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Experimental study on catalytic steam gasification of natural coke in a fluidized bed

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ABSTRACT

The gasification characteristics of natural coke from Peicheng mine with steam were investigated in a fluidized bed reactor. The effects of catalyst type, composition and dosage of catalyst on the yield, components and heating value of product gas, and carbon conversion rate were examined. The results show that fluidized bed gasification technology is an effective way to gasify natural coke. Also the results indicate that individual addition of K-, Ca-, Fe-, Ni-based catalyst effectively increases the gasification reaction rate of the natural coke samples. With the increase in catalyst dosage, the yield and heating value of product gas per hour increase obviously, and carbon conversion rate is improved substantially. Each of aforementioned catalysts has similar catalytic effect and trend, among which the effect of Ca-based catalyst is a little weaker. The optimum metal atom ratio of mixed catalyst is Fe/Ni/others = 35/55/10, and the mixed catalyst displays maximum catalytic performance when the catalyst dosage in the natural coke is about 4%. The experimental findings provide an interesting reference for large-scale development and utilization of natural coke.

1. Introduction

When coal bed was invaded, pyrolyzed and carbonized by high temperature magma, natural coke forms. It is a combustible solid fossil fuel with heating value of 18~30 MJ/kg [1–5]. Reserves of natural coke are abundant in China, specially in eastern area, such as in Shandong province and Anhui province according to the recent investigation [6,7]. Natural coke coexists with coal in the coal bed, but is discarded or left in the mine without scheduled exploitation because of lack of effective utilization technology, which would cause tremendous energy waste and harm to the environment. Therefore, considering the challenge of energy crisis sources, it is necessary to utilize it for power generation. Feasibility study of a power plant with two 1000MWe natural coke-firing PC boilers passed evaluation after completing pilot-scale and demostration tests in Shandong province.

Fluidized bed gasification technology has many advantages [8–11], such as its good coal flexibility and strong gasification intensity. Material in the fluidized bed is in a violent fluidization and could be quickly heated to the gasification temperature by the bed inventory with high temperature, so it is suitable to gasification of natural coke.

Natural coke is a high metamorphic grade coal with very complex chemical composition. In order to obtain better gasification results, the appropriate conditions for gasification and effective catalyst added to natural coke are necessary. Lots of work on the catalytic activity has been done so far. For example, Khan M R and Seshadri K [12] found that the addition of calcium oxide was in favor of the tar cracking and improved the coal gasification. Xu Xiufeng et al. [13] showed that Ca element led to higher gasification reactivity of chars loaded with iron or nickel. Chen D et al. [14] discovered that the carbon formation during CO_2 reforming of methane by a Ni/CaO-Al_2O_3 catalyst deactivated faster than the dry reforming. Lee W J and Kim S D [15] explored that potassium carbonate exhibits the highest catalytic activity of all the catalysts tested, since it is uniformly dispersed on the coal particles. Oxidative-reduction cycles involving the metal salts appear to be the best explanation of this catalytic activity. McKee D W and Chatterji D [16] proposed the reaction scheme for the Boudouard reaction. Lang R J and Neavel R C [17] found that for alkaline earth salts activity is significantly less than for the alkaline metal salts and they are more difficult to disperse among active sites in the carbon.

This paper presents the influences of catalyst type, component ratio of mixed catalyst and catalyst dosage on natural coke-steam gasification reaction.

2. Experimental

2.1. Experimental setup and procedure

A fluidized bed gasification system, shown in Fig. 1 was installed. The system consists of a high- temperature steam generation system, a coke feeding and ash removal system, a gasifier, a fuel gas clean-up, analysis and combustion system, and a temperature measuring and control system. The gasifier furnace body with 40 mm I.D. is made of heat-resistant stainless steel, and its effective height is 1600 mm, air-opening of the distributor is 2%. Natural coke fed via a rotary valve reacted with high-temperature steam in the gasifier. After removing ash in the cyclone separator, the product gas was introduced into the

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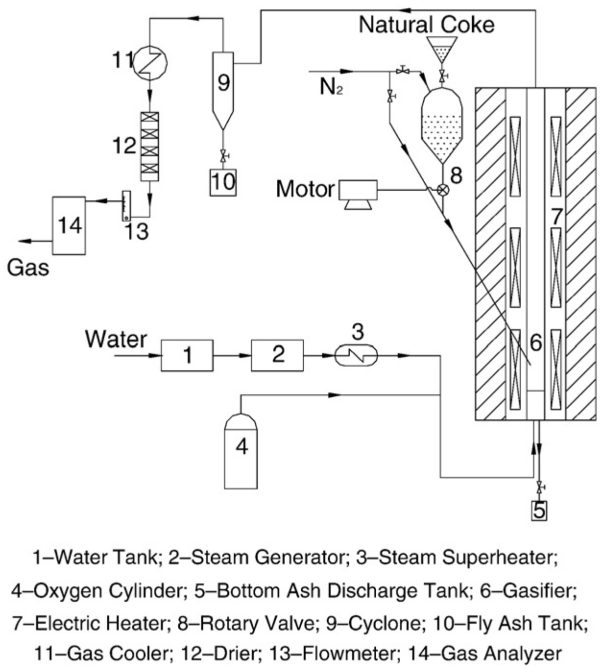

Fig. 1. Natural coke-steam fluidized bed gasification system.

cooler where the superheated steam was condensed and removed. Then the cooled gas was dehydrated in the dryer before passing through a flow meter, at last gas concentrations of CO, CO_2, CH_4, O_2 and H_2 in fuel gas were on-line measured with the multicomponent gas analyzer (NGA2000MLT1).

2.2. Experimental samples and conditions

Natural coke sample from Peicheng Mine, Jiangsu, China was crushed and sieved to particles with an average size of 1 mm. The proximate and ultimate analysis results of Peicheng natural coke, Xuzhou bituminous coal and petroleum coke are shown in Table 1. It is obvious by comparison that the natural coke has the lowest volatile, the highest ash and the lowest heating value. The bed material was quartz sand with the average size of 0.23 mm and density of 2400 kg/m^3. According to Geldart particle classification principle [18], two materials belong to Class B particles.

Candidate cataiysts were chosen based on comprehensive evaluation about their scientific and technical factors besides their economical consideration. Finally, calcium acetate, iron nitrate, nickel nitrate and potassium carbonate were selected as the catalyst in the experiments, and recorded as Ca-, Fe- Ni- and K-based catalyst, respectively. During the experiments, all catalysts were mechanically mixed with natural coke and their metal atom mass content was 2% of the natural coke quality except in the 3.3 section below.

Table 1
The proximate and ultimate analysis data of Peicheng natural coke, Xuzhou bituminous coal and petroleum coke.

Fuel	Proximate Analysis/% (mass, ad)				Ultimate Analysis /% (mass, daf)					Qnet,ad /MJ·kg^{-1}
	M	A	V	FC	C	H	O	N	S	
Natural coke	0.81	16.15	9.05	73.99	93.12	1.99	3.21	1.10	0.58	26.59
Coal	1.20	13.09	32.33	53.38	88.48	5.36	3.64	1.59	0.93	29.56
Pet coke	2.40	0.63	13.53	83.44	87.01	3.68	2.22	2.18	1.88	33.85

Basic experimental conditions were set as follows:

- Sample mass flow rate: 0.2 kg/h
- Steam mass flow rate: 1.05 kg/h
- Oxygen flow rate: 0.1 L/min
- Gasification reaction pressure: 0.1 MPa
- Gasification reaction temperature: 950 °C
- Period of time for each test: 30 min

2.3. Data dealt process

The product gas of natural coke-H_2O gasification is syngas, the gas heating value is the sum of heating value of every effective component gas, defined as:

$$Q_{vm} = 126[CO] + 108[H_2] + 359[CH_4] \quad (1)$$

The carbon conversion rate(X) is defined as:

$$X = \frac{12V([CO_2] + [CO] + [CH_4])}{22.4WC_{ad}} \times \frac{273}{273 + t_0} \times 100\% \quad (2)$$

Where, [CO], [CO_2], [H_2] and [CH_4] denotes its volume share in the whole product gas(%), respectively. Q_{vm} means the low heating value per volume of the syngas(kJ/m^3). V is the whole gas yield(m^3/h), W is the mass of natural coke(kg/h), C_{ad} is the air dry based carbon content in the natural coke(%), t_0 is the room temperature(°C).

The gas heating value per hour in the paper is the product value of gas heating value and gas yield(kJ/h).

The effective gas is the sum of CO, CH_4 and H_2.

3. Results and discussion

3.1. Influence of catalyst type on gasification reaction

The catalytic gasification experiments were conducted with Ni-, Fe-, K-, Ca-based catalysts separately mixed with natural coke in this section.

3.1.1. Influence of catalyst type on gas yield and carbon conversion rate

Experimental results of gas yield, carbon conversion rate of gasification reaction under the conditions with four kinds of metal salt catalysts and without catalyst are compared in Fig. 2. The addition of metal catalyst significantly increases the gasification rate and carbon conversion rate. Gas yield increases by more than 20%. The catalytic effect of each of the four catalysts on gas yield and carbon conversion rate is similar. However, gas yield and carbon conversion rate for Ca-based catalyst seem to be lower than the other catalysts. Previous research found that potassium carbonate exhibits the highest catalytic activity of

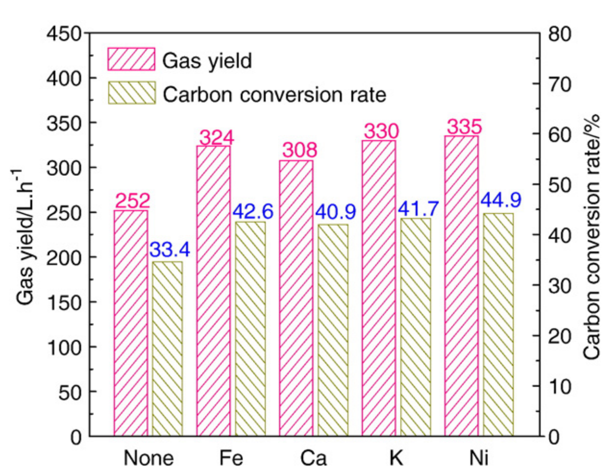

Fig. 2. Influences of catalyst type on gas yield and carbon conversion rate.