Combined Partial Oxidation and Carbon Dioxide Reforming Process: A Thermodynamic Study

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Abstract: Problem statement: CO_2 reforming is one of the methods to utilize a greenhouse gas to produce syngas, an important feed for methanol and Fischer-Tropsch synthesis. However, CO_2 reforming is strong endothermic reaction requiring large amount of supplied energy. Partial oxidation, an exothermic reaction, is combined with CO_2 reforming to serve the energy requirement. Thus, the optimum ranges of O_2 and CO_2 fed to the process corresponding to feedstock are needed to find. Moreover, one of the most important problems found in this process is solid carbon formation. Therefore, the operating range in which the carbon formation can be avoided is also required to study. **Approach:** In this study CH_4 was used as feedstock. The optimum rage of O_2 and CO_2 fed to the process was found by using thermodynamic equilibrium method based on minimization of Gibbs free energy. The Lagrange multiplier method was conducted to form the equations and they were solved by the Newton-Raphson method. The solid carbon formation zone was also simulated. **Results:** The simulation showed that higher reaction temperature caused higher CH_4 and CO_2 conversions. Syngas production increased with increasing temperature. Operating the process with high temperature or high O_2/CH_4 and CO_2/CH_4 rations could eliminate solid carbon formation. Increase of O_2/CH_4 ration higher than 0.1 led decreasing syngas while increase of CO_2/CH_4 ration caused increasing H_2 and CO. However, when CO_2/CH_4 ration was higher than 0.85, increasing CO_2/CH_4 ration showed insignificant change of syngas concentration. **Conclusion:** The combined partial oxidation and CO_2 reforming of method should be operated with reaction temperature of 1050 K. The optimum range of $CH_4:CO_2:O_2$ for this process is 1: 0.85-1.0:0.1-0.2.

Key words: Partial oxidation, carbon dioxide reforming, syngas production, solid carbon formation, greenhouse gases, increasing temperature, Fischer-Tropsch, thermodynamic study

INTRODUCTION

CO_2 is one of the most important greenhouse gases produced from combustion process (Al-Mutairi and Koushki, 2009; Bundela and Chawla, 2010; Khademi *et al.*, 2009). It can be utilized as reactant for hydrocarbon reforming to produce synthesis gas (also called syngas). The syngas, which consists of H_2 and CO, is a feedstock for the methanol and Fischer-Tropsch syntheses (Tsang *et al.*, 1995; Froment, 2000). CO_2 reforming process is sometime called dry reforming, which is strong endothermic reaction. Thus, it requires large amount of heat supplied to the process. CO_2 reforming has been widely investigated (Edwards, 1995; Wurzel *et al.*, 2000; Nagaoka *et al.*, 200; Li *et al.*, 2004). Both equilibrium model simulation and experiment were conducted by Haghighi *et al.* (2007) to study CO_2 reforming of CH_4. The result has been presented that equilibrium H_2/CO ratio at high temperature was about 1.0. However, at a specific temperature, higher pressure caused lower H_2/CO ratio.

Moreover, the authors indicated that a deposited carbon was also one of the major products obtained from CO_2 reforming. For coke (carbon) formation, it has been mentioned by many researchers that it is an important problem of the dry reforming reaction, because it leads to catalyst deactivation (Wurzel *et al.*, 2000; Nagaoka *et al.*, 200; Shamsi and Johnson, 2003).

Partial oxidation of hydrocarbon can be explained as a sub-stoichiometric combustion process and it is an exothermic reaction. The thermodynamic equilibrium of ethanol partial oxidation has been studied by Wang and Wang (2008). At complete conversion, 86.28-94.98% yield of hydrogen and 34.69-38.64% concentration of CO could be achieved at 1070-1200 K. Partial oxidation of methane to hydrogen and carbon monoxide over a Ni/TiO_2 catalyst has been experimentally investigated (Wu *et al.*, 2005). Use of fixed-bed reactors for the partial oxidation has shown a drawback of hot spot (Puwanto and Muharam, 2006). Hot spot formation is a common problem found in catalytic partial oxidation (Naito *et al.*, 2008) and it can cause deactivation of catalysts.

From the above information, the idea to combine the partial oxidation and CO_2 reforming processes is presented to solve the high energy requirement problem of CO_2 reforming. Heat produced from partial oxidation process is supplied to CO_2 reforming process. Therefore, the combined process is a thermally self-sustaining and may not need to consume external thermal energy. The combination of exothermic and endothermic reactions is called autothermal reaction. The combined steam reforming and partial oxidation, which is the well known hydrogen production process, is an example of the autothermal reaction.

In this study, the partial oxidation process combined with CO_2 reforming process is investigated through thermodynamic equilibrium model. Methane is chosen as feedstock. The effect of reaction temperature on CH_4 and CO_2 conversions is focused. Moreover, the reaction temperature is varied to observe the change of concentration of products. The formation of coke (carbon) is an important issue examined in this study. The effects of CO_2/CH_4 and O_2/CH_4 ratios on syngas production are also presented. Finally, the optimum condition to syngas yield is suggested.

MATERIALS AND METHODS

Chemical reactions: The major gas species considered in this study are CH_4, CO, CO_2, H_2 and H_2O. Solid carbon is also observed. The partial oxidation combined with CO_2 reforming of methane is involved with the predominance chemical reactions, which are listed below:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{1}$$

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \tag{2}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{3}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \tag{4}$$

$$CH_4 + C_2O \leftrightarrow 2CO + 2H_2 \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6}$$

$$2CO \leftrightarrow CO_2 + C \tag{7}$$

$$CH_4 \leftrightarrow 2H_2 + C \tag{8}$$

The chemical equilibrium model: The chemical equilibrium model can be categorized into 2 types. The first one is equilibrium model based on equilibrium constants. It is known as the stoichiometric model. This method requires the information of chemical reactions occurring in the process. Another kind of equilibrium model is non-stoichiometric model, so called the minimization of Gibbs free energy method in which no chemical reactions are involved. The equilibrium model used in this study is developed following the method discussed in Ref (Jarungthammachote and Dutta, 2008; Jarungthammachote, 2009). At equilibrium state, the total Gibbs free energy of the system is minimized. The total Gibbs free energy of system is defined as:

$$G^t = \sum_{i=1}^{N} n_i G_i = \sum_{i=1}^{N} n_i \mu_i \tag{9}$$

Where:

n_i and μ_i = The number of moles and the chemical potential of species i, respectively

G_i = The partial molar Gibbs free energy of species i

If all gases are assumed as ideal gas and all reactions take place at one atmospheric pressure. The chemical potential of species i can be presented by:

$$\mu_i = \Delta \bar{G}_{f,i}^o + RT \ln(y_i) \tag{10}$$

Where:

R and T = The universal gas constant and temperature, respectively

y_i = The mole fraction of gas species i and it is the ratio of n_i and the total number of moles in the reaction mixture

$\Delta \bar{G}_{f,i}^o$ = The standard Gibbs free of formation of species i

For solid carbon, the partial molar Gibbs free energy is:

$$G_{C(S)} \cong \Delta \bar{G}_{f,C(S)}^o \tag{11}$$

To find the minimum point, the Lagrange multiplier method is conducted with constraint of mass balance, i.e.:

$$\sum_{i=1}^{N} a_{ij} n_i = A_j, \, j = 1, 2, 3, ..., k \tag{12}$$

Where:

a_{ij} = The number of atom of the jth element in a mole of the ith species

A_j = Defined as the total number of atom of jth element in the reaction mixture

From Eq. 9-12, Lagrangian function is formed and partial derivative is applied. The final simultaneous equations, therefore, can be developed as:

$$\frac{\Delta \bar{G}_{f,i}^o}{RT} + \ln\left(\frac{n_i}{n_{tot}}\right) + \sum_{j=1}^{k} \frac{\lambda_j}{RT} a_{i,j} = 0, \qquad i = 1, ..., N \tag{13}$$

where, λ_j, $\lambda = \lambda_1,\ldots, \lambda_k$ are Lagrange multipliers.

The solutions n_i have to be real numbers in the boundary such that $0 \leq n_i \leq n_{tot}$. Equation 13 creates the set of non-linear equations and those are solved along with constraint equations by iteration technique, the Newton-Raphson method. The data from the NASA technical memorandum 4513 (McBride *et al.*, 1993) is employed to calculate all thermodynamic properties in this model.

RESULTS AND DISCUSSION

The effect of temperature on reactant conversions and gas yields: The simulation of combined partial oxidation and CO_2 reforming was conducted with $CH_4:CO_2:O_2$ feed ratio of 1.0:1.0:0.2. The conversion of reactants affected by reaction temperature is shown in Fig. 1. The conversions of CH_4 and CO_2 are defined in Eq. 14 and 15, respectively:

$$CH_4 \text{ conversion} (\%) = \frac{\left(CH_{4,in} - CH_{4,out}\right)}{CH_{4,in}} \times 100 \qquad (14)$$

$$CO_2 \text{ conversion} (\%) = \frac{\left(CO_{2,in} - CO_{2,out}\right)}{CO_{2,in}} \times 100 \qquad (15)$$

where subscripts in and out represent mole of substance at the inlet and outlet, respectively.

From Fig.1, it can be observed that the temperature strongly affects on CH_4 conversion. It increases when temperature increases. The conversion of 95% of CH_4 can be achieved at reaction temperature of 1050 K. For CO_2 conversion, it increases with increasing temperature. At higher temperature, CO_2 conversion dramatically increases because CO_2 reforming is endothermic reaction favoring high temperature. This reason is supported by increasing CO concentration when temperature increases, which is discussed in Fig. 2.

The equilibrium products from partial oxidation and CO_2 reforming are exhibited in Fig. 2. Increase of CO mole fraction shows similar trend as CO_2 conversion. As previously mentioned, high temperature favors CO_2 reforming and it produces CO. For H_2, its concentration increases with increasing temperature. However, at temperature higher than 1000 K, mole fraction of H_2 is quite constant. This is because CO_2 reforming and reverse water gas shift reactions are endothermic. High temperature not only supports CO_2 reforming reaction to product H_2 but also favors reverse water gas shift reaction to consume H_2. Decreasing H_2O is clearly observed at high temperature. That is the effect of reactions (3) and (4), which are strong endothermic reactions.

Figure 3 illustrates H_2/CO ratio and syngas (H_2+CO) production from combined partial oxidation and CO_2 reforming. The value of H_2/CO ratio is

higher at lower temperature. At 800 K, H_2/CO ratio is about 5, while H_2/CO ratio is 1.09 at 1000 K. It is clearly seen that H_2/CO ratio approaches to 1 at high temperature. This also confirms that CO_2 reforming is predominant (reaction (5)) at high temperature. However, at low temperature, the influence of partial oxidation of methane (reaction (2)) outstandingly
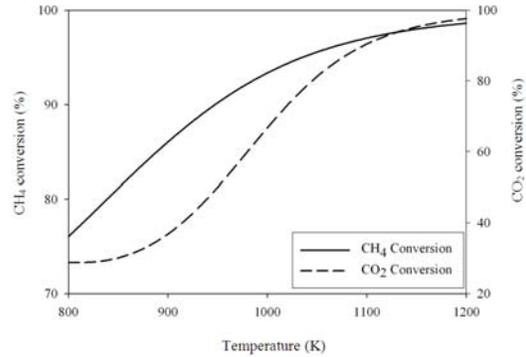
Fig. 1: Effect of temperature on CH_4 and CO_2 conversions
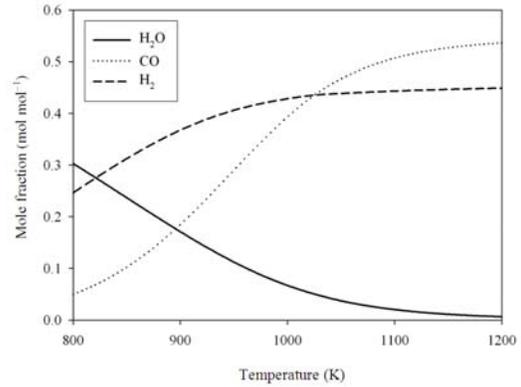
Fig. 2: Effect of temperature on reaction products
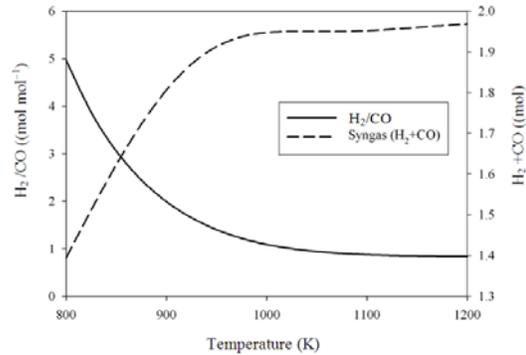
Fig. 3: Effect of temperature on H_2/CO ration and syngas production
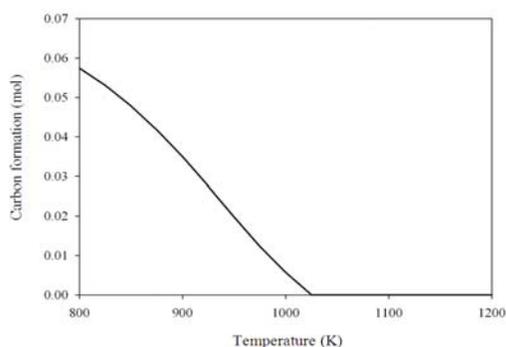
Fig. 4: Effect of temperature on solid carbon formation
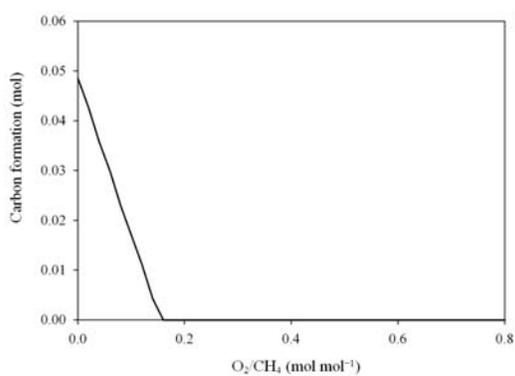
Fig. 5: Carbon formation affected by O_2/CH_4 ration
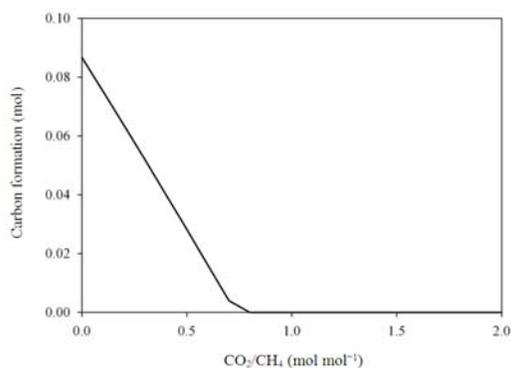
Fig. 6: Carbon formation affected by CO_2/CH_4 ration

presents. For syngas, it dramatically increases at low temperature and slightly changes after 1000 K. For Fig. 3, syngas production is about 5.5 mol for feeding 1 mol of CH_4 if the reactor is operated at temperature higher than 1000 K.

The solid carbon formed in this process is also investigated. It is an undesired component because it deactivates the catalyst and causes pressure drop in reactor. From Fig. 4, it elucidates that mole fraction of carbon formed in the process decreases with the increase in temperature. The solid carbon cannot be found when reaction temperature is higher than 1025 K.

Carbon formation: To study more about carbon formation in combined partial oxidation and CO_2 reforming process, the simulation is carried out at the reaction temperature of 1050K. Figure 5 presents that at CO_2/CH_4 ration of 1, higher fed O_2 leads to lower carbon formation because more O_2 introduced to the process can react more with carbon and forms CO and CO_2. Supplying O_2 where O_2/CH_4 ratio is higher than 0.15, it causes no carbon formation in the process. Comparing with Fig. 4, it can be implied that carbon formation can be limited at lower O_2 supply if the process is operated at higher temperature. At O_2/CH_4 ration of 0.2 and reaction temperature of 1050 K, carbon formation cannot be investigated at CO_2/CH_4 ratio higher than 0.8.

Effect of fed CO_2: The effect of CO_2 fed in to the process is investigated here. As shown in Fig. 1, at 1050 K, the CH_4 conversion is 95% and Syngas concentration nearly reaches the maximum.

From Fig. 5, H_2/CO ratio is also about 1 at this reaction temperature. Thus, the reaction temperature is fixed at 1050 K, while CO_2 supplied to the system is varied to study its effect on gas production. The other reactants, e.g., CH_4 and O_2 are also fixed at $CH_4:O_2$ of 1.0:0.2. Moreover, at 1050 K, solid carbon may not be observed. Even though the solid carbon is formed, its concentration is very low. Therefore, the equilibrium calculation omits to consider solid carbon.

Figure 7 exhibits the change of the mole fraction of some important products when CO_2/CH_4 ratio changes. The mole fraction of H_2 increases from 0.45-0.516 when CO_2/CH_4 increases from 0 to 0.45. Adding more CO_2 into the process, it causes dropping H_2 concentration. The similar behavior as H_2 is observed from the change of CO. The mole fraction of CO increases with increasing CO_2 fed to the process. However, as seen from Fig. 7, CO starts to decrease when CO_2/CH_4 is equal to 1.0. From the above discussion, it can be implied that feeding more CO_2 into the reactor, it may not provide good result. Excess CO_2 cannot be converted and it leads to increase of CO_2 in the product as exhibited in Fig. 7. The H_2O content increases with increasing CO_2/CH_4. That is the effect of reverse water gas shift reaction. Figure 8 presents the change of mole of syngas in the product compared with the change of CO_2/CH_4 ratio. The concentration of syngas sharply increases when CO_2/CH_4 ratio increases. Nevertheless, the increase of syngas is hardly observed after CO_2/CH_4 ratio is higher than 1. Finally, it can be concluded that at the reaction temperature of 1050 K, the optimum CO_2/CH_4 ratio range based on syngas yield is 0.85-1.0 and CH_4 conversion in this range of CO_2/CH_4 ratio is 95.3-96.5%.
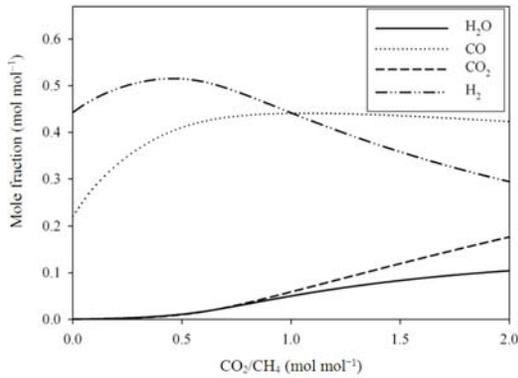
Fig. 7: Effect of CO_2/CH_4 ratio on gas compositions
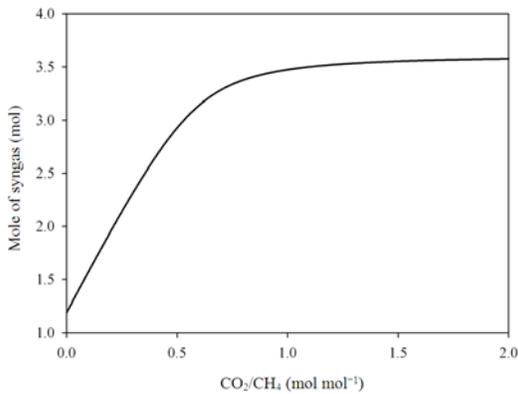
Fig. 8: Effect of CO_2/CH_4 ratio on syngas production
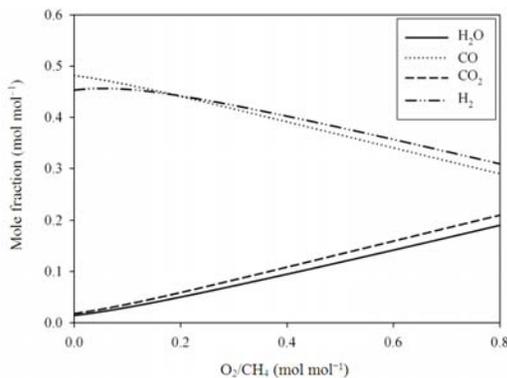
Fig. 9: Effect of O_2/CH_4 ratio on gas compositions

Effect of fed O_2: To study the effect of added O_2 on the production of combined partial oxidation and CO_2 reforming, the ratio of CO_2/CH_4 is fixed at 1 and the reaction temperature is also maintained at 1050 K, while the ratio of O_2/CH_4 is varied from 0 to 0.8. The results of equilibrium calculation are shows in Fig. 9 and 10. Figure 9 presents the mole fraction of H_2O, H_2, CO and CO_2. For CO, when more O_2 is added into the
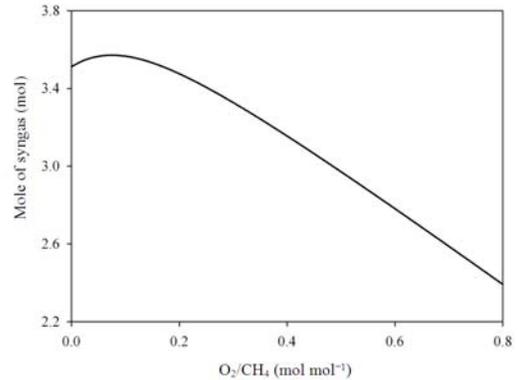
Fig. 10: Effect of O_2/CH_4 ratio on syngas production

process, its concentration starts to drop. However, CO_2 concentration is observed that it increases when fed O_2 increases. For the changes of CO and CO_2 concentration, they can be explained that, more O_2 added into the reactor causes CH_4 conversion to CO_2 and H_2O, that is reaction (1). Moreover, it is also due to CO and H_2 oxidation with O_2 formed CO_2 and H_2O, respectively (Amin and Yaw, 2007). onsequently, H_2 and CO contents reduce because they are converted to be H_2O and CO_2, respectively. This explanation is confirmed by increasing H_2O and CO_2 illustrated in Fig. 9. As seen from Fig. 10, the mole of syngas starts to reduce when O_2/CH_4 ratio is about 0.1. If the maximum syngas yield is considered, the optimum O_2/CH_4 ratio should be 0.1. However, the CH_4 conversion matching with O_2/CH_4 ratio of 0.1 is about 94% and 97% of CH_4 conversion can be achieved at O_2/CH_4 ratio of 0.2. Therefore, the optimum rage of O_2/CH_4 ratio is 0.1-0.2.

CONCLUSION

The thermodynamic equilibrium method was used to study combined partial oxidation and CO_2 reforming process. Methane was employed as feedstock. The first part of this study was done based on CH_4:CO_2:O2 feed ratio of 1.0:1.0:0.2. The results showed that higher reaction temperature caused higher CH_4 and CO_2 conversions. CO and H_2 production increased with increasing temperature. H_2/CO ratio was about 1 when the reaction temperature was higher than 1000 K. For syngas, it sharply increased at low temperature and slightly changed after 1000 K. Solid carbon formation could not be observed after 1025 K. The next study was carried out to investigate solid carbon formation due to the variation of O_2/CH_4 and CO_2/CH_4 rations at 1050 K. It was found that solid carbon formation could be eliminated by increasing O_2/CH_4 and CO_2/CH_4 rations. The effect of fed CO_2 and O_2 on syngas production was

observed at 1050 K. For O_2/CH_4 higher than 0.1, increase of O_2/CH_4 ration led decreasing H_2 and CO in product gas while increase of CO_2/CH_4 ration caused increasing H_2 and CO. However, when CO_2/CH_4 ration was higher than 0.85, increasing CO_2/CH_4 showed insignificantly change of syngas concentration. Finally, the results from this study presented that, at the reaction temperature of 1050 K, the optimum range of $CH_4:CO_2:O_2$ for combined partial oxidation and CO_2 reforming process was 1: 0.85-1.0:0.1-0.2.

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