Development of Anisotropic Texture in Co-Carbonization of Low Rank Coal and Pitch

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Abstract. The extent of development of anisotropic texture in cokes made from various coals or blends with pitch in co-carbonization systems was evaluated in terms of the hydrogen donor (D) and acceptor (A) abilities of coals, pitches and for various blending ratios of coal-pitch systems. Gieseler plastometry and high temperature H-NMR were also used to obtain information about the mobility in the co-carbonization systems. A good correlation was found between the extent of development of anisotropic texture, solidification temperature and the value of D/A for single or blend systems.

Introduction

For industry, the developing shortage of prime coking coals, their escalating costs and the increasing demands for improved quality of metallurgical coke have led to the consideration of the co-carbonization of blends of coals of lower rank with pitch additives derived from petroleum or coal.

Marsh et al. (1) have extensively studied the mechanism of modification in terms of the development of anisotropy in cokes from low grade coal.

Recently, it has been reported that the hydrogen donor (Da) and acceptor (Aa) abilities of pitch and coal are important factors governing mesophase development in the co-carbonization of low rank coal and pitch systems(2). Y. D. Park et al(3) applied the concept of Da and Aa to explain the phenomenon of the dissolution of mesophase from pitches into their distillates.

This paper is concerned with the chemistry of the co-carbonization of various coals with pitch. Mechanisms of modification are discussed in terms of the hydrogen donor and acceptor abilities of coal and pitch.

Experimental

Five different ranks of coal and pitch-A were selected as samples. The elemental analysis of the coals and the pitch used is shown in Table 1. The coals were crushed to pass through 100 Tyler mesh and dried before use.

<table>
<thead>
<tr>
<th>Coal</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ash(wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yallourn</td>
<td>66.0</td>
<td>3.9</td>
<td>0.5</td>
<td>0.2</td>
<td>29.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Tempoku</td>
<td>72.7</td>
<td>5.1</td>
<td>1.6</td>
<td>0.5</td>
<td>20.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Taheiyou</td>
<td>77.8</td>
<td>6.0</td>
<td>1.1</td>
<td>0.2</td>
<td>14.9</td>
<td>10.7</td>
</tr>
<tr>
<td>Akabira</td>
<td>83.0</td>
<td>6.4</td>
<td>1.8</td>
<td>0.1</td>
<td>8.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Yubarishiko</td>
<td>87.0</td>
<td>6.3</td>
<td>1.8</td>
<td>0.2</td>
<td>4.7</td>
<td>5.6</td>
</tr>
<tr>
<td>Pitch A</td>
<td>91.5</td>
<td>5.5</td>
<td>1.7</td>
<td>0.3</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

The hydrogen donor and acceptor abilities of coal and pitch were assessed using anthracene and 9,10-dihydroanthracene (9,10-DHA) as hydrogen acceptor and donor molecules respectively(4). Anthracene or 9,10-dihydroanthracene was mixed with coal or pitch (weight ratio 1:1) and heat-treated using a vertical infrared image furnace. The heating rate, the soaking temperature and soaking period were 10K/min, 673K and 5 min, respectively. The resulting product was dissolved in CDCl₃ and examined using H-NMR. Da was estimated from the intensity of 3.9 ppm which is due to the 9,10 positions of 9,10-DHA and is produced by the abstraction of transferable hydrogen in the sample. Aa was evaluated from the intensity of 8.4 ppm due to the 9,10 positions of anthracene.

The optical textures of polished surfaces of heat-heated specimens were assessed using a Nikon Apophoto optical microscope with polarized light and are defined according to the classification of Grint et al (5).
Results and Discussion

The values of hydrogen donor ability and hydrogen acceptor ability as a function of coal rank are represented in Figure 1(a) and 1(b), respectively. It can be seen that the hydrogen donor ability increases with increasing rank of coal and attains a maximum at about 87% carbon content. On the other hand, hydrogen acceptor ability decreases uniformly with increasing rank of coal. Yallourn brown coal has the highest hydrogen acceptor ability so far tested.

Table 2. Blending Ratios and D/A Values for Co-Carbonization Systems and Optical Texture of Resultant Coke.

<table>
<thead>
<tr>
<th>Coke texture</th>
<th>MF</th>
<th>D/A</th>
<th>Mn</th>
<th>D/A</th>
<th>MC</th>
<th>D/A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yallourn</td>
<td>1.3</td>
<td>0.21</td>
<td>1.7</td>
<td>0.27</td>
<td>2.5</td>
<td>0.40</td>
</tr>
<tr>
<td>Tempoku</td>
<td>1.1</td>
<td>0.23</td>
<td>1.5</td>
<td>0.27</td>
<td>2.3</td>
<td>0.41</td>
</tr>
<tr>
<td>Taiheiyo</td>
<td>1.0</td>
<td>0.20</td>
<td>1.5</td>
<td>0.29</td>
<td>2.0</td>
<td>0.38</td>
</tr>
</tbody>
</table>

Figure 1. Relation between D/a and A/a of coal.

In order to define the extent of hydrogen transfer in the co-carbonization system, we proposed the following parameter, which takes account of the fact that hydrogen transfer occurs between coal-coal, pitch-pitch and coal-pitch.

\[
\text{D/A} = \frac{\mathbf{m}_1/(\text{A} \times \text{pitch}) + \mathbf{m}_2/(\text{A} \times \text{coal})}{\mathbf{m}_2/(\text{A} \times \text{coal})}
\]

where \(\text{D/a}\) pitch and \(\text{D/a}\) coal are the hydrogen donor ability (mg/g. sample) of pitch and coal, respectively, \(\text{A/a}\) coal is the hydrogen acceptor ability of coal (mg/g. sample), and \(\mathbf{m}_1/\mathbf{m}_2\) is the blending ratio of pitch to coal (by weight). In equation (1), \(\text{A/a}\) pitch can be neglected because virtually no hydrogens from coal are transferred to the pitch.

Table 2 summarizes the values of D/A, the blending ratio for the co-carbonization systems and the extent of anisotropic texture of resultant coke. It is apparent that there is a good correlation between D/A values and the optical textures of the resultant cokes from low rank coals.

The relationship between D/A parameters and solidification temperatures obtained by the Gieseler method is shown in Figure 2. Figure 2 indicates a good correlation between D/A and solidification temperature. Solidification temperature rises with increasing D/A values. In addition, Figure 2 also shows a correlation between the extent of development of anisotropic texture and solidification temperature.

Conclusion

The proposed parameter, D/A, would not be out of place in a manual describing how to select and add pitch as a modifier to low grade coal used as a raw material for coke manufacturing.(6)

References

(6) Nakamura, K., Mori, M., Yokono, T. and Sanada, Y., This conference.