Investigation of The Structural Changes in Freeze-dried Low-rank Turkish Coals and in Their Supercritical Extracts

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Introduction

Coal structure consists of asset of clusters attached by groups containing bonds potentially capable of undergoing free rotation. The clusters contain aromatic and hydroaromatic systems. Most of the clusters are divergent, that is covalently bonded to only two other clusters. Some portion of the clusters are tri- or higher valent so that tridimensional macromolecules exist in the coal structures. Their presence in the coal causes the whole system to be linked into one large molecule, one in which a chain of covalent bonds attaches any atom to all other atoms. In addition to the covalent branch points, many branch points exist because of hydrogen bonding. Strongly basic solvents can break coal-coal hydrogen bonds. The results of solvent swelling in strongly basic solvents would be quite different from those obtained with the solvents which do not break hydrogen bonds. Swelling experiments are useful in terms of investigation and modification of the coal structure.

Lyophilizing is used to eliminate solvents in the interest of solute without destroying the structure reached after freezing. It is based on sublimation of freezeed solvent under vacuum.

Turkish Beyazpazi and Elbistan lignite samples were swollen in ethylene diamine and dimethyl sulfoxide, in the present work. The change of surface area and morphology of the coal particles after swelling and lyophilization experiments were compared with those of untreated samples.

Experimental

Beyazpazi and Elbistan lignite samples were used in the present work. Elemental analyses of these are given in the Table 1.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Beyazpazi</th>
<th>Elbistan</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>65.2</td>
<td>62.7</td>
</tr>
<tr>
<td>H</td>
<td>5.4</td>
<td>4.7</td>
</tr>
<tr>
<td>N</td>
<td>2.1</td>
<td>0.8</td>
</tr>
<tr>
<td>S (total)</td>
<td>5.4</td>
<td>4.0</td>
</tr>
<tr>
<td>O (by diff.)</td>
<td>21.9</td>
<td>27.8</td>
</tr>
</tbody>
</table>

The lignite samples were ground to ~100 mesh size before using. The swelling behavior of the lignite samples was studied by Liotta’s method. Approximately 100 mg of a sample was placed in a 6 mm o.d. tube and centrifuged for 10 minutes at 5000 rev/min. The height of the sample was measured as h1. Excess ethylenediamine or dimethyl sulfoxide (~1 ml) was added into the tube and the contents of the tube were mixed and the tube was centrifuged after 24 hours and the height of the sample in the tube (h2) was measured. Swelling kinetics of dried coals were determined until equilibrium.

The swollen Elbistan and Beyazpazi lignite samples were frozen in two different ways before lyophilization. The first method was to freeze samples directly in liquid N2. In the other method pre-cooled samples at -20°C were then frozen in liquid N2 as it was in the first method. The samples were lyophilized at room temperature and a pressure of 0.120 mbar by using a Christ ALPHA 1-2 LD lyophilizer. The lyophilized and raw samples were examined with a Gemini scanning electron microscope. All samples were coated with gold before taking any image because of insufficient conducting of the lignite samples. The change in the structure after lyophilization was compared with those of the raw samples.

Lyophilized samples were treated with supercritical carbon dioxide in a Thermo Haake C35P supercritical system at 50 bar and 80°C. Raw samples and supercritically treated samples were extracted in tetrahydrofuran, digested, for 24h at 20°C and in 130 rpm. Extracts obtained were analyzed using a Shimadzu GC-17A GC-MS system. The surface area of the raw and treated samples were measured using an ASAP 2000 Accelerated Surface Area and Porosimetry system manufactured by Micromeritics Co., USA.

Results and Discussion

Swelling ratios of Beyazpazi and Elbistan lignites in dimethylsulfoxide and ethylenediamine were measured until equilibrium values were attained. The swelling ratio of Beyazpazi lignite sample in dimethylsulfoxide and of Elbistan lignite sample in ethylenediamine were measured as 1.42 and 1.46, respectively.

Figure 1. Micrograph of raw Elbistan lignite sample.

Figure 2. Micrograph of pre-cooled to ~20°C and then cooled in liquid nitrogen and lyophilized Elbistan lignite sample.

Micrographs of raw and treated lignite samples (Figures 1-6) indicated the presence of disintegrated particles in the solvent swollen and lyophilized samples. Particles seemed to develop new porosity on the surface. Surface areas of the treated samples increased compared to those of the raw samples.

GC-MS analyses revealed differences in the composition of THF extracts obtained after supercritical carbon dioxide treated lyophilized lignite samples. The components present in the total ion chromatograms (TIC) of the raw lignite (Figure 7) seemed to contain fewer number of peaks compared to those of TIC’s of the extracts of treated lignite samples (Figure 8 and 9). Mass spectra of the components identified in the TIC’s indicated the presence of complex structures in the extracts.

The work is in progress and it is expected that the complete set of analysis of the material present in the extracts and the effect of lyophilization on the morphology of particles will be determined in the future studies.

References