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Molecular structure and size of asphaltene and preasphaltene from direct coal liquefaction

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ABSTRACT

The heavy organic components in the direct coal liquefaction residue (DCLR), such as asphaltene (AS) and preasphaltene (PA) have significant influence on the direct coal liquefaction (DCL) technology. In this paper, the molecular structure and size of two types of AS and PA from the DCLR of 6 t/d Shenhua process developing unit and a batch hydro-liquefaction in laboratory were characterized. Results indicated that two types of AS and PA from different liquefaction technologies respectively display similar distribution of fluorophors. 3 ~ 4 rings fused aromatic nucleus (ANs) and/or more rings peri-condensed ANs are the predominating structures in the AS and PA. The scale of PA molecule is significantly larger than that of AS molecule. The molecular model, in which several ANs linked by bridge bonds or hydrogenated aromatic rings, is valid at least for the PA. Both AS and PA from direct coal liquefaction can form aggregates while the PA exhibits stronger aggregation than the AS.

1. Introduction

Direct coal liquefaction (DCL) process is essentially a technology to transform coal into oil or oil products by modification of molecular structure and changing the proportions of hydrogen and carbon. In order to obtain an affordable, reliable and sustainable alternative of oil to ensure energy security, 'China Shenhua DCL technology' had been developed [1]. The first commercial DCL plant after Second Word War has produced successfully oil products since 2008. As a part of the development of Shenhua DCL technology, a 6 t/d process developing unit (PDU) was built in Shanghai in November 2004 [2]. However, the separation and disposition of liquefaction residue (DCLR), which contains about 30–50 wt % heavy liquid [3], is still an intractable issue [4].

It is generally known that the coal macromolecular structure is firstly depolymerized through cleavage of these cross-linking bonds in the DCL process, and then the fragments formed are stabilized by hydrogenation into various products such as oil, AS and PA. Meanwhile, there also are a lot of secondary reactions occurred in the DCL, such as hydrogenation and retrogressive reactions (formation of insoluble products) [5,6]. Therefore, in a conventional DCL process, the DCLR generally consists of organic component and inorganic component, and the former includes un-reacted organic substance of coal and heavy products, such as AS and PA [7]. For example, Zhong et al. [8] investigated the extraction of DCLR from the 6 t/d Shenhua PDU, and found that the DCLR contains more than 50% of extractable components consisting of about 58% of oil. Chen et al. [9] found significant change of coal macerals in the DCLR derived from a 0.1 t/d BSU.

Petroleum AS (p-AS) had been extensively investigated because it was considered among the largest molecular species and the most complex component in crude oil [10,11], and strongly affects the phase changes, viscosity and interfacial properties of crude oils [12]. So far, there are two different views of the AS structure, which can be categorized as the peri-condensed or island model and the archipelago model [13]. Yen-Mullins model suggested that the most probable p-AS MW is ~750 g/mol, with the island molecular architecture dominant. AS molecules can form nanoaggregates with an aggregation number less than 10, and the nanoaggregates further form clusters at higher concentrations [14]. Although a great lot of researches [15–17] proved the validity of island model of AS, the archipelago model was also supported by data from pyrolysis, oxidation, thermal degradation and small-angle neutron scattering techniques [18–20]. Recently, the quantitative evidence for bridged structures in AS by thin film pyrolysis further supported the archipelago structure of p-AS [20]. Therefore, there is still considerable debate regarding the structure of p-AS, especially the size of the aromatic groups and the linking between the aromatic groups and other structural groups [13].

Similar to the AS in petroleum, the AS and PA in DCLR have significant influences on the yield of oil, the operation of DCL process, and

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the utilization of DCLR. For example, the chemical structure of organic components in the residue affected on the viscosity of DCLR [21], and the molecular interactions involving polar functional groups are very important for defining the viscosity of coal-derived liquid [22]. Recently, Gu et al. [23,24] studied the molecular structure of heavy oil fraction and AS fraction from Shenhua DCLR in a 0.1 t/d bench scale unit (BSU). Their average molecular weights (MWs) determined by the method of the vapor pressure osmometry (VPO) were 339 amu and 1387 amu, respectively. Unfortunately, little information is known about the basic structural parameters of heavy products in DCLR, especially for the PA due to its extremely complex structure and macromolecular properties. Although ASs from various resources have similar solubility, there are some obvious differences between p-AS and coal derived AS (c-AS). Firstly, the c-AS generally contains more heteroatoms (mostly O and N) than the p-AS [25]. As a result, the hydrogen bonds largely involving phenolic OH have significant influences on the properties of c-AS, such as its solubility and viscosity [26]. Secondly, the c-AS is highly deficient in alkanes and has much smaller AS molecules than the p-AS [25]. For example, the size of c-AS molecules is about half of the size of p-AS molecules, and the c-AS molecules show very low MW (average MW ~350 amu [12,27,28], MW 400–600 amu [29]). The c-AS has less alkane carbon and is deficient in hydrogen in comparison to p-AS [29]. So c-AS has much higher fraction of aromatic carbon [25], and smaller ring systems than p-AS [27]. Recently, Andrews et al. [30] further found that p-AS had seven times as much carbon in long chains (more than 9 carbons) as c-AS. So the difference of average MWs between c-AS (402 amu) and p-AS (828 amu) apparently derived mainly from the difference in the aliphatic distributions. Meanwhile, the c-AS possessed relatively larger polycyclic aromatic hydrocarbons (PAH) (~6 fused rings). Therefore, it was suggested that the c-AS should be the island molecular architecture because of its small MW and fairly large polycyclic aromatic nucleus. However, to our knowledge, few researches on the MW and structures of PA in DCLR have so far been reported.

Since the AS and PA in DCLR, which were obtained from coal through hydrogenation and cracking, are different with the p-AS (virgin AS), the conditions of liquefaction maybe have influences on the structures and size of AS and PA. In the present work, two types of AS and PA, which were obtained from the DCLR from Shenhua 6 t/d PDU and the batch hydro-liquefaction in our laboratory, respectively, were separated into AS, PA and THF insoluble. The molecular structure, MW and MW distribution of AS and PA were characterized by Fourier transform infrared spectroscopy (FTIR), ultra-violet-visible spectroscopy (UV), fluorescence spectroscopy (FL), gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) techniques, and the aggregation in AS and PA were also discussed.

2. Experimental section

2.1. Materials

In the present work, two types of PA and AS were used. One was obtained by solvent extraction of the DCLR from a 6 t/d Shenhua PDU, and another was prepared by a conventional direct liquefaction in a batch autoclave with Shenmu-Fugu subbituminous coal (SFSBC) as feed. Ultimate and proximate analyses of SFSBC and DCLR were listed in Table 1. All reagents were commercially available without further purification.

2.2. Preparation of AS and PA

The original DCLR is a solid block at room temperature, and was ground to sizes smaller than 0.5 mm before use. The true density of DCLR is 1.59 g/cm^3 and softening point is 148 °C. It was successively extracted in a soxhlet extractor by n-hexane, toluene, and tetrahydrofuran (THF) solvents to separate into oil, AS and PA, respectively. The AS and PA from DCLR were denoted as PL-AS and PL-PA, respectively.

Table 1
Proximate and ultimate analyses (wt %) of SFSBC and DCLR.

Sample	Proximate analysis			Ultimate analysis					H/C
	A_d	M_{ad}	VM_{daf}	C_{daf}	H_{daf}	N_{daf}	$S_{t,d}$	O^{*}_{daf}	
SFSBC	5.5	9.3	38.2	80.1	4.9	1.4	0.5	>13.1	0.73
DCLR	20.6	0.4	33.8	85.1	4.7	0.8	1.8	>7.6	0.67

* by difference.

A conventional hydro-liquefaction was carried out in a batch 200 ml autoclave. The liquefied products were separated into oil + solvent, AS, PA and residues by solvent extraction. Typical liquefaction process is performed at 400 °C for 60 min under 5 MPa H_2 (initial pressure) in 2:1 (solvent: coal) tetralin solvent with 5% FeS + S (an equimolar mixture of FeS and S) as catalyst. A detailed procedure of hydro-liquefaction and separation can be seen elsewhere [31]. The AS and PA obtained by a batch liquefaction were denoted as BL-AS and BL-PA, respectively. All results were reported as an average of three parallel experiments with a relative deviation of less than 5%.

2.3. Characterization of AS and PA

The MALDI-TOF/MS measurements were performed using a Bruker Biflex III matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometer equipped with a 337 nm nitrogen laser. Both matrice 4-hydroxy-α-cyanocinnamic acid and sample were dissolved in 1:1 (v/v) acetonitrile: water with 1% trifuoroacetic acid. And 0.5 μl of this mixture solution was placed on a metal sample plate and air-dried at ambient temperature. Mass spectra were acquired in positive linear mode and using an acceleration voltage of 19 kV. External mass calibration was performed using a standard peptide mixture. Spectra were obtained by setting the laser power close to the thresold of ionization and generally 100 pulses were acquired and averaged.

FTIR spectra of PA and AS were obtained on a PE-Spectrum One FTIR spectrometer at ambient temperature. A normal KBr disk technique was used with a ratio of sample/KBr, 10 mg/200 mg. The spectra were recorded at a resolution of 4 cm^{-1}. The element analyses were carried out by Elementar Vario EL III. ^{1}H NMR spectra of PA and AS, which were dissolved in d_5-pyridine solvent, were obtained using a Brucker AM500 (500 MHz).

Dilute AS and PA solutions with THF as solvent were used to measure their absorption spectra, fluorescent spectra and GPC curves. These solutions were prepared by dissolution of the dried solid samples in THF, and then were left in ultrasonic bath for 30 min to assure complete dissolution. Finally, the samples were diluted with THF to certain concentration and stood overnight before determination.

Absorption spectra of samples were taken using a diode array spectrometer (Lambda 35 UV-vis) of 1 nm spectral resolutions. All measurements were made at room temperature. Quartz sample cell with 1 cm optical path was used. Fluorescence spectrum was recorded on a Hitachi F-4600 spectrophotometer with 150 W Xenon lamp as the excitation source. Fluorescence measurement was made using a classic optic mount at 90° signal observation. Emission and excitation slits were set at 5 nm. The scanning speed was kept constant (1200 nm/min). The spectral measurement at room temperature was made with the use of quartz cell of 1-cm path length.

A Shimadzu LC-20AT liquid chromatography, equipped with a SPD-20A UV/vis detector, was used to measure the GPC curve. The GPC column was a Shim-pack GPC-8025. THF was selected as eluent at 1 mL/min flow rate. The detective wavelength was set at 254 nm and the column temperature was controlled at 20 °C.