1-4-3  350°C程度の穏和な溶剤処理を利用した褐炭の改質

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Upgrading of Low Rank Coals Using Degradative Solvent Extraction at around 350°C

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SYNOPSIS: Recently, we proposed degradative solvent extraction at around 350°C as an efficient upgrading method of low rank coals. In this study eight low rank coals including lignites and subbituminous coals were thermally treated and fractionated by using 1-methylnaphthalene at 350°C. The coals were partly decomposed and were separated into three fractions having different molecular weights, Soluble, Deposit and Upgraded Coal. The yields of the three fractions respectively ranged from 17wt% to 27wt%, 4 wt% to 17 wt%, and 47 wt% to 64 wt% on d.a.f. coal basis. The carbon contents of the three fractions were much larger than those of the raw coals, suggesting that a significant amount of oxygen was effectively removed from the coal during the treatment. The interesting findings were that the Solubles obtained from the eight coals were very close to each other in elemental composition, chemical structure, molecular weight distribution, pyrolysis behavior, and softening/melting behavior. It was also the case with all the Deposits obtained from the eight coals. Thus, the proposed degradative solvent extraction method was found to be effective in converting low rank coals into solid fuels and compounds having very similar chemical and physical properties.

1. Introduction

Low rank coals are currently used just as fuels near coal mines, because their utilization is limited due to the high moisture content and the high spontaneous combustibility. Therefore, both dewatering and upgrading are necessary to utilize low rank coal more effectively even as just fuels. If we also think of the low rank coal as the feedstock of chemicals and materials, it is necessary to recover precursors of chemicals and/or materials from the low rank coals in addition to dewatering and upgrading. The authors have proposed a method to dewater, upgrade and fractionate coals by using non-polar solvent at below 350°C. In this work the proposed method was applied to eight low rank coals including lignites and subbituminous coals and the effect of coal type on the upgrading behavior was examined in detail.

2. Experimental

The thermal treatments of the eight low rank coals including six lignites and two sub-bituminous coals were performed in a batch reactor using 1-methylnaphthalene (1-MN) as a solvent as described in detail in a previous paper. The properties of the coals were shown in Table 1. The batch reactor with a stainless filter equipped at its bottom was heated up to 350°C, where it was kept for 60 min under autogenous pressure. The solvent containing extracts and the Upgraded Coal (UC or residue) were separated by opening the valve connected below the filter at the treatment temperature. And the extracts dissolved in the solvent at the extraction temperature were separated into Deposit (D) which precipitated at room temperature and Soluble (S) dissolved in solvent even at room temperature. The solvent dissolving the S was evaporated at around 140°C under reduced pressure to recover the S as solid. The yields of S, D, and UC were determined by weight. The gaseous products were analyzed by gas chromatograph, and the yield of H2O was determined by the oxygen balance.

<table>
<thead>
<tr>
<th>Coal</th>
<th>Ultimate analysis (wt%, d.a.f.)</th>
<th>Proximate Analysis (wt%, d.a.f.)</th>
<th>Moisture (wt%, d.a.f.)</th>
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<tr>
<td>NM</td>
<td>66.4  3.9  1.9  27.8</td>
<td>50.2  24.0  25.8</td>
<td>12.2</td>
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<tr>
<td>LY</td>
<td>66.7  4.7  0.9  27.7</td>
<td>51.5  47.0  1.5</td>
<td>66.3</td>
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<tr>
<td>WA</td>
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<td>50.5  47.9  1.5</td>
<td>37.0</td>
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<tr>
<td>BR</td>
<td>71.0  4.9  1.3  22.6</td>
<td>43.4  52.5  4.1</td>
<td>21.9</td>
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<tr>
<td>MB</td>
<td>71.7  4.8  1.7  21.9</td>
<td>42.8  52.6  4.6</td>
<td>24.1</td>
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<tr>
<td>PH</td>
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<td>51.5  36.7  11.8</td>
<td>25.8</td>
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<td>51.7  40.5  1.8</td>
<td>21.2</td>
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<td>TH</td>
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<td>41.6  49.2  9.2  10.3</td>
<td></td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1 Yields of extracts and UC

First, the water contained in the coal was completely removed while the coals were heated up to 350°C.

Fig. 1 shows the yields of S, D, UC, and gaseous products. The yields of the same fractions obtained from the eight coals were different, depending on the coal type. The S and D yields respectively ranged from 17 wt% to 27 wt% and from 4 wt% to 17 wt% on d.a.f. coal basis. This means that 22 wt% - 41 wt% of the coals were
extracted by the 1-MN. The gaseous products consisted almost solely of H₂O and CO₂. It means that the degradation of oxygen functional groups occurred during the treatment.

3.2 Properties of extracts and UC
The carbon contents of S were surprisingly from 81.8 wt% to 84.0 wt%, and the oxygen contents were as small as from 6.5 wt% to 10.2wt% on d.a.f. sample basis. So the elemental compositions of the S were rather close to that of bituminous coal. Fig. 2 shows the H/C vs. O/C diagram of fractions and raw coals. For the S, all of the data points converged on the values of H/C = 1.1 and O/C = 0.07 – 0.09. On the other hand, all the data points converged on the values of H/C = 0.77 – 0.91 and O/C = 0.12 – 0.18 for the D. These results show that the proposed degradative extraction can convert the wide range of low rank coals into S and D that respectively have similar elemental compositions. In addition, the carbon and oxygen contents of the UC were respectively increased and decreased as compared to those of the raw coals.

Fig. 3 Molecular weight distributions of S and D

Fig. 3 and Fig. 4 respectively show the molecular weight distributions (MWDs) measured by LD-TOFMS and hydrogen distributions measured by ¹H-NMR of S and D. The results show that the MWDs of S are very close to each other and the molecular weights ranged from 100 to 500. This was also the case with the D. And the molecular weights of all the D ranged from 300 to 800. The hydrogen distributions of the S and D are also respectively rather close to each other. Thus, it was found that the chemical structures of the S/D are rather close to each other.

Fig. 4 Hydrogen distributions of S and D.

Fig. 5 shows the thermogravimetric (TG) and the thermomechanical analysis (TMA) curves of the S and D during the heating to 900°C at a heating rate of 10 K/min. Both TG and TMA curves of S and D were respectively so close to each other. The Fig. 5 (b) shows that all of the S and D completely melted at lower than 100°C and around 250°C, respectively. Thus, the S/D have very similar pyrolysis, thermal plastic and melting behaviors, regardless of the coal type.

4. Conclusion
Eight low rank coals including lignites and sub-bituminous coals were thermally treated and fractionated by 1-MN at 350°C to obtain extracts (S and D) and UC. The carbon and oxygen contents of the S, D, and UC were respectively much higher and much lower than those of their parent coals. The S and D obtained from the eight coals were respectively very close to each other in elemental composition, chemical structure, MWDs, pyrolysis behavior, and softening/melting behavior. Thus, the proposed degradative extraction method was found to be effective in converting low rank coals into UC and compounds having similar chemical and physical properties.

[Acknowledgement]
The assistance of Kobe Steel Co. for construction of the extraction apparatus is gratefully acknowledged.

[Reference]
1) 蘭川ら, 第 18 回日本エネルギー学会大会発表論文集, p.48 (2009)