Research Article

Optimum Feed Ratio Analysis for Tri-Reforming of Methane Using Thermodynamic Equilibrium Method

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Abstract

Tri-reforming of methane was studied in this work through a method called Gibbs free energy minimization or thermodynamic equilibrium. Optimum feed ratios of H_2O/CH_4 and CO_2/CH_4 at a specific O_2/CH_4 ratio were investigated based on optimum conditions which are CH_4 and CO_2 conversions are equal to or higher than 90%, H_2/CO ratio is 2.0 and H_2 yield should be as high as possible. Carbon formation during reaction was also focused for each case of the optimum feed ratio. Moreover, heat required to raise the reaction temperature was calculated and presented in terms of CO_2 equivalent. Net CO_2 emission from the process was finally expressed. The results showed that the values of optimum H_2O/CH_4 and CO_2/CH_4 ratios reduce as O_2/CH_4 ratio increases. The values of carbon selectivity, reflecting solid carbon formation, are very low. The net CO_2 emission is in the range of 0.176-0.137 kmol per 1 kmol of CH_4

Keywords: Tri-reforming; CO_2 emission; Hydrogen production; Thermodynamic equilibrium

1. Introduction

Reforming of natural gas is the well-known method for syngas production. Steam reforming of natural gas is the most widely used method for hydrogen production in industrial scale [1]. Steam reforming of methane, shown in reaction (1), provides high H_2/CO ratio

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H^o_{298} = 206\ \text{MJ/kmol} \tag{1}$$

CO_2 reforming, also called dry reforming, is of interest to many researchers. It utilizes CO_2, a major green-house gas, to react with methane and produces syngas with H_2/CO ratio of 1.0, as presented in reaction (2).

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad \Delta H^o_{298} = 247.3\ \text{MJ/kmol} \tag{2}$$

The partial oxidation of methane can be explained as a sub-stoichiometric combustion of methane and it is an exothermic reaction which can be described as:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H^o_{298} = \text{-}36\ \text{MJ/kmol} \tag{3}$$

A new process, called tri-reforming, has been focused upon by researchers. It is the combination of three previous methods [2]. The idea of tri-reforming process shown in Ref. [2] is that the flue gas, which consists

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of CO_2, H_2O, and O_2, reacts with methane in a main reactor under controlled temperature condition. The desirable product is syngas or the mixture of H_2 and CO. Tri-reforming can produce syngas with H_2/CO ratio suitable for the production of methanol, dimethyl ether, and other liquid hydrocarbon [3]. One of the most important concepts of this process is that the reforming reactions (reactions (1) and (2)) are endothermic. However, the oxidation reaction (reaction (3)) is exothermic. The combination of these reactions contributes to energy saving because heat generated from reaction (3) compensates for the energy demand of the reforming reactions. Moreover, the tri-reforming process uses CO_2 as co-reactant. It, therefore, reduces CO_2 emission from industries and power plants. Song and Pan [2] have proposed and experimentally exhibited a tri-reforming process utilizing the power station flue gas for syngas production. The authors have also pointed out the advantage of the process is that O_2 and H_2O in co-reactant can reduce carbon deposition onto catalyst. Halmann and Steinfeld [4, 5] have done an analysis for tri-reforming of fossil fuel-fired flue gases. The resulting syngas was used for methanol, ammonia or hydrogen production. Fuel saving and CO_2 emission avoidance were observed. A chemical simulation program was performed by Zhang et al. [3] to simulate methanol production coupled to a tri-reforming process. The optimum CH_4/flue gas ratio was focused. The optimization of heat integration was also carried out to minimize both utility and capital costs. The influence of the feedstock composition on methane conversion, the H_2/CO molar ratio of the syngas obtained by tri-reforming of methane over $Ni/\beta\text{-SiC}$ based catalyst have been described by García-Vargas et al. [6]. H_2/CO ratio ranging from 1.9-2.1 was focused. The study was observed that the effect of both water and oxygen volume flow on the H_2/CO ratio was positive while that of methane and carbon dioxide volume flow was negative. Thermodynamic and economic studies for combined CO_2 and steam reforming and tri-reforming for syngas production have been presented by Cañete et al. [7]. The result showed that combined reforming and tri-reforming of CH_4 are competitive processes, with lower operating and capital costs in comparison with steam reforming.

A novel multi-tubular fixed bed tri-reformer assisted with hydrogen and oxygen perm-selective membranes was proposed by Rahimpour et al. [8]. A kinetic model was developed to study this novel reactor. This model requires information of chemical reactions taking place as well as flow phenomena in the reactor. Recently, the kinetic model was used to study the tri-reforming process coupled with steam reforming reaction in a double concentric tube multi-tubular reactor [9] and to study the thermally coupled reactor (styrene reaction and tri-reforming) [10].

From the literature review, tri-reforming has been studied through kinetic models. However, the disadvantages of this method are: 1.) it requires the information of the major chemical reactions and 2.) the complex numerical method must be applied to find the solution. To operate a tri-reforming process efficiently in terms of high CH_4 and CO_2 conversions as well as high H_2 yield, a suitable combination of co-reactant, CO_2, H_2O, and O_2 is desirable to know. Moreover, the suitable mixture of reactants must also lead to an appropriate H_2/CO ratio. Due to the complexity of the chemical reactions taking place in this process, a simulation method, called thermodynamic equilibrium based on Gibbs free energy minimization, is proposed to use, because it does not need the information about chemical reactions practically occurring in the process [11].

In this work, thermodynamic analysis of tri-reforming process is performed through Gibbs free energy minimization method or non-stoichiometric equilibrium method. The optimum feed ratios of CO_2/CH_4, H_2O/CH_4, and O_2/CH_4 are investigated. The energy required for each optimum case is found and net CO_2 emission is finally expressed.

2. Model Description

2.1 Non-stoichiometric Equilibrium Model

The thermodynamic equilibrium model can be developed using two approaches. The first one is an equilibrium model based on equilibrium constants known as the stoichiometric model. This method requires the information of chemical reactions occurring in the considered system. Therefore, it is not suitable for a chemical system in which many chemical reactions take place. The second method is a non-stoichiometric equilibrium calculation based on Gibbs free energy minimization. The concept of this method is that, at equilibrium state, total Gibbs free energy of system is minimum. The total Gibbs free energy of a system is defined as:

$$G^t = \sum_{i=1}^{N} n_i \mu_i \tag{4}$$

where n_i is the number of moles of species i ($i = 1, 2, ..., N$) and μ_i is the chemical potential of species i and it can be calculated as follows [11]:

$$\mu_i = \bar{G}_i^o + \bar{R}T \ln\left(\frac{f_i}{f_i^o}\right) \tag{5}$$

where $\bar{R}$ and T are the universal gas constant (8.3145 kJ/kmol·K) and temperature in Kelvin, respectively. f_i represents the fugacity of species i. $\bar{G}_i^o$ and f_i^o are the standard Gibbs free energy and the standard fugacity of species i, respectively. For reaction in gas phase, the fugacity can be calculated by:

$$\frac{f_i}{f_i^o} = \phi_i y_i \frac{P}{P_o} \tag{6}$$

where ϕ_i is the fugacity coefficient of component i. Substituting Eqs. (5) and (6) into Eq. (4), gives the following result.

$$G^t = \sum_{i=1}^{N} n_i \bar{G}_i^o + \sum_{i=1}^{N} n_i \bar{R}T \ln\left(\frac{\phi_i y_i P}{P_o}\right) \tag{7}$$

If solid carbon is involved in the system, Eq. (7) can be rewritten as [12]:

$$G^t = \sum_{i=1}^{N-1} n_i \bar{G}_i^o + \sum_{i=1}^{N-1} n_i \bar{R}T \ln\left(\frac{\phi_i y_i P}{P_o}\right) + n_{C(s)} \bar{G}_{C(s)}^o \tag{8}$$

The standard Gibbs free energy of chemical species i can be computed from the following equation.

$$\bar{G}_i^o = \bar{H}_i^o - T\Delta\bar{S}_i^o \tag{9}$$

The values of standard enthalpy, $\bar{H}_i^o$, and standard entropy, $\bar{S}_i^o$, are described in terms of polynomial equations. Data from the NASA technical memorandum 4513 [13] are used to calculate both thermodynamic properties. For the fugacity coefficient calculation, Peng-Robinson equation of state with van der Waals' mixing rules was used, as described in [14].

$$\ln(\phi_i) = \frac{B_i}{B}(Z-1) - \ln(Z-B) - \frac{A}{B\sqrt{8}} \ln\left[\frac{Z + \left(1+\sqrt{2}\right)B}{Z + \left(1-\sqrt{2}\right)B}\right] \left[\frac{\left(2\sum_k x_k A_{k,i}\right)}{A} - \frac{B_i}{B}\right] \tag{10}$$

$$A = \frac{aP}{\bar{R}^2 T^2},\ B = \frac{bP}{\bar{R}T},$$
$$a = \sum_i \sum_k x_i x_k a_{i,k},\ b = \sum_i \sum_k x_i x_k b_{i,k} \tag{11}$$

O'Connell and Haile [15] discussed that calculation of $a_{i,k}$ can be conducted by $a_{i,k}=\sqrt{a_i a_k}$ while b can be alternatively estimated by $b=\sum_i x_i b_i$. These calculations are applied in this study for a and b. Now, the problem is to find the values of n_i which minimize the objective function G^t. The appropriate method, which has been usually performed for minimization of Gibbs free energy problem, is Lagrange multiplier [11]. The constraint of this problem is that the number of moles of each element in the system remains unchanged [12]:

$$\sum_i^N n_i \kappa_{i,j} = \varphi_j \qquad (j = 1,2,...,E) \qquad (12)$$

where $\kappa_{i,j}$ is the number of atoms of the j element presenting in each molecule of species i and φ_j is total number of atoms of j element in the system. The Lagrangian function (L) is formed by multiplying the Lagrange multipliers of element j (λ_j) to constraints and subtracting these terms from G^t.

$$L = G^t - \sum_{j=1}^{E} \lambda_j \left(\sum_{i=1}^{N} \kappa_{i,j} n_i - \varphi_j \right) \qquad (13)$$

The minimum of this function is obtained by taking the partial derivative of Eq. (13) with respect to n_i and setting these equations equal to zero. In this step, N equations are formed and Eq. (12) provides E equations. These $N+E$ equations permit determination of $N+E$ unknowns ($n_i = n_1,...,n_N$ and $\lambda_j = \lambda_1,...,\lambda_E$). In this study, only 6 gas species are assumed to be found in the reactor. However, for some cases solid carbon is also considered. A computer code modified from previous work [11] is used to find the equilibrium compositions.

2.2 Energy Balance

The reactions occurring in the tri-reformer have both endothermic and exothermic reactions. The endothermic reactions consume heat generated from exothermic reactions. In some cases, energy supplied from external source for heating the mixture to reach the desired reaction temperature is required. To obtain the value of additional energy needed, the first law of thermodynamics or energy balance is applied to the process by:

$$Q_{req} + \sum_{R=react} H_R(T_R,P_R) = \sum_{P=prod} H_P(T_P,P_P) \qquad (14)$$

where Q_{req} is the energy in form of heat required to raise the reaction temperature. No heat transfer to the environment is assumed in this calculation. H_R and H_P are enthalpies of reactant and product mixtures at specific states, respectively. Both molar specific enthalpies can be calculated by:

$$\bar{h} = \bar{h}^D + \bar{h}^{ig} \qquad (15)$$

where $\bar{h}^{ig}$ and $\bar{h}^D$ are molar specific enthalpy of ideal gas and molar specific enthalpy departure, respectively. The enthalpy departure is given by the following equation [14]:

$$\bar{h}^D = RT(Z-1) + \frac{T\frac{da}{dT} - a}{\sqrt{8}b} \ln\left(\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right) \qquad (16)$$

In the calculation of heat required, the enthalpies of reactant and product can be computed in kJ/kmol and they are converted to kJ/kg. Due to mass conservation principles, mass of reactant is equal to mass of product. The units of both enthalpies are the same; therefore, the amount of heat can be estimated in kJ/kg and total heat required can be finally found in kJ or MJ. The calculation procedure described in this section is illustrated in Figure 1.

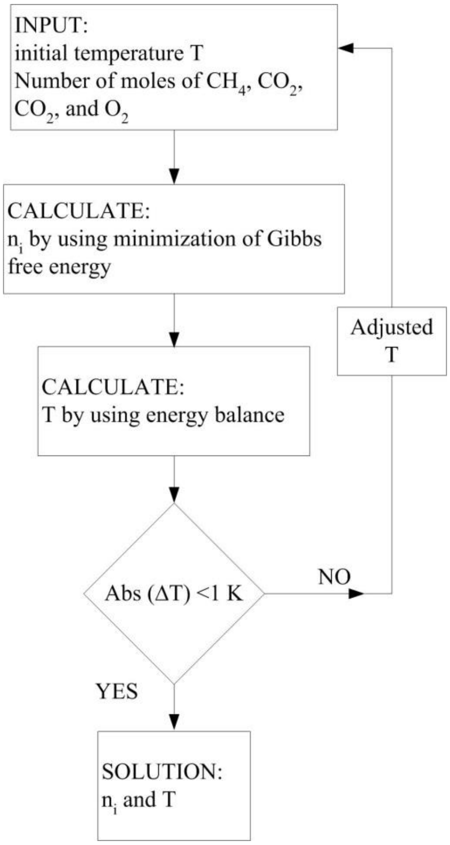


Fig.1. The calculation procedure.

3. Validation of Model

The thermodynamic equilibrium model developed in this study was validated by comparing the calculation results with that from other works. In the validation, the mole fractions of gas species in product gas were compared. For some cases, solid carbon was also focused. Six calculation cases obtained from Halmann and Steinfeld's works [4, 5] were used to compare with the results from the present model. All validation results show the agreement between calculation results from the model in this study and that from Halmann and Steinfeld's works with the maximum relative error less than 0.5%. Figure 2 illustrates an example of a validation case.

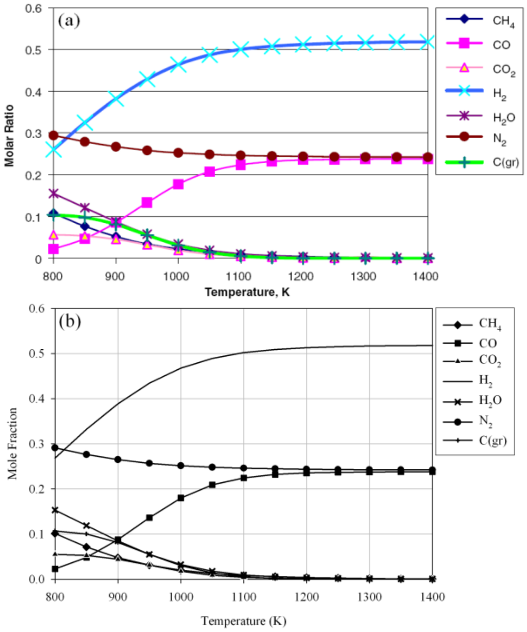


Fig.2. Comparison of equilibrium compositions in tri-reforming between (a) Halmann and Steinfeld's work, [4] and (b) present study, at given fixed feed ratio CH_4:CO_2:H_2O:O_2:N_2= 60:9:49:2.5:69.5, at 1 atm.

4. Results and Discussion

According to the information given by Zhang et al. [3] it can be found that hydrogen production and CH_4 conversion are suppressed as the pressure increases. Moreover, Zhang et al. [3] also pointed out that CO and H_2 productions reach maximum at a temperature of 850°C. Therefore, they recommended that the optimum reaction temperature and pressure are T=850°C and P=1 atm, respectively, and these conditions are also employed in this study.

For the feed compositions, Song and Pan, [2] informed that, for syngas production with H_2/CO =2.0, the best feed compositions should be CH_4:CO_2:H_2O:O_2 = 1:0.3-0.4:0.6-0.8:0.1-0.2. In this study, O_2/CH_4 ratio in range of 0.1-0.2 is considered. At a specific O_2/CH_4 ratio, feed ratios of CO_2/CH_4 and

H_2O/CH_4 are varied to investigate the optimum point. The optimal conditions are CH_4 conversion $\geq 90\%$, CO_2 conversion $\geq 90\%$, H_2/CO = 2.0, and maximum H_2 yield. CH_4 and CO_2 conversions as well as H_2 yield are defined as the following:

$$\text{CH}_4 \text{ conversion} (\%) = \frac{\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}}{\text{CH}_{4,\text{in}}} \times 100\% \qquad (17)$$

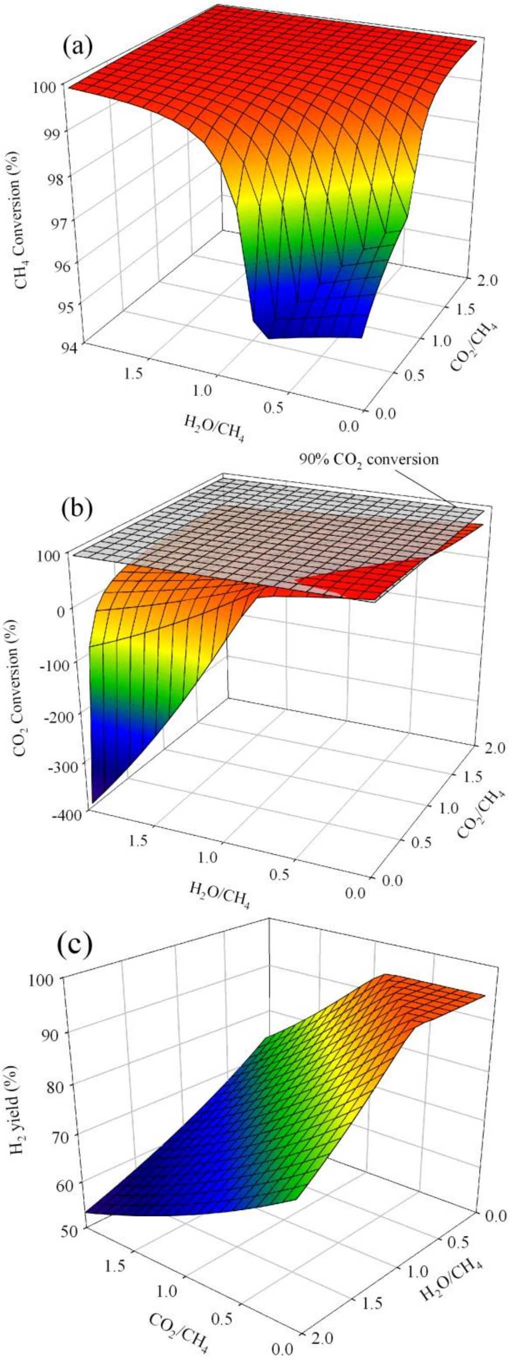
$$\text{CO}_2 \text{ conversion} (\%) = \frac{\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}}}{\text{CO}_{2,\text{in}}} \times 100\% \qquad (18)$$

$$\text{H}_2 \text{ yield} (\%) = \frac{\text{H}_{2,\text{out}}}{2\text{CH}_{4,\text{in}} + \text{H}_2\text{O}_{\text{in}}} \times 100\% \qquad (19)$$

4.1 Effects of CO_2/CH_4 and H_2O/CH_4 Ratios

To study the effects of different combinations of CO_2/CH_4 and H_2O/CH_4 ratios on syngas production, O_2/CH_4 ratio is initially fixed at 0.1. The reaction temperature and pressure are set at 850°C and 1 atm, respectively. The equilibrium calculation was done at different CO_2/CH_4 and H_2O/CH_4 ratios and the results are shown in Figure 3.

From Figure 3 (a), it is clearly observed that CH_4 conversion is higher than 90% in these ranges of CO_2/CH_4 and H_2O/CH_4 ratios. CH_4 conversion increases with increasing CO_2 or H_2O, because increases of oxidants can react with more CH_4. This phenomenon is also found in Ref. [16].



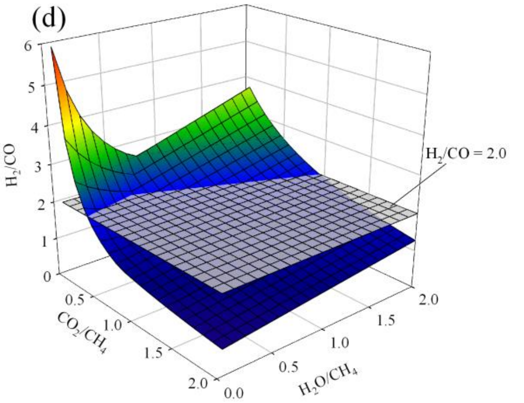


Fig.3. Effects of CO_2/CH_4 and H_2O/CH_4 on (a) CH_4 conversion, (b) CO_2 conversion, (c) H_2 yield, (d) H_2/CO ratio.

Figure 3 (b) illustrates CO_2 conversion. A horizontal plane indicates 90% CO_2 conversion level. In the figure, CO_2 conversion higher than 90% can be observed at low CO_2/CH_4 and H_2O/CH_4 ratios. Increase of H_2O content causes a significant decrease of CO_2 conversion, because H_2O is more chemical reactive than CO_2. Therefore, CH_4 reacts with H_2O rather than CO_2. Negative CO_2 conversion is found in this figure, especially at low CO_2/CH_4 and high H_2O/CH_4 ratios. From the definition of CO_2 conversion, it implies that CO_2 produced in the process is more than that added to the reformer. The negative conversion is also found in Ref. [16]. However, CO_2 conversion becomes positive when H_2O/CH_4 ratio is less than 0.9.

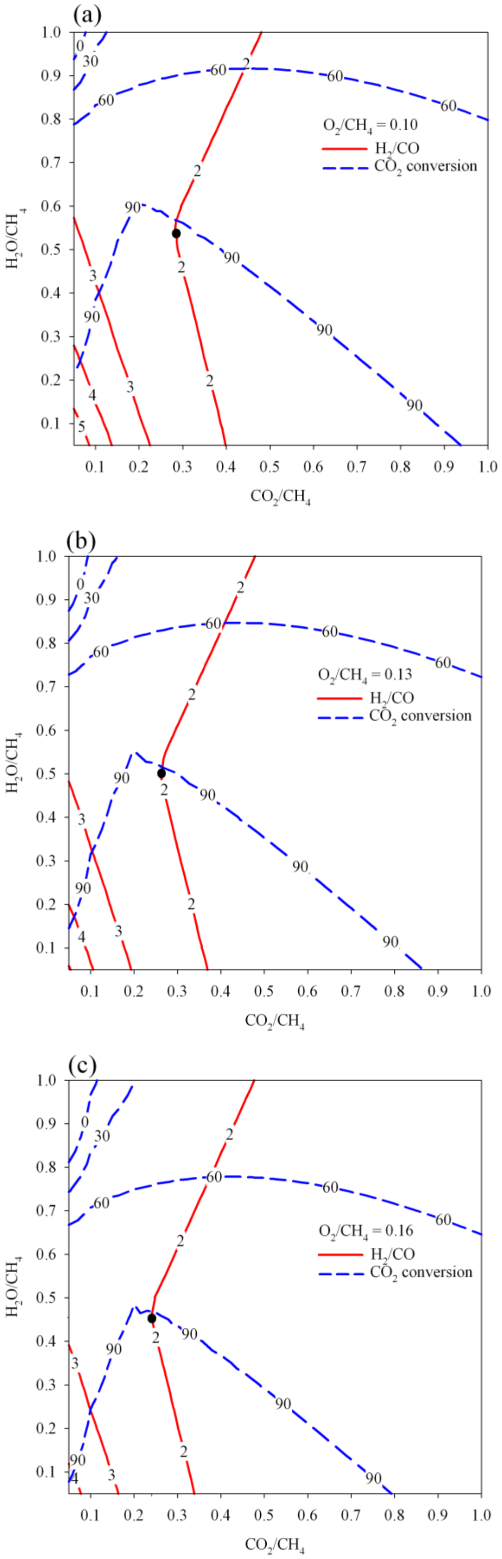
The equilibrium calculation of H_2 yield is shown in Figure 3 (c). H_2 production reaches maximum at low CO_2/CH_4 and H_2O/CH_4 ratios. Beyond the maximum H_2 yield location, reducing CO_2/CH_4 or H_2O/CH_4 ratio causes insignificant reduction of H_2 yield. Increases in H_2O and CO_2 contents induce decreasing H_2 yield. Adding more H_2O with fixed CH_4, O_2, and CO_2 can enhance H_2 production. However, from investigation of H_2O production, increase of H_2O in feed composition also causes more generation of H_2O in product gas. Additional H_2O increases the value of the denominator in Eq. (19) and consequently decreases H_2 yield. Increasing CO_2 content reduces H_2 production. The possible reason is the effect of reverse water gas shift reaction, which has become predominant [17].

For H_2/CO ratio, it is one of the most important parameters for the tri-reforming process. H_2/CO ratio was set to be equal to 2.0, which is suitable for methanol production. From Figure 3 (d), the plane indicated by $H_2/CO=2.0$ intersects with H_2/CO surface at low CO_2/CH_4 ratio. Moreover, it also shows that an H_2/CO ratio of 2.0 can be achieved in this range of H_2O/CH_4 and CO_2/CH_4 ratios in the feed gas.

4.2 Optimum CO_2/CH_4 and H_2O/CH_4 Ratios

As mentioned in the beginning of this section, the values of CO_2/CH_4 and H_2O/CH_4 ratios, obtaining optimal conditions, need to be found. In the first case, the optimum feed ratios of CO_2/CH_4 and H_2O/CH_4 for $O_2/CH_4 = 0.1$ are investigated. O_2 content, then, increases and new optimum feed ratios of CO_2/CH_4 and H_2O/CH_4 are observed.

Figure 4 depicts the optimum CO_2/CH_4 and H_2O/CH_4 ratios, based on the optimum conditions mentioned above, for different O_2/CH_4 ratios. In the figure, the dash line presents the CO_2 conversion profile, while the solid line illustrates the H_2/CO ratio. According to the optimum conditions, the optimum CO_2/CH_4 and H_2O/CH_4 ratios have to be positioned on the line H_2/CO ratio of 2.0 and in the area that CO_2 conversion is equal to or higher than 90%. It should be emphasized that CH_4 conversion in this study rage is found higher than 90%, (see Figure 3 (a)). Moreover, H_2 yield should be as high as possible.



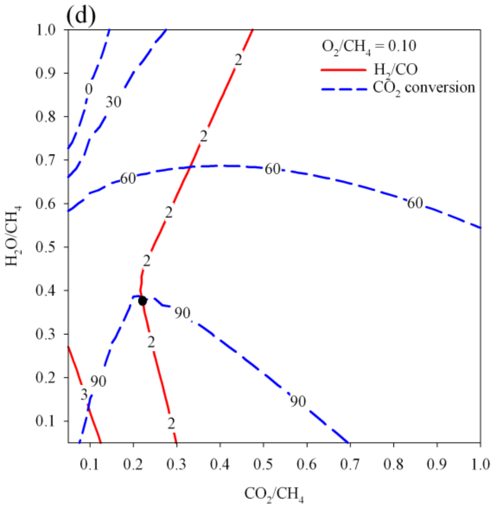


Fig.4. Optimum H_2O/CH_4 and CO_2/CH_4 ratios for different O_2/CH_4 ratios at T=850°C and P=1 atm.

For O_2/CH_4 ratio of 0.1, Figure 4 (a) expresses that the optimum CO_2/CH_4 and H_2O/CH_4 ratios are found at 0.282 and 0.574, respectively, indicated by a solid black circle. At these feed ratios, H_2 yield is 94.943%. As O_2 content in co-reactant increases, the area reflecting high CO_2 conversion ($\geq$90%) depletes. For O_2/CH_4 ratios of 0.13, 0.16 and 0.2, the optimum CO_2/CH_4 and H_2O/CH_4 ratios for each case slightly shift to lower values, as demonstrated in Figure 3 (b)-(d), the CO_2 conversions are, however, higher than 90%. Table 1 summarizes the optimum CO_2/CH_4 and H_2O/CH_4 ratios at different O_2/CH_4 ratios and other process parameters simulated at the optimum conditions. Optimum CO_2/CH_4 and H_2O/CH_4 ratios continuously reduce with increasing O_2/CH_4 ratio. From the table, each optimum operation point provides quite the same value of H_2 yield. It should be noticed that the optimum CO_2/CH_4 and H_2O/CH_4 ratios take place at the point that CO_2 conversion is about 90%. In fact, the maximum H_2 yield takes place at the point beyond the optimum CO_2/CH_4 and H_2O/CH_4 ratios shown in Table 1, but CO_2 conversion is lower than 90% at that point. However, the optimum feed ratios may not be at the intersection of 90%-CO_2

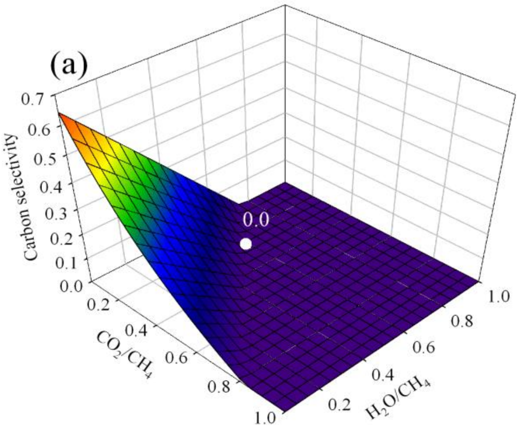
conversion and 2.0-H_2/CO ratio curves, because the intersection point may provide H_2 yield less than that at optimum CO_2/CH_4 and H_2O/CH_4 ratios, as shown in Table 1.

4.3 Solid Carbon Formation

Solid carbon formation is also of interest in this study. It is presented in terms of carbon selectivity, which is defined as:

$$\text{Carbon selectivity} = \frac{\text{total number of moles of C in solid phase}}{\text{total number of moles of C in feed}} \qquad (20)$$

This is due to the fact that more O_2 fed to the process can react with more carbon to form CO and CO_2. The solid carbon formations for the optimum feed ratios, expressed in Table 1, are indicated in Figures 5 (a)-(d) by white circles accompanying with values. The value of carbon selectivity is zero for the first case (Figure 5 (a)) and they are quite low for the rest. For the last case, it has little higher carbon selectivity (0.0122) compared with the previous cases. To operate at feed conditions without carbon formation, the optimum conditions may not be succeeded, for example, H_2/CO ratio is higher than 2.0. Increase of O_2 content may cause reduction of H_2 yield, but it does not favor solid carbon formation. Operating with higher temperature is one of the potential solutions. However, it requires energy to heat up the mixture.



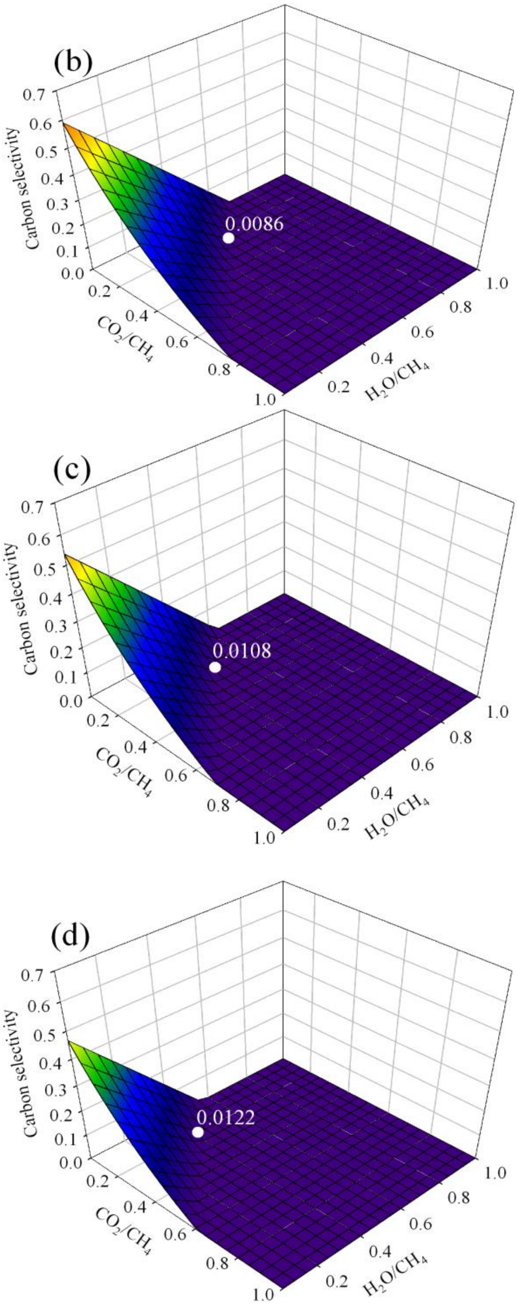


Fig.5. Carbon selectivity at optimum H_2O/CH_4 and CO_2/CH_4 ratios.

Table 1. Optimum CO_2/CH_4 and H_2O/CH_4 ratios at different O_2/CH_4 ratios and other simulation results.

Case	O_2/CH_4 ratio	Optimum ratio		CO_2 conversion (%)	H_2 yield (%)	H_2/CO ratio
		CO_2/CH_4	H_2O/CH_4			
1	0.10	0.282	0.574	90.0	94.943	2.003
2	0.13	0.257	0.500	91.5	94.746	2.003
3	0.16	0.238	0.456	91.0	94.745	2.001
4	0.20	0.212	0.400	90.1	94.744	2.001

4.4 Energy Requirement and CO_2 Emission

To produce syngas by tri-reforming process, flue gas from industries or power stations can be used as co-reactant. This is a method of flue gas treatment and CO_2 emission control. Therefore, the reduction of CO_2 emission from the tri-reforming process is focused in this section. However, it should be emphasized that N_2 is not considered in the co-reactant for this study.

The energy requirement for heating mixture in the reformer, for example from 150°C (Flue gas temperature at stack [2]) to 850°C, can be calculated by the first law of thermodynamics. This amount of energy required can be obtained from CH_4 combustion, as shown in reaction (22)

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -802.9\,\text{MJ/kmol} \tag{21}$$

From the above reaction, it can be implied that burning 1 kmol of CH_4 to provide 802.9 MJ of energy produces 1 kmol of CO_2. If the energy gained from CH_4 combustion can be utilized only 75%, CO_2 equivalent to energy requirement of 802.9 MJ is 1.33 kmol.

Table 2 reports the energy required for heating the mixture to the desired reaction temperature for each optimum case. The energy from combustion is, then, converted to be CO_2 equivalent and net CO_2 emission is finally presented. From the table, less O_2 content needs more energy to heat-up the mixture. Knowing that, addition of O_2 is necessary to promote the partial oxidation, which is exothermic reaction. Thus, from case 1 to case 4, the net CO_2 emission is found to continuously reduce. In case 1, 259.1 MJ of energy is required to convert 1 kmol of CH_4 in tri-reformer and this amount of energy is equivalent to 0.430 kmol of CO_2. The process needs 0.282 kmol of CO_2 and 0.028 kmol of CO_2 is found in the product gas. Therefore, the net CO_2 emission from this case is 0.176 kmol. In case 4, the energy required reduces 23.7% from case 1. Even through CO_2 is consumed only 0.212 kmol and CO_2 conversion is fair, the CO_2 generated from combustion process dramatically reduces. The net CO_2 emission, consequently, deceases about 22 % from case 1.

Table2. Energy requirement for heating mixture and CO_2 emission.

Case	Energy requirement ($MJ/kmol_{CH4}$)	CO_2 equivalent (kmol)	Net CO_2 emission (kmol)
1	259.1	0.430	0.176
2	237.4	0.394	0.159
3	220.3	0.366	0.149
4	197.8	0.328	0.137

5. Conclusion

The optimum H_2O/CH_4 and CO_2/CH_4 ratios at a specific O_2/CH_4 ratio were found for the tri-reforming process. Reaction temperature and pressure were set at 850°C and 1 atm, respectively. The result shows that, for the O_2/CH_4 ratio ranging from 0.1-0.2, the optimum H_2O/CH_4 and CO_2/CH_4 ratios are in the range of 0.574-0.400 and

0.282-0.212, respectively. Both optimum feed ratios reduce when O_2/CH_4 increases. The carbon formation was slightly observed in the optimum operation ranges. For net CO_2 emission, it strongly depends on CO_2 equivalent, estimated from heat required to raise the reaction temperature. Higher O_2 content decreases net CO_2 effluent. Based on 1 kmol of CH_4, net CO_2 emitted from the process is in the range of 0.176-0.137 kmol.

6. References

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