Study of Low Rank Greek Coals Using FTIR Spectroscopy

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Fourier transform infrared (FTIR) spectra of lignite and humic clay samples, collected from 2 boreholes located at Apofysis-Amynteo lignite deposit, NW Greece, as well as their insoluble organic matter, obtained by Soxhlet extraction with dichloromethane, were recorded between 400 and 4,800 cm$^{-1}$. In the same way, FTIR spectroscopy was used to study a xylite sample from Vevi xylite basin (north of Apofysis-Amynteo lignite deposit) and its chars, which are the solid products of pyrolysis, at 3 final fixed temperatures: 400°C, 600°C, and 800°C. In the Apofysis-Amynteo samples, oxygen-containing structures were observed in the 1,800–1,000 cm$^{-1}$ zone, aliphatic hydrogen in the 2,950–2,700 cm$^{-1}$ zone, aromatic out-of-plane structures in the 900–670 cm$^{-1}$ zone, and hydroxyl groups in the 3,400–3,600 cm$^{-1}$ zone. A great abundance of C=O and C−O−R structures in the 1,800–1,000 cm$^{-1}$ region were noticed, while clay and silicate minerals were identified in the 400–600 cm$^{-1}$ and 3,600–3,800 cm$^{-1}$ zones.

In the IR spectra of the initial xylite sample BEX, the major quantity of H$_2$O is at a wave number of 3,400 cm$^{-1}$. A strong peak at 1,032 cm$^{-1}$ in the xylite sample is evidence of the presence of phenolic and alcoholic C−O bonds as well as C−O−C bonds with aliphatic or aromatic carbons. The 800°C char, at the same wave number, presents only a weak peak.

Keywords char, FTIR, Greece, lignite, pyrolysis, Soxhlet extraction, xylite

Due to its origin, coal is a chemically and physically extremely complex and heterogeneous material, consisting of organic (carbon) and inorganic (minerals) constituents. The acceptance of a coal for particular processes in industry depends critically on both
components. The organic structure of coal can be regarded as consisting of heterogeneous aromatic structures, with aromaticity increasing from low rank (lignite, xylite) to high rank coals (semianthracite and anthracite). The organic part of coal also contains sulphur, oxygen, and nitrogen in functional groups. Fourier transform infrared (FTIR) spectroscopy is a widely used analytical technique for determining the different functional groups of a coal structure. This method, being able to reveal carbohydrogenated structures (aromatic and aliphatic) and heteroatomic functions (mainly oxygenated), as well as to detect the presence of minerals, is currently one of the most powerful techniques for coal characterization and thus is of paramount importance in the various utilization procedures of coal (industrial combustion, coke production processes, etc.) (Guiliano et al., 1990; Cloke et al., 1997; Ruau et al., 1997; Guo and Bustin, 1998; Gilfillan et al., 1999; Lu et al., 1999; Vandenberghe et al., 1999; Thomasson et al., 2000; Yaman et al., 2000; Zondrow et al., 2000; Alcañiz-Monge et al., 2001).

In this study, FTIR spectra of lignite samples from Apofysis-Amynteo lignite deposit, Northern Greece, were obtained in order to investigate the chemical structure of these low rank coals, as well as the vertical and lateral differentiation of their IR spectra in the Amynteo lignite deposit. The nonextractable material of the samples was also analyzed by FTIR spectroscopy in order to correlate raw lignites with nonextractable matter. FTIR spectroscopy was also used to study a xylite sample, collected from Vevi xylite basin, situated north of the Apofysis-Amynteo lignite basin. This sample was subjected to a pyrolysis procedure, which was repeated 3 times at 3 final fixed temperatures (400°C, 600°C, and 800°C), and the relationship in structural changes between the initial coal (xylite sample BEX) and the pyrolysis solid residues (chars) was also investigated.

**Experimental**

Eight lignite samples were collected from 2 boreholes situated in the Apofysis (samples “A”) and Amynteo (samples “B”) lignite mines, respectively (Figure 1). The sampling depth was between 60 and 85 m for samples “A,” and between 80 and 150 m for samples “B” (vertical depth from surface). The distance between boreholes was approximately 3 km. A LECO CHN-2000 apparatus determined carbon, hydrogen, and nitrogen content. A LECO SC-144DR apparatus was used for the measurement of the sulphur content. The insoluble organic matter was obtained by Soxhlet extraction with dichloromethane (24 h). These nonextractable materials were analyzed by FTIR along with raw material (lignite). A 2.5 kg quantity of a xylite sample named BEX has been collected from Vevi xylite basin (Figure 1). The sample was crushed into coarse fragments, air dried at room temperature for approximately 10 days, and then ground to a grain size down to 5 mm. The sample BEX was subjected to a pyrolysis procedure. During pyrolysis a thermal depolymerization (cracking) of macromolecules, like cellulose, semicellulose, and lignin, occurs in the absence of oxygen (van Krevelen, 1993). A solid, black residue (char), noncondensable gases, and a liquid/oily phase were produced (van Krevelen, 1993). In the present study, 3 pyrolysis experiments were performed at the final temperatures of 400°C, 600°C, and 800°C, respectively. For each experiment, the weight of the xylite sample in the reactor was 300 g, while the heating rate was approximately 3°C/min. The initial xylite (BEX) as well as its 3 chars (BEX 400°C, BEX 600°C, and BEX 800°C) were ground to a size down to 1 mm, and proximate and ultimate analyses followed. The gross calorific value was determined using an IKA C-400 adiabatic calorimeter. Carbon, hydrogen, nitrogen, and sulphur contents were determined as mentioned before.
Specimens for FTIR were prepared using the potassium bromide (KBr) pellet technique. A very small amount of each sample (approximately 0.5 mg) was mixed with 200 mg of KBr to produce the pellets. FTIR spectroscopy analysis was carried out on a Nicolet 510P spectrometer, equipped with a DTGS detector, at a resolution of 4 cm$^{-1}$. Spectra were recorded by coadding 128 scans. The infrared signal was recorded in the region between 400 and 4,800 cm$^{-1}$ wave number. Bands were identified by comparison to published assignments (Lide, 1991; van Krevelen, 1993; Mastalerz and Bustin, 1995; Ibarra et al., 1996; Mastalerz and Bustin, 1996; Cloke et al., 1997; Koch et al., 1998; Das, 2001).
Results and Discussion

Lignites and Insoluble Organic Matter from Apofysis-Amynteo Deposits

Results of proximate and ultimate analysis along with atomic ratios H/C and O/C are shown in Table 1.

The moisture content ranges between 16.1 and 25.1% (ad), while the ash content ranges between 11.1 and 50.6% (db) and the TOC content between 27.6 and 71.6% (daf). Samples B17 and B39 show very low total organic carbon contents (35.2% and 27.6%, respectively), a fact that may categorize them as humic clays rather than as lignites. Therefore the values of O/C and H/C ratios are preferentially increased.

The identification of the most prominent bands of FTIR spectra of both lignite and insoluble material is shown in Table 2.

Intense bands are observed at 466–470 cm\(^{-1}\) and 528–535 cm\(^{-1}\) (Figure 2), resulting from clay and silicate minerals, and at 3,618–3,628 cm\(^{-1}\) and 3,696–3,699 cm\(^{-1}\), attributed to kaolinite and illite minerals (Guiliano et al., 1990; van Krevelen, 1993; Öztas and Yürüm, 2000). As expected, all of the above bands became more evident in the FTIR spectra of solid residues. The most intense peaks at the 3,600–3,800 cm\(^{-1}\) region are revealed by samples A139, B17, and B39, a fact that may be attributed to their higher content in clay minerals. In the aliphatic stretching region (3,000–2,800 cm\(^{-1}\)), there are distinct peaks at 2,851 cm\(^{-1}\) and 2,918–2,926 cm\(^{-1}\), attributed to symmetric and asymmetric \(-\text{CH}_2\) stretching, respectively. A great abundance of C=O and C–O–R structures is noted, as revealed by the intensity of the peaks in the 1,800–1,000 cm\(^{-1}\) region. This zone of oxygen-containing functional groups is characterized by a very intense peak at 1,618–1,622 cm\(^{-1}\), which is attributed either to C=O or C=C aromatic ring stretching. The C=C bands, which should be placed between C–O and C=O bands, were not definitely distinguished, since low rank coals have high oxygen content and these bands almost masked the C=C structures (Yaman et al., 2000). At the 1,200–1,000 cm\(^{-1}\) region, a sharp, intensive peak is present in all lignite samples, which is broadening in the insoluble fractions (e.g., sample A158). The C–O groups in the 1,115–1,118 cm\(^{-1}\) and 1,032–1,047 cm\(^{-1}\) regions are also very distinct. The 1,032–1,047 cm\(^{-1}\) may also result from silicate minerals (Si–O bonds). A very prominent band at 669 cm\(^{-1}\) could be related to aromatic out-of-plane C–H deformations, rather than to mineral matter, because its intensity decreases in the FTIR spectra of the insoluble fractions (e.g., samples A129, A158, and B54). The intense bands at 3,402–3,416 cm\(^{-1}\) are attributed to \(-\text{OH}\) stretching from H\(_2\)O or phenol groups. The intensity of this band is slightly decreased in the IR spectra of the insoluble matter when compared to raw lignite spectra. Sample A139 has a broader peak at the \(-\text{OH}\) stretching band compared to other samples of the same borehole, which may be attributed to its higher O/C and H/C ratios. A great similarity between the spectra of raw lignites and insoluble fractions is observed (Figure 2). Aliphatic bands (3,000–2,800 cm\(^{-1}\)) and oxygenated functional groups (1,800–1,000 cm\(^{-1}\)) show lower intensities in the nonextractable material compared to raw lignites, thus revealing the effectiveness of the extraction with dichloromethane at these regions. The intensity of the mineral bands (in the 400–600 cm\(^{-1}\) and 3,600–3,800 cm\(^{-1}\) zones) was preferentially increased in the FTIR spectra of the insoluble material. The vertical and lateral differentiation in the FTIR spectra of both lignite and nonextractable matter is insignificant, since samples were collected from the same lignite deposit and all have the same maturity. The FTIR results were confirmed by \(^{13}\text{C}\) nuclear magnetic resonance (NMR) spectroscopy, applied in the same samples (Iordanidis, 2002). In particular,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (ad)</th>
<th>Ash (ad)</th>
<th>Ash (db)</th>
<th>TOC (daf)</th>
<th>C (daf)</th>
<th>H (daf)</th>
<th>N (daf)</th>
<th>O(^a) (daf)</th>
<th>S (daf)</th>
<th>O/C</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A129</td>
<td>16.1</td>
<td>9.3</td>
<td>11.1</td>
<td>66.4</td>
<td>57.6</td>
<td>4.6</td>
<td>0.8</td>
<td>34.2</td>
<td>2.8</td>
<td>0.45</td>
<td>0.97</td>
</tr>
<tr>
<td>A139</td>
<td>22.5</td>
<td>39.2</td>
<td>50.6</td>
<td>63.8</td>
<td>41.9</td>
<td>3.5</td>
<td>1.3</td>
<td>50.8</td>
<td>2.5</td>
<td>0.91</td>
<td>0.99</td>
</tr>
<tr>
<td>A158</td>
<td>23.7</td>
<td>21.2</td>
<td>27.8</td>
<td>71.0</td>
<td>58.6</td>
<td>4.1</td>
<td>1.9</td>
<td>32.7</td>
<td>2.7</td>
<td>0.42</td>
<td>0.83</td>
</tr>
<tr>
<td>A171</td>
<td>18.9</td>
<td>31.4</td>
<td>38.7</td>
<td>65.8</td>
<td>54.1</td>
<td>4.4</td>
<td>1.9</td>
<td>37.9</td>
<td>1.7</td>
<td>0.53</td>
<td>0.97</td>
</tr>
<tr>
<td>B17</td>
<td>25.1</td>
<td>25.1</td>
<td>33.5</td>
<td>35.2</td>
<td>28.3</td>
<td>2.4</td>
<td>1.1</td>
<td>66.5</td>
<td>1.7</td>
<td>1.76</td>
<td>1.02</td>
</tr>
<tr>
<td>B39</td>
<td>20.9</td>
<td>19.9</td>
<td>25.2</td>
<td>27.6</td>
<td>22.3</td>
<td>2.0</td>
<td>0.7</td>
<td>72.1</td>
<td>2.8</td>
<td>2.42</td>
<td>1.07</td>
</tr>
<tr>
<td>B46</td>
<td>25.1</td>
<td>25.1</td>
<td>33.5</td>
<td>58.2</td>
<td>48.1</td>
<td>3.6</td>
<td>1.3</td>
<td>45.0</td>
<td>2.0</td>
<td>0.70</td>
<td>0.90</td>
</tr>
<tr>
<td>B54</td>
<td>19.2</td>
<td>35.4</td>
<td>43.8</td>
<td>71.6</td>
<td>57.3</td>
<td>3.9</td>
<td>2.2</td>
<td>35.0</td>
<td>1.6</td>
<td>0.46</td>
<td>0.81</td>
</tr>
</tbody>
</table>

ad = air-dried; db = dry basis; daf = dry ash free basis.
\(^a\)by difference.
(All values in wt%, except O/C, H/C).
Table 2
Band assignments of the most prominent peaks in the FTIR spectra of lignite samples and CH$_2$Cl$_2$-insoluble matter

<table>
<thead>
<tr>
<th>Bands (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>466–470 and 528–535</td>
<td>Clay and silicate minerals</td>
</tr>
<tr>
<td>669</td>
<td>Aromatic out-of-plane bending (?)</td>
</tr>
<tr>
<td>1,032–1,047 and 1,115–1,118</td>
<td>Silicates (Si–O), C–O, and C–O–R structures</td>
</tr>
<tr>
<td>1,612–1,622</td>
<td>C=O aromatic stretching and C=O conjugated</td>
</tr>
<tr>
<td>2,851</td>
<td>Aliphatic symmetric –CH$_2$ stretching</td>
</tr>
<tr>
<td>2,918–2,926</td>
<td>Aliphatic asymmetric –CH$_2$ stretching</td>
</tr>
<tr>
<td>3,402–3,416</td>
<td>–OH stretching</td>
</tr>
<tr>
<td>3,618–3,628 and 3,696–3,699</td>
<td>Clay minerals (kaolinite and illite)</td>
</tr>
</tbody>
</table>

$^{13}$C cross polarization/magic angle spinning (CP/MAS) NMR spectroscopy was performed, indicating the presence of aliphatic, aromatic, and carboxylic groups along with carbohydrates, phenols, and methoxyls.

**Xylite and Char Samples (BEX, BEX 400°C, BEX 600°C, BEX 800°C) from Vevi Basin**

*The Pyrolysis Process.* The products of the pyrolysis procedure are mainly influenced by various parameters such as rank of the coal, final temperature, residence time, and

![Figure 2. FTIR spectra of a raw lignite sample (A) and the nonextractable matter of the same sample (B) after Soxhlet extraction with dichloromethane.](image-url)
FTIR Spectroscopy of Low Rank Greek Coals

The chars contain more carbon than the starting material but less volatile matter and moisture. The calorific value of the chars increases by the removal of low-energy components (Cloke et al., 1999). Decomposition reactions are starting just below 300°C and become more significant between 350 and 500°C. Pyrolysis products, such as CO₂, CO, CH₄, CₙHₘ, H₂, H₂O, H₂S, NH₃, and oil/tar are given off. No tar or pyrolytic water was formed after 600°C (Roy et al., 1985). The results of proximate and ultimate analyses and gross calorific value determinations of the xylite sample and its chars are shown in Table 3.

The as-received moisture (13.96%) decreased after pyrolysis to a minimum rate of < 0.5%, while the ash content (db) increased in the chars. The volatile matter content decreased from the initial 51.35% in the xylite sample to 3.88% (daf) in the 800°C char. The gross calorific value of 19,193 J g⁻¹ of the initial xylite sample BEX increased to 26,573 J g⁻¹ for the 600°C char. After the initial removal of oxygen, further heating tends to decrease the calorific value of the char as carbon and hydrogen are removed from the coal structure. This means that the calorific values of the chars go through a maximum (600°C) with increasing process temperature. A carbon content increase of approximately 15% was noticed from the xylite sample BEX to its 800°C char. On the contrary, the oxygen decreased from 21.37% in the initial xylite to zero in the temperature range of 800°C. The hydrogen content also decreased during the pyrolysis procedure. The total sulphur content decreased from 2.03% in the xylite sample to 1.6% in the 600°C char. This could suggest that the organic sulphur is driven off as a gas during pyrolysis and the inorganic sulphur remains in the solid residue. At the 800°C char the sulphur seems to be enriched, a fact that can be explained by a weight loss of the char at this high temperature. The weight loss from the initial xylite sample to the 800°C char was of 58.9%.

FTIR Determinations. A comparison of the FTIR spectra for the wavenumber region 400 to 4,800 cm⁻¹, for the xylite sample and its chars at the 3 different temperatures, is presented in Figure 3. The intensity of the characteristic bands of C‒H and C‒O decreases according to the loss of hydrogen and oxygen during devolatilization (Cerny, 1996; Jones et al., 1999). The xylite sample presents an intense band at 3,400 cm⁻¹. This band is attributed to the stretching vibration of the hydroxyl group (O‒H) due to the water content of the xylite sample. For the 400°C char the same peak (3,378 cm⁻¹) is weaker, because large amounts of the functional groups (‒OH) still remain in the sample. Some water content in the chars (Table 3) seems to be due to the absorption of air moisture by the chars. The 800°C char presents only a weak peak at 3,400 cm⁻¹, because of the remaining ‒OH. This is consistent with the ultimate analysis results, in which the oxygen content decreased with the pyrolysis temperature. The aliphatic C‒H bands attributed to symmetric and asymmetric ‒CH₂ are distinct at the 2,922‒2,851 cm⁻¹ stretching region and their intensity is decreasing as the pyrolysis temperature increases. The distinct peaks at 2,851 cm⁻¹ and 2,919 cm⁻¹ refer to the symmetric and asymmetric ‒CH₃ stretching, respectively. The aliphatic C‒H bands in the xylite sample BEX at 2,919 cm⁻¹ and 2,851 cm⁻¹ show lower intensities in the chars. A sharp and strong peak at the region 1,604‒1,591 cm⁻¹ observed for the xylite sample BEX may be attributed to carbonyl groups as well as to the aromatic C=‒C ring stretching vibration. This band again shows lower intensities in the 400°C and 600°C chars and disappears in the 800°C char. The 1,350‒1,000 cm⁻¹ band region is very complex because of the contribution of many different functional groups and the mineral matter present in the xylite (de la Puente et al., 1998). The band, due to stretching of C‒O from aliphatic ethers and alcohols
Table 3

Proximate and ultimate analysis results of the xylite sample from Vevi basin and of the pyrolysis solid products (chars)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture (ar) (wt%)</th>
<th>Volatiles (daf) (wt%)</th>
<th>Ash (db) (wt%)</th>
<th>Gross calorific value (J g⁻¹)</th>
<th>Ultimate analysis (wt%, daf)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>BEX</td>
<td>13.96</td>
<td>51.35</td>
<td>16.3</td>
<td>19,193</td>
<td>55.10</td>
</tr>
<tr>
<td>BEX 400°C</td>
<td>&lt; 0.5</td>
<td>42.17</td>
<td>18.4</td>
<td>24,842</td>
<td>60.70</td>
</tr>
<tr>
<td>BEX 600°C</td>
<td>&lt; 0.5</td>
<td>10.31</td>
<td>26.0</td>
<td>26,573</td>
<td>68.10</td>
</tr>
<tr>
<td>BEX 800°C</td>
<td>&lt; 0.5</td>
<td>3.88</td>
<td>27.2</td>
<td>26,137</td>
<td>69.64</td>
</tr>
</tbody>
</table>

ar = as received, db = dry basis, daf = dry ash free basis.

*By difference.
Figure 3. FTIR spectra of the xylite sample from Vevi basin (BEX) and its 400°C, 600°C, and 800°C chars.

at 1,032 cm\(^{-1}\) which represents oxygenated functional groups, shows lower intensity for the 800°C char (Guo and Bustin, 1998). Furthermore, the band may be due to the presence of any silicate mineral (Si–O bonds), including quartz and clays (Çetinkaya and Yürüm, 2000). With increasing temperature, the oxygenated groups are released mainly as H\(_2\)O and CO, but also as aldehydes, alcohols, and acids. The bands at 466–470 and 528–535 cm\(^{-1}\) could be related to the presence of clay and silicate minerals.

Conclusions

FTIR spectroscopy was applied to lignite and humic clay samples from Apofysis-Amynteo region, Northern Greece, as well as to a xylite sample from Vevi xylite basin and its solid pyrolysis products at 3 different final temperatures (chars), in order to investigate their chemical structure. The nonextractable material of the lignite and humic clay samples from Apofysis-Amynteo region was also analyzed in order to correlate raw lignites with nonextractable matter. IR spectra of lignite and humic clay samples from Apofysis-Amynteo region reveal a great abundance of C=O and C–O–R structures (1,800–1,000 cm\(^{-1}\) region), while clay and silicate minerals were identified in the 400–600 cm\(^{-1}\) and 3,600–3,800 cm\(^{-1}\) zone. The intensity of the mineral bands was preferentially increased, whereas –OH groups are slightly decreased in the FTIR spectra of the insoluble material.
A great similarity between the spectra of raw lignites and insoluble fractions was noted, while the vertical and lateral differentiation in the FTIR spectra of Amynteo lignites is insignificant, as expected for samples collected from the same region. During pyrolysis of a xylite sample (BEX) from Vevi basin, a weight loss of 58.9% and a volatile matter decrease from 51.35% (in the initial xylite sample) to 3.88% (in the BEX 800°C char) were noted. In the IR spectra of the xylite sample BEX the major quantity of H₂O is at a wave number of 3,400 cm⁻¹. A strong peak at 1,032 cm⁻¹ of the same sample is evidence of the presence of phenolic and alcoholic C–O bonds as well as C–O–C bonds with aliphatic or aromatic carbons. In the 800°C char, only a weak peak is present at the same wave number. The 800°C char contains only aromatic bonds C≡C, in accordance with the ultimate analysis results.

References


