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

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Abstract: Problem statement: CO₂ reforming is one of the methods to utilize a greenhouse gas to produce syngas, an important feed for methanol and Fischer-Tropsch synthesis. However, CO₂ reforming is strong endothermic reaction requiring large amount of supplied energy. Partial oxidation, an exothermic reaction, is combined with CO₂ reforming to serve the energy requirement. Thus, the optimum ranges of O₂ and CO₂ 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 CH₄ was used as feedstock. The optimum rage of O₂ and CO₂ 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 CH₄ and CO₂ conversions. Syngas production increased with increasing temperature. Operating the process with high temperature or high O₂/CH₄ and CO₂/CH₄ ratios could eliminate solid carbon formation. Increase of O₂/CH₄ ratio higher than 0.1 led decreasing syngas while increase of CO₂/CH₄ ratio caused increasing H₂ and CO. However, when CO₂/CH₄ ratio was higher than 0.85, increasing CO₂/CH₄ ratio showed insignificant change of syngas concentration.

Conclusion: The combined partial oxidation and CO₂ reforming of method should be operated with reaction temperature of 1050 K. The optimum range of CH₄:CO₂:O₂ 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

CO₂ 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 H₂ and CO, is a feedstock for the methanol and Fischer-Tropsch syntheses (Tsang et al., 1995; Froment, 2000). CO₂ reforming process is sometime called dry reforming, which is strong endothermic reaction. Thus, it requires large amount of heat supplied to the process. CO₂ 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 Haghhighi et al. (2007) to study CO₂ reforming of CH₄. The result has been presented that equilibrium H₂/CO ratio at high temperature was about 1.0. However, at a specific temperature, higher pressure caused lower H₂/CO ratio.

Moreover, the authors indicated that a deposited carbon was also one of the major products obtained from CO₂ 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/TiO₂ 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 (Pwanto 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 CO₂ reforming processes is presented to solve the high energy requirement problem of CO₂ reforming. Heat produced from partial oxidation process is supplied to CO₂ 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 CO₂ reforming process is investigated through thermodynamic equilibrium model. Methane is chosen as feedstock. The effect of reaction temperature on CH₄ and CO₂ 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 CO₂/CH₄ and O₂/CH₄ 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 CH₄, CO, CO₂, H₂ and H₂O. Solid carbon is also observed. The partial oxidation combined with CO₂ reforming of methane is involved with the predominance chemical reactions, which are listed below:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 &\rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\text{CH}_4 + \frac{1}{2}\text{O}_2 &\rightarrow \text{CO} + \text{H}_2 \\
\text{CH}_4 + \text{H}_2\text{O} &\leftrightarrow \text{CO} + 3\text{H}_2 \\
\text{CH}_4 + 2\text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + 4\text{H}_2 \\
\text{CH}_4 + \text{C}_2\text{O}_2 &\leftrightarrow 2\text{CO} + 2\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} &\leftrightarrow \text{CO}_2 + \text{H}_2 \\
2\text{CO} &\leftrightarrow \text{CO}_2 + \text{C} \\
\text{CH}_4 &\leftrightarrow 2\text{H}_2 + \text{C}
\end{align*}
\]

**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:

\[
G' = \sum_{i=1}^{N} n_i G_i = \sum_{i=1}^{N} n_i \mu_i
\]

Where:

- \( n_i \) and \( \mu_i \) = 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:

\[
\mu_i = \Delta G^o_{f,i} + RT \ln (y_i)
\]

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
- \( \Delta G^o_{f,i} \) = The standard Gibbs free of formation of species \( i \)

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

\[
G_{c(S)} = \Delta G^o_{f,c(S)}
\]

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

\[
\sum_{i=1}^{N} a_i n_i = A_j, j = 1, 2, 3, ..., k
\]

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:

\[
\frac{\Delta G^o_{f,i}}{RT} + \ln \left( \frac{n_i}{n_{\text{ref}}} \right) + \sum_{j=1}^{k} \frac{\lambda_j}{RT} a_{ij} = 0, \quad i = 1, ..., N
\]
where, $\lambda_j, \lambda_k = \lambda_1, \ldots, \lambda_k$ are Lagrange multipliers.

The solutions $n_i$ have to be real numbers in the boundary such that $0 \leq n_i \leq n_{\text{tot}}$. 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:

\[
\text{CH}_4 \text{ conversion} (%) = \frac{\text{CH}_4_{\text{out}} - \text{CH}_4_{\text{in}}}{\text{CH}_4_{\text{in}}} \times 100 \quad (14)
\]

\[
\text{CO}_2 \text{ conversion} (%) = \frac{\text{CO}_2_{\text{out}} - \text{CO}_2_{\text{in}}}{\text{CO}_2_{\text{in}}} \times 100 \quad (15)
\]

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 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$_2$O 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
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 CO₂ reforming process, the simulation is carried out at the reaction temperature of 1050 K. Figure 5 presents that at CO₂/CH₄ ratio of 1, higher fed O₂ leads to lower carbon formation because more O₂ introduced to the process can react more with carbon and forms CO and CO₂. Supplying O₂ where O₂/CH₄ 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 O₂ supply if the process is operated at higher temperature. At O₂/CH₄ ratio of 0.2 and reaction temperature of 1050 K, carbon formation cannot be investigated at CO₂/CH₄ ratio higher than 0.8.

**Effect of fed CO₂:** The effect of CO₂ fed in to the process is investigated here. As shown in Fig. 1, at 1050 K, the CH₄ conversion is 95% and Syngas concentration nearly reaches the maximum.

From Fig. 5, H₂/CO ratio is also about 1 at this reaction temperature. Thus, the reaction temperature is fixed at 1050 K, while CO₂ supplied to the system is varied to study its effect on gas production. The other reactants, e.g., CH₄ and O₂ are also fixed at CH₄:O₂ 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 CO₂/CH₄ ratio changes. The mole fraction of H₂ increases from 0.45-0.516 when CO₂/CH₄ increases from 0 to 0.45. Adding more CO₂ into the process, it causes dropping H₂ concentration. The similar behavior as H₂ is observed from the change of CO. The mole fraction of CO increases with increasing CO₂ fed to the process. However, as seen from Fig. 7, CO starts to decrease when CO₂/CH₄ is equal to 1.0. From the above discussion, it can be implied that feeding more CO₂ into the reactor, it may not provide good result. Excess CO₂ cannot be converted and it leads to increase of CO₂ in the product as exhibited in Fig. 7. The H₂O content increases with increasing CO₂/CH₄. 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 CO₂/CH₄ ratio. The concentration of syngas sharply increases with increasing CO₂/CH₄. 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 CO₂/CH₄ ratio. The concentration of syngas sharply increases with increasing CO₂/CH₄ ratio. Nevertheless, the increase of syngas is hardly observed after CO₂/CH₄ ratio is higher than 1. Finally, it can be concluded that at the reaction temperature of 1050 K, the optimum CO₂/CH₄ ratio range based on syngas yield is 0.85-1.0 and CH₄ conversion in this range of CO₂/CH₄ ratio is 95.3-96.5%.
Effect of fed O₂: To study the effect of added O₂ on the production of combined partial oxidation and CO₂ reforming, the ratio of CO₂/CH₄ is fixed at 1 and the reaction temperature is maintained at 1050 K, while the ratio of O₂/CH₄ is varied from 0 to 0.8. The results of equilibrium calculation are shown in Fig. 9 and 10. Figure 9 presents the mole fraction of H₂O, H₂, CO, and CO₂. For CO, when more O₂ is added into the process, its concentration starts to drop. However, CO₂ concentration is observed that it increases when fed O₂ increases. For the changes of CO and CO₂ concentration, they can be explained that, more O₂ added into the reactor causes CH₄ conversion to CO₂ and H₂O, that is reaction (1). Moreover, it is also due to CO and H₂ oxidation with O₂ formed CO₂ and H₂O, respectively (Amin and Yaw, 2007). Consequently, H₂ and CO contents reduce because they are converted to be H₂O and CO₂, respectively. This explanation is confirmed by increasing H₂O and CO₂ illustrated in Fig. 9. As seen from Fig. 10, the mole of syngas starts to reduce when O₂/CH₄ ratio is about 0.1. If the maximum syngas yield is considered, the optimum O₂/CH₄ ratio should be 0.1. However, the CH₄ conversion matching with O₂/CH₄ ratio of 0.1 is about 94% and 97% of CH₄ conversion can be achieved at O₂/CH₄ ratio of 0.2. Therefore, the optimum rage of O₂/CH₄ ratio is 0.1-0.2.

CONCLUSION

The thermodynamic equilibrium method was used to study combined partial oxidation and CO₂ reforming process. Methane was employed as feedstock. The first part of this study was done based on CH₄:CO₂:O₂ feed ratio of 1.0:1.0:0.2. The results showed that higher reaction temperature caused higher CH₄ and CO₂ conversions. CO and H₂ production increased with increasing temperature. H₂/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 O₂/CH₄ and CO₂/CH₄ ratios at 1050 K. It was found that solid carbon formation could be eliminated by increasing O₂/CH₄ and CO₂/CH₄ ratios. The effect of fed CO₂ and O₂ on syngas production was
observed at 1050 K. For O₂/CH₄ higher than 0.1, increase of O₂/CH₄ ration led decreasing H₂ and CO in product gas while increase of CO₂/CH₄ ration caused increasing H₂ and CO. However, when CO₂/CH₄ ration was higher than 0.85, increasing CO₂/CH₄ 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 CH₄:CO₂:O₂ for combined partial oxidation and CO₂ reforming process was 1: 0.85-1.0:0.1-0.2.

REFERENCES


