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Experimental investigation on the influence of the pyrolysis operating parameters upon the char reaction activity in supercritical water gasification

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ABSTRACT

Supercritical water gasification of coal is a clean and efficient method for coal utilization which can convert coal into H_2 and CO_2. In order to further reduce costs, a novel two-step cascade utilization method was proposed in this study: conducting traditional pyrolysis first and then gasifying the pyrolysis char in supercritical water. The influences of different pyrolysis operating parameters on gaseous products and char gasification in supercritical water were investigated. Quartz tube reactors were used to ensure the complete collection of gaseous products in pyrolysis process. The experimental results showed that both carbon and hydrogen conversion efficiency increased with temperature, and the increasing trend became not obvious after reaction for 5 min. The thermogravimetric curves showed that volatilization removal process was completed at the pyrolysis time of 5 min and higher pyrolysis temperatures were beneficial to the subsequent gasification process. The result also showed that residual weight was 15%–20% of the initial weight. Hydroxyl radicals kept stable during pyrolysis process with the absorption peak intensity increasing first and then decreasing, and mineral substance disintegrated gradually as time increased. As pyrolysis temperature increased, the peak of C–C double bonds decreased, turning into stable functional groups and carbonyl group increased. Dispersive pores occurred at the surface of coal as residence time increased with particle size decreasing, specific surface area and reactivity increasing. The results might be used for the design of a cascade utilization system based on coal gasification in supercritical water.

Introduction

Coal is the main energy resource in our country and its traditional utilization way, direct combustion, has caused serious environment pollution [1–5] such as nitrogen oxides and metal compounds [6], and the heat efficiency is low because the production of flue gas containing much non-recycled heat [7,8]. Thus, exploring a new way to control pollution and improve energy efficiency is of great importance [9–11]. Supercritical water gasification (SCWG) [12–15] is an environment-friendly technology for coal conversion as it can

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convert coal into H_2 and CO_2 and convert nitrogen and sulphur atom into inorganic salts which can be enriched [16]. Due to the unique physical and chemical properties [17,18], such as high diffusivity and low viscosity [19], supercritical water (SCW) provides a homogeneous and rapid reaction condition for coal gasification with high efficiency [20,21]. Therefore, many researches about gasification of coal in SCW were conducted [22–26].

It is worth mentioning that SCW must be excessive during the coal gasification process, which raised the cost compared with the pyrolysis process [27–30]. Organic compounds in coal mainly contains volatiles and fixed carbon and the former can be obtained through pyrolysis under low parameters [31–35]. Thus, conducting pyrolysis of coal under low pressure first and SCWG of pyrolysis product char then may provide a promising way for coal conversion, where part of the coal is consumed with lower costs than gasification directly. Moreover, the surface of pyrolysis char under low pressure contains abundant pore structures [36,37], which can absorb catalysts, provide more reaction sites and accelerate gasification reaction. Cheng [38] investigated the gasification of semicoke in supercritical water with a supercritical water fluidized bed reactor and drew the conclusion that the semicoke-water slurry of 30 wt% could be fed into the reactor continuously and could avoid blocking problem. CE of 95.26%, hydrogen yield of 85.9 mol/kg were obtained under the condition of 660 °C and 23 MPa. The semicoke, fixed carbon, obtained by the pyrolysis of coal can produce hydrogen efficiently and with the increase of temperature and alkali catalysts, CE and hydrogen yield increased.

Since the gas yield in the pyrolysis process changed dramatically with time, extracting and collecting the produced gases continuously was difficult, thus quartz tube reactor was used to collect enough gaseous products.

In this study, a novel two-step method, conducting pyrolysis first and then gasifying the pyrolysis product char, was proposed. Quartz tube reactor was used to collect pyrolysis gaseous products for further analyzing. Furthermore, the influence of different pyrolysis conditions on reaction characteristics of char was studied by infrared spectra and thermogravimetric analysis. SEM and nitrogen adsorption experiments were conducted to analyze the surface morphology, specific surface area and pore structure respectively.

Experimental section

Apparatus and experimental procedures

In this paper, the experiments were conducted in a micro quartz tube reactor and Hongliulin coal was selected as the feedstock since its low content of sulfur, phosphor and ash and high heat value. The raw coal used in this paper was as received, and its elemental and proximate analyses were listed in Table 1.

The quartz tube reactor is a cylinder (3 mm i.d. × 5 mm o.d. × 200 mm length) with one-end sealed and the maximum designed temperature and pressure of 1000 °C and 45 MPa, respectively. The excellent thermal conduction of quartz ensures the rapid heating and cooling of the reactor, and the effect of catalysis caused by metal reactors can be avoided.

In every single experiment, the coal sample (about 30 mg) measured by a precise electric balance was loaded into the reactor, after which the reactor was vacuumed and back-filled with argon to provide an oxygen-free environment for reaction, then the open end of the quartz tube was sealed by hydrogen flame. The prepared quartz tube was placed into the furnace when the temperature was steady around the designed reaction temperature and held for some time at this temperature. After the reaction, the quartz tube was moved out of the furnace quickly for cooling. For each operation condition, at least three identically repeated experiments were conducted (see Fig. 1).

Analytical methods

The analysis of the gaseous products was conducted using a gas chromatography (Agilent 7890A) with thermal conductivity detectors (TCDS) and high-purity argon was used as the carrier gas. Carbon conversion efficiency (CE), hydrogen conversion efficiency (HE) and the yield of a certain component in the gaseous products (YG) were utilized to evaluate the pyrolysis characteristics, and their definitions were as follows:

$$CE = \frac{\textit{the mass of carbon in gaseous products}}{\textit{the mass of carbon in feedstock}} \times 100\% \quad (1)$$

$$YG = \frac{\textit{the molar amount of a certain component in the gaseous products}}{\textit{the mass of the feedstock}} \times 100\% \quad (3)$$

Table 1 – Industry and element analyses of Hongliulin coal.

Elemental analysis (wt%)					Proximate analysis (wt%)				$Q_{b,\,ad}$ (MJ/kg)
C_{ar}	H_{ar}	S_{ar}	N_{ar}	O_{ar} [*a]	M_{ar}	A_{ar}	V_{ar}	FC_{ar}	
74.29	4.69	1.12	1.00	9.26	2.79	6.84	33.19	57.18	

[*a] By difference.

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