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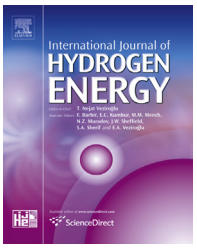

Study on rapid pyrolysis and in-situ char gasification characteristics of coal and petroleum coke

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ABSTRACT

Rapid pyrolysis characteristics of three different rank coals and two petroleum cokes were investigated using a drop tube furnace. Moreover, gasification characteristics of char samples were studied in an in-situ heating stage. The results showed that H_2 and CO were the main gaseous pyrolysis products of coal samples. The relative content of H_2 and CO increased with increasing pyrolysis temperature. The volume fraction of H_2 in syngas increased with increasing coal rank, whereas that of CO showed the contrary trend. Anthracite and petroleum cokes (Petcoke 1 and Petcoke 2) exhibited a great similarity in gas release characteristics. There was a maximum value for the specific surface area and graphitization degree of char samples with increasing pyrolysis temperature. The results of in-situ heating stage experiments indicated that the most of char particles reacted with CO_2 in the shrinking particle mode at the initial stage. Char samples of petcokes and anthracite were similar in slow consumption of particle skeleton during gasification. Interestingly, petcokes demonstrated particle migration, residual agglomeration, and rapid consumption at the later reaction stage. The variation trend of the area shrinkage ratio of char samples was well verified by the TGA results.

Introduction

Gasification is an key technology for clean and efficient usage of carbonaceous materials [1,2]. At present, coal is the main raw material used in industrial gasifiers. However, with the rapid consumption of coal, it is increasingly urgent to conduct researches on other alternative carbonaceous materials like petroleum coke (petcoke) and biomass.

Petroleum coke is an important by-product originating from delayed coking of oil. Production of this coke increases steadily as the demand of heavy crude oil is increasing continuously [3]. Meanwhile, there are some distinctive characteristics of petroleum coke such as higher heating value and carbon content, lower volatile compounds and ash content compared to coal. These different properties of petcokes may lead to different reaction characteristics during pyrolysis or gasification process. As a result, a comprehensive

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comparison of thermal reaction characteristics between petroleum coke and coal may be required for making full use of petroleum coke.

Pyrolysis is the fundamental step of gasification, and it involves removal of volatiles and evolution of matrix structure, which may impact the gasification process. Pyrolysis is not only an effective way for coal desulfurization, but also a significant method for value added gaseous or liquid products, such as H_2, aromatic compounds etc [4,5]. Many factors, such as pyrolysis temperature, heating rate and residence time, may affect pyrolysis characteristics and gasification reactivity. Zhu et al. investigated the influence of heating rate and pyrolysis temperature on the char structure and gasification reactivity [6]. The results showed that the structure of samples remained almost unchanged at a low heating rate but expanded at a high heating rate. The gasification reactivities of chars was enhanced at a higher heating rate or a at a lower pyrolysis temperature. Jayaraman et al. reported that the production of light gases (i.e. H_2, CH_4, etc) was enhanced at higher heating rates during coal pyrolysis process [7], which agreed well with the results proposed by Yan et al. [8]. Liu et al. showed that the graphitization degree and regularity of microcrystal structure of petroleum coke increased with increasing pyrolysis temperature [9].

Recently, although numerous studies on rapid pyrolysis of coal using wire-mesh reactors or drop tube furnaces have been reported [10–12], the rigorous comparison of rapid pyrolysis and gasification characteristics between petroleum coke and coal is relatively rare. Generally, gasification experiments are mostly conducted in black-box equipment, resulting in high challenges for the analysis of real reaction situation in gasifiers. In our previous studies, the interaction between catalyst and coal at the gasification stage was visually revealed. We also recorded the morphological variations of coal loaded with catalyst on-line using a heating stage microscope [13,14]. Nonetheless, the application of such in-situ visual technique on the gasification processes of fast-pyrolysis chars of petroleum coke or coal is rare.

The present work is aimed to carry out rapid pyrolysis experiments of coals with different ranks and two petroleum cokes. A drop tube furnace was used to make comprehensive comparison on the pyrolysis gas release and char structure evolution between coals and petroleum cokes. Furthermore, the in-situ analysis of char gasification reactivities was performed using a heating stage microscope coupled with a thermogravimetric analyzer (TGA). It was not only beneficial to deeply understand the characteristics of rapid pyrolysis and char gasification from two kinds of carbonaceous materials, but also to provide fundamental data for the industrial application of petroleum coke or the mixture of petroleum coke and coal in gasifiers.

Experimental section

Samples preparation

Three Chinese typical coals, Neimeng lignite (NM), Shenfu bituminous coal (SF), Zunyi anthracite (ZY), and two petroleum cokes obtained from Jinling Refinery Plant, China (Petcoke 1) and VALERO company, America (Petcoke 2) were selected as raw materials. The experimental samples were dried, ground and sieved to the size fraction of 80–120 μm. Properties of tested samples are summarized in Table 1.

Rapid pyrolysis in a DTF

The rapid pyrolysis experiments of raw materials were conducted in a drop tube furnace (DTF). The device is composed of sample feeding system, high temperature furnace, gas supply system, and products collector. Detailed description of the device can be found in our previous study [15].

The raw materials were put into the hopper at first during pyrolysis procedures. Meanwhile, nitrogen was fed for ~30 min at a rate of 1 L min^{-1} in order to sweep away residual air in the reactor. Then the furnace was heated up to the desired temperature (800–1400 °C with the interval of 200 °C) under continuous nitrogen flow. Afterwards, the screw fitter was turned on and the tested samples were fed continuously into the reactor and passed through the isothermal zone rapidly. Finally, char samples and pyrolysis gases were collected.

Gas chromatography analysis

The relative and absolute amounts of light gaseous species including H_2, CO, CO_2, and CH_4 were measured by using Agilent 7890A gas chromatography [16].

According to the volume percentage of each gas product from the gaseous analyzer, the yields of light gaseous species were obtained as gas generation per unit mass of coal (g) in dry basis.

In calculation, N_2 was adopted as a tracer gas. The total volume of nitrogen in the outlet was assumed to be the same as that supplied to the furnace. Table 1 indicates that nitrogen content of all carbonaceous materials was less than 1.5 wt.%, thus it is rational to adopt N_2 as tracer gas in DTF. Detailed formula for quantitative analysis of gaseous products was as follows:

$$n_i = \frac{\left(\frac{Q_{N_2}}{V_{N_2}} \times V_i\right)}{m \times V_m} \quad (1)$$

Note: n_i denotes gaseous yield of component i (mmol·g^{-1}); Q_{N_2} denotes the flow rate of N_2 (L·min^{-1}); V_{N2} denotes the volumetric percentage of N_2 in exhaust gas (vol.%); V_i denotes the volumetric percentage of component i in exhaust gas (vol.%); m denotes feed rates of coal or petcoke (g·min^{-1}); V_m denotes the molar volume of gaseous product (L·mol^{-1}).

Structural tests of char samples

Micromeritics ASAP 2020 Analyzer was used to analyze the pore structure of char samples. Nitrogen and carbon dioxide gases were chosen as the adsorbent to measure the mesopore and macropore at −196 °C and micropores around 0 °C, respectively.

Carbon crystallite structure of char samples was characterized by Rigaku D/max-2550VB/PC X-ray diffraction within the diffraction angle range of 10–80°. KBr pellet pressing

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