Synchronous fluorimetric characterization of heavy intermediates of coal direct liquefaction

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**A B S T R A C T**

In order to understand the molecular structure of coal and the mechanism of coal direct liquefaction, the heavy intermediates of coal liquefaction such as asphaltene (AS) and preasphaltene (PA) were separated into different sub-fractions by column chromatography, respectively. The distributions of fused aromatic nucleuses (FAN) of sub-fractions were determined by synchronous fluorescence combined with the fitting technique of multiple peaks of spectrum. The results indicated that the PA and AS obtained from liquefactions of three Chinese coals were separated into 4 and 2–4 sub-fractions, respectively. The content of three rings FAN was the highest in the major sub-fractions of AS. The major sub-fractions of PA contained not only more single ring aromatic nucleus but also larger FAN than those of AS. Meanwhile, there were more complex aggregations in PA compared to AS.

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1. Introduction

Preasphaltenes (PA) and asphaltenes (AS) are very important heavy intermediates of direct liquefaction of coal (DCL) [1,2]. They have high density, heteroatom content, carbon residue, and low hydrogen/carbon ratio. These pose many difficulties in hydro-refining process of liquefied products, such as the deposition on the catalyst resulting in the deactivation of catalyst, and the sedimentation and/or coking on the devices causing the plugging of lines and equipment. Meanwhile, they also dominate.

The efficiency of DCL, especially for the oil yield. Therefore, it is essential to investigate the properties of PA and AS, especially for Chian, which is nearly to the commercialization of DCL.

Although the chemical identification of PA and AS is nearly impossible due to their very complex constitution and poor solubility, some structural characterizations, such as the determinations of functional groups and structural parameters, have been extensively carried out by modern analytical technique. Kanda et al. [1] suggested that one molecule of original AS consists of 1–3 structural unit on average, in which there are 2 or 3 aromatic rings with 1 or 2 naphthenic rings, 0 or 1 alkyl carbon atom, 0 or 1 OH group and 0 or 1 hetero-ring. In general, the aromatic structural features of PA and AS such as the size of aromatic ring and the degree of condensation are important for their upgrading and stability. Ultraviolet spectrometry (UV) and fluorescence spectrometry (FL) are always used to determine the aromatic system in crude oil and coal derivatives [3–5]. However, the PA and AS all show very wide peak with no structural characteristic in their UV spectra before being fine separated [5]. Similarly, the FL spectrometry is also limited in the determinations of PA and AS because there are very complex phosphors and energy transfers [3]. In addition, 1H NMR and 13C NMR can be used to determine the contents of aromatic hydrogen and carbon but they can not give the distribution of aromatic ring number. For example, Seshadri et al. suggested by the characterizations of 13C NMR and FTIR that AS and PA separated from the products of DCL are ‘oligomeric’ in structure, in which aromatic clusters being linked by carbon bridges and containing different functional groups [6].

Synchronous fluorescence spectrometry (SFL) introduced by Lloyd has been widely used to determine complex mixtures, and provides fingerprints of complex samples, such as crude oils and extracts of coals [7–10]. By SFL characterization, it was found that the thermolysis products of hard coal consist of the aromatic compounds with 2–5 condensed aromatic rings [8]. Compared to conventional fluorescence at fixed monitoring wavelength, SFL shows much higher spectral resolution of the complex mixtures by selecting the difference of wavelength according to the sample structure [9]. Despite the limitation of the method that some molecules give only weak peaks, Katoh et al. thought that it was the potential usefulness of SFL as a method of analysis of complex mixtures such as coal-derived liquids [10]. Kister et al. determined quantitatively the polyaromatic hydrocarbons (PAHs) in extractables of coal by SFL, in which three main synchronous fluorescence spectral regions were fined according to the number of lineally condensed aromatic rings [11]. Kershaw et al. found that the tar from the pyrolysis of Loy Yang coal showed two characteristic peaks in the constant-energy synchronous spectrum, and suggested that constant-energy SFL is
a valuable method for monitoring the concentration of the larger aromatic ring systems in pyrolysis tars [3]. Li et al. found that the pyridine-solubles of coal consisted of 3–5 aromatic rings by the SFL at a constant wavelength difference of 14 nm [12]. In our previous works, the fluorescence spectroscopy had been used to characterize the structures and aggregations of AS and PA from the liquefaction products of coal, respectively [13,14]. In order to determine the distribution of condensed aromatic rings in the heavy liquefied products, the sub-fractions separated from AS and PA, were respectively analyzed by the SFL.

2. Experiments

2.1. Preparation and fractionation of AS and PA

AS and PA were defined as the n-hexane insoluble/toluene solubles and the toluene insoluble/tetrahydrofuran (THF) solubles, respectively, and prepared by the soxhlet extraction of coal liquefaction products. In this work, three Chinese coals including Shenfu sub-bituminous coal (SF), Shengli lignite (SL) and Xiaolongtan lignite (XLT), were hydro-liquefied to prepare corresponding AS and PA. In this work, three Chinese coals including Shenfu sub-bituminous coal (SF), Shengli lignite (SL) and Xiaolongtan lignite (XLT), were hydro-liquefied to prepare corresponding AS and PA in a batch autoclave at 400 °C, 5 MPa (initial pressure) H2 with tetralin solvent for 30 min. The reaction mixture was recovered from the autoclave by washing out and soxhlet extraction with THF. After THF was removed by rotary evaporation, THF-soluble was extracted by n-hexane to separate into n-hexane-soluble and n-hexane-insoluble, and the latter was separated by toluene extraction into toluene soluble (AS) and toluene insoluble (PA). AS and PA were dried on vacuum at 80 °C overnight and weighted, respectively. Liquefaction yields and elemental analyses of PA and AS were respectively listed in Table 1. A detailed description can be found elsewhere [15].

AS and PA were further fractionated by column chromatography, in which 200 mesh silica was used as adsorbent, and toluene, mixing solvents of THF/toluene with different ratios, THF, methanol were used as eluents, respectively. In a typical run, 0.5 g sample was mixed well with 1 g silica. The mixture was placed on the top of the column, and the column was eluted sequentially with the following solvents: toluene (only used in the fractionation of AS), toluene/THF (4:1, by volume), toluene/THF (1:2, by volume), THF and methanol. After eluting the column with a particular solvent, the solvent was removed by rotary evaporation and drying on vacuum oven at 80 °C. The sub-fractions, which defined sequentially as A1, A2, A3, A4 and A5 for AS, and P1, P2, P3 and P4 for PA according to eluents, were weighted and used for further analysis. After the column was eluted by all solvents, the THF extraction showed that there was hardly the residue on silica. Therefore, all components of AS and PA were almost eluted.

2.2. Characterization of sub-fractions

Sub-fraction sample was dissolved in THF. The solution was put on in ultrasonic bath for 30 min and subsequently was standing overnight to assure complete dissolution. Finally, the solution was diluted with THF to 5 mg/l. The synchronous fluorescence spectrum was recorded on a Hitachi F-4600 spectrophotometer with 150 W Xenon lamp as the excitation source. A slit width of 5 nm was selected. The spectrum was scanned from 200 to 650 nm at a speed of 240 nm/min and a constant wavelength difference of 17 nm. All graphs were plotted using origin 7.0 software. The elemental analysis was carried out in Elementar Vario EL III.

3. Results and discussion

3.1. Assignment of synchronous fluorescence spectral peaks

SFL spectra of PAHs and their artificial mixtures have been extensively investigated [11,16]. Fig. 1 lists the SFL peak positions of partial PAHs and their derivates as shown in Ref. [11]. Considering the influences of solvent and wavelength difference, the SFL spectra of toluene, naphthalene, 1-methylnaphthalene, anthracene and pyrene were determined in THF solvent with 17 nm constant wavelength differences in present work as shown in Fig. 2, and their peak positions are also showed in Fig. 1. In general, the PAHs with different number of rings have different fluorescing properties. The PAHs with more linearly fused aromatic rings in the system fluoresce at longer wavelengths than those with fewer rings, and aromatic heterocycles can produce a bathochromic effect [11]. Fig. 2 shows that the SFL spectra of these aromatics have a limited number peaks (1–3) within a definite spectral range. THF solvent only shows a very weak SFL peak at 272 nm, and it hardly influences the SFL of PAHs. Therefore, the determination conditions, such as wavelength difference and solvent, only have an acceptable influence.

Taking into account the relation between the SFL spectrum and the structure of fluorophor, the SFL spectral region of fused aromatic nucleus (FAN) was roughly assigned in Fig. 1 according to the ring numbers of FAN. Here, the SFL peaks at less than 300 nm, 300–340 nm, 340–400 nm, and more than 400 nm were attributed to the fluorophors containing 1, 2, 3, and 4 rings respectively. This assignment is agreement with Refs. [11,16] and may be applied to characterize the sub-fractions of AS and PA from DCL.

3.2. Characterization of AS sub-fractions

Table 2 shows the distributions of AS sub-fractions of three coal liquefaction products and their elemental analysis results. It was found that the distributions of AS sub-fractions varied with the parent coals. The AS from SL could be separated into four sub-fractions as A1, A3, A4 and A5, and A1 and A4 were the major sub-fractions. Although the AS from XLT could be also separated into four sub-fractions as A2, A3, A4 and A5, but A2 and A3 were the major sub-fractions. However, the major sub-fraction A2 and minor sub-fraction A5 were only obtained in the AS from SF. The ASs from SF and XLT could not be eluted by toluene though they

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Parent coal</th>
<th>Yield (%)</th>
<th>Wad (%)</th>
<th>H/C</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
<td>S</td>
<td></td>
</tr>
<tr>
<td>PA</td>
<td>SF</td>
<td>22.0</td>
<td>79.16</td>
<td>7.84</td>
<td>1.41</td>
</tr>
<tr>
<td></td>
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<td>77.91</td>
<td>6.31</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>XLT</td>
<td>20.1</td>
<td>73.38</td>
<td>6.37</td>
<td>2.28</td>
</tr>
<tr>
<td>AS</td>
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<td>14.0</td>
<td>80.61</td>
<td>6.65</td>
<td>1.58</td>
</tr>
<tr>
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<td>SL</td>
<td>11.0</td>
<td>73.74</td>
<td>7.09</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>XLT</td>
<td>9.8</td>
<td>76.87</td>
<td>6.31</td>
<td>2.35</td>
</tr>
</tbody>
</table>

* By difference.
were toluene extracts. The yields of all minor sub-fractions were less than 7%. The yield of sub-fraction decreased with increasing polarity of eluant except for those derived from SL. With the increase of eluant polarity, the oxygen content of sub-fraction distinctly increased, but the carbon content decreased for all ASs. The atomic ratios of H/C and O/C of AS sub-fractions from SL were significantly higher than those from SF and XLT. Compared with other AS sub-fractions, those from XLT showed the lowest H/C, and those from SF showed the lowest O/C.

Similar to the SFL spectrum of sub-fraction A1 from SL shown in Fig. 3, the SFL spectra of AS sub-fractions all showed multiple peaks in the range of 250–550 nm. Definitely, these SFL peaks ought to originate from different fluorophors rather than the same fluorophor. Therefore, the fitting technique of multiple peaks was applied to calculate the distributions of FAN with different ring numbers in the AS sub-fraction. Fig. 3 shows that four fitted peaks were obtained with $R^2$ (correlation coefficient) = 0.9992. Three peaks at 286 nm, 325 nm and 359 nm, respectively were narrow but the fourth peak at 385 nm was a broad peak. So the former three peaks could be attributed definitely to single-ring, double-ring and three-ring FAN. Since the signal of SFL are only obtained at wavelength ranges where excitation and emission spectra overlap, the wide SFL speak indicates that the fluorophor has wide excitation and emission spectra, which are easy to produce a wide overlap range. Barashkov et al. suggested that the anthracene associates show a broad band along with the monomeric component [17]. According to the FL spectra of PA and AS [13,14], the aggregation of PA and AS can result in a broadening fluorescence peak. It suggested that the last broad peak at 385 nm may originate from the aggregates and/or its exciplex.

Table 3 shows the fitting results of the SFL spectra from all AS sub-fractions. Since the aggregation and exciplex effects can cause the red shift of spectrum, the fourth broad band of A1 and A2 should be attributed to the aggregates of three-ring FAN and that of other sub-fractions should be attributed to the aggregates of double-ring FAN. So the major sub-fractions (A1 or A2) contained a large number of three-ring FAN, but other sub-fractions contained mainly single-ring and double-ring aromatic nucleus. A few of four-ring FANs were found in the A3 of SL and A4 of XLT, except for the A5 of XLT. Therefore, the AS obtained from different coals liquefaction had similar distributions of FAN, and the content of three-ring FAN was higher than those of single-ring and double-ring nucleus in their major sub-fractions.

### 3.3. Characterization of PA sub-fractions

Table 4 shows the distributions and elemental analysis results of PA sub-fractions from three coal liquefaction products. Although four sub-fractions were all obtained from three PAs by the column
chromatography, their yields varied obviously with different PAs. The yield of P1 was the highest in the PAs from SF and XLT, but the yield of P2 was the highest in the PA from SL. The yield of P4 was less than 10% in all PAs. With the increase of eluant polarity, the oxygen content of sub-fractions increased basically but the carbon content of sub-fractions from SL and XLT decreased. Compared with the corresponding AS sub-fractions, the PA sub-fractions from SF and XLT showed higher H/C and O/C, but those from SL coal were on the contrary.

Fig. 3. Synchronous fluorescence spectrum and fitting result of multiple peaks of sub-fraction A1 from SL coal liquefaction.

Table 2
Results of AS separation and their sub-fractions elemental analyses.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Parent coal</th>
<th>Yield (%)</th>
<th>W_{daf} (%)</th>
<th>H/C</th>
<th>O/C</th>
</tr>
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<tr>
<td>A1</td>
<td>SL</td>
<td>72.1</td>
<td>79.28</td>
<td>8.03</td>
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</tr>
<tr>
<td></td>
<td>SF</td>
<td>93.7</td>
<td>81.26</td>
<td>6.68</td>
<td>1.58</td>
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<tr>
<td>A2</td>
<td>XLT</td>
<td>69.0</td>
<td>78.48</td>
<td>6.41</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
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<td>75.32</td>
<td>7.53</td>
<td>1.61</td>
</tr>
<tr>
<td>A3</td>
<td>XLT</td>
<td>20.9</td>
<td>75.77</td>
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</tr>
<tr>
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<td>73.03</td>
<td>7.50</td>
<td>1.12</td>
</tr>
<tr>
<td>A4</td>
<td>XLT</td>
<td>4.9</td>
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<td>2.37</td>
</tr>
<tr>
<td></td>
<td>SF</td>
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<td>70.89</td>
<td>6.20</td>
<td>1.67</td>
</tr>
<tr>
<td>A5</td>
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<td>55.61</td>
<td>5.65</td>
<td>1.86</td>
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<td></td>
<td>XLT</td>
<td>5.2</td>
<td>62.00</td>
<td>4.91</td>
<td>2.96</td>
</tr>
</tbody>
</table>

* By difference.

Table 3
Yields of AS sub-fractions and results of synchronous fluorescence analysis.

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<tr>
<th>Fractions</th>
<th>Parent coal</th>
<th>Fused ring distribution (%)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 2 3 Widen peak</td>
</tr>
<tr>
<td>A1</td>
<td>SL</td>
<td>6.8 19.2 27.1 46.9(385)</td>
</tr>
<tr>
<td></td>
<td>SF</td>
<td>11.1 19.4 28.8 40.7(380)</td>
</tr>
<tr>
<td>A2</td>
<td>XLT</td>
<td>10.6 16.9 20.1 52.3(389)</td>
</tr>
<tr>
<td></td>
<td>SL</td>
<td>30.1 – 2.3 52.6(326), 15.0(410)</td>
</tr>
<tr>
<td>A3</td>
<td>XLT</td>
<td>66.7 26.5 – 6.8(415)</td>
</tr>
<tr>
<td></td>
<td>SL</td>
<td>43.7 23.7 4.3 28.3(367)</td>
</tr>
<tr>
<td>A4</td>
<td>XLT</td>
<td>31.1 1.3 4.3 48.0(327), 17.2(405)</td>
</tr>
<tr>
<td></td>
<td>SF</td>
<td>40.6 21.2 3.6 34.7(353)</td>
</tr>
<tr>
<td>A5</td>
<td>SL</td>
<td>44.9 22.8 3.9 28.3(351)</td>
</tr>
<tr>
<td></td>
<td>XLT</td>
<td>73.6 31.0 11.4 –</td>
</tr>
</tbody>
</table>

* The value in the parentheses is the i_{max} of wide peak.

Table 4
Results of PA separation and their sub-fractions elemental analyses.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Parent coal</th>
<th>Yield (%)</th>
<th>W_{daf} (%)</th>
<th>H/C</th>
<th>O/C</th>
</tr>
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<tbody>
<tr>
<td>P1</td>
<td>SF</td>
<td>52.2</td>
<td>79.28</td>
<td>8.03</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
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<td>24.2</td>
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</tr>
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<td>53.2</td>
<td>76.24</td>
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<td>2.36</td>
</tr>
<tr>
<td>P2</td>
<td>SF</td>
<td>31.1</td>
<td>79.32</td>
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<td>53.2</td>
<td>78.31</td>
<td>6.09</td>
<td>1.96</td>
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<td>30.8</td>
<td>73.06</td>
<td>6.78</td>
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</tr>
<tr>
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<td>SF</td>
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<td>10.45</td>
<td>0.76</td>
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<td>76.63</td>
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<td>1.27</td>
</tr>
<tr>
<td></td>
<td>XLT</td>
<td>6.3</td>
<td>73.73</td>
<td>6.97</td>
<td>1.95</td>
</tr>
<tr>
<td>P4</td>
<td>SF</td>
<td>3.0</td>
<td>56.90</td>
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<td>1.88</td>
</tr>
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<td>68.70</td>
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<td>1.88</td>
</tr>
<tr>
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<td>XLT</td>
<td>9.7</td>
<td>58.58</td>
<td>5.08</td>
<td>2.40</td>
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</table>

* By difference.

Fig. 4 shows the SFL spectra and the fitting results of sub-fraction P1 from three coals. Similar to AS sub-fractions, PA sub-fractions from different coals all showed SFL spectra with multiple peaks. Further Fig. 4, shows that the SFL spectra of PA sub-fractions could also be successfully fitted into more peaks than those of AS sub-fractions with the R^2 more than 0.999. There were especially several broad fitted peaks in most of sub-fractions, suggesting that there were more complex aggregations in PA than in AS. The more aggregated structure of heavy products might be one of the main reasons of solubility difference between PA and AS [18].

The fitting results of SFL spectra of all PA sub-fractions are shown in Table 5. Except for several broad peaks, the narrow peak mainly originated from the single-ring aromatic nucleus. Taking into account of the broad peaks, there were some FANs with more
than three rings in most of PA sub-fractions. Meanwhile, the content of single-ring aromatic nucleus in the major sub-fraction of PA was higher than that in the major sub-fraction of AS. So PA contained more diversified FANs compared to AS, and the single rings aromatic nucleus is easy to form liquefied oil in the conversion of PA into AS. Further, it was found from the intensity and position of broad peak that the P1 contained more and larger FANs than other sub-fractions. The difference of the condensation degree of aromatic ring was mainly reflected in major sub-fraction P1, and the distributions of FAN in other sub-fractions were similar. In addition, the heavy intermediates of XLT liquefaction, either PA or AS, showed less rings FAN than those of SF and SL liquefaction.

4. Conclusion

PA and AS obtained from three Chinese coals liquefaction were respectively separated by column chromatography into different sub-fractions. Although four sub-fractions were obtained in each PA with increasing polarity of eluant, only 2–4 sub-fractions could be separated from AS varying with parent coals. In general, the

Table 5

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Parent coal</th>
<th>Condensed ring distribution (%)</th>
<th>Widen peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 2 3 4 Widen peak</td>
<td></td>
</tr>
<tr>
<td>P1</td>
<td>SF</td>
<td>26.1 7.4 3.7 – 47.4(402), 15.4(473)&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SL</td>
<td>21.0 – 3.8 4.6 – 56.8(373), 8.5(471), 5.3(507)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>XLT</td>
<td>23.4 – 6.0 – 34.3(338), 29.0(399), 7.3(466)</td>
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</tr>
<tr>
<td>P2</td>
<td>SF</td>
<td>47.5 – 2.8 – 16.1(321), 33.6(424)</td>
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</tr>
<tr>
<td></td>
<td>SL</td>
<td>30.8 2.3 3.1 0.5 33.3(346), 30.0(432)</td>
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<td>41.1 1.6 2.2 – 34.9(326), 20.2(410)</td>
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<tr>
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<td>SF</td>
<td>54.0 – 3.0 – 20.2(324), 22.8(418)</td>
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<td>43.0 1.9 2.8 – 32.8(323), 19.5(413)</td>
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<td>SF</td>
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<tr>
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<td>SL</td>
<td>44.3 1.8 2.0 – 37.0(324), 14.9(408)</td>
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<td>XLT</td>
<td>46.9 4.8 3.0 – 45.3(335)</td>
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</table>

<sup>a</sup> The value in the parentheses is the <i>λ</i><sub>max</sub> of wide peak.
major constituents eluted by weak polar solvent showed higher carbon content and lower oxygen content than the minor constituents eluted by strong polar solvent. By the multiple peaks fitting of SFL spectrum, it was found that the AS obtained from different coals had similar distributions of FANs. In AS major sub-fraction, the content of three-ring FAN was the highest. However, PA major sub-fractions contained not only more single ring aromatic nucleus but also larger FAN than AS major sub-fractions, suggesting that the hydrogenation of large FAN occurred in the conversion of PA into AS. Meanwhile, it was also found that PA shows more complex aggregations than AS by the SFL characterization of their sub-fractions.

Acknowledgements

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