Research article

Effects of alkali and alkaline-earth metals and retention time on the generation of tar during coal pyrolysis in a horizontal fixed-bed reactor

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A B S T R A C T

To reduce the tar yield, a horizontal fixed bed is proposed to replace a conventional fluidized bed in the pyrolysis stage of two-stage gasification. Effects of alkali and alkaline-earth metals on the generation of tar are studied. Roles of the interparticle and inner-furnace retention time are also investigated. Ultraviolet–visible spectrophotometry was used to determine the aromatic compounds in tars. The results showed that absorbance intensity of the tar solution increased linearly with its concentration within the examined concentration range. The removal of alkali and alkaline-earth metals increased the tar yield of coal. Increase in the absorbance intensity of tar is attributed to the increase in aromatic ring systems. Ion-exchangeable Na plays a dominant role in the retention of tar precursors, mainly polycondensed aromatic rings, by connecting them with the char matrix. Increasing the retention time in interparticle diffusion decreased the yield of tar, especially for polycondensed aromatic rings. Increasing the retention time in inner-furnace diffusion slightly decreased the tar yield. Introduction of a fixed bed could effectively solve the problems of high tar yield from coal and low catalyst contents in char.

1. Introduction

Gasification is considered a clean and efficient way to utilize fossil and renewable fuels [1, 2]. Low-temperature gasification is attracting growing attention because of its high cold gas efficiency and simultaneous low oxygen consumption [3]. The thermodynamics of coal/biomass gasification with steam show the theoretical possibility of complete conversion of low-rank fuels (brown coal, subbituminous coal, and biomass) at temperatures above 750 °C [3]; however, the presence of undesirable tar in syngas, particularly polycondensed aromatic ring compounds in the tar, and low char reactivity limit its application [4]. Hayashi [3] proposed the concept of two-stage gasification (Fig. S1), in which the rapid pyrolysis of low-rank fuel is separated from gasification of the char and conducted in a fluidized state. The tar is reformed into gases with hot steam; however, incomplete conversion of tar remains [5], especially in low-rank fuel with high volatiles content. In addition, > 80% of alkali and alkaline-earth metals (AAEM) were released from the coal after its pyrolysis in a fluidized bed [6, 7].

In this study, a horizontal fixed-bed reactor (HFBR), without inert gas flow through the intervals between coal particles, was introduced into the two-stage gasification system (Fig. S2) for the pyrolysis of low-rank coal. A large-reserve Zhundong coal (1.64×10^{11} t) [8], with high

sodium and volatiles contents, was used in this study. Two factors are crucial to the generation of tar: first, the thermal decomposition of substrate coal; second, diffusion and reaction of the thermally cracked fragments (as tar precursors) toward the gas phase [9, 10]. The latter appears in all three types of diffusion of tar precursors: intraparticle, interparticle, and inner-furnace diffusion (Fig. 1). The effects of AAEM (mainly sodium) and retention time in the diffusion processes on the reactions of tar precursors were studied. These two factors were selected based on actual operating conditions during pyrolysis of coal in a continuously fed HFBR, e.g., changing contents of AAEM, height of the coal bed, and flowrate of the carrier gas.

AAEM species play important roles in the intra- and interparticle reactions (Fig. S3). Effects of the AAEM on the yield and composition of tar during pyrolysis of coal have been widely studied. Li et al. [11] reported that AAEM species greatly suppressed the volatilization of larger aromatic ring systems during coal pyrolysis in a WMR. Hayashi et al. [12] showed that removal of metal species (Ca, Mg, Fe, Na, and Al) by acid washing increased the tar yield from coal pyrolysis in a drop-tube reactor, while leaving the aliphatic-to-aromatic carbon conversion almost unchanged. They also reported that the AAEM species, especially Na, catalyzed the reaction of nascent tar with steam from the pyrolysis of coal [13]. Yan et al. [14] reported that AAEMs catalyzed

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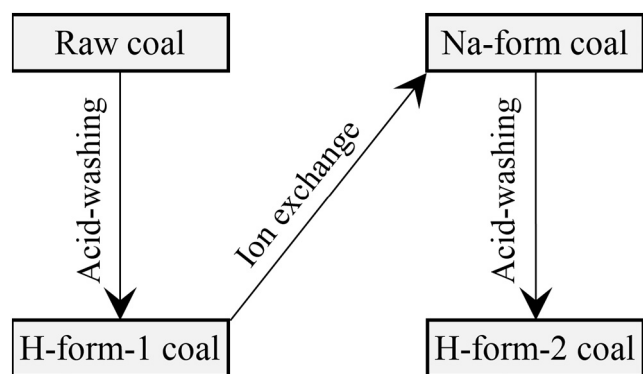
Fig. 1. Preparation of H-form-1, Na-form, and H-form-2 coal samples.

Table 1
Ultimate and proximate analyses of raw and H-form-1 coals (wt%).

Coal sample	Proximate analysis (d)			Ultimate analysis (daf)				
	A	V	FC	C	H	N	S	O[a]
Raw	3.57	32.22	64.21	73.52	6.55	0.91	0.51	18.51
H-form-1	0.95	31.83	67.22	81.84	3.69	0.68	0.55	13.24

[a] By difference.

the decomposition of phenols and condensed aromatics to light aromatic hydrocarbons during coal pyrolysis in a Py–GC/MS. Coal particles are stacked at the bottom of the reactor during their pyrolysis in a HFBR. Owing to the tight contact between coal particles, the effects of AAEM during pyrolysis of coal in a HFBR differ from those in other reactors. In addition, the release of AAEM in the HFBR is special because there is no carrier gas flow between the coal particles. Few studies have simultaneously investigated the release of AAEM and their effects on tar composition during coal pyrolysis in a HFBR.

Secondary pyrolysis of primary tars, from primary pyrolysis of coal, has a significant effect on the tar yield. The destruction of tar was possible when volatiles were forced through a char bed, which may be attributed to volatile–char interactions [15, 16]. The tar yield from pyrolysis of a brown coal in a fluidized bed reached a maximum at temperatures above 600 °C because of secondary pyrolysis [17]. Sathe et al. [9] found that tars could be completely released within 10 s at temperatures above 500 °C in a WMR. In a HFBR, however, the primary volatiles must diffuse through the coal/char bed toward the carrier gas. The retention time of primary tars in the coal/char bed (i.e., interparticle diffusion) changes with the bed height. For the inner-furnace diffusion of tar precursors, the retention time changes with the flowrate of the carrier gas. The effects of interparticle and inner-furnace secondary reaction time on the generation of tar have not been systematically investigated in a HFBR.

In this work, the generation of tar was studied in the three diffusion processes of tar precursors during coal pyrolysis in a HFBR. Ultraviolet–visible (UV–vis) spectrophotometry was used to characterize the aromatic compounds in tar. The influence of tar concentration on UV–vis absorbance spectra was investigated. The role of AAEM was studied by comparing the yield and composition of tars formed from raw coal and its acid-washed form. A further investigation was conducted by loading ion-exchangeable Na onto the coal, and comparing the yield and composition of tars produced from sodium-loaded and acid-re-washed coal. The influence of retention time in interparticle diffusion was investigated by changing the height of the coal bed, whereas that in inner-furnace diffusion was investigated by changing the flowrate of the carrier gas. The total volatiles yield was also monitored in the present study as an experimental control.

2. Experimental

2.1. Sample preparation

A subbituminous coal from Wucaiwan Colliery, Zhundong, China, was used. After being pulverized and partially dried at room temperature [18], the coal was sieved to collect samples with particle sizes between 109 and 180 μm. The composition of raw coal is shown in Table 1. The contents of atomic sodium, potassium, magnesium, and calcium in the raw coal were 0.26, 0.01, 0.12, and 1.07 mass%, respectively, on a dry basis (db).

Acid washing of the raw coal was conducted by mixing it with 0.1 mol/L H_2SO_4 solution [9]. The sample was labelled as H-form-1 coal, and its composition are also given in Table 1. After acid washing, there was a large decrease in the ash content, but only a slight decrease in the volatiles content. The sodium, potassium, magnesium, and calcium contents of H-form-1 coal were negligible.

Ion exchange between Na^+ and H^+ of carboxyl was conducted by adding H-form-1 coal in the CH_3COONa solution and stirring for about 20 h at pH 8.3 (adjusted by adding NaOH solution) in an argon atmosphere. After repeated washing with deionized water and filtration, the Na-form coal was obtained, as described in Fig. 1. The Na-form coal was rewashed with sulfuric acid to prepare H-form-2 coal. The sodium content in Na-form coal was 2.07 mass% (db), whereas that in H-form-2 coal was negligible.

2.2. Pyrolysis

A horizontal fixed-bed quartz tube reactor, similar to that introduced by Zhang et al. [19] and Liu et al. [20] was used in this study. Fig. 2 shows a schematic diagram of the experimental setup for coal pyrolysis. The temperature in the reactor was measured by a thermocouple with an accuracy of ± 2.0 °C. The flat-temperature zone was about 700 mm in length (Fig. S4). Argon with a flowrate of 1 L/min was used as carrier gas, which also supplied an inert atmosphere throughout the reactor. An alumina boat, containing ca. 1.0 g of dry coal, was quickly introduced into the furnace that preheated to the desired temperature. After a holding time of 20 min, the boat was pulled out and cooled quickly in the water-cooled pipeline section.

Total volatiles yield was determined by difference in mass of the sample-containing alumina boat before and after the pyrolysis of coal. The tar generated during pyrolysis was absorbed using a mixed solution of chloroform and methanol (80:20 by volume) in two gas-wash bottles [21]. The tar condensed along the pipeline was also recovered by repeated washing with the mixed solution. After total volume measurement, about 40 mL of the tar solution was transferred into an aluminum dish and then heated in an argon-purged oven controlled at 35 °C for 4 h to evaporate the chloroform and methanol [9]. The mass gain of the dish was obtained to calculate the tar yield. The average result from triplicate measurements is reported; the error bars indicate the standard deviation. The char, tar, and volatiles prepared from the pyrolysis of raw coal were denoted as raw char, raw tar, and raw volatiles, respectively. All samples employed an analogous labelling scheme.

2.3. Ultraviolet–visible spectroscopic analysis of aromatic compounds

Massive large-molecule compounds present in the primary tar are too heavy to be observed by GC/MS [22]. These compounds condensed easily on the downstream equipment. Nelson et al. [23] reported that only about 20–30 mass% of tar obtained from the pyrolysis of coals at temperatures between 400 and 600 °C can be detected by GC. The remaining compounds, with high boiling points, were aromatic rings bonded with long-chain alkyl groups [24] or heavy aromatic compounds with 6–12 carbon rings [25]. UV–vis absorbance spectra were used to characterize the aromatic compounds in the tar.

UV–vis spectra in the wavelength range of 200–800 nm at 0.2 nm