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Thermodynamic equilibrium analysis of CO₂ reforming of methane: elimination of carbon deposition and adjustment of H₂/CO ratio

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Abstract

Dry (CO₂) reforming of methane (DRM) is considered as a promising technique to produce syngas. In this study, to optimise the operating conditions for elimination of carbon deposition, thermodynamic calculations were carried out to understand the effect of various temperatures (550-1200 °C), pressures (0.05-5MPa) and CH₄/CO₂ mole ratios (0.5-2) on the product of H₂/CO ratio as well as the formation of carbon deposition. The suggested DRM operating conditions for carbon free regime are at a temperature greater than 1000 °C with CH₄/CO₂ mole ratio = 1 and pressure P = 0.1MPa. The operating temperature of carbon free regime could be switched to lower temperature by either lowering the CH₄/CO₂ mole ratio or decreasing the reaction pressure. The results illustrated that the temperature range for severe carbon formation was between 546 °C and 703 °C. CH₄ decomposition and CO disassociation reaction are considered as the major reactions contributing to carbon formation. The former was promoted at operating conditions of P ≤ 0.1MPa and 550 °C ≤ T ≤ 1000 °C, while the latter was enhanced at operating conditions of P ≥ 0.1MPa and T ≤ 700 °C. The syngas produced from optimised carbon free regime operating conditions, could be used to synthesis olefin, heavy hydrocarbons and oxygenated compounds. H₂/CO ratio could be adjusted by the changing CH₄/CO₂ mole ratio and/or pressure to satisfy F-T process for different application. Since the latter is only effective when operating temperature is lower than 900 °C, the former is proposed as a more efficient method to adjust H₂/CO ratio. When the operating temperature of DRM is over 700 °C, H₂/CO ratio obtained at CH₄/CO₂ mole ratio of DRM ≤ 1 and P = 0.1MPa is more preferable to be used for the synthesis of olefin, heavy hydrocarbons and oxygenated compounds. Otherwise the syngas is more suitable for producing alkane (C₁–C₅).

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1. Introduction

Methane could be reformed to produce syngas containing hydrogen and carbon monoxide, which could then be used as the feedstock of Fischer-Tropch (F-T) process [1, 2]. To date, the conversion of CH₄ to syngas has been widely studied, with main focus on the steam reforming (SR), partial oxidation (PO) and dry (CO₂) reforming of methane (DRM). Among these technologies, SR has been commercialised. However, SR consumes huge amount of water, and the H₂/CO mole ratio is far higher than that required in F-T process. Since PO process employs pure oxygen as oxidant at high temperature, it is hampered by high cost of pure oxygen and high possibility of explosion. The DRM is regarded as a promising technique because it utilises CO₂ as a feedstock, which is a kind of greenhouse gas, and the H₂/CO ratio of the product gas is more suitable for F-T process to synthesise value-added liquid products [3-5]. However, the formation of carbon deposit is the biggest problem for DRM, which is the obstacle to its commercialisation [6-8]. Regardless of carbon deactivation, the operating cost of DRM is 20% less than other reforming processes [9]. Hence, a lot of efforts have been made to minimize carbon formation during the DRM [5-9]. Generally, valuable liquid products are synthesized via F-T process using syngas with a H₂/CO mole ratio in the range of 1.0-2.5. Technically, alkanes (C₁–C₅) are favourable products when H₂/CO ratio is ≥ 2. And, olefin, heavy hydrocarbon (i.e. wax) and oxygenated compounds (i.e. alcohols, methanol and DME) are the products when H₂/CO ratio is in the range of 1 – 2 [10]. As H₂/CO mole ratio of syngas dictates the products from F-T process, it is therefore important to adjust H₂/CO mole ratio to obtain required liquid products by optimising the operating conditions of DRM. In comparison to ‘Trial and Error’ approach, modelling is a more cost-effective approach to find the optimal operating conditions [11, 12]. Therefore, in this research, thermodynamic analysis was conducted using FactSage to study carbon elimination and the adjustment of H₂/CO mole ratio by optimising the operating conditions of DRM.

2. Methodology

A thermodynamic equilibrium analysis on methane dry reforming was simulated with FactSage software by minimizing the total Gibbs energy of the multi-reaction system. When the reaction stays at the equilibrium state, the differential of total Gibbs free energy is zero [13, 14]. For complex systems with N kinds of components, total Gibbs free energy in differential form can be described as:

$$dG = -SdT + VdP + \sum_{i=1}^N v_i du_i$$

Where S is the system entropy, T is the system temperature, V is the system volume, P is the system pressure, v_i is stoichiometric coefficients of component i and u_i is the chemical potential of component i . As total Gibbs free energy is always calculated in an isolated system for a given temperature and pressure, the total Gibbs free energy can be expressed as:

$$G = \sum_{i=1}^N v_i u_i$$

The total Gibbs free energy of the reaction in an isolated system at equilibrium state can be calculated by comparing with the standard Gibbs free energy of pure substance at same conditions, which is shown by the equation

$$G = \sum_{i=1}^N v_i u_i = \sum_{i=1}^N v_i u_i^0 + RT \ln K_i$$

Where R is the molar gas constant, K_i is the equilibrium constant of component i .

3. Results and discussion

3.1 Thermodynamic analysis

To illustrate the DRM, thermodynamic equilibrium reaction with CH_4/CO_2 mole ratio of 1 and pressure at 0.1 MPa as a function of temperature was calculated (Table 1). As shown in Table 1, the enthalpy of MDR is +247KJ/mole, which indicates the reaction is highly endothermic. The equilibrium state temperature for $\Delta G \leq 0$ is $T \geq 643^\circ\text{C}$, which means DRM requires large amount of energy to react in the forward direction at high temperature over 643°C . Basically, DRM reaction is very complex that several side reactions related to carbon formation including CH_4 decomposition (Equation (2)), CO_2 gasification (Equation (3)), and CO disassociation reaction (Equation (4)) always take place along with DRM. Among them, CH_4 decomposition and CO disassociation are reported as major reactions producing carbon deposition. Table 1 illustrates that CH_4 decomposition is slightly endothermic and occurs at $T \geq 546^\circ\text{C}$, and CO disassociation is moderately exothermic and comes up when $T \leq 703^\circ\text{C}$. Whereas, CO_2 gasification, which consumes carbon solid, is moderately endothermic and takes place at $T \geq 703^\circ\text{C}$. Hence carbon formation is inferred to take place significantly in temperature range of $546\text{-}703^\circ\text{C}$.

Table 1: Thermodynamic analysis of related reactions in MDR

Reaction	Equation	ΔH_{298K} (KJ/mole)	T: $\Delta G_T \leq 0$ ($^\circ\text{C}$)	No.
MDR	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO}$	+247	≥ 643	(1)
CH_4 decomposition	$\text{CH}_4 \leftrightarrow \text{C(s)} + 2\text{H}_2$	+75	≥ 546	(2)
CO_2 gasification	$\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$	+171	≥ 703	(3)
CO disassociation	$2\text{CO} \leftrightarrow \text{C(s)} + \text{CO}_2$	-171	≤ 703	(4)

3.2 Carbon formation

Carbon deposit, mainly caused by reactions (2) and (4), tends to lead catalysts deactivation which is regarded as the major obstacle to DRM commercialisation. Thus, it is necessary to eliminate carbon deposit during the reaction by optimising the operating conditions. In this research, thermodynamic analysis of the effect of CH_4/CO_2 mole ratio on carbon formation was simulated at 0.1 MPa, and the effect of pressure on carbon formation was simulated at CH_4/CO_2 mole ratio of 1. Figure 1 (left) shows that at $P = 0.1\text{MPa}$ carbon formation decreased with the increase in temperature from 550 to 1200°C , especially in the temperature range of $550\text{-}700^\circ\text{C}$. The reason for this is that although carbon deposit mainly comes from reactions (3) and (4), the exothermic reaction (4) will be prohibited more significantly than the endothermic reaction (3) with the increase in temperature, and reaction (4) will not occur at

temperature over 703 °C. Moreover, carbon formation increased as CH₄/CO₂ mole ratio decreased, which indicates that reaction (2) will be promoted to eliminate carbon formation with larger CH₄/CO₂ mole ratio. However, as CO₂ separation from a gaseous mixture is expensive, the CH₄/CO₂ mole ratio of 1 is the suggested operating condition. Also from Figure 1 (left), carbon free conditions at the atmosphere pressure would be achieved at the CH₄/CO₂ mole ratio less than 1, and the lower the CH₄/CO₂ mole ratio, the lower the temperature of carbon free conditions achieved. As shown in Figure 1 (right), carbon deposit decreased with the decrease in the pressure from 5 to 0.05 MPa and it also decreased in the temperature range of 550 °C and 1200 °C at CH₄/CO₂ mole ratio of 1. The curve of carbon formation moved to higher temperature zone as the pressure increased, which indicates higher pressure would suppress reaction (3) and enhance the carbon formation. Figure 1 (right) demonstrates that carbon free conditions would shift from lower temperature to higher temperature as the pressure increases. Furthermore, it indicates that reaction (2) and reaction (3) are preferable taking place at low pressure and high temperature, but reaction (4) is preferable occurring at high pressure and low temperature.

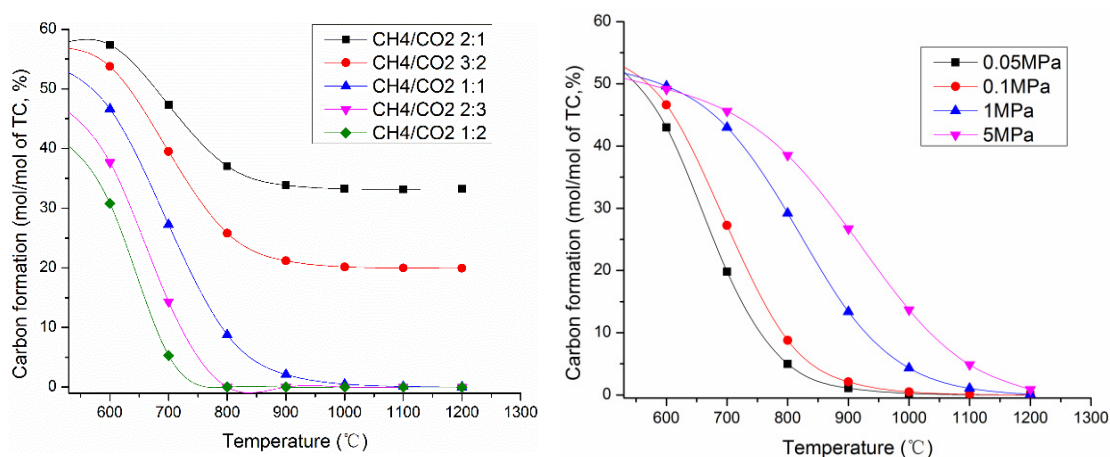


Figure 1: Carbon formation as a function of (left) CH₄/CO₂ mole ratio and temperature at 0.1 MPa, and (right) pressures and temperature with CH₄/CO₂ mole ratio is 1.

3.3 H₂/CO mole ratio

To obtain typical liquid products from F-T process for different applications, tuning the H₂/CO mole ratio is becoming more important. In DRM, the H₂/CO mole ratio could be adjusted by changing the operating temperature, pressure and CH₄/CO₂ mole ratio to satisfy different F-T process requirements. In this research, thermodynamic equilibrium analysis of the effect of CH₄/CO₂ mole ratio on product of H₂/CO mole ratio was calculated at 0.1 MPa, and the effect of pressure on H₂/CO mole ratio was simulated at CH₄/CO₂ mole ratio of 1. As shown in Figure 2 (left), the H₂/CO mole ratio decreased with the increase in temperature from 550 °C to 800 °C, and then there is stability at T ≥ 800 °C. The increase of CH₄/CO₂ mole ratio leads to an increment of H₂/CO mole ratio for the whole temperature range. For the DRM of CH₄/CO₂ mole ratio ≤ 1.5, the syngas produced at temperature over 800 °C is fit for synthesising olefin, heavy hydrocarbon and oxygenated compounds without any adjustment. However, for DRM occurring at operating conditions of CH₄/CO₂ mole ratio ≥ 2, and at the temperature range of 550-1200 °C, the syngas is only fit for alkane (C₁-C₅) synthesis as the H₂/CO mole ratio is always ≥ 2. Figure 2 (right) illustrates that H₂/CO mole ratio is slightly affected by pressures at the temperature range of T ≥ 900 °C, which is close to 1 and is suitable for producing olefin, heavy hydrocarbon and oxygenated compounds from F-T process. When operating temperature of DRM is less than 900 °C, the H₂/CO mole ratio increased with the

increase in operating pressure and with the decrease in the operating temperature. The syngas from DRM at low temperature range of 550- 650°C would be used for alkane ($C_1 - C_5$) synthesis when operating pressure ≥ 0.1 MPa. And when the operating pressure is greater than 0.1MPa, the H_2/CO mole ratio of the syngas obtained from DRM at low temperature range of $T \leq 700^\circ C$ would too high to be used as the feedstock for F-T process. The results show that to adjust H_2/CO mole ratio, changing the CH_4/CO_2 mole ratio is more efficient than changing the pressure. It is only when operating temperature of DRM $\leq 900^\circ C$ that changing pressure could be used as an alternative method for adjustment of H_2/CO mole ratio in compare to changing CH_4/CO_2 mole ratio.

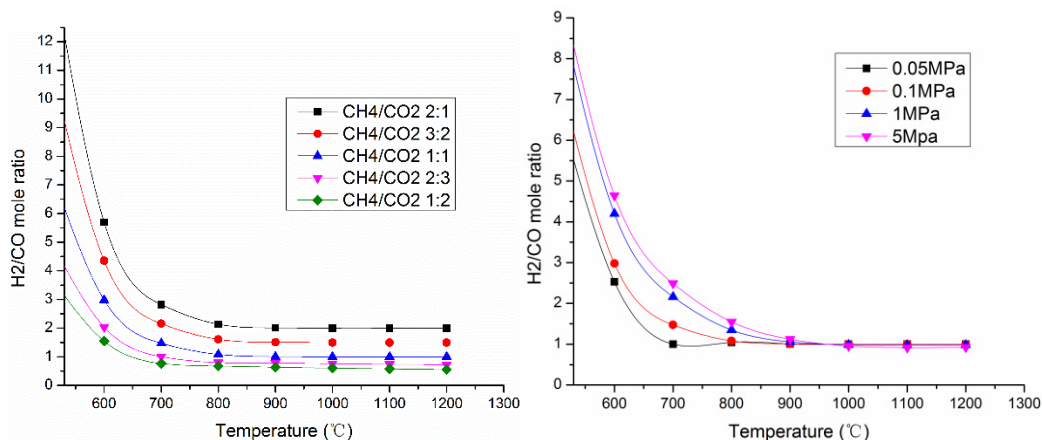


Figure 2: H_2/CO mole ratio as a function of (left) CH_4/CO_2 mole ratio and temperature at 0.1MPa, and (right) pressures and temperature with CH_4/CO_2 mole ratio is 1.

4. Conclusion

A thermodynamic equilibrium analysis on methane dry reforming was simulated with FactSage by minimizing the total Gibbs energy of the multi-reaction system. Thermodynamic calculation was employed to optimise the operating conditions for elimination of carbon deposition and the adjustment of H_2/CO mole ratio. Thermodynamic calculation demonstrated that carbon deposition would take place significantly in the temperature range of 546-703°C, and the optimum operating conditions for carbon free regime were $T \geq 1000^\circ C$, CH_4/CO_2 mole ratio = 1 and pressure = 0.1MPa. In terms of carbon formation contributors, CH_4 decomposition was promoted at operating conditions of $P \leq 0.1$ MPa and $546^\circ C \leq T \leq 1000^\circ C$, while CO dissociation was enhanced at operating conditions of $P \geq 0.1$ MPa and $T \leq 703^\circ C$. Thus, decreasing the CH_4/CO_2 mole ratio would achieve the carbon free regime at lower temperature. Similarly, the temperature for carbon free regime shifts to lower temperature with the decrease in reaction pressures. The H_2/CO mole ratio produced at optimal carbon free operating conditions could be used to synthesise olefin, heavy hydrocarbon and oxygenated compounds. The H_2/CO mole ratio decreased with increasing the reaction temperature, until the stability was achieved at $T \geq 900^\circ C$. Increasing both the CH_4/CO_2 mole ratio and pressures could lead to increment of H_2/CO mole ratio. H_2/CO mole ratio could be adjusted by changing CH_4/CO_2 mole ratio and pressures to synthesise different required hydrocarbon products. Since the latter could be effective only when $T \leq 900^\circ C$, the former was proposed as a more efficient way than the latter. In practice, these optimal operating conditions based on thermodynamic calculations would be directly tested in future experiments to improve efficiency.

5. Copyright

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References

1. Lunsford, H.J., *Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century*. Catalysis Today 2000. **63**: p. 165-174.
2. Lavoie, J.M., *Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation*. Front Chem, 2014. **2**: p. 81.
3. Gao, J.H., Z; Lou, H; Zheng,X, *Dry (CO₂) Reforming.*, in *Fuel Cell: Technologies for Fuel Processing* 2011, Elsevier: Oxford.
4. Nikoo, M.K. and N.A.S. Amin, *Thermodynamic analysis of carbon dioxide reforming of methane in view of solid carbon formation*. Fuel Processing Technology, 2011. **92**(3): p. 678-691.
5. Paksoy, A.I., B.S. Caglayan, and A.E. Aksoylu, *A study on characterization and methane dry reforming performance of Co–Ce/ZrO₂ catalyst*. Applied Catalysis B: Environmental, 2015. **168-169**: p. 164-174.
6. Guzzi, L., et al., *Methane dry reforming with CO₂: A study on surface carbon species*. Applied Catalysis A: General, 2010. **375**(2): p. 236-246.
7. Wang, C., et al., *The Properties of Individual Carbon Residuals and Their Influence on The Deactivation of Ni-CaO-ZrO₂Catalysts in CH₄Dry Reforming*. ChemCatChem, 2014. **6**(2): p. 640-648.
8. Mette, K.K., S; Dudder, H; Kahler, K; Tarasov, A; Muhler, M; Behrens, M, *Stable Performance of Ni Catalysts in the Dry Reforming of Methane at High Temperatures for the Efficient Conversion of CO₂ into Syngas*. ChemCatChem, 2014. **6**: p. 100-104.
9. Pakhare, D. and J. Spivey, *A review of dry (CO₂) reforming of methane over noble metal catalysts*. Chem Soc Rev, 2014. **43**(22): p. 7813-37.
10. Klerk, P.M.M.A.d., *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. 2013: WILEY-VCH.
11. Zhao, H.L., X; He, J; Peng, C; Wu, T, *Recovery of elemental sulphur via selective catalytic reduction of SO₂ over sulphided CoMo/γ-Al₂O₃ Catalysts*. Fuel, 2015. **147**: p. 67-75.
12. Zhao, H.Y., G; Gao, X; Wu, T, *H₂O-Temperature-programmed surface reaction and its application on the investigation of metal oxides for H₂O capture*. Fuel 2016. **181**: p. 1089-1094.
13. Sun, Y., et al., *Thermodynamic analysis of mixed and dry reforming of methane for solar thermal applications*. Journal of Natural Gas Chemistry, 2011. **20**(6): p. 568-576.
14. Hack, K., *A self-tuition package on computational thermochemistry*. 2011, FactSage.

Biography

Professor Tao Wu is an active researcher and currently leading the Municipal Key Laboratory of Clean Energy Conversion Technologies at the University of Nottingham Ningbo China. He has over 20 years of experience on utilization and conversion of fossil fuels and biomass. His current research interests focus on clean energy saving and conversion technologies, waste reduction and recycling technologies.