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## Experimental Study of Petroleum Coke Steam Gasification Catalyzed by Black Liquor in a Fluidized Bed

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### Abstract

Steam gasification of petroleum coke with black liquor (BL) was conducted in a fluidized bed. The reaction characteristics was investigated to allow an insight into the catalytic mechanism, and thus to justify the feasibility of H<sub>2</sub> production from petroleum coke using the fluidized bed gasification technology. The results showed that BL could not only greatly enhance the gasification rate but also increase the H<sub>2</sub> content in the produced gas. In comparison with non-catalytic gasification, the temperature of realizing similar reaction activity decreased by about 200 °C when loading with 10 wt.% BL, and the corresponding hydrogen amount increased by about 9 percentage point.

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*Keywords:* Petroleum coke; Steam gasification; Catalytic; Black liquor; Fluidized bed

### 1. Introduction

Petroleum coke is the final by-product from the coking process (mainly delayed coking) in the refinery. The amounts of petroleum coke, especially these with high sulfur content have been greatly increased because of the degradation of raw oil and the deep conversion refining technology<sup>[1]</sup>. Petroleum coke is characterized by low ash, low volatile content and highly condensed carbon structure. As a result, it usually has low reaction activity and cannot be gasified directly using the conventional fluidized bed technology. Most of petroleum coke is combusted for steam and power generation, and in turn caused great environmental problems in terms of high SO<sub>x</sub> and NO<sub>x</sub> emission. It has been well proved<sup>[2,3]</sup> that alkaline and alkaline earth metal (AAEM) species could greatly promote the gasification reactivity of carbonaceous materials, such as biomass, coal and their char products. However, it is economically unfeasible of using pure AAEM species as the catalyst in commercial gasification process due to the high price and recovery problems. Black liquor (BL) is the by-product from pulping process in paper making industry and usually contains abundant amounts of alkaline salts. Its catalytic effects on petroleum coke

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gasification have been widely studied<sup>[4,5]</sup>. In this study, petroleum coke steam gasification catalyzed by BL was conducted in a fluidized bed reactor in the temperature range of 700-1000 °C, thus to demonstrate the feasibility of hydrogen production from petroleum coke by the fluidized bed gasification technology.

## 2. Experimental Section

### 2.1. Sample preparation

Petroleum coke from Daqing Petrochemical Refinery was used and BL was provided by a local paper-making plant in Beijing, China. Petroleum coke was pulverized by a ball mill, then dried at 105 °C for 4 h and sieved into the samples with specified size distribution. For the catalytic gasification, the pulverized petroleum coke was impregnated with dewatered BL in deionized water for 24 h, then dried and sieved. The loading amount of BL varied in the range of 5-20 wt.% according to the mixture of petroleum coke and BL on dried basis. Table 1 shows the proximate and ultimate analyses of petroleum coke and dewatered BL. The main components of BL ash are illustrated in Table 2.

Table 1. Proximate and ultimate analyses and high heating value of petroleum coke and dewatered BL

Samples	Proximate analysis (wt.%, ad <sup>a</sup> )				Ultimate analysis (wt.%, daf <sup>b</sup> )					HHV <sup>c</sup> (MJ/kg)
	M	V	A	FC	C	H	N	S	O <sup>d</sup>	
Petroleum coke	5.76	9.97	0.17	84.10	92.66	4.09	1.65	0.48	0.95	35.22
Dewatered BL	0.64	47.45	43.38	9.17	55.78	3.74	1.64	0.67	38.17	ND <sup>e</sup>

<sup>a</sup>ad: air-dried basis; <sup>b</sup>daf: dry ash-free basis; <sup>c</sup>HHV: high heating value; <sup>d</sup>O: calculated by difference; <sup>e</sup>ND: not detected.

Table 2. Composition analysis of ash from BL

Components	Na <sub>2</sub> O	K <sub>2</sub> O	SiO <sub>2</sub>	SO <sub>3</sub>	Cl	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
Content (wt.%, d)	49.73	4.48	4.39	3.62	2.64	0.11	0.09	0.06	0.04	0.01

### 2.2. Experimental setup

Petroleum coke gasification was conducted in a fluidized bed reaction system, mainly including the parts of control system, gas and steam supply, reaction zone and product analysis. The fluidized bed reactor was made of quartz tube with an inner diameter of 30 mm (H=400 mm) and an enlarged upper section of 50 mm (H=200 mm). The reactor was divided into the preheating (with inert Al<sub>2</sub>O<sub>3</sub> balls) and the reaction zone by a gas distributor. Steam and nitrogen was used as fluidizing gas. Steam also was the gasification reagent, while nitrogen was the purging gas during the experimental intervals and used as the calibrating gas to determine the gas yield. The samples were instantly introduced into the reactor downwards via the two-stage valve after the reactor was heated to the designed temperature. The gas product was successively filtered, washed, dried and analyzed with a GC (Micro GC 3000, Agilent).

### 2.3. Analysis methods and data processing

The components in BL ash were analyzed by the X-ray fluorescence (XRF) spectrometry (AXIOS, PANalytical). The variation of the functional groups for the different samples was characterized with FTIR (TENSOR 27, Bruker) scanning in a range of 400-4000 cm<sup>-1</sup>. The carbon conversion ratio  $X$  of petroleum coke gasification was defined as Eq. (1), where  $X$  (%) is the conversion ratio;  $V$  (L) is the volume of gas products at end of the reaction;  $C_{CO}$ ,  $C_{CH_4}$  and  $C_{CO_2}$  (vol.%) stands for the volume fractions

of CO, CH<sub>4</sub> and CO<sub>2</sub>, respectively;  $m_o$  (g) is the sample mass and  $\alpha$  (wt.%) is the mass fraction of BL in the sample;  $w_{PC}$  and  $w_{BL}$  (wt.%) stands for the carbon fractions in the petroleum coke and BL, respectively;  $T_o$  (°C) is the environment temperature during the gas collection.

$$X = \frac{12V(C_{CO_2} + C_{CO} + C_{CH_4})}{22.4[m_o(1-\alpha)w_{PC} + m_o\alpha w_{BL}]} \times \frac{273}{273 + T_o} \times 100\% \quad (1)$$

### 3. Results and discussion

#### 3.1. BL loading amount

Figure 1 shows the effect of BL loading amounts on gasification rate (Fig. 1a) and gas composition (Fig. 1b) of petroleum coke gasification at 850 °C. The completion time of carbon conversion in non-catalytic gasification was about 250 min, while the time reduced by half (120 min) when loading 5 wt.% BL, and the time further declined to about 50 min with 10 wt.% BL. Meanwhile, the corresponding hydrogen content in the produced syngas increased from 58 vol.% (without BL) to about 67 vol.% (with 10 wt.% BL). As a result, BL as a catalyst, could not only enhance the gasification reactivity of petroleum coke, but also increase the H<sub>2</sub> concentration in produced gas. The conversion time hardly shortened when further increasing the BL loading amount from 10 wt.% to 20 wt.%. However, excessive BL added in petroleum coke could certainly decrease the treating capacity. The optimal loading amount of BL was thus chosen to be 10 wt.%.

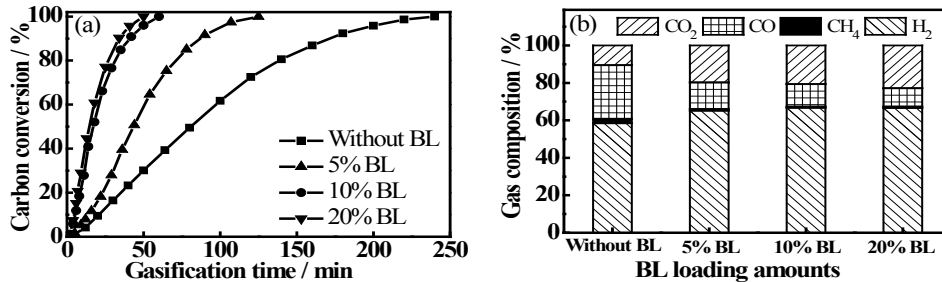


Fig. 1. Effects of BL loading amounts on carbon conversion (a) and gas composition (b) for steam gasification of petroleum coke

#### 3.2. Gasification temperature

The effect of temperature on carbon conversion time was shown for both non-catalytic (Fig. 2a) and catalytic steam gasification (Fig. 2b) of petroleum coke. High temperature would no doubt facilitate carbon conversion both with and without BL, especially for non-catalytic gasification. For example, the completion time of pure petroleum coke gasification was 240 min at 850 °C, while greatly reduced to about 85 min at 1000 °C. Petroleum coke could not be fully converted at the temperature lower than 850 °C, and while the temperature of complete carbon conversion was decreased to about 700 °C when adding 10 wt.%. Only 40 min was needed for the petroleum coke catalytic gasification at 850 °C.

Figure 3 shows the gas composition varied with temperature for the non-catalytic and catalytic steam gasification of petroleum coke. As for the carbon steam gasification, high temperature would inhibit water gas shift reaction due to its exothermic effect, consequently declining H<sub>2</sub> concentration in the produced gas. Steam gasification of petroleum coke was restricted by the conflicts of slow reaction rate at low temperature and H<sub>2</sub> decrement at high temperature. Using BL as catalyst could enhance both the gasification rate and also H<sub>2</sub> concentration. All of these show that black liquor could be an effective catalyst for petroleum coke gasification to produce hydrogen-rich syngas.

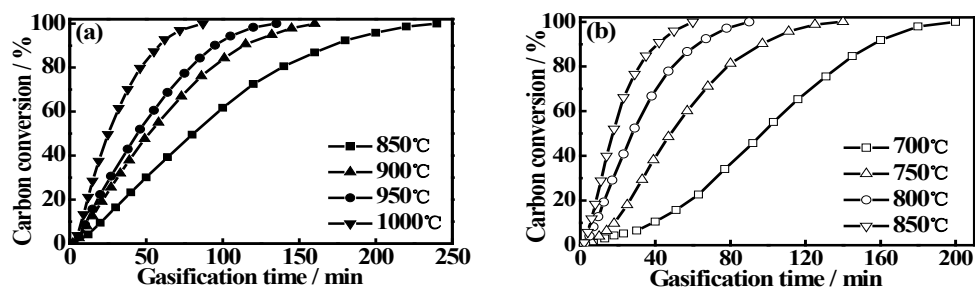


Fig. 2. Carbon conversion versus time of petroleum coke gasification at different temperatures without (a) and with BL (b)

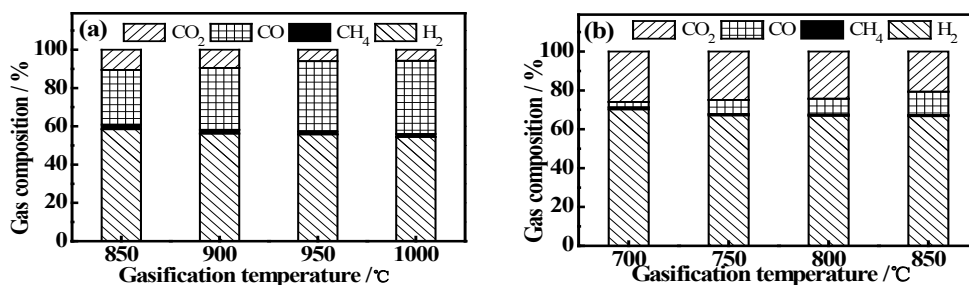


Fig. 3. Gas composition versus temperature of petroleum coke gasification without (a) and with BL (b)

#### 4. Conclusion

Co-gasification of petroleum coke and black liquor was conducted in a fluidized bed reactor to investigate the reaction behaviour, thus to justify the feasibility of hydrogen production from petroleum coke by conventional fluidized bed gasification process. The results showed that black liquor was an effective catalyst for petroleum coke steam gasification in light of both enhancing reaction rate and increasing hydrogen content in the produced syngas. Moreover, the temperature for complete carbon conversion was decreased by about 200 °C, thus to solve the contradiction of slow reaction rate at low temperature and H<sub>2</sub> concentration decrement at high temperature.

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#### Biography

Dr. Yuming Zhang is an associate professor from State Key Laboratory of Heavy Oil Processing, Chinese University of Petroleum. He obtained his PhD degree on Chemical Engineering in 2013 from IPE, Chinese Academy of Sciences. His work has focused on thermal conversion process, such as heavy oil processing, coal pyrolysis and gasification.