Studies on the chemistry of thermal drying of lignite in inert atmosphere

Joy Mukherjee, Ms Puspa Singh & Abhijit Sarkar*
Central Fuel Research Institute, Dhanbad 828 108, India

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Drying of lignite and its storage for sufficient length of time in dried conditions has been an integral part of industrial economy, yet a fundamental understanding of the physico-chemical changes involved still lags far behind the practical use. Moisture is generally held in lignite by surface forces and oxygenated groups. Elimination of carboxyl groups by thermal decarboxylation has been found to reduce moisture holding capacity of lignite. In this paper a relationship has been shown to exist between carboxyl-oxygen and moisture of lignite at 60 percent relative humidity (RH) condition. Thermal behaviour of carboxylic acid functionality has been studied. Dehydroxylation was not observed at optimum temperature of decarboxylation. The nature and disposition of carboxylic acid functionality in lignite has been indicated.

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Lignitic coal generally contains considerable amount of bed-moisture which, as a rule, is driven out either by passing hot flue gas or imposing super heated steam under pressure prior to its combustion in boiler. But the ultimate aim to store the lignite in sufficiently dry condition is hardly achievable because of the fact that readsorption of moisture can not be avoided when it is kept exposed to humid atmospheric conditions. The inherent property of moisture adsorption is related to both physical1-3 and chemical4 nature of lignite. Moisture in lignite is reported to be held in three distinct ways: (i) surface bound moisture, (ii) pores and macropores bound moisture and (iii) hydrogen bonded moisture with polar oxygenated groups such as –COOH and –OH. By simple thermal drying5 at a temperature of about 100 to 110°C moisture removal or drying of lignite is apparently possible but on exposure to atmospheric conditions the moisture gets slowly accumulated on the dried surface of lignite provided the pores and micropores are not destroyed and their physical structure not altered during thermal drying.

Readsorption may vary depending on the surface conditions, atmospheric conditions and time of exposure. Hydrogen-bonded moisture, on the other hand, remains almost constant and proportional to the amount of oxygen present in general, and to the hydroxyl and carboxyl-groups in particular. Unlike the surface moisture, the hydrogen bonded moisture remains almost unchanged unless the oxygenated groups are removed. In this background, some studies were undertaken to develop a method of deoxygenation of lignite without any significant amount of carbon loss or for that matter much alteration of carbon-hydrogen matrix and then to study verification of moisture holding capacity of lignite at 60 percent relative humidity (RH) condition.

Experimental Procedure

A freshly mined lignite was procured from Neyveli Lignite Corporation. All studies were done on the sample (-72 mesh B.S.S.) the characteristic features of which are shown in Table 1. Experiments were designed to accomplish decarboxylation and dehydroxylation by heating lignite at temperatures ranging from 200 to 350°C for 1h under nitrogen atmosphere to prevent auto-oxidation by air.

A known weight of lignite sample (5g) was spread in a thin layer in a retort through which nitrogen gas was passed in order to maintain an inert atmosphere. After each experiment the –COOH and –OH contents of the thermally treated lignite were determined6,7. The equilibrated moisture at 60 percent RH condition was also determined8,9. Infra red

* For correspondence
(E-mail: joy_mukherjee_in@yahoo.com; Fax: 0326-2381113)
analysis of the samples was carried out with a Perkin-Elmer model 1760X-FT-Spectrometer using KBr pellets.

Results and Discussion

In the case of a lignite the total content of carboxylic acid functionality is 2-3 times more than those of the matured coals and most of the functionalities are in reactive form, which can be decomposed below 400 °C. During decarboxylation, an elimination reaction occurs, very smoothly, if a moderately good electron acceptor exists adjacent to the carboxyl.

A summary of all experimental results on decarboxylation is presented in Table 2. Carboxyl-oxygen of raw lignite could be brought down from 5.3 to 1.3 percent and 60 percent RH moisture value was simultaneously reduced from its original value of 14.2 to as low as 7-8 percent. A relationship was found to exist between the carboxyl-oxygen and 60 percent RH moisture of the heat treated lignite. It was observed that lower the carboxyl-oxygen lower was the moisture retention of the product. The OOH value of the heat treated lignite did not show any change.

It is also interesting to note from Table 2 that, the decomposition pattern appeared under relatively mild condition (e.g. 200 to 350°C) suggests that the reactive functional groups consisted of different groups of functionalities.

The IR spectra of the heat treated products revealed that bands characteristic of aliphatic -CH₂ and -CH₃ groups at 2920 cm⁻¹ and 2840 cm⁻¹ and at 1450 cm⁻¹ and 1370 cm⁻¹ were identical with that of the original lignite. The marked reduction in intensity at 1710 cm⁻¹ is indicated. No changes were observed in the intensities of aromatic out-of-plane vibrations in the region 900-700 cm⁻¹, or in the band at 1600 cm⁻¹ partly ascribed to aromatic clusters. Thus, the aromatic/ hydroaromatic structure appears to be unaffected by the treatment. The hydroxyl stretching absorption is rather broad and indicates the presence of both free and bonded hydroxyl groups. Analytical results and spectroscopic measurements are consistent with decarboxylation having taken place.

In order to avoid decomposition of lignite and evolution of tar and gas, all experiments were conducted much below pyrolytic point of lignite. Although decarboxylation could be achieved but dehydroxylation at this temperature was not found possible. FT-IR data also show practically no change in the region 3650-3350 cm⁻¹. Nevertheless thermal decomposition pattern of lignite further suggests that some amount of residual carboxylic acid functionalities remain in the product beyond 350 °C.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Temperature (°C)</th>
<th>Moisture (60% RH)</th>
<th>Ash (dmf)</th>
<th>O₃COOH (dmf)</th>
<th>O₃OH (dmf)</th>
<th>Moisture (60% RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>7.1</td>
<td>3.6</td>
<td>3.9</td>
<td>5.1</td>
<td>12.3</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>6.3</td>
<td>3.7</td>
<td>3.6</td>
<td>4.9</td>
<td>11.2</td>
</tr>
<tr>
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<td>275</td>
<td>5.6</td>
<td>3.8</td>
<td>2.3</td>
<td>5.0</td>
<td>10.4</td>
</tr>
<tr>
<td>4</td>
<td>300</td>
<td>4.5</td>
<td>3.7</td>
<td>1.9</td>
<td>5.8</td>
<td>9.4</td>
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<tr>
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<td>6.4</td>
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</tr>
<tr>
<td>6</td>
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<td>7.6</td>
</tr>
</tbody>
</table>

All data are expressed in percent.
Literature survey\textsuperscript{10} reveals that carboxylic groups attached to aromatic system are in the stable form and decompose above 400°C. However, it is difficult to delineate with these data the actual structure of the reactive carboxylic acid functionality in lignite. But at least, one may assume that lignite has much of a natural product like carboxylic acid functionality in the macromolecular network structure.

Conclusion

The present study has amply demonstrated that both hydroxyl and carboxyl groups are mainly responsible for adsorption of moisture. Of the two oxygenated groups, the thermally unstable carboxyl groups can be removed, to a large extent, via decarboxylation during heating, but it is difficult to eliminate the hydroxyl groups under similar situation. As a consequence, the moisture level of the heat treated lignite may be reduced to a desired level.

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References