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Thermodynamics Analysis of Hydrogen-Rich Production from Biogas Reforming

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ABSTRACT

Investigating the reforming characteristics and optimal operating circumstances of the biogas reforming reaction for the hydrogen-rich gas generation was the target of this work. Besides, parametric broadcast studies were executed, to increase the hydrogen generation and methane conversion rate, wherein there were the differences of the CH4 flow ratio, steam flow ratio, CO2 flow ratio, and catalyst adding in the reactor. Temperature (100–1000 oC), pressure (1–20 atm) and steam to fuel (S/F) ratio (1–9) were three general varieties of settings to discover equilibrium composition of the products. S/F ratio indeed was effective on hydrogen generation, through the whole range of temperature examination. On the other hand, hydrogen mole fraction dropped by developing the pressure starting 1 to 20 atm. At varied S/F ratios, temperatures and pressures, the solid carbon formation does not found a problem during the biogas reforming. When the temperature reach 750 oC, the conversion of methane was maximized in different pressure and S/F ratio. The maximum hydrogen mole fraction was obtained in S/F ratio of 9 at atmospheric pressure, however; by increasing the pressure to 20 atm, hydrogen decreased significantly. Energy consumption was increasing by rising the temperature in both different pressure and S/F ratio for all gases.

KEY WORDS: *Hydrogen; Biogas Reforming; Aspen Plus*

1.0 INTRODUCTION

There has been a considerable attention recently over the growing transpiration of greenhouse gases involving CO2 (resulted from fossil fuel burning) and CH4 (resulted from natural gas, oil and coal mines processes). Furthermore, both methane and carbon dioxide are unnaturally resulted from anaerobic ingestion operations which known as ''biogas''. Biogas typically contains 50–80 % CH4, and 20–50 % CO2 and small quantity of other gases e.g. NH3, H2S and H2 [1-3]. In biogas, the methane and carbon dioxide contents can differ relying on the operating conditions and the features of raw material of biomass [3]. Nowadays, as an additional fuel for production of steam in refinery and electricity production, biogas that made by human is extensively employed. Conversely, because of the existence of CO2, the custom usage of biogas can afford two problems; first, participates to its straight emission into the air and second, reduces the heating amount of biogas. For this reason, the reforming of biogas, or the segregation of CO2 from biogas, is of great importance [4-9].

For the combination gas or syngas generation (CO + H2), the biogas reforming can be measured to be comparable to CH4 and CO2 reforming which is employed as an essential feed in many refinery operations e.g. methanol or by the so-called Fischer–Tropsch combination to liquid fuel. Since the emission of CO2 can be diminished with a more appreciated yield of syngas, It is very exciting to employ biogas for straight CH4 reforming with CO2 [10].

To our knowledge, there is limited topic in previous studies experimentally work on biogas reforming [11-14]; whereas, for the first time the thermodynamics modelling of hydrogen-rich production from biogas reforming in R-Gibbs reactor was theoretically investigated in this study. The influence of temperature on equilibrium product composition and energy

consumption and also the influence of operational parameters in the biogas reforming, such as different temperature, pressure and S/F ratio was considered in this investigation.

2.0 MODEL AND TEST METHOD

Aspen Plus 8.8 software has been applied for the calculations of Gibb's free energy to measure the equilibrium combinations. For the reaction calculations this code needs characteristics of the system. The R-Gibbs reactor using the Ideal property technique has been elected for the calculations. To model the biogas reforming, CH_4 and CO_2 with small quantity of H_2S, and water were considered as the feedstock of the reforming. In the existence of steam, these gases were the clean gases observed distinctly at reforming processes.

Apart from the characteristics of the inlet combination and reactants, other factors like the reaction temperature, the pressure, the steam to fuel ratio and the inlet temperature and pressure of the reactants, are of great importance. In the design of a reforming system the usage of thermal energy is an important concern. In steam reforming process it was found that if the temperature of the reactor is controlled at a particular value, the input feed temperature of reactants does not impact the thermodynamic outcomes. The reason is that the temperature of the steam reforming reactor is specified via the outer heat transfer to the reactor [15]. The reactor temperature was given as a feedstock factor for the determination of the thermodynamic computations. Even though to characterize an actual reformer with temperature alterations in the pivotal direction of the catalyst tubes there is a doubt in selecting a particular temperature and between them, equilibrium examination still delivers a truthful approximation of the level of reaction [16]. Reactor temperature varied from 100–1000 oC, pressure from 1 to 20 atm and steam to fuel ratio (S/F) from 1 to 9. The outcomes are shown as molar fractions of the gaseous yields on dry basis.

Reactions below are of interest in this study:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad (2)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (3)$$

3.0 SIMULATION RESULT

3.1 Effect of Temperature in Equilibrium
As revealed in Figure 1, the maximum hydrogen molar fraction is achieved at temperature of 700 oC and a little decline of hydrogen mole fraction happens at T > 700 oC. The CH_4 mole fraction declines with the growth of temperature and reaches to zero at T > 770 oC. It can be resulted that the steam reforming of methane is enhanced with the growing temperature and participates to the creation of H_2. It is worth mentioning that the CO mole fraction

rises at T > 420 oC and CO_2 declines at T > 550 oC. It can be clarified via the improved converse WGSR at high temperatures, which may also afford the decrease of H_2 in this condition. same subtitle or sub-subtitles.

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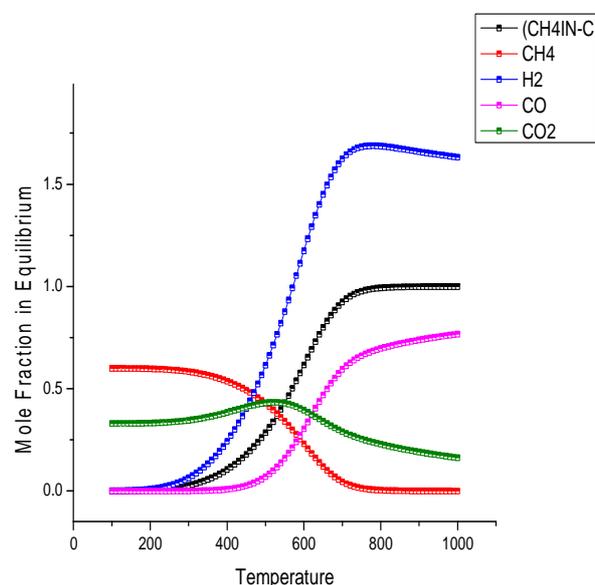

Figure 1: Biogas reforming-Effect of temperature on equilibrium product composition at S/F=5 (C2H2 and Carbon result is not presented due to its relatively small value).

3.2 Effect of Steam to Fuel Ratio (S/F)
In the reforming reaction steam to fuel ratio plays an essential duty which its influence depends on the temperature. Figure 2, shows the molar fraction of the gaseous yields as a function of the steam to fuel ratio and the temperature. Steam to fuel variation has momentous influence on the mole fraction of hydrogen which means that under S/F=9, hydrogen generation has a maximum of 2.3 at 520 oC while at this temperature it is only around 0.5 at the S/F=1 variation (Fig. 2, H2). Increasing S/F from 1 to 9 gives outcomes in 35% growth in mole fraction of hydrogen at 700 oC.

Steam to fuel ratio also impact the methane concentration (Fig. 2, CH4). The highest is the S/F, the lowest is the methane mole fraction at 500 oC. At upper temperatures where reforming and WGSR conquer, the necessity of carbon monoxide on the amount of steam is pretty strong with the uppermost concentration achieved at the smallest S/F (Figure. 2, CO). The production of

carbon monoxide is negligible up to 400 oC, whereas the result of S/F ratio comes to be essential at temperatures upper than 500 oC. The maximum production of carbon dioxide obtained at S/F=9 and the lowest at S/F=1; however, there is significant decrease after T=550 oC for all S/F ratio in the CO2 mole fraction.
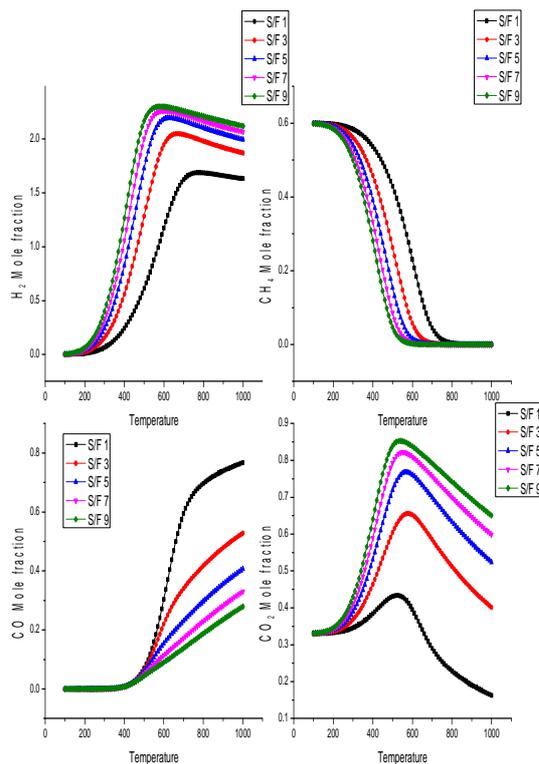

Figure 2: Biogas reforming—effect of steam to fuel ratio on production of hydrogen, methane, carbon monoxide and carbon dioxide composition.

Since the unwanted carbon formation can disable the catalysts affectedly, carbon deposition is an important issue in the (oxygenated) hydrocarbon and biogas reforming to generate hydrogen [17, 18]. However, the carbon deposition section which determined for the reforming of biogas in this study was zero; thus, the figure was ignored due to its low value.

3.3 Effect of Pressure

Apart from reaction temperature and S/F ratio, the influence of pressure on the distribution of the products made by reforming of oxygenates was also explored. The equilibrium compositions at stable S/F=5 and several pressures are offered in Figure 3 as a function of temperature. Pressure moves to an excessive level the

yield distribution in the temperature sort between 500 oC. Hydrogen and methane are the two gases typically impacted via the pressure. Increasing the pressure from 1 to 20 atm gives outcomes in a decline of hydrogen molar fraction at 500 oC from 2.22 to 0.5. Above the same circumstances, methane content drops from 0.4 to zero. The direct relation between hydrogen and methane demonstrates that steam reforming of methane is the foremost route of hydrogen generation. At temperatures upper than 800 oC the influence of pressure is insignificant, because at this level the supply of the yields is mostly specified by water gas shift balance, a reaction with no volume variation. Increased pressure does not favour carbon formation, which leftovers slight above all circumstances observed S/F=5 and temperature 100–1000 oC (not shown). As revealed in Figure.3, there was no important impact on CO molar fraction under all pressures whereas interesting decrease of CO2 at 500 oC from 0.85 to 0.52.

3.4 Energy Consumption

Energy Consumption also is an important role to estimate the cost of the reaction in the real experiment. The influence of this factor is complex by the point that its impact relies on the temperature. Figure 4, shows the energy uses of all gaseous products as a function of the temperature in different S/F ratio and different pressure. The simulation showed that the unit energy consumption decreased at 500 oC as pressure was being increased from 1 to 20 atm. This result can be clarified by the better operation of all gases pressure, which permits the improvement of consistent decrease in the prices. Furthermore, energy prices also reduced if the quantities of water for vaporization reduced [19]. Nevertheless, important decreasing of the energy consumption is owing to increasing S/F ratio in all temperatures. These effects exhibited that the maximum pressure and S/F ratio resulted the smallest consumption of energy.
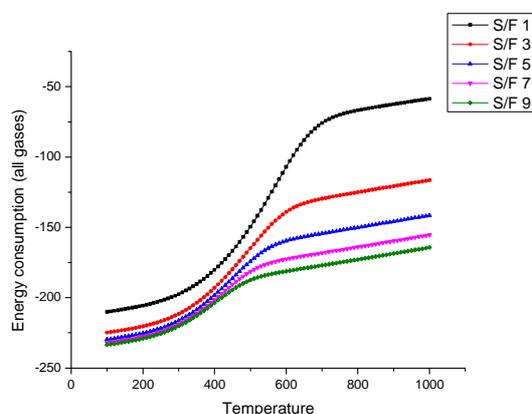
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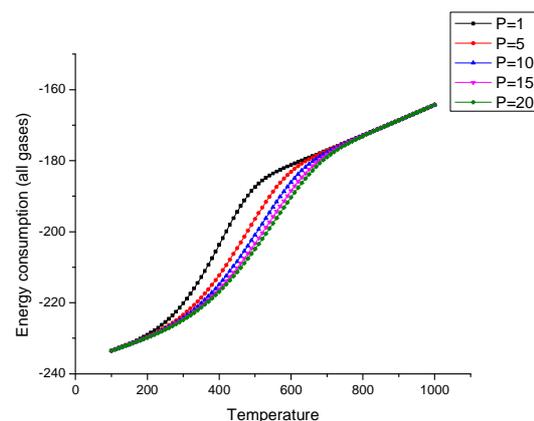
Figure 4: Energy consumption in different pressure (left) and different S/F ratio (right).

4.0 CONCLUSION

Simulation of the biogas reforming, (CH_4 and CO_2 with small amount of H_2S, and water as the products of the reforming) was the focus of this study. Biogas reforming is a potentially feasible path for hydrogen generation. A thermodynamic examination via the ASPEN plus software was showed to identify the circumstances affecting biogas reforming. The biogas product are simply converted even at low temperatures creating a mixture of H_2, CO, CO_2, CH_4, C, C_2H_2, C_2H_4 with changing configuration. Temperature, steam to fuel ratio and pressure are the operating variables which impact to an excessive level of the equilibrium composition. Temperature increase effects the production of hydrogen up to 700 oC where extreme concentration of hydrogen is achieved. The volume of steam to the inlet combination defines to a great extent the hydrogen. The upper is the S/F ratio the greater is the hydrogen concentration and lower methane mole fraction. Best results concerning hydrogen molar fraction are achieved at atmospheric pressure and maximum S/F ratio for all gases. Carbon free operation, C_2H_2 and C_2H_4 is not possible at all temperatures, S/F ratios and pressures. Methane and carbon dioxide are the main product at low temperatures for all simulation product minimizing at 100 oC. Simulations for a complete system at the optimal circumstances (T=700 oC, atmospheric pressure and S/F=9) shows that maximum pressure and S/F ratio resulted the smallest consumption of energy which is the optimal result of this study.

ACKNOWLEDGEMENTS

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