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Comparison of steam-gasification characteristics of coal char and petroleum coke char in drop tube furnace☆

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ABSTRACT

The steam-gasification reaction characteristics of coal and petroleum coke (PC) were studied in the drop tube furnace (DTF). The effects of various factors such as types of carbonaceous material, gasification temperature (1100–1400 °C) and mass ratio of steam to char (0.4:1, 0.6:1 and 1:1 separately) on gasification gas or solid products were investigated. The results showed that for all carbonaceous materials studied, H_2 content exhibited the largest part of gasification gaseous products and CH_4 had the smallest part. For the two petroleum cokes, CO_2 content was higher than CO, which was similar to Zun-yi char. When the steam/char ratio was constant, the carbon conversion of both Shen-fu and PC chars increased with increasing temperature. When the gasification temperature was constant, the carbon conversions of all char samples increased with increasing steam/char ratio. For all the steam/char ratios, compared to water gas shift reaction, char-H_2O and char-CO_2 reaction were further from the thermodynamic equilibrium due to a much lower char gasification rate than that of water gas shift reaction rate. Therefore, kinetic effects may play a more important role in a char gasification step than thermodynamic effects when the gasification reaction of char was held in DTF. The calculating method for the equilibrium shift in this study will be a worth reference for analysis of the gaseous components in industrial gasifier. The reactivity of residual cokes decreased and the crystal layer (L_{002}/d_{002}) numbers of residual cokes increased with increasing gasification temperature. Therefore, L_{002}/d_{002}, the carbon crystallite structure parameter, can be used to evaluate the reactivity of residual cokes.

1. Introduction

Gasification reaction of coal and petroleum coke (PC) is important for fundamental research in gasification technology. Since the middle of the twentieth century, researchers have deeply and systematically studied on the characteristics of coal gasification reaction, and they have designed and built several methods to study coal gasification. A lot of valuable information has been obtained in experiments which provided an important direction of the industrialization of coal gasification. Moreover, coal, which is a main raw material of gasification, belongs to the non-renewable energy. Nevertheless, petroleum coke, as a carbonaceous material abundant in carbon, which comes from the delay-coke plant, is still going up in its production. The gasification of petroleum coke for the production of steam, power, and hydrogen has widely generated interests due to the broad application perspective [1]. Therefore, it is necessary to study the structure and reaction characteristics of petroleum coke for full use in industrial gasification in the future.

The gasification reaction characteristics of carbonaceous material were widely studied with the usage of thermogravimetric analyzers (TGA), self-made fluidized bed reactors and fixed bed reactors [2–5]. Zhan *et al.* [2] studied the effects of blending methods on the co-gasification of petroleum coke and lignite from experiments performed at atmospheric pressure and 1000 °C with a heating rate of 25 °C·min^{-1} by TGA. Kim *et al.* [4] used a horizontal fixed bed reactor in the char-CO_2 gasification experiments and studied the effects of coal type and particle size on char-CO_2 gasification *via* gas analysis. Their experiments were carried out at different reaction temperatures (1050–1400 °C) with a slow heating rate (20 °C·min^{-1}). Tay *et al.* [5] performed the gasification of a Victorian brown coal at 800 °C in a novel fluidised-bed/fixed-bed reactor and the changes in char reactivity and structure were compared under two different gasifying agents (O_2 and CO_2).

Most of the previous studies were carried out at a low temperature (≤1100 °C) or a slow heating rate (≤100 °C·s^{-1}). With the development of entrained-flow gasification technology, a great many gasification reactions data obtained in the conditions of high temperature, rapid

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heating and short residence time are needed for the design and operation of gasifiers. The drop tube furnace (DTF), with characteristics of rapid heating and high gasification temperature, is close to industrial entrained-bed gasifier.

In previous research, DTF was often used to study carbonaceous material combustion or char-CO_2 gasification characteristics [6–10]. Chen *et al.* [6] simulated the process of pulverized coal injection (PCI) in a blast furnace with the usage of DTF and investigated the characteristics of volatiles release, particle formation and reactivities of unburned char and soot of two different coals. Ahn *et al.* [7] and Kajitani *et al.* [8] carried out experiments on char-CO_2 gasification in DTF. The effect of pore diffusion on gasification reaction at high temperature was studied and the corresponding kinetic models were established. Milenkova *et al.* [9] studied the behavior of three fuel-grade petroleum cokes of different origination under pulverized fuel combustion conditions in DTF. However, to the best of our knowledge, there are rare reports about steam-gasification characteristics of coal or petroleum coke in DTF [11]. In the present, water-coal (coke) slurry gasification technology has been extensively applied. Therefore, it is necessary to study char-steam gasification reaction characteristics for process parameter optimization of water–coal (coke) slurry gasification unit.

The present work aims to study the characteristics of steam gasification reaction of coal char and PC char under high temperature (≥1100 °C) and rapid heating rate (10^3–10^4 °C · s^{-1}) in DTF. Effects of various factors such as types of carbonaceous material, gasification temperature and concentration of gasification agent (steam/char ratio) on gasification gas production, carbon conversion, structure and gasification reactivity of residual cokes were investigated. Meanwhile, the main reaction balances in DTF were calculated based on the concept of equilibrium temperature interval so as to provide a worth reference for the analysis of product gas composition from the industrial gasifier.

2. Experimental

2.1. Samples

Nei-meng (NM) coal, Shen-fu (SF) coal, Zun-yi (ZY) coal, Jin-ling (PC1) petroleum coke and Hui-zhou (PC2) petroleum coke were used for this study. The coals and petroleum cokes were crushed and sieved, and the size fraction of 80–120 μm was chosen as sample. The proximate and ultimate analyses and ash fusion temperatures of samples are summarized in Table 1.

2.2. Apparatus

As shown in Fig. 1, a drop tube furnace (0.054 m.i.d. × 1.5 m high) was designed and built for the present study. In this work, coals or chars were fed into the upper surface of the isothermal zone of the furnace with a water-cooling nozzle. The particles flowed through a screw feeder from a hopper with a feeding capacity of 0.3–0.4 g · min^{-1}, and Ar was used as a carrier gas during the pyrolysis process. The stability of the feeding rates for different samples was measured in the preliminary testing. The feeding amount in 5 min of each sample was recorded for several tests. Standard deviation in population (STDEVP) was adopted to evaluate the stability of the feeding rates. As shown in Table 2, the values of STDEVP are small enough to ensure the feeding stability for different carbonaceous materials. When char-steam gasification experiments were carried out, N_2 was used as a carrier gas (also gas tracer), and water was pumped into a vaporizer by a double-type axial piston pump for steam generation. The steam was mixed with N_2 and heated to 220 °C for injection into the reactor. During the char-steam gasification process, the char particles were carried by small gas flow rates (around 1 L · min^{-1}) to ensure a laminar flow, and the residence time of particles was nearly 2 s in the main reaction zone. The furnace was heated by three compartments of silicon and molybdenum rod high-temperature electric heating elements which could heat the reaction zone to 1400 °C. Each heating compartment was controlled separately to maintain a constant temperature over the reactor length. The product gases and residues were quenched and separated in a char collector. The heating rate in DTF is 10^3–10^4 °C · s^{-1}, which is similar to that in the industrial coal gasifier. The temperature profiles in DTF were measured by a K-type thermocouple. Fig. 2 shows that the isothermal zone is about 600 mm along the tube, and the maximum temperature difference between the external surface of reaction wall and gas in the internal isothermal zone of the tube is less than 20 °C. Thus, the practical gas temperature in the main reaction zone of the alumina tube was approximately represented with the corresponding temperature of the external surface of reaction wall (1100–1400 °C).

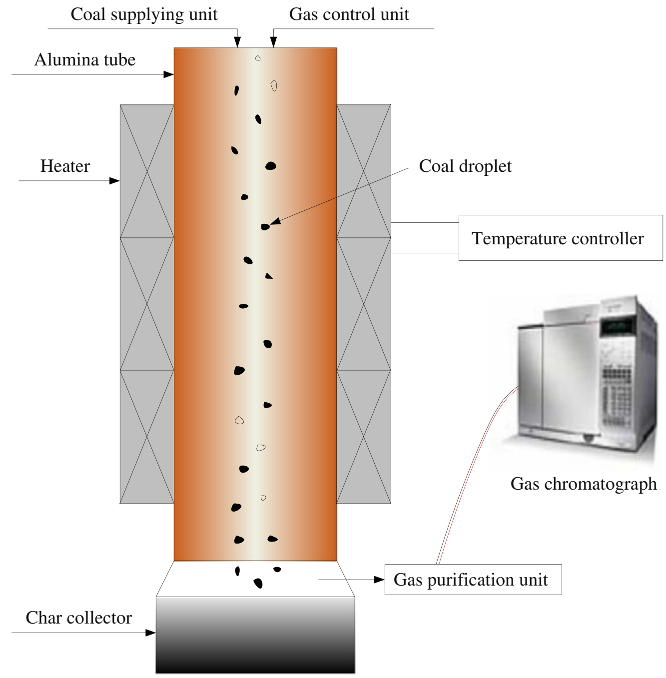

Fig. 1. Schematic diagram of drop tube furnace setup.

Table 1
Proximate and ultimate analyses and ash fusion temperature of coals and petroleum coke samples

Sample	Proximate analysis *d* (by mass)/%			Ultimate analysis *d* (by mass)/%					Ash fusion temperature/°C			
	VM	FC	Ash	C	H	N	S	O*	DT	ST	HT	FT
NM	42.09	43.60	14.31	61.18	2.35	1.21	0.64	20.31	1119	1169	1200	1218
SF	35.42	58.29	6.29	79.14	2.32	1.12	0.77	10.36	1152	1167	1175	1179
ZY	7.59	73.46	18.95	76.57	2.13	1.10	0.83	0.42	1345	1370	1395	1463
PC1	9.51	90.22	0.27	89.15	3.72	0.75	2.08	4.02	–	–	–	–
PC2	10.33	89.38	0.29	92.24	3.20	1.48	2.77	0.02	1453	1537	1539	1542

Note: O* was calculated by difference.