FTIR STUDY OF TWO DIFFERENT LIGNITE LITHOTYPES FROM NEOCENE ACHLADA LIGNITE DEPOSITS IN NW GREECE

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Abstract

The FTIR spectra for both Neogene xylite and matrix lignite samples from Achlada NW Greece show significant differences, which are mainly evident in aliphatic stretching region (3000-2800 cm⁻¹) where the intensities of the vibrations are reduced in matrix lignite lithotype compared to xylite one. The intense bands in the region 3402-3416 cm⁻¹ are attributed to -OH stretching of H₂O and phenol groups. The bands at ~3697 cm⁻¹ and ~3623 cm⁻¹ as well as at ~538 cm⁻¹ and 470 cm⁻¹, which are more evident in the FTIR spectra of matrix lignite, are attributed to higher content of clay minerals in the samples of this lithotype. The stretching vibration appears at ~1032 cm⁻¹ is intense in all matrix lignite samples and it is broadening in the xylite ones. The FTIR spectra of all samples confirm the progressive elimination of aliphatic vibrations from xylite lithotype to matrix lignite one and the appearance of clay minerals in the latter. As a whole the FTIR spectra of both xylite and matrix lignite confirm the significant differences between these two lignite lithotypes.

Key words: FTIR, Neocene, lignite, xylite, Achlada, Greece.

1. Introduction

At the end of diagenesis the polycondensed organic residue, called lignite in coal swamps, also contains varying amounts of largely unaltered refractory organic material (Killops and Killops, 1993). Therefore, the organic structure of coal can be regarded as consisting of heterogeneous aromatic structures, with aromaticity increasing from low rank (lignite, brown coal) to high rank coals (semi-anthracite, anthracite). The term lignite refers to the maturity stage of coals, while the terms xylite and matrix refer to lignite lithotype. Fourier Transform Infra Red (FT-IR) method is a widely used analytical technique for determining the different functional groups of coal structures. Infrared (IR) spectroscopy has been extensively employed in the characterization of the mineral and organic matter of coals (Guiliano et al., 1990; Cloke et al., 1997; D’Alessio et al., 2000; Georgakopoulos et al., 2003; Kalaitzidis, 2007; e.t.c).

In Greek lignites a limited number of studies have been published up to now, using FTIR method for coal characterization. Georgakopoulos et al. (2003) resulted in the presence of phenolic and alcocholic C-O bonds as well as C-O-C bonds with aliphatic carbons (strong peak at 1032 cm⁻¹) concerning the initial xylite sample BEX from Vevi region. In the same study the FT-IR spectra of lignite and humic clay samples, from Apofysis-Amynteo lignite deposits NW Greece, revealed the great
abundance of C=O and C-O-R structures (1800-1000 cm⁻¹ region) as well as clay and silicate minerals in the 3600-3800 cm⁻¹ and 400-600 cm⁻¹ region, respectively.

No study has been published concerning the investigation by FTIR method of the organic beds of Achlada lignite deposits, Florina sub-basin, NW Greece.

The present study is part of a research of both xylite and matrix lignite aimed at their structural characterization by Fourier transform infrared spectroscopy (FTIR) and focuses on their significant differences. X-ray diffraction (XRD), thermo-gravimetric (TG/DTG) and differential thermal analysis (DTA) were also employed for this purpose.

2. Geological setting

The studied samples obtained from the lignite-bearing sequence of Neocene Achlada lignite deposits, which are located at the east margins of Florina sub-basin, NW Greece.

The Neocene-Quaternary sediments that fill the basin, overlay unconformably both Palaeozoic metamorphic rocks and Mesozoic crystalline limestones and consist of conglomerates, sands, marls, sandy marls, clays, lignite beds, lateral fans and alluvial deposits (Pavlides and Mountrakis, 1987).

3. Methods

Lithological features of each of the studied samples were macroscopically described and the lignite lithotype determined according to guidelines established by the International Committee for Coal and Organic Petrology (I.C.C.P., 1993), as well as by Taylor et al. (1998). Samples with less than 10% by volume woody tissues were logged as matrix lignite, whereas those of immiscibly woody tissues were classed as xylite.
Several xylite and matrix lignite samples were examined using the FTIR method of analysis. The IR measurements were carried out using a Fourier Transform Infrac Red (FT-IR) spectrophotometer (Perkin Elmer GX-1). The FT-IR spectra, in the wavenumber range from 4000 cm⁻¹ to 400 cm⁻¹, were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample:KBr, approximately 1:200), at 8 tons/cm². Bands were identified by comparison to published studies (Wang and Griffith, 1985; Lide, 1991; Sobkowiak and Painter, 1992; Van Krevelen, 1993; Mastalerz and Bustin, 1995, 1996; Ibarra et al., 1996; Cloke et al., 1997; Koch et al., 1998; Das, 2001; e.c.t). Bands assignments used in this paper are listed in table 1.

Peak areas representing the hydroxyl group region (3100-3700 cm⁻¹), aliphatic stretching region (2931-2855 cm⁻¹), aromatic carbon (peaks at 1618 and 1606 cm⁻¹), aliphatic bending region (1509-1371 cm⁻¹), cellulose and lignin region (1300-1000 cm⁻¹) and the aromatic out-of-plane region (900-700 cm⁻¹) were measured. Additionally, intense vibrations at 3698 cm⁻¹, 3620 cm⁻¹, 531 cm⁻¹ and 469 cm⁻¹ are attributed to clay and silicate minerals.

The same xylite and matrix lignite samples were also examined by means of X-ray diffraction (XRD) analysis, as well as thermo-gravimetric (TG/DTG) and differential thermal (DTA) analysis. X-ray power diffraction patterns were obtained using a Bruker D-8 Focus diffractometer, with Ni-filtered CuKα1 radiation (λ=1.5405 Å), operating at 40 kV, 30mA, while TG/DTG/DTA were obtained simultaneously using a thermal analyzer (Mettler, Toledo 851) at a heating rate of 10°C/min, at air atmosphere and temperature range 25°C-1200°C.

4. Results and Discussion

4.1 FTIR study of xylite and matrix lignite samples

Representative FT-IR spectra of xylite and matrix lignite samples are shown in figure 2. The spectra differ significantly in the peaks due to mineral matter, as well as to phenolic (C-O) and aliphatic carbon (C-H) groups.

Both representative spectra show typical infrared characteristics of the organic matter of low-rank coals, including aliphatic C-H stretching bands at 2924 cm⁻¹ and 2856 cm⁻¹, C=C or C=O aromatic ring stretching vibrations at ~1610 cm⁻¹ and at ~1506 cm⁻¹, as well as aliphatic C-H stretching bands, at 1455 cm⁻¹, 1370 cm⁻¹ and 822 cm⁻¹.

Due to the fact that the present functional groups are different for xylite and matrix lignite samples it is more convenient to describe them separately.

Studying the FTIR spectra of the representative xylite sample (Fig. 2a), from the Achlada lignite deposits in NW Greece, the following conclusions resulted:

- The broad band at 3392 cm⁻¹ is attributed to -OH stretching vibrations of hydrogen-bonded hydroxyl groups of absorbed water of clay minerals as well as to -OH of phenol groups.
- The strong peak at ~2931 cm⁻¹ is due to asymmetric aliphatic C-H stretching vibrations of methylene (-CH₂).
- The band at ~1606 cm⁻¹ is attributed either to C=O or C=C aromatic ring stretching vibrations.
- The band at ~1505 cm⁻¹ is due to C=O stretching vibrations.
- The band at ~1454 cm⁻¹ is attributed to symmetric aliphatic C-H vibration of methylene (CH₃) and methoxy (OCH₃).
- The peak at ~1370 cm⁻¹ is due to symmetric aliphatic C-H bending vibration of methyl groups (OCH₃).
- The band at ~1265 cm⁻¹ are attributed to C-O stretching vibrations.
The peak at ~1033 cm$^{-1}$ is due to C-O-H bonds in cellulose as well as to C-O stretching vibrations of aliphatic ethers (R-$\text{O}$-$\text{R}$) and alcohols (R-$\text{OH}$).

The band at ~821 cm$^{-1}$ is due to out-of-plane aryl ring with isolated C-H groups.

In the FT-IR spectra of the matrix lignite samples bands corresponding to the most abundant minerals were detected confirming the occurrence of clay minerals (e.g. kaolinite bands at ~3698 cm$^{-1}$, 3620 cm$^{-1}$, 1030 cm$^{-1}$, 915 cm$^{-1}$, 531 cm$^{-1}$, and 469 cm$^{-1}$). The small peaks at ~3698 cm$^{-1}$ and 3620 cm$^{-1}$ can be assigned to the crystal water which exists in clay minerals of the matrix lignite samples (Geng et al., 2009).

Studying the FTIR spectra of the representative matrix lignite sample (Fig. 2b), from the Achlada lignite deposits in NW Greece, the following conclusions resulted:

- The small peak at ~3698 cm$^{-1}$ arises from the in-phase symmetric stretching vibration of the OH groups, either “outer” or “inner” surface OH of the octahedral sheets, which form weak hydrogen bonds with the oxygen of the next tetrahedral layer (Balan et al., 2001). The peak at ~3620 cm$^{-1}$ is due to the stretching vibrations of the “inner OH groups” lying between the tetrahedral and octahedral sheets (Madejova, 2002; Geng et al., 2009).
- The broad band at ~3406 cm$^{-1}$ is attributed to -OH stretching vibration of absorbed water either of clay minerals or of the organic matter of the matrix lignite sample.
- The bands at ~2925 cm$^{-1}$ and ~2855 cm$^{-1}$ are attributed to asymmetric and symmetric aliphatic $\text{–CH}_2$ stretching vibrations respectively.
- The strong band at ~1618 cm$^{-1}$ is attributed either to C=O or C=C aromatic ring stretching vibrations, as well as to OH bending vibrations of adsorbed water.

Fig. 2: FTIR spectra of representative xylite (a) and matrix lignite (b) samples.
The ~1030 cm\(^{-1}\) and 1013 cm\(^{-1}\) bands arise from the Si-O-Si and Si-O-Al\(\text{VI}\) vibrations, respectively.

The ~914 cm\(^{-1}\) band arises from the bending vibrations of “inner” OH groups of Al-OH-Al of kaolinite structure.

The band at ~680 cm\(^{-1}\) could be related to aromatic out-of-plane C-H vibrations, rather than to mineral matter (Georgakopoulos, 2003).

The band at ~531 cm\(^{-1}\) originates from Si-O-Al\(\text{VI}\) vibrations (Al in octahedral co-ordination) of clay minerals.

The main FTIR absorption bands of both xylite and matrix lignite samples are summarized in table 1.

The comparative FT-IR spectroscopy of xylite and matrix lignite lithotypes showed that:

- An intense and broad hydroxyl band of the xylite sample with a maximum at ~3392 cm\(^{-1}\), was displaced relatively to the matrix lignite band which appears at ~3406 cm\(^{-1}\). The latter peak is accompanied by two other small peaks around 3698 cm\(^{-1}\)and 3620 cm\(^{-1}\) due to mineral matter (Georgakopoulos, 2003).

- The predominant FTIR feature for xylite samples (Fig. 2b), in contrast to matrix lignite ones, is the high intensity of aliphatic C-H stretching vibration at ~2931 cm\(^{-1}\), which appears at slightly lower wavenumbers (2925 and 2856 cm\(^{-1}\)), in matrix lignite samples.

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The comparative FT-IR spectroscopy of xylite and matrix lignite lithotypes showed that:

- An intense and broad hydroxyl band of the xylite sample with a maximum at ~3392 cm\(^{-1}\), was displaced relatively to the matrix lignite band which appears at ~3406 cm\(^{-1}\). The latter peak is accompanied by two other small peaks around 3698 cm\(^{-1}\)and 3620 cm\(^{-1}\) due to mineral matter, which is more abundant in the matrix lignite.

- The predominant FTIR feature for xylite samples (Fig. 2b), in contrast to matrix lignite ones, is the high intensity of aliphatic C-H stretching vibration at ~2931 cm\(^{-1}\), which appears at slightly lower wavenumbers (2925 and 2856 cm\(^{-1}\)), in matrix lignite samples.

Significant differences of the containing functional groups are also present in the 1700-1100 cm\(^{-1}\) region. More specifically:

- The stretching vibrations at ~1506cm\(^{-1}\) due to C=O structures tend to decrease in matrix lignite. As far as, the bands at this region (~1506 cm\(^{-1}\)) practically disappear at the stage of bi-

**Table 1.** Characteristic FTIR bands of functional groups of low rank coals.

| Wavenumber (cm\(^{-1}\)) | Assignment |
|--------------------------|------------|
| 3400 | O-H stretching vibrations of hydrogen-bonded hydroxyl groups in polymeric association |
| 2930 | Asymmetric aliphatic C-H stretch vibrations–methylene (CH2) |
| 2850 | Symmetric aliphatic C-H stretch vibrations–methylene (CH2) |
| 1610 | Aromatic ring (C=C in plane) stretching symmetric |
| 1510 | C=O stretching vibrations |
| 1458 | Asymmetric aliphatic C-H deformation of methylene and methoxyl |
| 1430-1420 | aromatic C=C stretching vibrations |
| 1370 | Symmetric aliphatic C-H bending of methyl groups CH3 |
| 1266 | C-O stretch vibration (in lignin-gualacyl ring with C-O stretch) |
| 1224 | C-O stretch vibration (in lignin-gualacyl ring and C-O stretch) |
| 1031 | C-O-H deformation in cellulose |
| 822 | Aromatic out-of-plane-rings with 2 neighboring C-H groups |
| ~534 | Si-O-Al\(\text{VI}\) vibrations (Al in octahedral co-ordination) of clay minerals |
| ~468 | Si-O-Si bending vibrations of clay minerals |
tuminous coal (Ibarra et al., 1996), the progressive elimination of stretching vibrations in this region probably indicates increasing coalification from xylite to matrix lignite lithotype.

- The vibrations due to the aliphatic C-H and C-O groups at ~1455 cm\(^{-1}\), 1370 cm\(^{-1}\), 1265 cm\(^{-1}\) and 1224 cm\(^{-1}\), as well as the out of plane vibration due to the C-H bonds at 823 cm\(^{-1}\) also decrease in matrix lignite (Ibarra et al., 1996).
- Strong vibrations corresponding to the occurrence of clay minerals (e.g. kaolinite bands at ~3698 cm\(^{-1}\), 3620 cm\(^{-1}\), 1031 cm\(^{-1}\), 915 cm\(^{-1}\), 531 cm\(^{-1}\), and 469 cm\(^{-1}\)) were detected in the FT-IR spectra of the matrix lignite samples, while for the xylite ones a limited number of these vibrations are present, which are also quite weak.
- The prominent band at ~680 cm\(^{-1}\) in matrix lignite sample, could be related to aromatic out-of-plane C-H deformations, rather than to mineral matter (Georgakopoulos, 2003).

4.2 X-ray diffraction (XRD) analysis of xylite and matrix lignite samples

The X-ray diffraction (XRD) analysis revealed that the minerals present in matrix lignite are mainly,
kaolinite and gypsum (Fig. 3aA), while anhydrite is present in both heated samples (Fig. 3bA,B). Illite (+muscovite) is identified by the sharp diffraction peaks at d_{001}=~10 Å and d_{003}=~3.34 Å, while kaolinite by its typical peaks at d_{001}=~7.1 Å and d_{002}=~3.5 Å. In the same figure gypsum is identified by its characteristic peak at d_{020}=~7.56 Å. Minerals in minor contribution such as quartz at d_{101}=3.34 Å and d_{100}=4.26 Å and calcite at d_{104}=~3.03 Å have been detected, too. It is important to be mentioned that the formation of anhydrite, in the heated samples at d_{020}=~3.49 Å and d_{210}=~2.85 Å indicates the presence of gypsum in raw materials.

From the X-ray diagrams (Fig. 3a) it becomes clear that clay minerals are present in the matrix lithotype, while in the xylite one these are absent. This observation confirms the FTIR results, in which the typical bands of clay minerals are absent from xylite spectrum. This may be attributed to the nature of xylite samples that prevent the water movement through the xylite mass.

In addition, the samples were heated up to 550°C for 2 hours, in a static oven (Fig. 3b). Samples were then cooled at room temperature and examined by X-ray power diffraction (XRD). A decrease in the intensity of the characteristic diffraction pattern at d=7.57 Å, due to the collapse of gypsum, as well as the presence of typical peaks at d=3.50 Å and d=2.85 Å (Fig. 3b), indicates clearly the presence of anhydrite for both xylite and matrix lignite lithotypes.

4.3 TG/DTG and DTA study of xylite and matrix lignite samples

The thermal study results of the Achlada low rank coal samples examined after heating up to 1200°C, at a rate of 10°C/min, are shown in Fig. 4a,b. The TG curves of the examined samples showed a continuous weight loss during heating up to ~650°C and 900°C, for xylite and matrix lignite samples, respectively. More specifically:

- The steep slope of the xylite TG curve, in the temperature range from 200°C to 500°C, due to the rapid weight loss is attributed to the high devolatilization rate of organic matter.

- In the same temperature range, a big and sharp devolatilization peak observed at the DTG curve indicates the high devolatilization rate of xylite lithotype comparing to matrix one. This sharp peak at ~380°C (Fig. 4a) can be attributed to cellulose content of xylite sample (Charland et al., 2003). Taking into consideration that this peak height can provide a relative measure of the reactivity, the xylite seemed to be more reactive, as far as its decomposition rates were higher than those corresponding to the matrix lignite (Vamvuka et al., 2004). On the other hand, the bulk of the burning process for matrix lignite occurred mainly between 450°C and 600°C.

- An endothermic peak at ~380°C (DTA curve) is associated with the decomposition of cellulose, while the decomposition of lignin is characterized by an exothermic one, in the temperature range from 200°C to 400°C (Fig. 4a).

- Xylite samples present higher weight loss up to 1000°C (67.35% wt), comparing to matrix lignite ones (37.66% wt). The water that is evolved during pyrolysis arises from OH of constituent water as well as from the condensation of phenols (MacPhee et al., 2004), as it is shown in the following equation:

\[
\text{Phenol} + \text{OH}_2 \rightarrow \text{Phenol}_2 + \text{H}_2\text{O}
\]

The thermogravimetric curves of the Achlada low rank coal samples examined show that:

- The first peak of DTG curve at 100°C, which is associated with sample drying phase (Fig. 4b).
In the temperature range from 200°C to 560°C, the weight loss is less than in xylite sample and this is indicated by the slight slope of the TG curve. The TG curve of the matrix lignite samples showed a continuous weight loss during heating up to ~900°C, originated from the lignin content, that is quite difficult to decompose, as well as from the presence of inorganic material.

The exothermic peak in the temperature range from 200°C to 400°C of DTA curve is characteristic of lignin and can be attributed to the destruction of aliphatic grouping, CH groups, carbohydrate components and to some extent of oxygenous (alcoholic, phenolic) and amino groups (Kucerik et al., 2004).

The endothermic peak at ~500°C is attributed to the dehydroxylation of the kaolinite, (due to the loss of OH groups, surrounding the Al\textsuperscript{VI} atoms) and the progressive transformation from the octahedral co-ordinated Al, in kaolinite, to a tetrahedral co-ordinated form, in metakaolinite, through the breaking of OH bonds (Van Jaarsveld et al., 2002). A part of the weight loss in this temperature range comes from the decomposition of siderite according to the reaction

Fig. 4: TG/DTG/DTA diagrams of representative xylite (a) and matrix lignite (b) samples.
FeCO₃ → FeO+CO₂. Chlorite and illite (+muscovite) give endothermic peaks at higher temperatures.

5. Conclusions

Studying the xylite and matrix lignite lithotypes from the organic beds of Achlada lignite deposits, Florina sub-basin, NW Greece, by FT-IR spectroscopy, in combination with X-ray diffraction and thermoanalytical methods (TG/DTG and DTA), the following conclusions were taken:

- The FTIR spectra of all samples confirm the progressive elimination of aliphatic vibrations from xylite lithotype to matrix lignite one and the appearance of clay minerals in the latter.
- The aliphatic stretching regions at 3000-2800 cm⁻¹ and 1700-1100 cm⁻¹, where the vibrations of C-H and C-O groups at ~1458 cm⁻¹, 1370 cm⁻¹, 1267 cm⁻¹ and 1224 cm⁻¹ are present, reduced in matrix lignite.
- The vibrations corresponding to the occurrence of clay minerals (~3697 cm⁻¹, 3620 cm⁻¹, 1034 cm⁻¹, 915 cm⁻¹, 531 cm⁻¹, 469 cm⁻¹ and 435 cm⁻¹), are more evident in matrix lignite samples and very weak in xylite ones.
- According to X-ray analysis the minerals present in the matrix lignite are mainly illite (+muscovite), kaolinite, and gypsum, while in the xylite samples these minerals are absent. The formation of anhydrite in the heated samples indicates the presence of gypsum in both raw materials.
- The TG/DTG/DTA curves of xylite lithotype present higher weight loss comparing to matrix lignite lithotype, as well as a sharp DTG peak at ~380 °C, accompanied with an endothermic peak of DTA curve, that is characteristic of cellulose decomposition. In contrast, the lignin decomposition is characterized by an exothermic peak in the temperature range from 200°C to 400°C.

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