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# Reactivity and kinetics for steam gasification of petroleum coke blended with black liquor in a micro fluidized bed ☆

Yuming Zhang [a,b], Meiqin Yao [b], Shiqiu Gao [b,*], Guogang Sun [a], Guangwen Xu [b,*]

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum-Beijing, Beijing 102249, China
[b] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

## HIGHLIGHTS

- Steam gasification of petroleum coke with black liquor (BL) was conducted in a micro fluidized bed.
- Using BL evidently enhanced gasification reaction and increased $H_2$ content in the produced gas.
- The work studied the effects of BL loading amount, reaction temperature and oxygen content in steam.
- The shrinking core model well described the steam gasification of petroleum coke to estimate kinetic parameters.
- Activation energy of petroleum coke gasification was decreased by BL catalysis and $O_2$ addition into steam.

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## ABSTRACT

Steam gasification of petroleum coke catalyzed by black liquor (BL) was conducted in a micro fluidized bed to investigate the reaction characteristics and kinetics, including the effects of temperature, particle size, BL loading amount and oxygen content in steam on product gas composition and reaction rate. The completion time of petroleum coke steam gasification at 900 °C decreased from 120 min for pure coke to about 40 min for the coke blended with 10 wt.% BL. The corresponding hydrogen fraction in the produced syngas increased by 9 vol.%. The gasification reaction was further enhanced by introducing a small amount of oxygen into the steam. The shrinking core model (SCM) and homogenous model (HM) were used to calculate the kinetics of petroleum coke gasification, finding that SCM enabled the better correlation with experimental data than HM did. Using SCM the activation energy was 77 kJ·mol$^{-1}$ for coke gasification with 10 wt.% BL as catalyst, which was much lower than 120 kJ·mol$^{-1}$ for the case without BL blended. The activation energy was further reduced to about 63 kJ·mol$^{-1}$ by adding 5% oxygen into the steam, showing a synergistic effects of BL and $O_2$ on petroleum coke gasification. The study also justified the feasibility of syngas production from petroleum coke via fluidized bed gasification.


## 1. Introduction

Petroleum coke is the final by-product from the delayed coking process in refinery, and its amount has increased rapidly with the development of deep conversion refining technology. There is also gradually more petroleum coke with high sulfur content in response to the quality deterioration of crude oil. High-sulfur petroleum coke is usually combusted as fuel for generation of steam or power, which would cause serious environmental impacts. Petroleum coke gasification can produce syngas ($CO + H_2$) for the production of hydrogen required by hydrogenation [1–4]. Meanwhile, the inherent sulfur in petroleum coke is mainly transformed into $H_2S$ in gasification to be easily recovered as S. However, the low gasification reactivity of petroleum coke greatly restricted its use in actual gasifiers, especially for fluidized bed gasification at temperatures of about 1000 °C [5,6].

It is well known that the gasification of carbonaceous materials, such as coal, biomass and their char can be catalyzed by various alkali and alkaline earth metal (AAEM) compounds [7–10]. However, the use of pure AAEM compounds as catalyst is expensive and economically unfeasible for practical applications because its recovery and treatment after gasification has still great difficulty. Cheap and effective catalyst is urgently needed for petroleum coke

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* Corresponding authors. Tel.: +86 10 82544885.
*E-mail addresses:* sqgao@ipe.ac.cn (S. Gao), gwxu@ipe.ac.cn (G. Xu).

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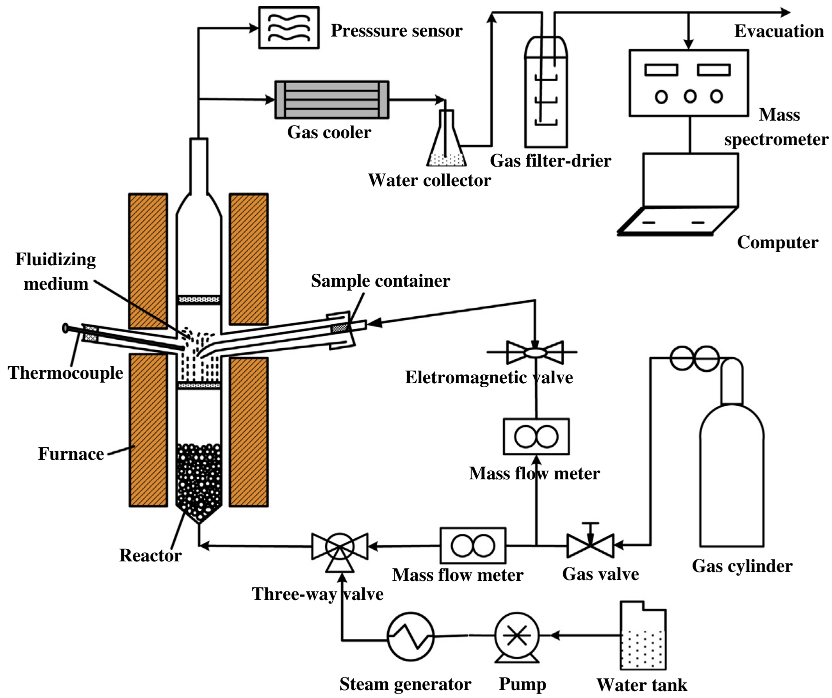


**Fig. 1.** A schematic diagram of the micro-fluidized bed reactor analyzer.

**Table 1**
Proximate and ultimate analyses of tested samples.

| Samples | Proximate analysis (wt.%, ad) | | | | Ultimate analysis (wt.%, daf) | | | | | HHV (MJ/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| | M | V | A | FC | C | H | N | S | O | |
| Petroleum coke | 5.76 | 9.97 | 0.17 | 84.10 | 92.66 | 4.09 | 1.65 | 0.48 | 0.95 | 35.22 |
| Fugu coal | 4.57 | 33.75 | 4.44 | 57.24 | 82.92 | 4.66 | 1.26 | 0.22 | 10.94 | 31.90 |
| Dewatered BL | 0.64 | 47.45 | 43.38 | 9.17 | 55.78 | 3.74 | 1.64 | 0.67 | 38.17 | 9.85 |

M: moisture; V: volatile matters; A: ash; FC: fixed carbon; ad: air dry; daf: dry ash-free; HHV: higher heating value; O: by difference.

**Table 2**
Composition analysis of BL ash by XRF.

| Components | $Na_2O$ | $K_2O$ | $SiO_2$ | $SO_3$ | Cl | $Al_2O_3$ | $P_2O_5$ | CaO | $F_2O_3$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Content (wt.%, d) | 49.73 | 4.48 | 4.39 | 3.62 | 2.64 | 0.11 | 0.09 | 0.06 | 0.04 | 0.01 |

gasification. Black liquor (BL) is generated in pulping process and contains usually alkaline salts and some organic compounds (lignin, cellulose and hemicellulose). Naqvi et al. [11–13] have investigated BL gasification by direct causticization for syngas and liquid fuel production integrated with a pulp mill that have shown to have good catalytic effect on carbonaceous materials [14–17]. Guo et al. [15] suggested that the sodium salts (e.g., NaOH and $Na_2CO_3$) in BL could be an effective catalyst on the alkali lignin pyrolysis and gasification. Zou et al. [16] demonstrated that the gasification rate of petroleum coke was more effectively enhanced by wet grinding with BL than by dry grinding. In a thermogravimetric analyzer (TGA), Zhan et al. [17] found that loading 5 wt.% BL into petroleum coke has made its reactivity with $CO_2$ higher than that of Shenfu coal at 1273 K. These studies on co-gasification of petroleum coke and BL are conducted in TGA and using $CO_2$ reagent, while there was almost no studies on the reaction kinetics. The understanding of gasification reactivity and kinetics for petroleum coke is of not only scientific value but also of practical importance on the gasifier design.

The characteristics and kinetics for gasification of the carbonaceous fuels, like, coal, biomass and their chars, have been extensively studied [18–21] also with various gas–solid reaction models. Zhang et al. [19] studied the reactivity and kinetics of gasification with steam and $CO_2$ for six typical Chinese anthracite chars in TGA using homogeneous model and shrinking core model. Generally, petroleum coke has different pore properties from that of coal or biomass chars. It has usually a highly condensed layer of carbon but few pores on its surface when comparing with that of coal and biomass chars. The reaction models for coal or biomass char might not be applicable to the petroleum coke gasification. The kinetics from TGA is based on weight loss of a sample in a specified heating program. The sample is confined into a fixed crucible during the reaction, which leads to serious inhibition on mass and heat transfers. Thus, the experimental results from TGA cannot be directly extrapolated to the conditions of fluidized bed which are greatly different from these in TGA.

The so-called micro fluidized bed reaction analyzer (MFBRA) [22] has been developed to enable the pulse feed of reactant particles in micro grams, rapid heating of reactant and effective suppression of external diffusion, while it allows also the real-time measurement of the gaseous product through an on-line mass spectrometer (MS). The MFBRA has already been used to measure different kinds of gas–solid reactions [23,24], such as biomass

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