

Article ID: 1671-8224(2007)03-0155-06

To cite this article: ZHANG Jia-yuan, ZHOU Jie-min. Modeling the kinetics of methane conversion in steam reforming process of coke-oven gas based on experimental data [J]. J Chongqing Univ: Eng Ed (ISSN 1671-8224), 2007, 6(3): 155-160.

Modeling the kinetics of methane conversion in steam reforming process of coke-oven gas based on experimental data *

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Received 3 December 2006; revised 10 April 2007

Abstract: Steam-reforming is an effective approach for upgrading methane and hydrocarbon of coke-oven gas into CO and H₂, but the kinetic behavior needs more study. We investigated the conversion of methane in coke-oven gas by steam reforming process in an electric tubular flow at 14 kPa with temperature varying from 500 °C to 950 °C, and developed a kinetic model for , ignoring the effects of adsorption and diffusion. The optimal dynamic conditions for methane conversion 14 kPa are as follows: the ratio of the amount of water to the amount of methane is from 1.1 to 1.3; the reaction temperature is from 1 223 K to 1 273 K. The methane conversion rate is larger than 95% when the ratio of the amount of water to the amount of methane is 1.2 at a temperature above 1 223 K with the residence time up to 0.75 s.

Keywords: coke oven gas; steam reforming; kinetics model; conversion rate

CLC number: TQ522.61

Document code: A

1 Introduction

With the development of the coke industry, the discharge of coke-oven gas has been increasing, of which a large portion is not disposed properly, leading to environmental pollution and a waste of resources [1-2]. Converting coke-oven gas into synthesis gas as metallurgical reduction gas or raw material for producing chemicals such as methanol, ammonia, etc., is an imposing technology [3-5].

The so-called coke-oven gas is a by-product of coking plants during the production of blast furnace coke. Besides CO and H₂, there is a large portion of hydrocarbons in the gas, which include methane, benzene, naphthalene, etc. For use as synthesis gas, reduction gas or fuel gas, those hydrocarbons have to

be converted [1,6]. Steam reforming, non-catalytic and catalytic partial oxidation of methane are the current technologies for making synthesis gas from coke-oven gas [7]. The methane conversion rate is claimed to be more than 95% for the three processes. Nevertheless, steam reforming has a disadvantage that it requires a high temperature up to 500 °C and pressure; therefore, high-temperature and pressure resistant materials are needed [8-9]. Non-catalytic partial oxidation and catalytic partial oxidation of methane are mild exothermic reactions, but the unfavorable thermodynamics limits their commercial feasibility [10-11].

To develop a process for upgrading coke-oven gas, the conversion of methane in the presence of H₂O was studied. A mathematics model of CH₄ conversion was proposed based on the kinetics of the reaction revealed by the experimental data.

2 Experimentals

The compositions of tested coke-oven gas are listed in Table 1.

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* Funded by the Postdoctoral Foundation of China under the grant No. 2910001

Table 1 Composition of raw coke-oven gas for experiments

Volume fraction in coke-oven gas/%					
H ₂	CO	CO ₂	CH ₄	C _m H _n	N ₂
58.17	4.6	1.6	25.2	5.9	3.2

Experiments were performed in an electric tubular flow reactor of quartz with a 200 mm internal diameter and a 1 500 mm length as shown in Fig. 1 at 14 kPa with temperature varying from 500 °C to 950 °C.

Axial temperature was measured by platinum-

rhodium thermocouples which were movable in a small quartz tube of 5 mm diameter. The coke-oven gas was metered in storage cylinders. Its flow into the reactor was fixed at 18 m³ h⁻¹. The water flow was controlled by a high precision syringe pump. The steam of about 300 °C was blown into the furnace with coke-oven gas. The desired mole fractions were adjusted by controlling the temperature in saturators. The flow and composition of the coke-oven gas were kept constant during the experiments, the volume of the reactor (namely the conversion time) was adjusted with the insert depth of the outlet. The product gas was analyzed with Testo-360 data equipment.

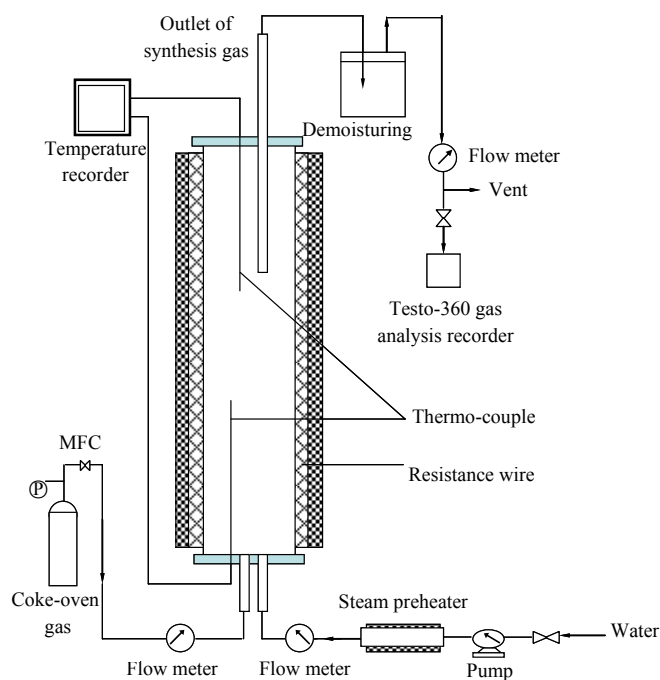


Fig. 1 The schematic flow sheet of experimental set-up

The results of experiments show that the optimal dynamic conditions for methane conversion are the H₂O/CH₄ ratio from 1.1 to 1.3 and the conversion temperature from 1 223 K to 1 273 K. In addition, the methane conversion rate are more than 95% when the H₂O/CH₄ ratio is 1.2, the conversion temperature is above 1 223 K and the residence time is up to 0.75 s.

3 Kinetics

3.1 Integral conversion equation

The experimental reactor can be approximately considered as an ideal piston-integral-reactor, a reactant goes through the reactor at constant

volumetric flow rate u and is converted constantly. The composition of outlet gas is the integration result of the whole reactor [12], as shown in Fig. 2.

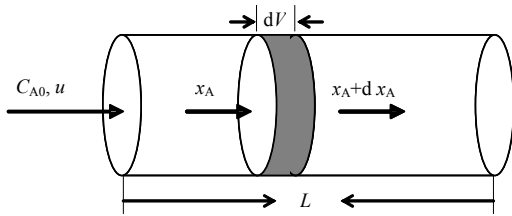


Fig. 2 The schematic of integral reactor

Assume that the original amount of substance concentration of A is C_{A0} , A flows into the reactor at a speed u , the conversion rate of A is x_A when A enters a micro bulk dV , and that is $x_A + dx_A$ when A departs. When the conversion process reaches a steady state, according to the matter equilibrium theory,

$$uC_{A0} dx_A = r_A dV, \text{ and } dV/(uC_{A0}) = dx_A/r_A.$$

Then, the dynamical integral equation of conversion rate is

$$V/(uC_{A0}) = \int_0^x \frac{dx_A}{r_A}, \quad (1)$$

where V is the volume of reactor; u the flow rate of reactant; C_{A0} the original amount of substance concentration of A; x_A , the conversion rate of A; and r_A , the conversion velocity of A.

3.2 Conversion rate equation

In the reactor, with the soot and nitrogen counted out, there are 5 components: CH₄, CO₂, CO, H₂O and H₂, which involves three elements: C, H and O. So, methane in a steam conversion system has two independent reactions as follows [13-14]:



whose steam conversion rates of methane are calculated by respectively

$$r_1 = K_1 C_{t,\text{CH}_4}^\alpha C_{t,\text{H}_2\text{O}}^\beta,$$

$$r_2 = K_2 C_{t,\text{CH}_4}^\theta C_{t,\text{CO}_2}^\gamma.$$

The total conversion rate of CH₄ is

$$R_{t,\text{CH}_4} = r_1 + r_2 = K_1 C_{t,\text{CH}_4}^\alpha C_{t,\text{H}_2\text{O}}^\beta + K_2 C_{t,\text{CH}_4}^\theta C_{t,\text{CO}_2}^\gamma, \quad (2)$$

where R_{t,CH_4} is the total methane-conversion rate; r_1 and r_2 the methane-conversion rates of respectively Reactions I and II; K_1 and K_2 are the rate constants of respectively Reactions I and II; C_{t,CH_4} , C_{t,CO_2} , and $C_{t,\text{H}_2\text{O}}$ are the instantaneous amount-of-substance concentrations of respectively CH₄, CO₂ and H₂O; α , β , θ , and γ are conversion indices.

The original amount-of-substance concentrations of CH₄, CO₂ and H₂O are assumed to be C_{0,CH_4} , C_{0,CO_2} , and $C_{0,\text{H}_2\text{O}}$, respectively.

Suppose the converted amount of CH₄ at a certain time is Y . The amount-of-substance concentration of CH₄ at this moment is $C_{t,\text{CH}_4} = C_{0,\text{CH}_4} - Y$. At the same time, the converted quantities of H₂O and CO₂ are mY and nY , respectively. According to the relation of chemical measurement by the reaction formulae I and II, we obtain

$$mY + nY = Y, \text{ namely, } m + n = 1.$$

So, the amount-of-substance concentrations of H₂O and CO₂ can be obtained as follows.

$$C_{t,\text{H}_2\text{O}} = C_{0,\text{H}_2\text{O}} - mY;$$

$$C_{t,\text{CO}_2} = C_{0,\text{CO}_2} - nY.$$

Substituting the expressions of C_{t,CH_4} , C_{t,CO_2} , and $C_{t,\text{H}_2\text{O}}$ into Eq. (2) leads to

$$R_{t,\text{CH}_4} = K_1 (C_{0,\text{CH}_4} - Y)^\alpha (C_{0,\text{H}_2\text{O}} - mY)^\beta + K_2 (C_{0,\text{CH}_4} - Y)^\theta (C_{0,\text{CO}_2} - nY)^\gamma. \quad (3)$$

3.3 Reaction rate constant K

Considering the possibility of integration, the assumed values of α , β , θ , and γ are as listed in Table 2 [15-16]. Then, the reasonable value is confirmed by experiment data.

Table 2 Assumed values of $\alpha, \beta, \theta,$ and γ

Case No	α	β	θ	γ
1	1	1	1	1
2	1	0	1	1
3	1	1	1	0

When $\alpha, \beta, \theta,$ and γ are all assigned a value of 1,

$$R_{1,CH_4} = K_1(C_{0,CH_4} - Y)(C_{0,H_2O} - mY) + K_2(C_{0,CH_4} - Y)(C_{0,CO_2} - nY).$$

Let $a = (mK_1 + nK_2)C_{0,CH_4} / (K_1C_{0,H_2O} + K_2C_{0,CO_2})$.

Then, uC_{0,CH_4}

$$R_{CH_4} = (mK_1 + nK_2)C_{0,CH_4}^2(1-x)\left(\frac{1}{a} - x\right), \tag{4}$$

where $x = Y/C_{0,CH_4}$.

Substituting Eq. (4) into (1) gives

$$\frac{V}{(uC_{0,CH_4})} = \int_0^x \frac{dx}{(mK_1 + nK_2)C_{0,CH_4}^2(1-x)\left(\frac{1}{a} - x\right)}. \tag{5}$$

Integrating Eq. (5), and supposing that

$$b = nK_2C_{0,CO_2} + mK_1C_{0,H_2O} - (mK_1 + nK_2)C_{0,CH_4},$$

$$\ln(1-x) = -bV/(uC_{0,CH_4}) + \ln(1-ax). \tag{6}$$

In this study, u and C_{0,CH_4} were kept constant; V was changed by adjusting the inset depth of the outlet; the conversion rate x of CH_4 was measured and calculated. The relationship of $V/(uC_{0,CH_4})$ with $\ln(1-x)$ is illustrated in Fig. 3.

The result shows that the relationship of $V/(uC_{0,CH_4})$ and $\ln(1-x)$ is approximately linear. The intercept and the slope of the line are the values of respectively $\ln(1-ax)$ and $-b$. At the same temperature, K_1 and K_2 stay constant, So, a and b are also constant. Then, we can get the values of a and b , thus get the corresponding values of K_1 and K_2 . The results are shown in Table 3.

The values of K_1 and K_2 for Cases 2 and 3 can also be calculated similarly. The results are shown in Table 4.

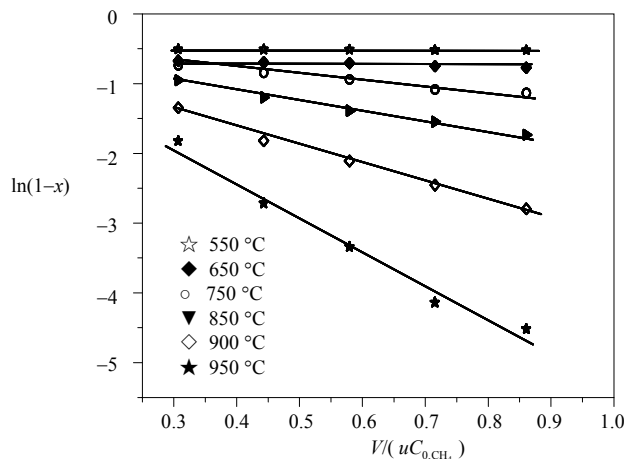


Fig. 3 Relationship of $V/(uC_{0,CH_4})$ with $\ln(1-x)$ at different temperature

Table 3 Values of a, b and K_1, K_2 for Case 1 when $\alpha, \beta, \theta,$ and γ all equal 1

Temperature/°C	a	b	K_{11}	K_{12}
550	0.108	0.037	0.163	0.201
650	0.154	0.329	0.31	0.338
750	0.105	0.711	0.70	0.411
850	0.108	1.461	1.46	0.975
900	0.106	2.853	2.86	2.305
950	0.114	5.415	5.34	4.075

Table 4 Values of K_1 and K_2 for Cases 2 and 3

Temperature/°C	K_{21}	K_{22}	K_{31}	K_{32}
550	-32.46	13.24	0.129	0.113
650	-16.26	28.06	0.426	0.234
750	10.82	-3.04	0.689	1.072
850	50.27	-41.94	0.846	2.133
900	-39.18	46.75	2.543	2.727
950	701.9	-744.90	3.807	7.415

3.4 Conversion indices

According to Arrhenius theory, the relationship of K and T is

$$K = A e^{-E/RT}, \quad (7)$$

and

$$\ln K = \ln A - \frac{E}{RT}, \quad (8)$$

where A is the apparent frequency-factor; E is the apparent activation energy which is constant; R is the gas constant; and T is temperature.

The relationship of $\ln K$ and $1/T$ should be linear, by which the reasonability of the above assumed could be judged. The curves of $\ln K$ versus $1/T$ are shown in Fig. 4, plotted with the data in Tables 3 and 4.

The results show that the relationships of $\ln K_{11}$ and $\ln K_{12}$ with $1/T$ are reasonable, but those of $\ln K_{21}$ and $\ln K_{22}$ are not, so the value of $(\alpha, \beta, \theta, \gamma)$ should be (1,1,1,1).

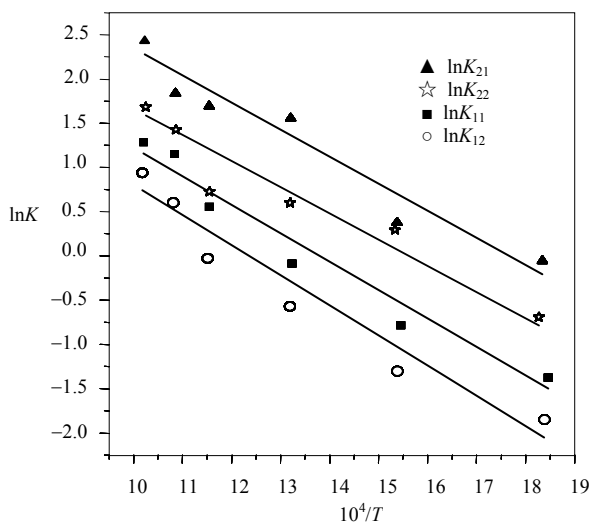


Fig. 4 Plot of $\ln K$ to $1/T$

3.5 Kinetics equation

The apparent frequency factors are $A_1 = 4.56 \times 10^9$ and $A_2 = 8.06 \times 10^8$.

The apparent activation energies are $E_1 = 21\,373.4 \text{ J mol}^{-1}$, $E_2 = 20\,843.7 \text{ J mol}^{-1}$.

The kinetics conversion rate equation of CH_4 is

$$R_{\text{CH}_4} = 4.56 \times 10^9 \times e^{-\frac{21373.4}{T}} C_{\text{t,CH}_4} C_{\text{t,H}_2\text{O}} + 8.06 \times 10^8 \times e^{-\frac{20843.7}{T}} C_{\text{t,CH}_4} C_{\text{t,CO}_2}.$$

4 Summary

The experiments of converting coke-oven gas into synthesis gas with steam in an ideal piston-integral reactor demonstrated that at 14 kPa, the optimal dynamic conditions for methane conversion are the $\text{H}_2\text{O}/\text{CH}_4$ ratio from 1.1 to 1.3 and the conversion temperature from 1 223 K to 1 273 K. Only the chemical reaction was taken into account; adsorption and diffusion effects on the conversion were ignored. The kinetic data were obtained by systematic variation of the reaction conditions, and the kinetics conversion rate equation of CH_4 was obtained.

Notations

- A: Reactant;
- A : Apparent frequency factor;
- C_{A0} : Original amount-of-substance concentration of A;
- $C_{\text{t,CH}_4}$: Instantaneous amount-of-substance concentration of CH_4 ;
- $C_{\text{t,CO}_2}$: Instantaneous amount-of-substance concentration of CO_2 ;
- $C_{\text{t,H}_2\text{O}}$: Instantaneous amount-of-substance concentration of H_2O ;
- E : Apparent activation energy;
- K_1 : Rate constant of Reaction I;
- K_2 : Rate constant of Reaction II;
- r_A : Conversion velocity of A;
- r_1 : Conversion rate of Reaction I;
- r_2 : Conversion rate of Reaction II;
- R : Gas constant;
- $R_{\text{t,CH}_4}$: Total conversion rate of CH_4 ;
- u : Flow rate of reactant;
- V : Volume of reactor;
- x_A : Conversion rate of A;
- α, β, θ and γ : Conversion indices.

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Edited by LUO Min