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Thermodynamic Analysis of Hydrogen Production from Ethanol-Glycerol Mixture through Steam and Dry Reforming

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Abstract

Thermodynamic properties of ethanol-glycerol steam and dry reforming have been studied with the method of Gibbs free energy minimization for hydrogen production. Equilibrium compositions were determined as a function of H_2O/ethanol-glycerol molar ratios (WEG)(1:1-12:1) for ethanol-glycerol steam reforming and CO_2/ethanol-glycerol molar ratios (CEG)(1:1-12:1) for ethanol-glycerol dry reforming where ethanol-glycerol is 1:1; reforming temperatures at 573-1273 K and 1 bar pressure. Production trends for H_2, CO, CO_2 and C were compared between both steam and dry glycerol reforming. Steam reforming (WEG 1:1) produced the highest H_2 (4.2 kmol) at 1173K. Dry reforming produced higher CO and CO_2 compared to steam reforming. Higher WEG and CEG ratio did not encourage hydrogen formation. Carbon formation could be thermodynamically inhibited better when steam reforming is employed.

Keywords: Ethanol-Glycerol Mixture; Dry Reforming; Steam Reforming; Hydrogen Production

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1. Introduction

The recent global increase in energy consumption and environmental pollution elevate the need for cleaner and sustainable fuel. Hydrogen is considered as the most suitable alternative for future energy to reduce the dependence on fossil fuels and carbon emissions. Currently, hydrogen is produced from hydrocarbon reforming and electrolysis processes [1]. Both processes are practical but involved high processing cost due to the expensive feed price. Hence, a more reliable cheaper option to attain hydrogen is required, thus leading to new processes which are more environmentally friendly and economical for hydrogen production. Glycerol, a derivative of biodiesel production by transesterification of vegetable oils and acyl acceptor, has been considered a brilliant candidate for hydrogen production. Numerous on-going studies for the catalytic glycerol steam and dry reforming to hydrogen have been reported [1-3]. The combination of glycerol and ethanol, another renewable biomass to produce hydrogen seems to be an interesting yet potential research area to be further explored [2]. Glycerol and ethanol have similar basic hydroxyl properties as they belong in the same functional group. By utilizing renewable biomass such as glycerol and ethanol, sustainable production of hydrogen can be realized.

Production of hydrogen by glycerol steam reforming [3], ethanol steam reforming [5], glycerol dry reforming [6] and ethanol dry reforming [7] have been widely investigated individually. Little is known about the combination of glycerol-ethanol steam and dry reforming towards hydrogen and syngas. The combination of ethanol-glycerol for steam and dry reforming could be an attractive process and it is worth to compare both reforming reactions. Both steam and dry reforming possessed their own strength. Steam reforming employs H_2O which is cheap, clean, easy to store and readily available. On the other hand, dry reforming enable the utilization of undesired CO_2 gas to be converted into synthesis gas, thus reducing the amount of green house gases produced globally. This is a huge benefit and reduces the pressure on carbon capture and storage (CCS) technology in the quest to remove CO_2 from the carbon biosphere cycle [8]. To the best of our knowledge, no literature has been reported regarding the comparison of such feed as ethanol-glycerol steam and dry reforming to hydrogen. Therefore, this thermodynamic analysis could be significant as a first step.

The aim of this work is to understand the possibility of ethanol-glycerol steam and dry reforming for hydrogen production and comparison of both methods by employing total Gibbs free energy minimization method. This study attempts to illustrate the effects of the process variables, H_2O and CO_2 to ethanol-glycerol ratio for steam reforming (WEG) and dry reforming (CEG), towards temperature at 1 bar pressure. The comparative effects toward carbon formation for both reforming were investigated as well.

2. Methodology

The minimization of the total Gibbs energy using HSC Chemistry software version 5.1 taking into account of chemical species involved is the approach of this investigation. The Gibbs program identifies the most stable species mixture and seeks out the phase compositions where the Gibbs energy of the system reaches its minimum at a fixed mass balance, constant temperature and pressure. Species considered in this study were ethanol, glycerol, CO_2 and H_2O as feed. On the other hand, H_2, CO, CO_2 and coke were the reaction products. Reaction products were assumed to be in thermodynamic equilibrium at the exit of the reactor. The total number of moles of the reactants including ethanol-glycerol and H_2O or CO_2 were fixed at 2. The operating temperature range was between 573 and 1273 K while H_2O:ethanol-glycerol (WEG) and CO_2: ethanol-glycerol (CEG) ratios were 1:1, 3:1, 6:1, 9:1 and 12:1. At all conditions, 1 bar pressure was used. Complete conversion of ethanol-glycerol and positive product yields were observed in all the cases, indicating the feasibility of the ethanol-glycerol steam and dry reforming process.

3. Results and discussion

The study was primarily aimed at comparing the hydrogen production from both ethanol-glycerol steam and dry reforming. In addition, the production of carbon monoxide, carbon dioxide and coke were analyzed as well. The formation of hydrogen from ethanol-glycerol steam and dry reforming is illustrated in Fig. 1. Moles of hydrogen produced increases with the temperature. Rapid hydrogen production can be observed from WEG 1:1 and CEG 1:1.