

Glycerol steam reforming for production of hydrogen ethylene and ethane: Thermodynamic Analysis

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ABSTRACT

Thermodynamic equilibrium for glycerol steam reforming to hydrogen, carbon dioxide, carbon monoxide, methane, ethylene and ethane was investigated using Gibbs free energy minimization method. 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: temperature 600–1000 K, and water-to-glycerol feed ratio 2-10%. 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 >600 oC, atmospheric pressure, and a molar ratio of water to glycerol of 10%. Under these conditions methane production is minimized, and the carbon formation is thermodynamically inhibited.

KEY WORDS: *Phenol Steam Reforming, Hydrogen Production, Thermodynamic Analysis.*

1.0 INTRODUCTION

The last century witnessed the rise of the petroleum-based chemistry and the exploitation of fossil resources for the production of energy and chemicals. Nevertheless the diminishing availability of these resources, together with the environmental issues related to greenhouse gas emissions, renders the birth of a new chemical industry essential (Nichele et al., 2012).

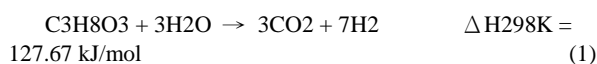
Hydrogen is considered as the future energy vector (Calles et al., 2009), because it is clean and carbon-free and it can be used directly by either thermal combustion or converted into electrical energy by means of fuel cells (Benito et al., 2007). Currently hydrogen is produced from fossil fuels, so the amount of carbon dioxide formed during its production is the same as that formed by direct combustion of these fuels (Czernik et al., 2002). To reduce effectively the greenhouse effect and the global warming, hydrogen should be produced from renewable resources. In this context glycerol has emerged as a promising source of hydrogen, because it has a high hydrogen content and it is safe and non toxic (Pompeo et al., 2010); moreover glycerol is the main by-product (approximately 10 wt%) in biodiesel production from transesterification of vegetable oils extracted from biomass (Haas et al., 2006), so its employ would be highly desirable for several reasons. First of all, the expected increase in biodiesel production will cause a glut of waste glycerol, whose disposal will rise even further the price of biodiesel itself; it is then essential to find useful applications for this by-product. Besides that, glycerol is a cheap and renewable source of hydrogen, so its employ for hydrogen production would be advantageous from both the economical and environmental point of view.

It has already been shown, thermodynamically, hydrogen can be generated from glycerol steam reforming (SRG) (Wang et al., 2008), dry reforming (DRG) (Wang et al., 2009), autothermal reforming (ATR) (Wang et al., 2009), partial oxidation (POG) (Rennard et al., 2009) and dry autothermal reforming (DATRG) (Kale and Kulkarni, 2010). POG and ATR processes have the

merit of fast start-up time because of the exothermic nature of the oxidation reaction. However, the steam reforming process provides the higher hydrogen yield and lower side-reactions rate.

A gas phase steam reforming of glycerol was also studied. Adhikari et al. (Adhikari et al., 2007) analyzed the effect of process variables for glycerol steam reforming by the direct minimization of Gibb free energy. They found that the best condition for producing hydrogen is at the temperature of higher than 900 K, atmospheric pressure, and the molar ratio of water to glycerol of 9.

However, most of these studies focused on different reactants (e.g. glycerol, CO₂ and/or H₂O) in reforming reactions. Only Ding et al. (Chen et al., 2009) reported adsorption-enhanced steam reforming of glycerol, which combined glycerol steam reforming with in situ removal of CO₂. Their results, based on a thermodynamic analysis, showed the maximum number of moles of hydrogen that is produced can be increased from 6 to 7, which can be explained by the Le Chatelier's principle through the following overall reaction:



H₂, CH₄, CO, CO₂, and C were the total product of previous study (Hirai et al., 2005; Soares et al., 2006; Adhikari et al., 2007). However in addition to the mentioned products, in this work products such as C₂H₄ and C₂H₆ was also calculated. 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 aim of this study is to analyze the production of hydrogen and other compounds and the effects of the process variables such as temperature and water-to-glycerol feed ratio (WGFR) with considering new products such as C₂H₄ and C₂H₆ which is the main finding of the current work. 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: temperature 100–1200 oC and WGFR 2-10%.

2.0 METHODOLOGY

Aspen plus 8.6 software has been used for the analysis. The R-Gibbs reactor with Peng–Robinson property method has been chosen for the thermodynamic analysis. Glycerol is the main component with the maximum composition of the mixture chosen to simulate the reforming of the glycerol steam reforming. C₂H₄, C₂H₆, CH₄, CO, CO₂, and H₂ were measured as the reforming based products on experimental result for Aspen Plus code requirement of product definition. The glycerol concentration and reaction temperature as a part of reactants condition must be stated. The input parameter set in the steam reforming is because the reactor temperature in the steam reforming for thermodynamic analysis is controlled by external heat transfer to the reactor and not the reactor itself (Seo et al., 2002). The range

of 100-1200 oC and 2-10% were varied for temperature and glycerol concentration respectively and the result was shown by molar fractions of gas products.

3.0 RESULTS

Production of hydrogen and other compounds at different temperatures and WGFRs has been analyzed. The steam reforming of glycerol produces C₂H₄, C₂H₆, CH₄, CO, CO₂, and H₂ together with the unreacted water and glycerol. Over the temperature 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 Ethylene and Ethane production

Fig. 2 (a) depicts the ethylene moles and molar fraction at different temperatures and WGFRs. As can be seen from this figure, the number of moles of ethylene increases with increasing temperature until 550 and decreases again until 750 °C. Similarly, the number of moles of ethylene increases with the increasing WGFRs. The molar fraction of ethylene is found to be higher in case of high WGFRs. This is mainly due to the significant amount of glycerol present in the product at high WGFRs. The unreacted water reduces the molar fraction of ethylene but not necessarily the quantity. The greatest quantity of hydrogen is produced at highest amount of concentration. C₂H₆ almost shows identical result with C₂H₄. Fig. 2 (b) shows the ethane molar fraction as a function of temperature. C₂H₆ production increases between the temperature range of 100 to 400 °C. Molar fraction of C₂H₆ also increases with the increase WGFR with the highest amount at 10% WGFR.

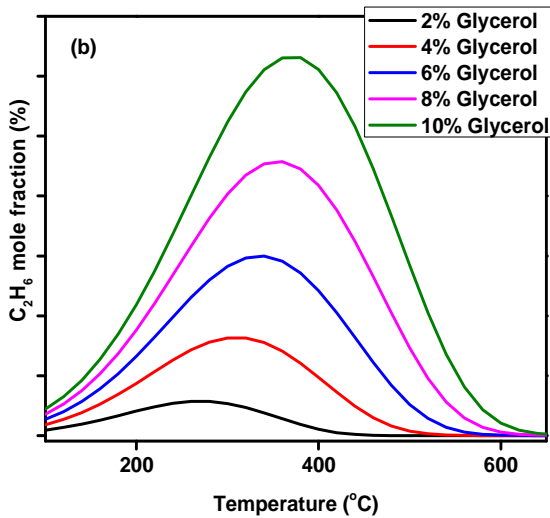


Figure 2. Effect of temperature and glycerol composition on C₂H₄ molar fraction(a) and C₂H₆ molar fraction(b)

1.2. Hydrogen production

Fig. 3 depicts the hydrogen moles and molar fraction at different temperatures and WGFRs. As can be seen from Fig. 3, the number of moles of hydrogen increases with increasing temperature. Similarly, the number of moles of hydrogen increases with the decreasing WGFRs. 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. At higher WGFRs, 10%, the number of moles of hydrogen produced at 1000K is lower than in 600 °C. The number of moles of hydrogen is at its maximum at 600 °C and decreases thereafter in both cases. A similar observation was made by Semelsberger and Borup (Semelsberger and Borup, 2006) in dimethyl ether steam reforming.

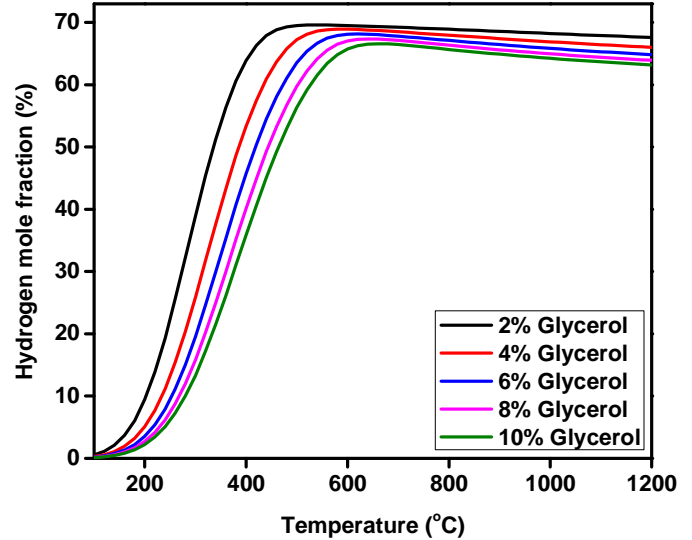
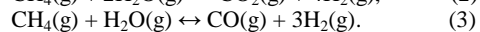
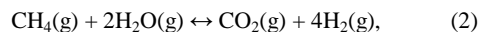


Figure 3 Effect of temperature and glycerol composition on H₂ molar fraction

1.3. Methane production

CH₄ competes against H₂, and obviously CH₄ is not a desirable product in the case of H₂ production. Fig. 4 shows the methane molar fraction as a function of temperature and WGFR. Methane production decreases when the temperature and the WGFR increase. Molar fraction of CH₄ also decreases with the increase in temperature and WGFR. At higher temperatures (>600 °C), the formation CH₄ is almost inhibited. As the temperature increases, moles of water and CH₄ decrease with increasing CO, CO₂, and H₂. This can be attributed to the methane steam reaction to produce CO or CO₂ and H₂ as given by the following equations (Amphlett *et al.*, 1981):



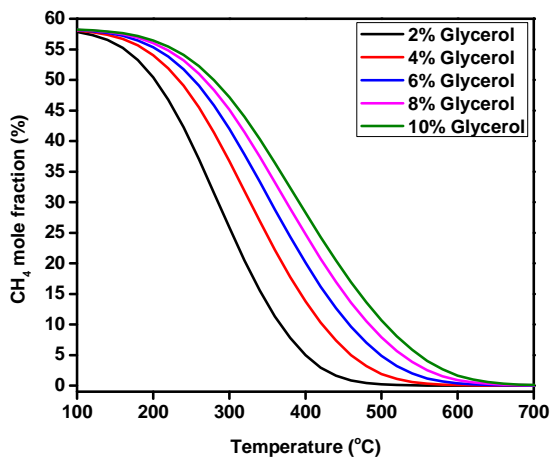


Figure 4 Effect of temperature and glycerol composition on CH₄ molar fraction

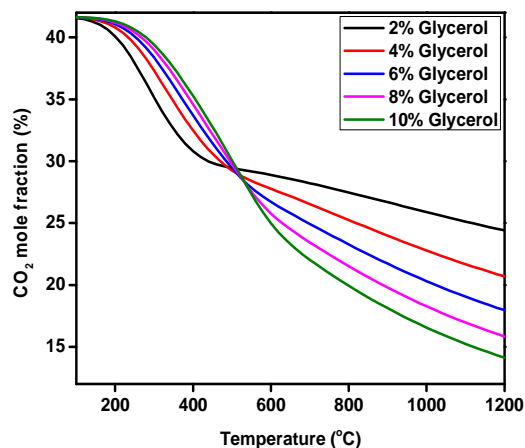


Figure 5 Effect of temperature and glycerol composition on CO and CO₂ molar fraction

1.4. Carbon monoxide and carbon dioxide production

1.5.

Oxygenated compounds CO and CO₂ are considered impurities because they do not compete against H₂. Fig. 5 shows the number of moles of CO and CO₂ 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 smallest number of moles of CO₂ was at lowest WGFR (2%) but this occur became reverse after 550 oC untill the highest amount of temperature. This behavior may be attributed to the reformation of CH₄ with CO₂ (Eq. (4)) (Fatsikostas *et al.*, 2002):



3.0 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, atmospheric pressure and high WGFRs favor the hydrogen production. The study revealed that the best conditions for producing hydrogen is at a temperature >600 oC and a molar ratio of water to glycerol of 9:1. Under these conditions methane production is minimized, and carbon formation is thermodynamically inhibited. 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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