Effect of Pressure, Temperature and Steam to Carbon Ratio on Steam Reforming of Vegetable Oils: Simulation Study

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Abstract—The steam reforming process of vegetable oil was simulated in ChemCad 6.4 to study the effect of temperature, pressure and steam-to-carbon (S/C) ratios on the process. Pressures from 1 to 20 bar and temperatures from 300 to 1000°C were considered with S/C ratios of 3, 6 and 9. The vegetable oil was modelled by triolein and the data show that the main reforming products under the operating conditions used are H2, CO2, CO, CH4 and carbon. Higher H2 production happens at low pressure, high temperatures and high S/C ratios. Lower operating temperatures and pressures must be avoided to prevent significant carbon formation. Higher S/C ratio reduces carbon formation.

Keywords—Pressure, temperature, steam-to-carbon ratio, reforming, vegetable oil

I. INTRODUCTION

Vegetable oils can be subjected to varied treatment processes in order to produce biofuel. Various reports on processes such as vegetable oils transesterification with alcohols for biodiesel production [1-3], cracking [4,5], hydrotreatment [6-8] and steam reforming [9, 10] are available in literature. Marquevich et al. [9-13] have shown that sunflower oil could be satisfactorily converted into hydrogen by steam reforming using commercial based catalysts. They have also indicated that equivalent yields and rates of hydrogen formation can also be obtained with other vegetable oils such as rapeseed oil, corn oil, and soybean used as feedstocks for the process [10]. Most of these studies mainly report kinetic data and very little is known on process thermodynamic equilibrium. The information on a system thermodynamic equilibrium is very important as it can reveal operating conditions that are favourable to the process and hence facilitate better process design. To the best of our knowledge, only few studies [11-13] on thermodynamic analysis of vegetable oils steam reforming process have been reported to date. Yenumala and Maity [11] have reported a thermodynamic analysis on reforming of vegetable oil for the production of hydrogen. They considered the vegetable oils as a mixture of tripalmitin, tristearin and trioleate and used the Gibbs free energy minimization method. They found optimum operating conditions as 875-925K with S/C ratios of 5-6 at atmospheric pressure. Most of the previous studies have considered CO, CO2, H2 and CH4 as the only products for vegetable oil steam reforming and did not report on carbon formation. Information on carbon formation during the reforming process is very useful as it will assist in selecting operating conditions that will minimize catalyst deactivation rate.

This study aims at systematically determining the effect of temperature (400-1000°C), pressure (1-20 bar) and S/C ratio (3-9) on the vegetable oils steam reforming process. In particular the effect of temperature, pressure and SC ratio on the formation of H2, CO, CH4, CO2 and carbon will be established. This will be done by performing a thermodynamic analysis using ChemCad 6.4 simulation package.

II. METHODOLOGY

The simulation of steam reforming of vegetable oils was performed with ChemCad 6.4 simulation package. The feed to the reforming reactor was chosen as 1 000 Kg/h of vegetable oil and mixed with steam to achieve S/C ratios of 3, 6 and 9. The simulation was performed at 1, 5, 10, 15 and 20 bar between 300 and 1000°C. The vegetable oil was modeled by triolein and the reforming process was modeled by Gibbs free energy minimization in ChemCad. The Gibbs reactor model is based on the principal that at chemical equilibrium the total Gibbs energy of the system has its minimum value. By attempting to minimize the total energy of the system, individual equilibrium constants are not considered. Rather, the possible reaction species are noted, and the distribution of these species is established using a general mathematical technique to give a minimum free energy for the system [14]. The selected possible components in the predicted equilibrium product included H2, CO, CO2, alkanes (C1 to C15), olefins (C2 to C15), cyclic hydrocarbons, aromatic compounds, light ketones, alcohols, carboxylic acids and solid carbon. All the selected components with their physical and chemical properties were available in ChemCad 6.4 components database.
III. RESULTS AND DISCUSSION

The simulation of vegetable oil modeled by triolein under the operating conditions used in this study, i.e. S/C ratios of 3, 6 and 9; 1 to 20 bar in the range of 300 to 1000°C predicts the formation of H₂, CO, CO₂, CH₄ and carbon as the major products in agreement with reported experimental studies [4, 10]. The amounts of H₂ produced as a function of reforming temperature and pressure for various S/C ratios are reported in Fig. 1. For all S/C ratios used, the data show a decrease in H₂ formation with an increase in operating pressure. For example for a S/C ratio of 3 (Fig. 1a) and a reforming temperature of 300°C, H₂ production was 14.3, 4.8, 3.1, 2.4 and 2.0 kmol/h at 1, 5, 10, 15 and 20 bar respectively. No significant effect of pressure on H₂ production was observed around 900 and above. Lower operating pressures are therefore the most thermodynamically appropriate for H₂ production by steam reforming of vegetable oils. The data also show that at the same operating pressure, H₂ production increases with the increase in reforming temperature following an S-shape pattern. This increase is less in the 300-400°C temperature range compared to the 400-700°C range where the temperature effect is more pronounced before flattening off at about 700°C and above. In some cases the H₂ production even reached a maximum value and decreased with further increase in temperature. For example with a S/C ratio of 9 (Fig. 1c), maximum H₂ production was reached at ca. 700°C for the data at 1 bar and at ca. 800°C for the data at 5, 10, 15 and 20 bar.

H₂ production is found to increase with an increase in S/C ratio as indicated by the plotted data which slightly move up as the S/C ratio is increased. For example with a S/C ratio of 3 (Fig. 1a), the highest values for H₂ production are about 138 kmol/h compared to 155 and 164 kmol/h for S/C ratios of 6 (Fig. 1b) and 9 (Fig. 1c) respectively.

The CO₂ formation data as function of pressure, temperature and S/C ratios are reported in Fig. 2. CO₂ production increases with an increase in operation pressure and this effect is only observed in the 300-500°C temperature range above which no pressure effect is observed. CO₂ formation increases with an increase in temperature and passes through a maximum around 700°C for all the S/C ratios used. The increase in SC ratio increases the formation of CO₂.

Fig. 3 shows the production of carbon for the various operating conditions used in this study. Operating conditions leading to carbon formation must be avoided as much of possible because of the negative effects that this brings to the reforming process which is usually solid-catalysed. The formed carbon would deposit on the catalyst surface and would cause its deactivation. Carbon formation decreases with the increase in pressure in the 300-800°C temperature range for all the S/C ratios used. For example, for S/C ratio of 6 (Fig. 3b) and a temperature of 400°C, carbon production of ca. 40, 15, 8, 6 and 4 kmol/h are predicted at 1, 5, 10, 15 and 20 bar respectively. This effect is not observed at 800°C and above. The data also show that carbon production decreases with an increase in temperature. They suggest that lower operating temperatures and pressures must be avoided to prevent significant carbon formation. An increase in S/C ratio slightly decreases the carbon formation. For example carbon formation of ca. 42, 40 and 37 kmol/h were predicted at 1 bar and 400°C for S/C ratios of 3 (Fig. 3a), 6 (Fig. 3b) and 9 (Fig. 3c) respectively.

Fig. 1 H₂ formation as function of temperature, pressure and steam to carbon ratio: a) S/C ratio = 3; b) S/C ratio = 6 and c) S/C ratio = 9
The methane formation (Fig. 4) increases with an increase in pressure and decreases with an increase in temperature. Also an increase in S/C ratio slightly decreases the methane formation. For example as it can be observed from the data generated for 20 bar, the methane formation is almost zero about 1000°C for S/C ratio of 3 (Fig. 4a) compared to the equivalent temperatures of 900 and 800°C for S/C ratios of 6 (Fig. 4b) and 9 (Fig. 4c) respectively. This suggests that lower operating pressures, and higher temperatures and S/C ratios must be selected to avoid more methane in the reforming products.

The data in Fig. 4 suggest that pressure has no significant effect on CO formation which increases with temperature (from ca. 400°C) and decreases with the increase in S/C ratio. The highest CO formation was ca. 43, 30 and 23 for SC of 3 (Fig. 5a), 6 (Fig. 5b) and 9 (Fig. 5c) respectively.

If the vegetable oil steam reforming aims at producing H2 or synthesis gas, an optimal combination of conditions minimizing carbon and methane formation, and maximizing H2 and CO formation must be chosen. The understanding of the effect of operating conditions (pressure, temperature and S/C ratios) on H2, CO2, CO, CH4 and carbon formation as discussed in this study is very critical to the optimization study.
Fig. 4 CH₄ production as function of temperature, pressure and steam to carbon ratio: a) S/C ratio = 3; b) S/C ratio = 6 and c) S/C ratio = 9

Fig. 5 CO production as function of temperature, pressure and steam to carbon ratio: a) S/C ratio = 3; b) S/C ratio = 6 and c) S/C ratio = 9

IV. CONCLUSION

The effect of temperature, pressure and S/C ratios on vegetable oil steam reforming process has been studied using process simulation in ChemCad 6.4. The data show that the main reforming products under the operating conditions used are H₂, CO₂, CO, CH₄ and carbon. Higher H₂ formation happens at low pressure, high temperatures and high S/C ratios. Lower operating temperatures and pressures must be avoided to prevent significant carbon formation. Higher S/C ratio reduces carbon formation.

REFERENCES


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