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RESEARCH

Effect of pyridine extraction on the tar characteristics during pyrolysis of bituminous coal

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Abstract: Extensive research has shown that coal has an extractable small molecular compound, which was associated with non-covalent bonding coal molecules. In addition, the reactivity of coal extract and residue is different. In this work, a bituminous coal was acid washed and extracted by pyridine to destroy the electrostatic interactions and hydrogen bonds. The pyrolysis behavior of the extracts and residue was studied by thermogravimetry (TG) and a fixed bed reactor. The H/C atomic ratio for the pyridine extract was significantly higher than that of raw coal, indicating hydrogen-rich components. The pyridine extract (E1) gave a higher tar yield of 44.4%, as well as more gas, while the tar yield of residue (R1) was lower than raw coal in an N_2 atmosphere. However, the residue gave more than two times the amount of tar under H_2 than that of N_2 because developed porous structure was formed by pyridine extraction, which would facilitate hydrogen diffusion into the pore structure and reduce the polycondensation reaction.

Key words: coal; extraction; pyrolysis; tar; non-covalent bonding

Coal is a heterogeneously complex structure with organic and inorganic macromolecules is one of the most important energy sources[1], especially in China, where approximately 70% of primary energy is from coal. Pyrolysis is the basis of coal thermal utilization because it occurs in initial period of a conversion process[2]. However, the complicated structure of coal has been the primary hindrance to get a comprehensive understanding of coal pyrolysis because of the powerful correlation between coal pyrolysis and coal structure. To clarify the structure of coal, several models of the represented structures have been proposed, bringing forth the two-phase structure concept[3–9], which assumes that the macromolecular network is a stationary phase and that small molecules are a mobile phase[10,11]. The macromolecular network is insoluble in any solvent, and relatively small amounts of solvent-soluble low molecular weight substances are trapped in the networks.

It is shown that extraction is a separable and nondestructive way to isolate organic species from coal and its derivatives at milder conditions[12–14]. Different polar solvents can break different interactions in coal framework, such as electrostatic interactions, hydrogen bonds and π-π interactions[15]. Nishioka et al[16,17] found that a carbon disulfide/*N*-methyl-2-pyrrolidinone (CS_2/NMP) mixed solvent (1:1 by volume) gave high extraction yields for some bituminous coals at room temperature. Wang et al[18] studied the extracts and final residue of Shenmu char powder by sequential extraction with petroleum ether, carbon disulfide, dichloromethane, acetone, and methanol. Li et al[13] studied the extraction of three low rank bituminous coals; the results show that extraction yields with NMP are 2–3 times of that with other solvents. Previous studies have shown that elements associated with the organic part, with ion-exchangeable cations present, were easily removed from coal by acetic acid washing[19]. Pyridine has been regarded as a good hydrogen bond acceptor, whereas CS_2/NMP has an even higher extraction yield due to distracting hydrogen bonds and π–π interactions between aromatic rings in intermolecular structure of coal. Coal extraction has targeted its methods to break non-covalent bonds and study its influence on conversion processes. However, a non-covalent interaction differs from a covalent bond, in which it does not involve sharing of electrons, and breaking of non-covalent interaction will not produce a radical during coal pyrolysis. Therefore, it is improper to generalize coal pyrolysis as a radical

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mechanism without considering the nature of non-covalent interaction. Since coal-derived small molecular extracts are very considerable for some bituminous coals, the role of small molecular on tar yield during pyrolysis should not be neglected. Thus, it is necessary to study the feature of coal-derived materials, such as coal extracts and residues, involved in coal pyrolysis.

Removing part of the micro-molecules from coal would affect its pore structure, which determines the inherent spaces and passageways for gas storage and diffusion[20–22]. Busch et al. summarized three distinct diffusion mechanisms within coal porous system[20]: inter-molecular collisions between gas molecules, which is significant for large pore sizes and/or high gas pressures; collisions between gas molecules and pore walls, which is significant for small pore sizes and low gas pressures; surface diffusion, where the adsorbed molecular species move along the pore wall surface. There, it is important to reduce the polycondensation reaction from a mass diffusion point of view.

In this work, a bituminous coal was washed by acetic acid and extracted by pyridine to break the electrostatic interactions and hydrogen bonds. The pyrolysis characteristics of raw coal, their extract fractions and residues were investigated and compared. In addition, the influence of non-covalent interaction on coal pyrolysis was deduced, and the role of extraction and pore structure in pyrolysis of coal was discussed from mass diffusion.

1 Experimental

1.1 Coal sample

Shihezi bituminous coal (Shihezi, abbreviated to SHZ) from Xinjiang province, China was crushed and sieved to 0.25–0.55 mm for experiment, which property is shown in Table 1. The coal sample was dried at 110°C for 2 h before use.

1.2 Coal extraction

Typically, raw coal (approximately 100 g) was mixed with acetic acid[19] (20%, 500 mL) in a 1000 mL flask at room temperature for 24 h. The mixture was filtrated to separate solid residue from the aqueous solution. The solid residue was washed three times using distilled water and vacuum-dried at 80°C for 12 h. The acetic acid washed coal (AC) was subjected to a Soxhlet extraction with pyridine at 75°C for 12 h, followed by an acetone Soxhlet extraction in order to replace the pyridine. After rotary evaporation, the extract was dried under vacuum for 12 h at 80°C. The extract and residue from the pyridine extraction was abbreviated as E1 and R1, respectively. E1 was fractionated with hexane and tetrahydrofuran (THF), respectively, to obtain a hexane-soluble (HS), THF-soluble (TS) and THF-insoluble (TI).

Elemental analyses of raw coal, AC, E1 and R1 were performed using a Vario EL elemental analyzer (Germany). The iodine numbers of raw coal, AC and R1 were analyzed using an analysis based on the Chinese standard method (GB/T 7702.7—2008). Before experiments all samples were vacuum-dried at 80°C for 4 h.

1.3 TG analysis

A thermogravimetric analyzer (Netzsch STA 449F3) was used to study pyrolysis properties of raw coal and its derived extract and residues. About 10 mg sample was placed in a ceramic crucible and heated from 45 to 900°C at 10°C/min, using 30 mL/min nitrogen as a carrier gas.

1.4 Pyrolysis experiments

All pyrolysis experiments were performed in a fixed bed reactor (150 mm × 35 mm I.D.) containing a 90 g sample from room temperature to 600°C for coal at 10°C/min under 600 mL/min N_2 atmosphere at ambient pressure. The volatile generated in a fixed bed reactor contains permanent gases, water and a condensable hydrocarbon. The liquid products including tar and water were collected in a cold trap; the water was separated by centrifugation. Products contained in the piping were washed three times by THF, and the solution merged with the products mentioned above. THF was stripped off, and the remaining part was weighed as tar. Subsequently, the tar was separated into maltene (*n*-hexane soluble) and asphaltene (*n*-hexane insoluble) fractions. The solid product remained in the reactor was defined as char.

The tar and char were weighed, and their yield was calculated according to the following equations.

Tar yield: $w_{tar}=W_{tar}/W_0\times100\%$

Char yield: $w_{char}=W_{char}/W_0\times100\%$

Where, W_{tar}: the mass of tar; W_{char}: the mass of char; W_0: the mass of coal.

Table 1 Proximate and ultimate analyses of SHZ coal sample.

Coal sample	Proximate analysis w_{ad}/%				Ultimate analysis w_{daf}/%				
	M	*A*	*V*	F	C	H	N	S	O
SHZ Coal	3.07	5.63	32.99	58.31	79.94	4.76	1.25	0.41	13.64