Air Oxidation of Turkish Beypazarı Lignite. 2. Effect of **Demineralization on Structural Characteristics in Oxidation** Reactions at 150 °C

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Demineralized (HCl/HF) samples of Beypazarı lignite were oxidized in air at 150 °C for up to 120 h in a ventilated oven. Elemental analyses, diffuse reflectance Fourier transform infrared (DRIFT), solid-state ¹³C CP/MAS/TOSS NMR, and pyrolysis mass (Py-MS) spectroscopies as well as solvent swelling were used for the characterization of the oxidized and unoxidized samples. It was found that the removal of 90.1% of the mineral matter from Beypazarı lignite facilitated the access of oxygen into the coal structure and permitted the occurrence of diffusion-controlled reactions. This was confirmed by the observation of linear relationships between the decrease in the intensity of aliphatic CH_2 and CH_3 groups, the increase of the O/H atomic ratio and the decrease in the aliphatic factor, and the square root of the duration of oxidation. It was observed from swelling measurements in pyridine before and after the oxidation that aryl esters and anhydrides, which were the major oxidation products, probably acted as covalent cross-links. Aliphatic groups oxidized more rapidly than aromatic structures and, in fact, methylenes oxidized more rapidly than methyls. The decrease in the intensity of the molecular ion series alkylphenols, alkyldihydroxybenzenes, alkylbenzenes, and alkylnaphthalenes arising from pyrolysis mass spectrometry of oxidized samples was approximately consistent with the corresponding increase in the intensity of CO_2^+ , CH_3COOH^+ , and CO^+ molecular ions.

Introduction

It is well-known that coals are heterogeneous, complex, and noncrystalline macromolecules containing both organic and inorganic materials. Due to this heterogeneity it is quite difficult to understand the structure of coals and then reactivity in different processes.¹⁻³ One finds that the low-temperature air oxidation affects both the organic and inorganic constituents of coals under even mild conditions causing structural alterations⁴⁻²⁰ which modify and change the technological behavior of the coal,

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usually for the worse in such processes as pyrolysis,²¹ combustion,²² liquefaction,²³⁻²⁶ and gasification.^{22,27}

The effect of demineralization on some of those processes has also been studied. A decrease in char reactivity^{28,29} and an increase in the pyrolytic yields of tar and gaseous hydrocarbons³⁰ were observed as a consequence of demineralization. Dilatometric properties were affected ad-

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Table 1. Elemental Analysis of Beypazarı Lignite

element	% (daf)	element	% (daf)
carbon	61.2	nitrogen	2.3
hydrogen	5.5	oxygen (difference)	25.7
sulfur (total)	5.3	ash (dry basis)	24.3%

versely by the removal of mineral matter.³¹ It has also been observed that low-rank coals have higher extractability in pyridine than bituminous coals after demineralization.³² Again, after demineralization, solvent extraction through such chemical reactions as depolymerization, reduction, amidomethylation, succinoylation, reductive acylation, and alkylation revealed a decrease in the yield of benzene/methanol extract.³³

Thus, the published literature suggest that there exist significant advantages in the removal of mineral matter from coals so as to obtain better understanding of the above-mentioned processes. While any alterations which may occur in the coal structure during the demineralization process should be noted, one should always take precautions to prevent the air oxidation of the demineralized coals. The removal of mineral matter has revealed the necessity for such techniques as maceral separation,³⁴ quantitative EPR,³⁵ and ¹³C NMR³⁶ studies of coal organic matter. The effect of HCl/HF demineralization on the macromolecular structure of six coals varying in carbon content between 69 and 86% was studied by Larsen et al.³⁷ They reported the occurrence of ion-exchange phenomenon in which carboxylic acid groups were formed from carboxylate anions but they found no significant bond cleavage due to demineralization.

It is quite surprising that the number of studies concerned with the effect of air oxidation on demineralized coals are very few. Demineralization of a low-rank French coal caused an increase in the amount of carboxyl and carbonyl groups particularly in the early stages of air oxidation, at 20 °C.38 It was concluded that the removal of mineral matter increased the oxidation at that temperature. The air oxidation of original Bevpazarı lignite proceeded in three consecutive stages in which the alterations in the organic structure started after almost 24 h of oxidation due to the formation of iron(II) sulfate.³⁹ Esters and anhydrides were also formed in the organic structure of Beypazarı lignite in different oxidation stages.

In this study, the oxidation pathway and the effect of air oxidation on the structural characteristics of demineralized Beypazarı lignite were investigated both qualitatively and quantitatively at 150 °C as a function of time.

Experimental Section

The elemental analysis of the Beypazarı lignite used in this study is shown in Table 1. Sample preparation and oxidation procedure have been described elsewhere.³⁹ Samples were subjected to oxidation at 150 °C after demineralization. The samples were characterized by diffuse reflectance Fourier transform infrared, pyrolysis-mass spectrometry, and solid-state ¹³C

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O/C

Figure 1. van Krevelen diagram of demineralized and of oxidized Beypazarı lignite (the numbers on the graph show the time of oxidation in hours).

FT-NMR The analytical procedures have previously been described in detail.³⁹

HCl/HF Demineralization. Approximately 1.6 L of aqueous 40% HF was added to 200 g of lignite in a Nalgene beaker and this mixture was stirred for approximately 24 h under a nitrogen blanket. After filtering, the lignite was washed with 1 L of distilled water and transferred to a glass beaker. Then, 2 L of 6 N HCl was added to the wet lignite and the suspension was stirred for 24 h under a nitrogen atmosphere. This mixture was filtered and washed with distilled water till the filtrate became neutral after which the lignite was dried to a constant weight at 110 °C under vacuum.

Solvent Swelling. The volumetric swelling measurements were carried out essentially as described by Green, Kovac, and Larsen.⁴⁰ The swelling ratios, Q_v , were obtained with pyridine by measuring the height of swollen and unswollen samples in a tube of 6 mm o.d.

Results and Discussion

Elemental Composition. In this study, the term "oxidized sample" refers to a sample that was first demineralized and subsequently oxidized for various different oxidation times. Figure 1 presents the elemental analysis of demineralized and oxidized Beypazarı lignite samples, plotted on a van Krevelen diagram (H/C vs O/C). During the whole oxidation period the hydrogen release was faster than the oxygen gain at 150 °C. The fast decrease of the H/C atomic ratio and the slow increase of the O/C atomic ratio is a consequence of the elimination of water from the organic structure during oxidation. This trend was also observed clearly at the third stage of the oxidation of the parent lignite.³⁹ However, the oxygen gain was significantly faster than the hydrogen loss at the second stage of the oxidation for that lignite. For a coal, a linear relationship between gas uptake and the square root of time confirms the existence of a diffusion-controlled reaction, as was observed for the sorption of methane by a coal at different temperatures.⁴¹ A diffusion-controlled reaction was also observed for a catalyst poisoning phenomenon in which there was a similar linear relationship between the fraction of catalyst reacted and the square root of time.⁴² In this study, in order to confirm a diffusioncontrolled reaction during the oxidation of demineralized Beypazarı lignite, the square root of time was used as the time scale of all the time-depended graphs. The O/H

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Time of oxidation $(h^{1/2})$

Figure 2. Plot of the change of O/H atomic ratio of demineralized and of oxidized Beypazarı lignite versus the square root of the oxidation time at 150 °C.



Figure 3. Difference spectra between 4000 and 600 cm⁻¹ at 150 °C : A, 120 h ; B, 72 h ; C, 24 h.

atomic ratio of the oxidized and unoxidized samples is plotted with respect to the square root of time in Figure 2. Figures 1 and 2 suggest that air oxidation of demineralized Beypazarı lignite at 150 °C proceeded in a single stage since the removal of 90.1% of the mineral matter whereas the original lignite had oxidized in three consecutive stages at the same temperature.³⁹ It seemed that the oxidation of demineralized Beypazarı lignite was diffusion-controlled at 150 °C.

Structural Analysis. As a result of the HCl/HF treatment of Beypazarı lignite, its ash content decreased from 24.3 to 2.4% and its swelling ratio in pyridine increased from 1.7 to 2.0. This enhanced swelling need not imply the removal of ionic cross-links as discussed by Larsen et al. for other coals,³⁷ but the removal of 90.1%of the mineral matter may have relaxed the structure of the demineralized Bevpazari lignite and made it easier to oxidize than the parent lignite.39

The oxidation pathway can be confirmed most accurately by observing the removal of aliphatic hydrocarbons rather than the formation of oxygen containing functionalities, particularly in low-rank coals. It was shown recently³⁹ that, during the interaction of molecular oxygen with the original Beypazarı lignite, some functional groups originally existing in the coal may have interacted with each other prior to the initiation of oxidation reactions. Figure 3 presents the difference spectra obtained by subtracting the spectra of the oxidized samples at different oxidation times at 150 °C from that of the demineralized Beypazarı lignite. The oxidation process affected both the carbonyl region at 2000–1600 cm^{-1} and the aliphatic region at 3000-2500 cm⁻¹. In Figure 4 the intensities of



0.8

0.4

0.2

Intensity

2 8 10 12 6 Time of oxidation $(h^{1/2})$

Figure 4. Plot of the change in intensity of the CH₂ 2926-cm⁻¹ band and CH₃ 2872-cm⁻¹ band relative to the 1610-cm⁻¹ band versus the square root of the oxidation time at 150 °C.



Time of oxidation (h^{1/2})

Figure 5. Plot of the change in aliphatic factor versus the square root of the oxidation time.

the bands near 2926 and 2872 cm⁻¹ which were due to C-H stretching vibrations of aliphatic CH2 and CH3 groups relative to the intensity of the aromatic vibrations at 1610 cm⁻¹ versus the square root of the oxidation time are presented. Figure 4 shows that the intensity of the aliphatic CH₂ and CH₃ groups decreased at different rates as the oxidation time was increased as diffusion-controlled in one stage. The rate of disappearance of aliphatic CH_2 and CH₃ groups indicated similar trend with the parent lignite.³⁹ It is also claimed for some other coals that these groups react with molecular oxygen at the initial stage of the oxidation.^{15,43-46} However, the oxidation of aliphatic CH_2 and CH_3 groups was prevented by the formation of iron(II) sulfate at the initial stage of oxidation of the parent lignite and the aliphatic CH₂ and CH₃ groups oxidized in three consecutive stages.

The interesting point is the confirmation of the existence of diffusion-controlled processes by the use of different analytical techniques. The decrease in the infrared intensity of aliphatic CH₂ and CH₃ groups (Figure 4), the increase of the elemental O/H atomic ratio (Figure 2), and the decrease in the aliphatic factor (Figure 5) showed a linear relationship with the square root of the oxidation time.

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Figure 6. CP/MAS/TOSS ¹³C NMR spectra of demineralized and those of oxidized Beypazarı lignite samples (120 h at 150 °C): (A) fresh; (B) 48 h; (C) 120 h.

Table 2. f_a and f_{al} Values Calculated from ¹³C CP/MAS/ TOSS NMR Spectra of Fresh and Oxidized Demineralized Beypazarı Lignite

<i>t</i> (h)	fa	fal		
0	0.49	0.43		
6	0.51	0.39		
12	0.49	0.36		
24	0.48	0.34		
48	0.52	0.31		
120	0.63	0.26		

It is quite evident from Figure 4 that the oxidation of methylene groups was more rapid than methyl groups. It has been suggested that most methylenes in vitrinites and inertinites could be attached to electron-withdrawing centers such as aromatics.⁴⁷ The absorption bands at 26 and at 33 ppm in ¹³C NMR spectra can be assigned to α -methyl groups Ar-*CH₃ and to α -methylenes Ar-*CH₂- CH_3 to aromatic rings, ⁴⁷ respectively (Figure 6). The band corresponding to terminal methyl groups $Ar-(CH_2)_n-*CH_3$ at 15 ppm was observed as a shoulder in the ¹³C NMR spectrum of demineralized Beypazarı lignite (Figure 6). In addition, the band which appeared at 43 ppm can be attributed to methylene bridges connecting aromatic rings and/or to methine groups⁴⁷ (Figure 6). As the time of oxidation increased the intensity of the aliphatic bands decreased and also the aliphatic factor changed from 0.43 to 0.26 (Table 2).

The results reported so far demonstrate that the aliphatic CH_2 and CH_3 groups were significantly affected



Figure 7. Low-voltage pyrolysis mass spectra of demineralized and of oxidized Beypazarı lignite samples: (A) fresh; (B) oxidized lignite (120 h at 150 °C).

by oxidation at 150 °C. This was confirmed by Py-MS examination of the solid products. Figure 7 presents the low-voltage pyrolysis mass spectra of demineralized Beypazarı lignite and of the 120 h oxidized product. The overall effect of the oxidation on the structures of demineralized and of the parent Beypazarı lignite was similar.³⁹ However, the intensities of equivalent pyrolysis mass spectrometric products from demineralized Beypazarı lignite (Figure 8) were different from the parent lignite. The changes in the intensities of the peaks in the Py-MS spectra were calculated in the same way as was done for the original Beypazarı lignite.³⁹ The intensities of the peaks of alkylphenols, m/z 94, 108, 122, and 136, and alkyldihydroxybenzenes, m/z 110, 124, and 128, which are known to be the main components of the network phase of the organic structure⁴⁸ were decreased more by oxidation than such components of the mobile phase⁴⁸ as alkylbenzenes, m/z 78, 92, 106, 120, and 134, and alkylnaphthalenes, m/z 128, 142, 156, and 170 (Figure 8). There was also a significant alteration in the intensities of the molecular ion series of alkyls, m/z 43, 57, 71, and 85. Methylene and methyl groups were the alkyl substituents of aromatic rings oxidized to generate carbonyl and carboxyl groups (Figures 7 and 8). These new oxygenated groups reacted further

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m / z



with each other at 150 °C to form anhydrides and especially esters eliminating water, as shown in the van Krevelen diagram (Figure 1). The quantities of the molecular ion series of alkyls, alkylphenols, and alkyldihyroxybenzenes of the demineralized Beypazarı lignite decreased more than of the parent lignite. In addition, the oxidation affected more m/z 108 C₁-alkylphenol, m/z 170 C₃-alkylnaphthalene, m/z 106 C₂-alkylbenzene, and m/z 124 C₁-alkyldihydroxybenzene molecular ions than the other homologs in each of the molecular ion series of the demineralized Beypazarı lignite as was observed for the oxidation of the parent lignite.³⁹

Oxidation for 120 h diminished the solvent swelling of the demineralized lignites from 2.0 to 1.5. This decrease may point to some reorientation of the macromolecular structure in which the formation of esters and anhydrides could possibly act as covalent cross-links. It is also accepted that oxygen principally causes some cross-linking reactions.⁴⁹ As far as the air oxidation of the low-rank coals are concerned, esters and anhydrides are the main oxidation products.^{7,8,15,26,43,50-53} The infrared difference spectra (Figure 3) showed a band at 1785 cm⁻¹ due to aromatic esters to be the major products whose concentration steadily increased during the oxidation by diffusion-controlled interactions (Figure 9). Esters and anhydrides were formed at virtually the same rate (Figure 9). The anhydrides being recognized by a characteristic infrared band at 1833 cm⁻¹ (Figure 3). Esters were also the major oxidation products of the parent lignite. However, the quantities of esters in the parent lignite were more than in the demineralized lignite after oxidation. Similar trend was also observed for the formation of anhydrides during oxidation.39

Absorption by aromatic ethers, phenols, and anhydrides occur in the region between 164 and 148 ppm in solidstate ¹³C NMR spectra.^{47,50} The band approximately 148



Time of oxidation $(h^{1/2})$

Figure 9. Plot of the change in K-M unit of the 1785-cm⁻¹ aryl ester band and the 1833-cm⁻¹ anhydride band versus the square root of the oxidation time.

ppm can be assigned to anhydrides (Figure 6). The absorption bands between 188-174 and 174-164 ppm may be due to carboxylic acids and esters, respectively.⁵⁰ The band near 170 ppm can be attributed to aryl esters. As the duration of oxidation increased the intensities of the band due to aryl esters increased and broadened and the intensity of the carboxylic band at 188 ppm decreased (Figure 6). There was no absorption at lower fields around 200 ppm whereas the bands of ketones and aldehydes appeared at that field in ¹³C NMR spectra of the parent lignite.³⁹ The existence of aromatic ethers was also confirmed by the DRIFT spectra (Figure 3) which showed aromatic carbon-oxygen vibrations at 1175 cm⁻¹; the intensity of this band remained almost unchanged during oxidation. ¹³C NMR measurements supported this observation; the bands at 75 and 154 ppm could be attributed to carbon atoms in Ar-*CH2-O-Ar and Ar-CH2-O-*Ar ethers, respectively. The intensity of these bands increased slightly as the time of oxidation increased (Figure 6). Thus, DRIFT and ¹³C NMR measurements showed the two major oxidation products of demineralized Beypazarı lignite that were esters and anhydrides. They were also observed as the major oxidation products of the parent lignite after oxidation.³⁹ The pyrolysis of these oxidation products produced the CO_2^+ (m/z 44) and CH_3COOH^+ (m/z 60) molecular ions in the pyrolysis mass spectra. The alterations in the intensities of these ions were more significant

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than those of CO⁺ $(m/z \ 28)$ molecular ion (Figure 8). It was observed that the quantities of the CO₂⁺ $(m/z \ 44)$ and CH₃COOH⁺ $(m/z \ 60)$ molecular ions of demineralized Beypazarı lignite were in excess compared to that of the parent lignite. This also indicated that the demineralized Beypazarı lignite was affected significantly by oxidation compared to the parent lignite.

As was observed for the parent lignite³⁹ by us and by some other authors,⁵⁰ oxidation at 150 °C did not affect the aromatic structures in the demineralized lignites significantly; difference spectra showed that there was no change in the intensity of the aromatic band at 1610 cm⁻¹ (Figure 3). However, the aromaticity increased slightly after 48 h of oxidation from 0.52 to 0.63 (Table II). This might be due to, first, the formation of anhydrides which give an absorption band at 148 ppm within the aromatic region⁵⁰ of the ¹³C NMR spectra, and second, the contribution of mineral matter⁵⁴ which could not be removed completely by demineralization. It was suggested that those factors caused the increase in the aromaticity factor of the demineralized Beypazarı lignite.

Conclusions

The 150 °C air oxidation of demineralized Beypazarı lignite showed a linear decrease in the intensity of aliphatic CH_2 and CH_3 groups, a linear increase in the O/H atomic ratio and a linear decrease in the aliphatic factor with respect to the square root of the oxidation time. This indicated the existence of diffusion-controlled reactions during the oxidation. The van Krevelen diagram (H/C vs O/C) of oxidized and unoxidized samples showed a similar linearity as the time of oxidation increased. However, apart from the alteration of the aliphatic factor, other parameters mentioned above were changed in three stages with respect to the time of oxidation of the parent lignite.³⁹ It has therefore been concluded that the removal of 90.1%of the mineral matter advanced the oxidation of Beypazari lignite as a diffusion-controlled process. Aromatic structures appeared more stable than aliphatic structures. The methylenes and methyls substituents of aromatic rings in demineralized lignite oxidized rapidly, whereas aliphatic groups of the parent lignite oxidized with greater difficulty, in three stages, forming esters and anhydrides. However, aromatic structures showed similar behavior for both lignites. The formation of arvl esters and anhydrides by oxidation decreased macromolecular mobility within the organic structure. It is suggested that these oxidation products acted as covalent cross-links in the organic network. The concentrations of alkylphenols (characterized by mass spectral peaks m/z 94, 108, 122, and 136) and alkyldihydroxybenzenes (characterized by mass spectral peaks m/z 110, 124, and 128) liberated by flash pyrolysis of network phase components were diminished more by oxidation than the concentrations of alkylbenzenes (characterized by mass spectral peaks m/z 78, 92, 106, 120, and 134) and alkylnaphthalenes (characterized by mass spectral peaks m/z 128, 142, 156, and 170) liberated by flash pyrolysis of the mobile phase. This decrease in the quantity of alkylphenols and alkyldihydroxybenzenes was approximately consistent with the increase in the quantities of CO₂, CH₃COOH, and CO liberated by flash pyrolysis following oxidation. The quantities of the CO_2^+ (m/z 44) and CH₃COOH⁺ (m/z 60) molecular ions of demineralized Beypazarı lignite were much more than that of the parent lignite. It was concluded that the effect of the oxidation on the demineralized Beypazarı lignite was more significant than the parent lignite.

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