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Thermodynamic equilibrium analysis of CO_2 reforming of methane: elimination of carbon deposition and adjustment of H_2/CO ratio

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Abstract

Dry (CO_2) 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℃), pressures (0.05-5MPa) and CH_4/CO_2 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℃ with CH_4/CO_2 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 CH_4/CO_2 mole ratio or decreasing the reaction pressure. The results illustrated that the temperature range for severe carbon formation was between 546℃ and 703℃. CH_4 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℃ ≤ T ≤ 1000℃, while the latter was enhanced at operating conditions of P ≥ 0.1MPa and T ≤ 700℃. The syngas produced from optimised carbon free regime operating conditions, could be used to synthesis olefin, heavy hydrocarbons and oxygenated compounds. H_2/CO ratio could be adjusted by the changing CH_4/CO_2 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℃, the former is proposed as a more efficient method to adjust H_2/CO ratio. When the operating temperature of DRM is over 700℃, H2/CO ratio obtained at CH_4/CO_2 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 (C_1 –C_5).

Keywords: carbon elimination; MDR; thermodynamic calculation; Fischer-Tropch.

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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 CH_4 to syngas has been widely studied, with main focus on the steam reforming (SR), partial oxidation (PO) and dry (CO_2) reforming of methane (DRM). Among these technologies, SR has been commercialised. However, SR consumes huge amount of water, and the H_2/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 H_2/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 H_2/CO mole ratio in the range of 1.0-2.5. Technically, alkanes (C_1 –C_5) are favourable products when H_2/CO ratio is $\geq$ 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 H_2/CO mole ratio of syngas dictates the products from F-T process, it is therefore important to adjust H_2/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 H_2/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 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 be 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 ≥ 643℃, which means DRM requires large amount of energy to react in the forward direction at high temperature over 643℃. 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 ≥ 546℃, and CO disassociation is moderately exothermic and comes up when T ≤ 703℃. Whereas, CO_2 gasification, which consumes carbon solid, is moderately endothermic and takes place at T ≥ 703℃. Hence carbon formation is inferred to take place significantly in temperature range of 546-703℃.

Table 1: Thermodynamic analysis of related reactions in MDR

Reaction	Equation	ΔH_{298K} (KJ/mole)	T: $\Delta G_T \leq 0$ (℃)	No.
MDR	$CH_4 + CO_2 \rightarrow 2H_2 + 2CO$	+247	≥643	(1)
CH_4 decomposition	$CH_4 \leftrightarrow C(s) + 2H_2$	+75	≥546	(2)
CO_2 gasification	$C + CO_2 \leftrightarrow 2CO$	+171	≥703	(3)
CO disassociation	$2CO \leftrightarrow C(s) + CO_2$	-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 = 0.1MPa carbon formation decreased with the increase in temperature from 550 to 1200℃, especially in the temperature range of 550-700℃. 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℃. Moreover, carbon formation increased as CH_4/CO_2 mole ratio decreased, which indicates that reaction (2) will be promoted to eliminate carbon formation with larger CH_4/CO_2 mole ratio. However, as CO_2 separation from a gaseous mixture is expensive, the CH_4/CO_2 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 CH_4/CO_2 mole ratio less than 1, and the lower the CH_4/CO_2 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℃ and 1200℃ at CH_4/CO_2 mole ratio of 1. The curve of carbon formation moved to higher temperature zone as the pressure increased, which indicates higher pressure would supress 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.
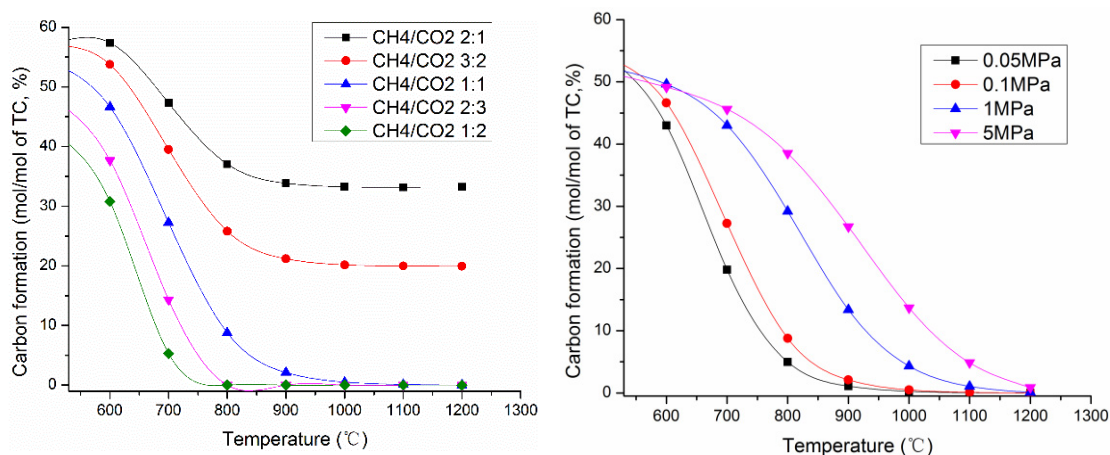

Figure 1: Carbon formation as a function of (left) CH_4/CO_2 mole ratio and temperature at 0.1MPa, and (right) pressures and temperature with CH_4/CO_2 mole ratio is 1.

3.3 H_2/CO mole ratio

To obtain typical liquid products from F-T process for different applications, tuning the H_2/CO mole ratio is becoming more important. In DRM, the H_2/CO mole ratio could be adjusted by changing the operating temperature, pressure and CH_4/CO_2 mole ratio to satisfy different F-T process requirements. In this research, thermodynamic equilibrium analysis of the effect of CH_4/CO_2 mole ratio on product of H_2/CO mole ratio was calculated at 0.1 MPa, and the effect of pressure on H_2/CO mole ratio was simulated at CH_4/CO_2 mole ratio of 1. As shown in Figure 2 (left), the H_2/CO mole ratio decreased with the increase in temperature from 550℃ to 800℃, and then there is stability at T ≥ 800℃. The increase of CH_4/CO_2 mole ratio leads to an increment of H_2/CO mole ratio for the whole temperature range. For the DRM of CH_4/CO_2 mole ratio ≤ 1.5, the syngas produced at temperature over 800℃ is fit for synthesising olefin, heavy hydrocarbon and oxygenated compounds without any adjustment. However, for DRM occurring at operating conditions of CH_4/CO_2 mole ratio ≥ 2, and at the temperature range of 550-1200℃, the syngas is only fit for alkane (C_1 –C_5) synthesis as the H_2/CO mole ratio is always ≥ 2. Figure 2 (right) illustrates that H_2/CO mole ratio is slightly affected by pressures at the temperature range of T ≥ 900℃, 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℃, the H_2/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℃ would be used for alkane (C_1 –C_5) synthesis when operating pressure ≥ 0.1MPa. 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 ≤ 700℃ 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 ≤900℃ 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.
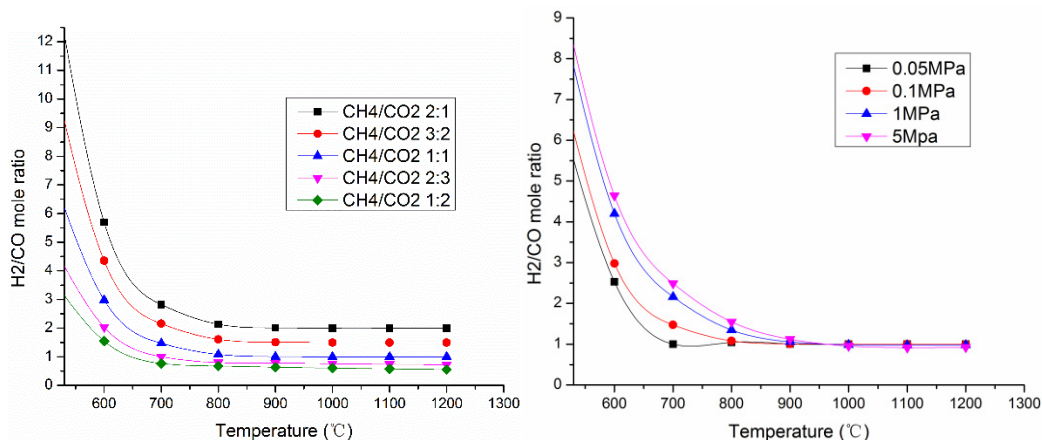

Figure 2: H2/CO mole ratio as a function of (left) CH_4/ CO_2 mole ratio and temperature at 0.1MPa, and (right) pressures and temperature with CH_4/ CO_2 mole ratio is1.

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℃, and the optimum operating conditions for carbon free regime were T ≥ 1000℃, 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 ≤ 0.1MPa and 546℃≤T≤1000℃, while CO dissociation was enhanced at operating conditions of P ≥ 0.1MPa and T ≤ 703℃. 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≥900℃. 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≤900℃, 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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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.