



Review

Thermodynamic and kinetic model of reforming coke-oven gas with steam

Jiayuan Zhang, Xiaohui Zhang*, Zhuo Chen, Li Li

School of Energy Science and Engineering, Central South University, Changsha, 932 South Lushan Rd, Hunan 410083, PR China

ARTICLE INFO

Article history:

Received 31 October 2009

Received in revised form

26 March 2010

Accepted 30 March 2010

Available online 6 May 2010

Keywords:

Coke-oven gas

Steam reforming

Kinetics model

Conversion rate

Thermodynamic

ABSTRACT

The experiments of reforming the methane of coke-oven gas with steam were performed. The effects of the thermodynamic factors, such as the H_2O/CH_4 ratio, the conversion temperature (T) of methane and the reaction time (t), on the methane conversion rate have been investigated. The experimental results show that the H_2O/CH_4 ratio within the range of 1.1–1.3 and the temperature 1223–1273 K are the reasonable thermodynamic conditions for methane conversion. A methane conversion of more than 95% can be achieved when the H_2O/CH_4 ratio is 1.2, the conversion temperature is above 1223 K and the conversion time is up to 15 s respectively. In addition, kinetic data of different reaction conditions were measured, and a dynamic model of methane conversion was proposed and verified. All results demonstrated that the results of the dynamic models agree well with the experiments, of which the deviation is less than 1.5%.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

The coke-oven gas (COG) is a by-product from coking plants during the production of blast furnace coke. It contains CO, H_2 , and large amount of hydrocarbons compounds like methane, benzene and naphthalene. Along with the development of the coke industry, a large amount of the coke-oven gas has not been utilized properly, which leads to serious environmental pollution and resource waste [1,2]. Reforming coke-oven gas into a synthesis gas, which can be used as metallurgical reduction gas or raw material for the production of chemicals such as methanol or ammonia etc., is a promising technology [3–6]. With regard to the use of the product gases, hydrocarbons should be converted first [1,7].

Reforming of coke-oven gas can be performed with or without catalysts. According to relevant literature, Steam reforming can also be combined with partial oxidation. Yang et al. [8] investigated the steam reforming of COG over the catalyst NiO/MgO, and found that the NiO/MgO catalyst possessed good catalytic activity, and the conversions of CH_4 and CO_2 were greatly affected by the reaction temperature and steam/carbon (S/C) mole ratio. Cheng et al. [9] introduced the characteristics of hot coke-oven gas (HCOG) over the catalyst Ni/Mg(Al)O, and pointed out the Ni/Mg(Al)O may be a promising catalyst in the catalytic reforming of HCOG.

Current research rarely reported studies of kinetic model of the COG reform process. Patel [10] produced a kinetic model for

oxidative steam reforming of methanol using Langmuir–Hinshelwood (LH) approach over Cu/ZnO/CeO₂/Al₂O₃ catalyst. Agrell et al. [11] studied the Cu/ZnO/Al₂O₃ catalyst for methanol steam reforming and produced strategies for suppression of CO formation and the kinetic model which agreed well with the experimental data. Mastalir et al. [12] investigated the Cu/ZrO₂/CeO₂ catalyst for methanol steam reforming from the viewpoint of dynamics, and point out that the content of Cu has an effect on the methanol steam reforming rate.

This paper is based on an enterprise industrial test of making metallurgical reduction gas with coke-oven gas. For coke-oven gas will cause damages to the catalyst (poisoning and pollution), catalyst loses efficacy in short-term, therefore, we have adopted 1Cr18Ni9Ti tube as reactor. Compared to the ordinary steel pipe, the 1Cr18Ni9Ti tube has a certain catalytic effect under the reasonable level of temperature and reaction time. The non-catalytic device we developed fully meets the requirements of the industrial transformation. Experiment and kinetic model were done on the basis of above work.

As a contribution to the development of a process to reform the coke-oven gas, the conversion of COG in the presence of H_2O has been studied in this paper. Experiments have been performed, and the optimal thermodynamic conditions as well as a mathematic model of CH_4 conversion have been proposed.

2. Experimental apparatus

The experiments were carried out on a laboratory-scaled apparatus. A schematic diagram of experimental system is shown in Fig. 1.

* Corresponding author. Tel.: +86 731 88876111.

E-mail address: xiaohui6064@sina.com (X. Zhang).

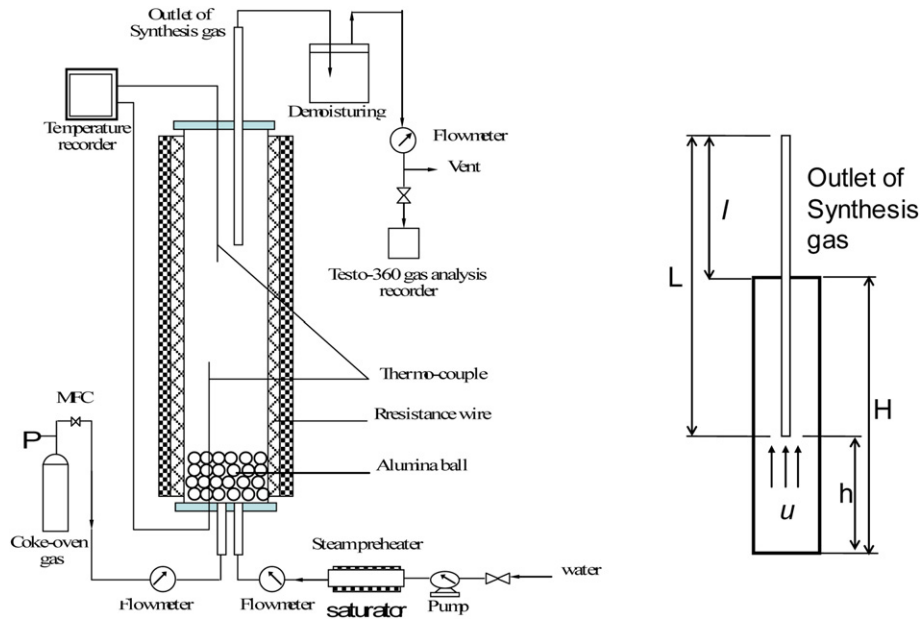


Fig. 1. The lay-out of experimental system.

A tubular electric flow reactor which is made of 1Cr18Ni9Ti is used to heat and maintain the furnace at a desired temperature. Alumina balls are put on the bottom of the furnace to keep an evenly distributed flow field. Temperature of the furnace can be controlled in a range of 773–1323 K. Axial temperatures are measured by platinum–rhodium thermocouples that can be shifted in a small quartz tube of 5 mm diameter. The coke-oven gas are metered from the storage cylinders and flow into the reactor at the fixed rate of $0.5 \text{ m}^3 \text{ s}^{-1}$ ($1.4 \times 10^5 \text{ Pa}$, 299 K) during the experiments. The flow rate of water is controlled by high precision syringe pump. Steam of about 573 K is generated by a saturator and mixed with the coke-oven gas at a certain molar ratio. The mixture is then blown into the furnace.

The measurement/analysis system includes elements for flow measurement, temperature measurement and gas analysis. The flow rates of steam and coke-oven gas are measured with a used vortex flowmeter (Sailsors TF130, Canada). The temperature is monitored and recorded by a 0.3 mm-wire thermocouple (K-type) and a data analysis device (Fluke, Hydra Data Logger 2625A, Germany). The product gas is analyzed and recorded by the Testo-360 (Germany) and Gasboard-3200L (China) which is capable of analyzing H_2 , CO, CO_2 and CH_4 .

Experiments were carried out under a pressure of $1.4 \times 10^5 \text{ Pa}$ and temperature of 773–1323 K. The compositions of the coke-oven gas for the experiments are listed in Table 1.

Table 2 shows the calibrated range, accuracy and relative error of the equipment. Errors may occur in experiments due to instrument conditions, calibration, observation, reading and test planning. The accuracy of the experiments has to be validated with an error analysis. This was done by using the method of average value and polynomial regression [13]. The average value of data was calculated by results of identical experimental condition. Then each data was analyzed by polynomial regression. For a given data set of x , y pairs, a polynomial regression of this kind can be generated as in Eq.

Table 1
Compositions of raw coke-oven gas for experiments.

Composition	H_2	CO	CO_2	CH_4	C_mH_n	SO_2
Content/mol%	58.17	4.6	1.6	25.2	5.9	3.2

(1). A standard error ($S_{y/x}$) was calculated by Eq. (2). The standard errors of the maximum values in H_2 selectivity, H_2 yield, CO selectivity, CO yield and CH_4 conversion rate were 1.13%, 0.96%, 1.16%, 1.02% and 2.33%, respectively.

$$y = a_0 + a_1x + a_2x^2 + a_3x^3 + a_4x^4 + \dots \quad (1)$$

$$S_{y/x} = \sqrt{\frac{\sum_{i=1}^n (y_i - a_0 - a_1x_i - a_2x_i^2)^2}{n - m - 1}} \quad (2)$$

3. Experimental results and discussions

During the experiments, influences of factors including $\text{H}_2\text{O}/\text{CH}_4$ mixing ratio, reaction temperature and time on methane conversion have been investigated. The conversion temperature varied from 773 K to 1323 K, and the $\text{H}_2\text{O}/\text{CH}_4$ ratio varied in 0.8–1.6. Conversion time was changed by adjusting the depth of outlet. The results of experiments are shown in Figs. 2 and 3.

As shown in Fig. 2, the methane conversion rate increases with increasing of temperature and conversion time. It reveals from Fig. 2 that the conversion reaction is close to an equilibrium state and the methane conversion rate reaches the maximum value when conversion time is up to 15 s and the temperature is above 1223 K.

Fig. 3 shows that the rate of methane conversion rate increases with the $\text{H}_2\text{O}/\text{CH}_4$ molar ratio when the $\text{H}_2\text{O}/\text{CH}_4$ ratio lies in 0.8–1.4, and the methane conversion rate is above 85%. When the $\text{H}_2\text{O}/\text{CH}_4$ ratio lies in 1.4–1.6, methane conversion decreases as $\text{H}_2\text{O}/\text{CH}_4$ ratio increases. It is known that the gas conversion rate is

Table 2
Calibrated range, accuracy and relative error of measurement.

Measurement	Equipment	Calibrated range	Accuracy	Relative error
Gas meter	Sailsors TF130	0–50 L/min	± 0.1	± 0.01
Gas temperature	K-type(D: $\phi 0.3$)	0–1643 K	$\pm 1 \text{ K}$	± 0.25
Gas analysis	Testo-360	CH_4 : 0–100%, CO_2 : 0–50%	± 0.02	± 0.02
	Gasboard-3200L	H_2 : 0–50%, O_2 : 0–25%		

Download English Version:

<https://daneshyari.com/en/article/1735090>

Download Persian Version:

<https://daneshyari.com/article/1735090>

[Daneshyari.com](https://daneshyari.com)