n_i	number of moles of species i	μ_i	chemical potential of species i

catalyst [6]. Carbon occurrence may arise due to the decomposition of CO or CH_4 or the reaction of CO_2 or CO with H_2 [7] and detail mechanisms will be discussed later. Conditions that are conducive to as well as that inhibit carbon formation can be determined from a thermodynamic analysis. However, it should be noted that the thermodynamic analysis does not include the effect of the catalysts.

The overall reaction of hydrogen production by steam reforming of $C_3H_8O_3$ is given as

$$C_3H_8O_3(g) + 3H_2O(g) \rightarrow 7H_2(g) + 3CO_2(g). \tag{1}$$
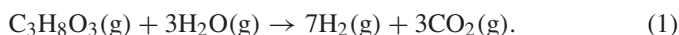
Although few studies on glycerol reforming for hydrogen production have appeared, a thermodynamic analysis has not been carried out. Steam reforming of glycerol for hydrogen production involves complex reactions. As a result, several intermediate byproducts are formed and end up in the product stream affecting the final purity of hydrogen produced. Furthermore, the yield of the hydrogen depends on several process variables, such as system pressure, temperature, and water-to-glycerol feed ratio (WGFR). The first step to understanding the effects of the aforementioned variables is a complete thermodynamic analysis. From this study, ideal reaction conditions for the steam reforming reaction of glycerol to maximize hydrogen yield and minimize undesirable products can be determined.

The aim of this study is to analyze the production of hydrogen and other compounds and the effects of the process variables (temperature, pressure, and WGFR). The equilibrium concentrations of different compounds were calculated by a direct minimization of G. This analysis has been performed for the steam reforming process of glycerol over the following variable ranges: pressure 1–5 atm, temperature 600–1000 K, and WGFR 1:1–9:1.

2. Methodology

If the pressure and the temperature of the system are constant, the equilibrium of the system is given as follows [8]:

$$dG = \sum_{i=1}^{K} \mu_i \, dn_i. \tag{2}$$

The objective is to find the set of n_i's which minimize the value of G. This can be solved in two ways [9]: (i) stoichiometric

and (ii) non-stoichiometric thermodynamic approaches. In the stoichiometric approach the system is described by a set of stoichiometrically independent reactions, and they are typically chosen arbitrarily from a set of possible reactions [10]. On the other hand, in a non-stoichiometric approach the equilibrium composition is found by the direct minimization of the Gibbs free energy for a given set of species [11]. The advantages of non-stoichiometric approach over the stoichiometric approach are as follows [7]: (a) a selection of the possible set of reactions is not necessary, (b) no divergence occurs during the computation, and (c) an accurate estimation of the initial equilibrium composition is not necessary. The non-stoichiometric approach has been used in this study.

From Eq. (2), we can write

$$G = \sum_{i=1}^{K} \mu_i n_i. \tag{3}$$

In order to find the n_i that minimize the value of G, it is necessary that the values of n_i satisfy the elemental mass balances, i.e.,

$$\sum_{i=1}^{K} a_{li} n_i = b_l, \quad l = 1, \ldots, M. \tag{4}$$

Eq. (3) can be further expressed as [11,12]

$$G = \sum_{i=1}^{K} n_i \Delta G_i^0 + RT \sum_{i=1}^{K} n_i \ln y_i + RT \sum_{i=1}^{K} n_i \ln P. \tag{5}$$

At low pressure and high temperature, the system can be considered as ideal [11,12]. The objective function (5) is minimized using Mathcad version 11 [13]. It is also solved by the Lagrange's multiplier method using Mathcad version 11 while satisfying the elemental mass balances as given in Eq. (4). The results are found to be the same from both methods. We considered the possible products from glycerol steam reforming to be hydrogen (H_2), methane (CH_4), carbon monoxide (CO), CO_2, unreacted water and $C_3H_8O_3$, and carbon (C). Three elements carbon, hydrogen (H), and oxygen (O) are contained in all the products considered in this study, and therefore only C, H, and O are used for elemental mass balance. Total Gibbs free energy is considered to be independent of carbon, since solid carbon's free energy of formation is zero, and it has no

vapor pressure [12]. Therefore, carbon is included only in the elemental constraints but not in the objective function. As entry data the program needs pressure, temperature, number of compounds, number of atoms, values of the Gibbs free energy of formation, and initial guesses for n_i's in the equilibrium. Thermodynamic data were obtained from Lide [14], Yaws [15], and Rossini [16].

3. Results and discussion

Production of hydrogen and other compounds at different temperatures, WGFRs, and pressures has been analyzed. The steam reforming of glycerol produces H_2, CH_4, CO, CO_2, and C, together with the unreacted water and glycerol. Only these compounds were included in the study because they are the primary products formed in the steam reforming of glycerol [5,17]. Over the temperature, pressure, and WGFR ranges analyzed, the conversion of glycerol was always greater than 99.99%, and it can be considered that the conversion was complete.

3.1. Hydrogen production

Fig. 1 depicts the hydrogen moles and molar fraction at different temperatures and WGFRs. As can be seen from Fig. 1(a), the number of moles of hydrogen increases with increasing temperature. Similarly, the number of moles of hydrogen increases with the increasing WGFRs, and increases with decreasing pressure (see Fig. 2(a)). The effect of the pressure on the glycerol steam reforming process is found to be consistent with methanol and ethanol steam reforming processes [6,7,12]. The molar fraction of hydrogen is found to be higher in case of low WGFRs. This is mainly due to the significant amount of water present in the product at high WGFRs. The unreacted water reduces the molar fraction of hydrogen but not necessarily the quantity. The greatest quantity of hydrogen is produced at excess water at all temperatures. The best conditions to produce hydrogen will be with excess water if the purification problems can be overcome. The upper limit

of the moles of hydrogen produced per mole of glycerol is 6 at 960 K, WGFR = 9:1, and $P = 1$ atm vs the stoichiometric value of 7. At higher WGFRs, i.e., 9:1 and 6:1, the number of moles of hydrogen produced at 1000 K is lower than in 950 K. The number of moles of hydrogen is at its maximum at 960 K and decreases thereafter in both cases. A similar observation was made by Semelsberger and Borup [18] in dimethyl ether steam reforming. Moles of hydrogen decrease together with CO_2 at temperatures >960 K, and at the same time, moles of CO and water increase. Perhaps, this can be explained by the following equation:

$$CO_2(g) + H_2(g) \leftrightarrow CO(g) + H_2O(g). \tag{6}$$
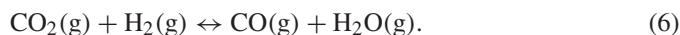
3.2. Methane production

CH_4 competes against H_2, and obviously CH_4 is not a desirable product in the case of H_2 production. Fig. 3 shows the moles of methane and the methane molar fraction as a function of temperature. CH_4 production decreases when the temperature and the WGFR increase. Molar fraction of CH_4 also decreases with the increase in temperature and WGFR. However, higher pressure favors the formation of CH_4 (see Fig. 2(b)). At higher WGFRs, i.e., 9:1 and 6:1, and at higher temperatures (> 950 K), the formation CH_4 is almost inhibited. As the temperature increases, moles of water and CH_4 decrease with increasing CO, CO_2, and H_2. This can be attributed to the methane steam reaction to produce CO or CO_2 and H_2 as given by the following equations [6]:

$$CH_4(g) + 2H_2O(g) \leftrightarrow CO_2(g) + 4H_2(g), \tag{7}$$

$$CH_4(g) + H_2O(g) \leftrightarrow CO(g) + 3H_2(g). \tag{8}$$
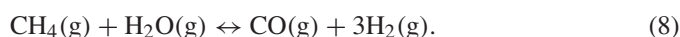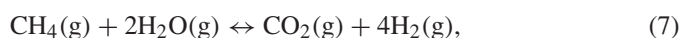
However, at WGFR 1:1 the CH_4 formation is lower compared to other feed ratios analyzed in the study. This can be due to the significant amount of carbon formation (see Fig. 5). Although, CH_4 formation is low at low WGFR, the molar fraction is higher than other feed ratios analyzed in the study. As can be seen
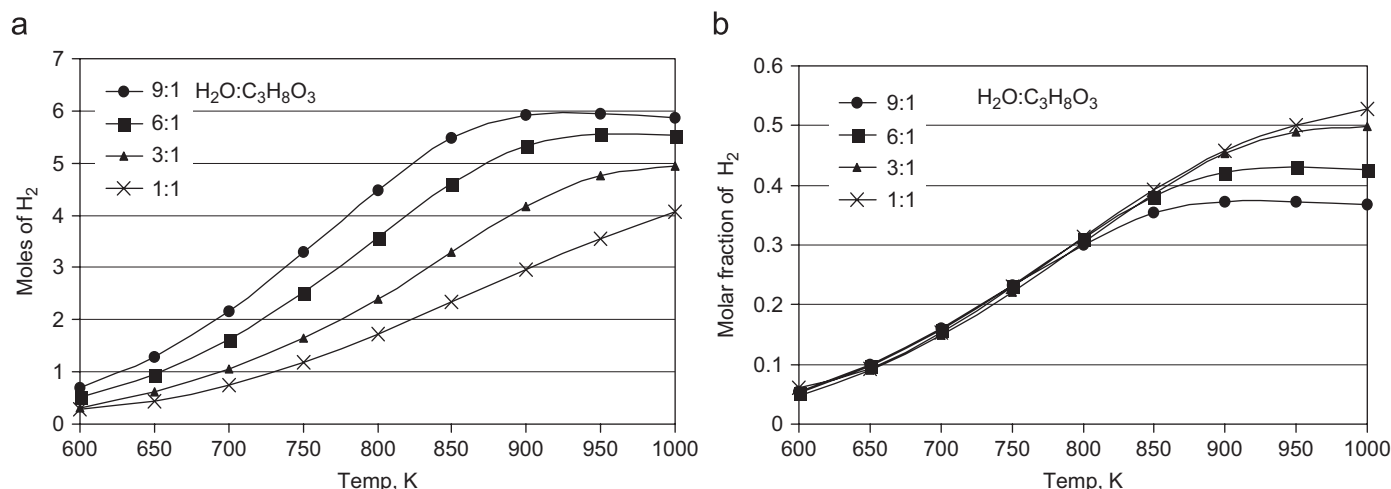

Fig. 1. (a) Hydrogen moles vs temperature at different WGFRs at $P = 1$ atm, (b) mole fraction of hydrogen vs temperature at different WGFRs at $P = 1$ atm.
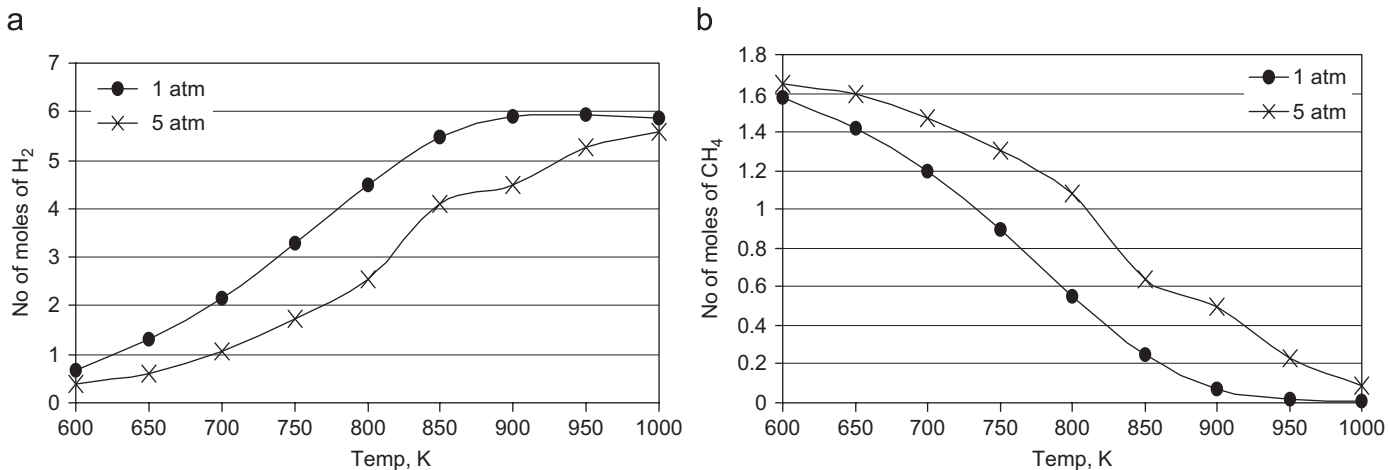
a

b

Fig. 2. (a) Hydrogen and (b) methane moles produced at selected pressure and WGFR = 9:1.
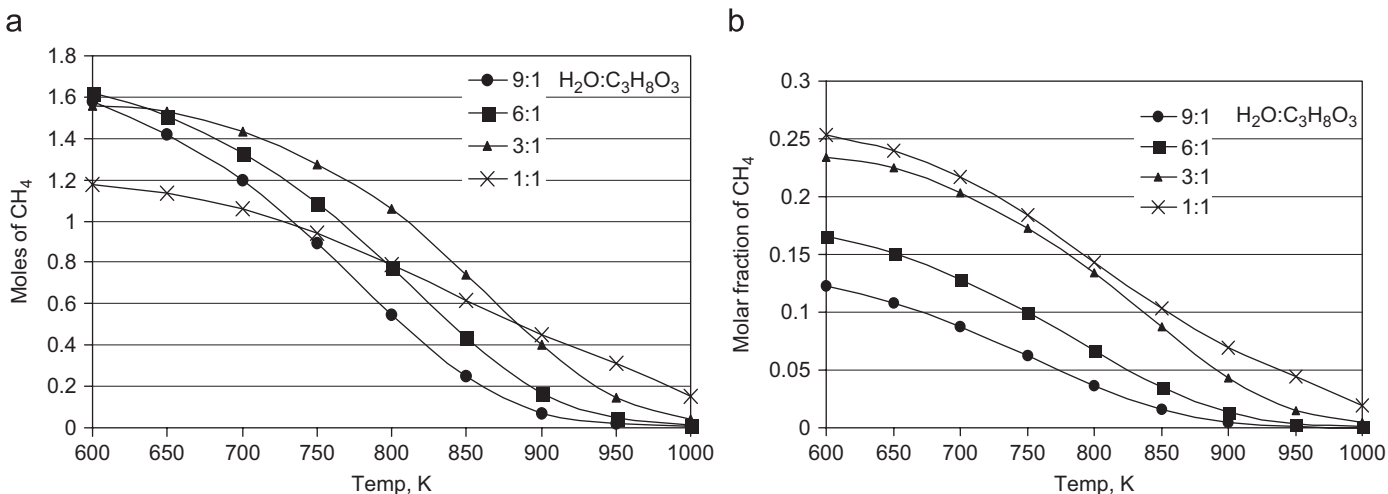
a

b

Fig. 3. (a) Moles of methane vs temperature at different WGFRs at $P = 1$ atm, (b) mole fraction of methane vs temperature at different WGFRs at $P = 1$ atm.
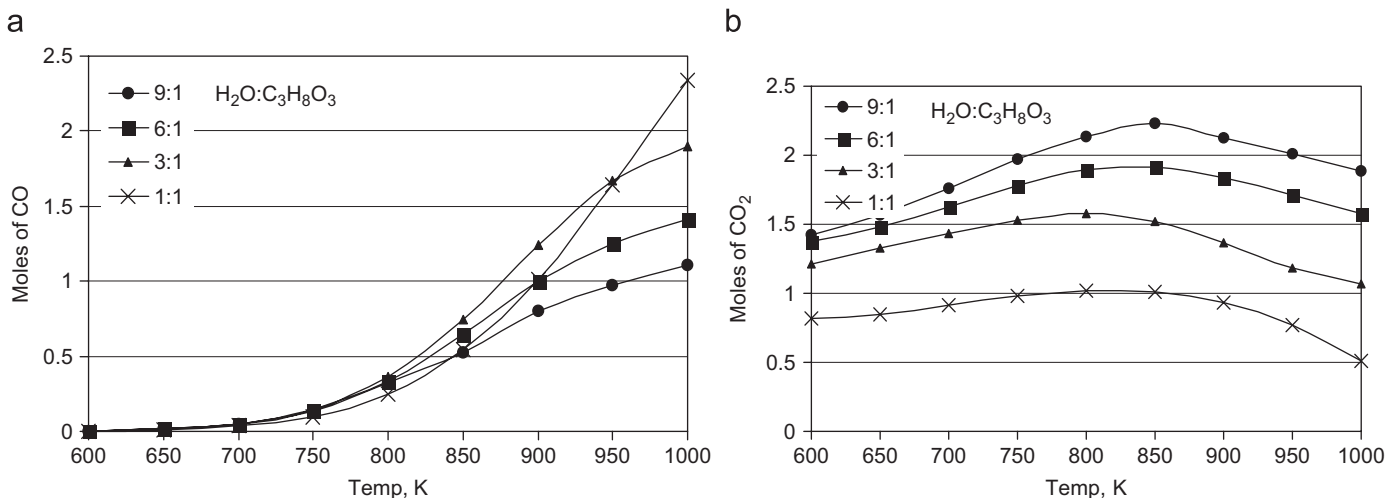
a

b

Fig. 4. (a) Moles of CO vs temperature at different WGFRs at $P = 1$ atm, (b) moles of CO_2 vs temperature at different WGFRs at $P = 1$ atm.
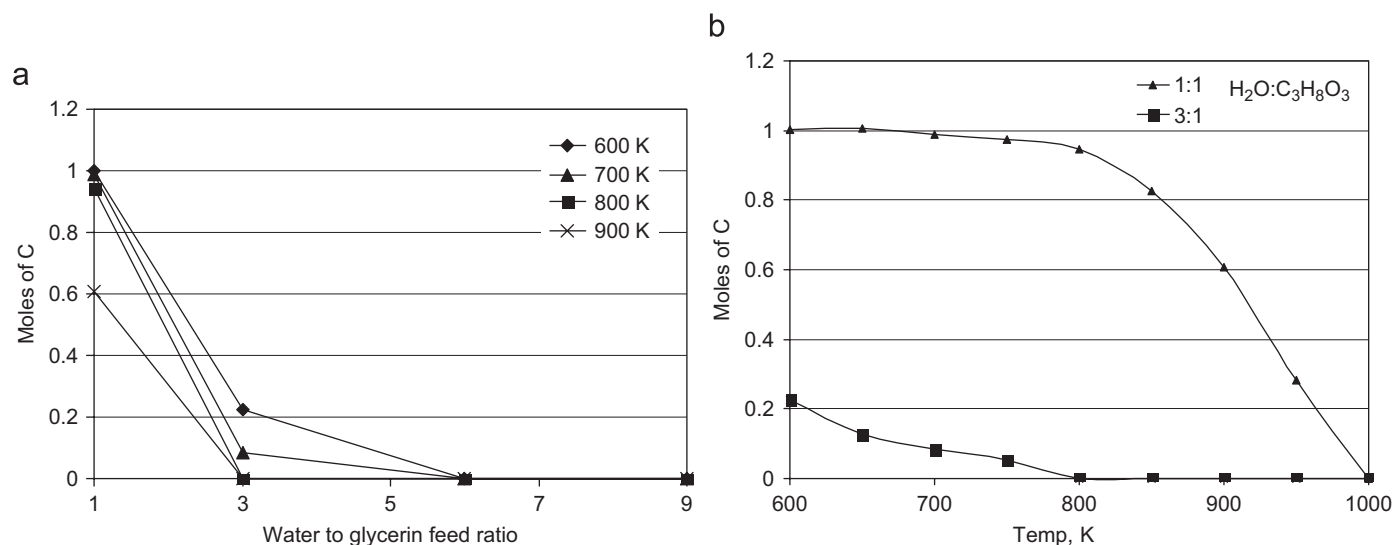
Fig. 5. (a) Moles of carbon formation at different WGFRs at selected temperatures at $P = 1$ atm, (b) moles of carbon formation at different temperatures at selected WGFRs at $P = 1$ atm.

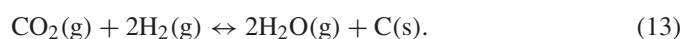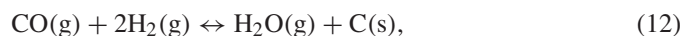from Fig. 3(b), as we increase temperature and WGFR, mole fraction of CH_4 decreases.

3.3. Carbon monoxide and carbon dioxide production

Oxygenated compounds CO and CO_2 are considered impurities because they do not compete against H_2. Fig. 4 shows the number of moles of CO and CO_2 at different temperatures under selected WGFRs. Number of moles of CO increases with the increase in temperature but decreases with the increasing WGFR. However, the number of moles of CO_2 increases with increasing temperature, goes through maximum at around 850 K, and then decreases at higher temperatures. This behavior may be attributed to the reformation of CH_4 with CO_2 (Eq. (9)) [19]

$$CH_4(g) + CO_2(g) \leftrightarrow 2CO(g) + 2H_2(g). \tag{9}$$
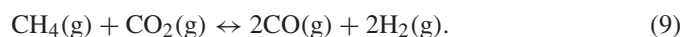
3.4. Carbon production

The possible reactions that can be attributed to carbon formation are given as follows:

$$2CO(g) \leftrightarrow CO_2(g) + C(s), \tag{10}$$

$$CH_4(g) \leftrightarrow 2H_2(g) + C(s), \tag{11}$$

$$CO(g) + 2H_2(g) \leftrightarrow H_2O(g) + C(s), \tag{12}$$

$$CO_2(g) + 2H_2(g) \leftrightarrow 2H_2O(g) + C(s). \tag{13}$$

As discussed earlier, the coke formation is not desirable in the steam reforming process. Fig. 5 shows the range of the conditions under which the solid carbon formation is possible. At 1000 K no carbon is formed at any WGFR. At WGFRs 6:1 and 9:1, carbon formation was thermodynamically inhibited at any temperature analyzed in this study. While

increasing WGFRs from 1:1 to 3:1, carbon formation drops significantly.

4. Conclusion

A thermodynamic analysis for hydrogen production by steam reforming of glycerol has been performed. The number of moles of hydrogen produced is calculated based on minimizing the Gibbs free energy. High temperatures, low pressures, and high WGFRs favor the hydrogen production. The study revealed that the best conditions for producing hydrogen is at a temperature > 900 K and a molar ratio of water to glycerol of 9:1. Under these conditions methane production is minimized, and carbon formation is thermodynamically inhibited. The upper limit of the moles of hydrogen produced per mole of glycerol is 6 vs the stoichiometric limit of 7. Although water-rich feed increases the hydrogen production, a significant amount of unreacted water is resulted in the products. The behavior of this system is very similar to that of steam reforming of ethanol.

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