Air Oxidation of Turkish Beypazarı Lignite. 1. Change of Structural Characteristics in Oxidation Reactions at 150 °C

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The oxidation of Beypazarı lignite was carried out in air at 150 °C for up to 168 h. Oxidized samples were withdrawn from a ventilated oven at different periods of time and characterized by elemental analysis, diffuse reflectance Fourier transform infrared (DRIFT), solid-state ¹³C CP/ MAS/TOSS NMR, and pyrolysis mass (Py-MS) spectroscopies. It was found that oxidation influenced the organic structure and the inorganics at different periods of the oxidation. Iron(II) sulfate was formed in 24 h, during which time there was almost no change of aliphatic CH₂ and CH₃ groups. After the formation of iron(II) sulfate, aliphatic CH_2 and CH_3 groups started to oxidize. Thus, the formation of iron(II) sulfate apparently prevented the oxidation of organic structure of Beypazari lignite during the first 24 h. The van Krevelen diagram (H/C vs O/C), the change of the O/H atomic ratio, and the rate of loss of aliphatic CH_2 and CH_3 groups showed the organic structure of Beypazari lignite to have continued in three stages. Aromatics seemed to be more stable than aliphatics during the oxidation process. The functional groups produced by the oxidation included ketones, carboxyls, and anhydrides but the major oxidation products were aryl esters. The abundance of CO_2^+ , CO^+ , CH_3COOH^+ , and SO_2^+ molecular ions increased in the pyrolysate of the oxidized sample whereas the molecular ions alkylphenols, dihydroxybenzenes, and alklynaphthalenes decreased after the oxidation.

Introduction

The low-temperature oxidation of coal and its mechanism have been investigated for many years and there is still great interest. It was early established that oxidation, weathering, and drying readily change the physical and chemical characteristics of coals.¹⁻³ Oxidation affects the technological properties of coal adversely in the sense that coking and caking behavior,⁴⁻⁶ extractability,⁷ tar yields,⁵ softening and swelling behavior,⁸ heats of combustion,⁵ and calorific values⁹ decrease sharply. In terms of elemental composition, the carbon and hydrogen contents fall, the oxygen content rises, and the macromolecular structure reorientates itself during oxidation.⁹ Air oxidation also causes the formation of ether or ester crosslinks which affect the fluid properties of the coal.¹⁰⁻¹⁴ Despite all this, there have been surprisingly few studies

- Chapters 6 and 7.
 (3) Berkowitz, N. An Introduction to Coal Technology; Academic Press: New York, 1979; Chapter 5.
 (4) Gray, R.; Rhoades, A. H.; King, D. T. AIME Trans. 1976, 260, 334.
 (5) Meuzelaar, H. L. C.; McClennen, W. H.; Cady, C. C.; Metcalf, G. S.; Winding, W.; Thurgood, J. R.; Hill, G. R.; Prepr. Pap.—Am. Chem. Soc., Div. Fuel. Chem. 1984, 29 (5), 166.
 (6) Crelling, J. C.; Schrader, R. H.; Benedict, L. G. Fuel 1979, 58, 542.
 (7) Larsen, J. W.; Lee, D.; Schimidt, T.; Grint, A. Fuel 1986, 65, 595.
 (8) Mahajan, O. P.; Komatsu, M.; Walker, P. L. Fuel 1980, 59, 3.
 (9) Cherenkov, I. O.; Shafir, G. S.; Eremin, I. V.; Bronovets, T. M. Khim. Tverd. Topl. 1985, 19 (6), 33.
 (10) Brooks, J. D.; Maher, T. P. Fuel 1957, 36, 51.
 (11) Wachowska, H. M.; Nandi, B. N.; Montgomery, D. S. Fuel 1974, 53, 212.

53. 212.

which aim at controlling the air oxidation of low-rank coals and lignite.15

Since coals are highly heterogeneous, containing both organic and inorganic components, the low-temperature oxidation of coal is a complex process which involves several reactions.^{11-13,16-20} Time resolved in situ FT-IR spectroscopy showed that at least three interrelated reactions occurred during the oxidation of Illinois No. 6 coal (25-100 °C).²¹ It is generally accepted that the initial stage of oxidation involves the attack of molecular oxygen on certain aliphatic moieties, generally methylenes α to aromatic rings or to -OR groups²⁴ to produce peroxides and hydroperoxides.^{11,22,23} Hydroperoxides and peroxides are unstable and decompose above 70 °C to form such oxygen-containing functional groups as hydroxyl, carbonyl,

(13) Painter, P. C.; Coleman, M. M.; Snyder, R. W.; Mahajan, O.; Komatsu, M.; Walker, Jr. P. L. Appl. Spectrosc. 1981, 32, 106.

- (14) Liotta, R.; Brons, G.; Isaacs, J. Fuel 1983, 62, 781.
- Vanov, S. K.; Rouchev, D. D.; Markove, K. I. Fuel 1980, 59, 273.
 Nandi, B. N.; Brown, T. D.; Lee, G. K. Fuel 1977, 56, 125.
- (17) Ignasiak, B. S.; Clugstone, D. M.; Montgomery, D. S. Fuel 1972, 51. 76.
- (18) Wachowska, H. M.; Angelova, G. Fuel 1977, 56, 422.
 (19) Ignasiak, B. S.; Nandi, B. N.; Montgomery, D. S. Fuel 1970, 49, 214.
- (20) Rhoads, C. A.; Senfle, J. T.; Coleman, M. M.; Davis, A.; Painter, P. C. Fuel 1983, 62, 1387.
- (21) Gethner, J. S. Fuel 1987, 66, 109.
- (22) Cronouer, D. C.; Ruberto, R. G.; Jenkins, R. G.; Davis, A.; Painter,
 P. C.; Hoover, D. S.; Starsinic, M. E.; Schlyer, D. Fuel 1983, 62, 1124
- (23) Khan, M. R.; Usmen, R.; Newton, E.; Beer, S.; Chisholm, W. Fuel 1988, 67, 1668.
- (24) Kouchi, J. K. Free Radicals; John Wiley and Sons: London, 1973, Vol. 1, Chapter 7.

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⁽¹⁾ van Krevelen, D. W. Coal; Elsevier: Amsterdam, 1961; Chapters 7 and 8.

⁽²⁾ Dryden, I. G. C.; Landers, W. S.; Donaven, D. J. In Chemistry of Coal Utilization; Lowry, H. H., Ed.; Wiley: New York, 1963; Suppl. Vol.; Chapters 6 and 7.

⁽¹²⁾ Painter, P. C.; Snyder, R. W.; Pearson, D. E.; Kwong, J. Fuel 1980, 59, 282.

Table I. 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	24.3 <i>%</i>	

and carboxyl.^{11,25} Painter et al.²⁰ observed that an overall increase in carbonyl and carboxyl groups in Lower Kinnating coal during oxidations at 140 and 60 °C depended on temperature and found that the loss of aliphatic groups was responsible for the subsequent loss of Geisler fluidity. It has also been experimentally confirmed that air oxidation under pressure took place on the surface of particles, there being no uniform oxidation of the particles throughout their bulk even at 300 °C after 30-60 min.9

Meuzelaar et al.²⁶ studied the effect of low-temperature air oxidation reactions of pyrolysis mass spectra and showed that as one would expect the abundance of carbon monoxide, carbon dioxide, and aliphatic carboxylic acids increased with time, temperature, and rank, but in lowrank coals the abundance of phenols and dihydroxybenzenes formed by oxidation decreased. Khan et al.²³ observed the chemistry of high-volatile (hv) bituminous coal oxidation at 150 °C for up to 48 h using ESR spectroscopy and concluded that the hydrogen-rich pyridine extract was more sensitive to oxidation than the hydrogen poor residue. ¹³C CP/MAS NMR and FT-IR spectroscopic studies on oxidation of different coals showed that the aromatic moieties were less reactive than aliphatic²⁷⁻²⁹ whereas MacPhee and Nandi³⁰ reported that there was an increase in the ratio of aromatic to aliphatic carbons as a function of oxidation time in air at 105 °C and concluded that the aromatic structure in coal was more sensitive to oxidation than aliphatics.

The effect of oxidation on the inorganic material is as important as the effect on the organic structure. Pyrite is well-known to be a sensitive mineral to oxidation even at low temperatures. The ferrous(II) sulfate, szomolnokite, which is the principal product of pyrite oxidation, is formed in air at 50 °C and gives characteristic bands at 1090 and 980 cm⁻¹ in FT-IR spectrum.^{31,32}

The purpose of the present study was to investigate the effect of air oxidation on the structural characteristics of Beypazarı lignite at 150 °C and to determine both the quantitative and qualitative changes as a function of time. It was hoped that this would lead to proposals of methods for both controlling oxidation and upgrading lignite.

Experimental Section

The Beypazarı lignite used in this study was ground and sieved under a nitrogen atmosphere to -65 mesh ASTM and stored under nitrogen at -5 °C until it was used. The elemental analysis of this lignite is given in Table I. Oxidations were carried out in a ventilated oven at 150 °C for up to 168 h. Samples were spread in open vessels each containing 5 g of sample. As reaction proceeded oxidized samples were removed from the oven after varying periods of time and characterized by elemental analysis (C, H, N, S), pyrolysis mass spectrometry, and diffuse reflectance Fourier transform infrared (DRIFT) and solid-state ¹³C FT-NMR spectroscopies.

DRIFT Measurements. Four percent (w/w) of oxidized or unoxidized lignites was mixed with pure NaCl powder. Sodium chloride of 90-75 mesh was dried first at 700 °C overnight in a muffle oven and then at 110 °C before use. After mixing, samples were dried in a vacuum oven at 50 °C overnight and placed in a 3 mm deep, 13 mm diameter cup. The IR spectra were recorded by a Perkin-Elmer Model 1700 FT-IR spectrometer using a Michelson interferometer with rotary scan and bidirectional data collection improved by a single beam and Servo interferometer alignment. The optics were sealed and fitted with molecular sieve desiccant, with a Ge-coated beamsplitter, and a variable Jacquinot stop. A temperature-stabilized ceramic source operating at 1400 K and a temperature-stabilized, coated FR-DTGS (fast recovery deuterated triglycine sulfate) detector with a moisture resistant CsI window as standard were used. All spectra were measured between 4000 and 600 cm⁻¹ by adding 10 scans at a resolution of 2 cm⁻¹. The intensities of diffuse reflectance spectra were calculated using the Kubelka-Munk function.33 Since the concentration and measurement conditions were the same for all samples, difference spectra were obtained as A - kB, where k was equal to 1. For all spectra, the sample chamber was purged with nitrogen gas.

Py-MS Measurements. Pyrolysis mass spectrometry experiments were performed on fresh and 120-h oxidized lignite using automated Curie-point pyrolysis mass spectrometer system, FOMautoPyMS. Coal samples of 50 μ g were coated on ferromagnetic wires from slurries in water. Py-MS conditions were as follows: Curie-point temperatures, 1043 K; heating time, 0.1 s; total pyrolysis time, 0.8 s; temperature of the expansion chamber 475 K; ionization, electron impact (15 eV); mass range scanned, m/z 25-225; scan speed, 10 scan s⁻¹; total number of averages spectra, 200.

¹³C NMR Measurements. Solid-state ¹³C CP/MAS FT-NMR spectra were obtained at a frequency at 75.468 MHz on a Brucker MSL-300 spectrometer in a static magnetic field of 7.05 T. A 7-mm double air bearing, magic angle spinning probe was used at room temperature. The rotor for holding the sample was made of aluminum oxide and was spun at approximately 4.5 kHz. Proton decoupling and cross polarization was used. For sideband suppression, the TOSS (total suppression of spinning sidebands) pulse program with 180° carbon pulses of about 8.7 μ s width was used. The operating parameters were as follows: proton pulse width, 5.4 μ s; contact time, 1 ms; acquisition time, 4.1 ms; pulse repetition time, 100 ms; total accumulation 14 000-290 000. The duration Dn between carbon pulses could be calculated: values were about 20-25, 9-10, 40-44, 210-220, and 160-180 µs for samples D25, D26, D27, D28, and D29, respectively. The peak areas of ¹³C CP/MAS/TOSS spectra were used for quantitative determination of aliphatics and aromatics.

Results and Discussion

Elemental Composition. The elemental analysis data for fresh and oxidized Beypazarı lignite samples are plotted on a van Krevelen diagram³⁴ (H/C vs O/C) in Figure 1. These samples were oxidized at 150 °C for increasing periods of time, and Figure 2 shows the O/H atomic ratio as a function of the oxidation time. As can be seen from Figures 1 and 2, the oxidation of Beypazarı lignite can be divided into three stages. During the first stage, there was little change in the H/C and O/C atomic ratios (the

⁽²⁵⁾ Lynch, B. M.; Lancaster, L.; MacPhee, J. A. Fuel 1987, 66, 979. (26) Jakab, E.; Hoesterey, B.; Windig, W.; Hill, G. R.; Meuzelaar, H. L. C. Fuel 1988, 67, 73.

⁽²⁷⁾ Calemma, V.; Rausa, R.; Margait, R.; Girardi, E. Fuel 1988, 67, 764.

⁽²⁸⁾ Rausa, R.; Calemma, V.; Ghelli, S.; Girardi, E. Fuel 1989, 68, 1168. (29) Joseph, J. T.; Mahajan, O. P. In Coal Science II; Schobert, H. H., Bartle, K. D., Lynch, L. J., Eds.; ACS Symp. Ser. No. 461; Washington

DC. 1991. 299.

⁽³⁰⁾ MacPhee, J. A.; Nandi, B. N. Fuel 1981, 60, 169.
(31) Cooke, N. E.; Fuller, O. M.; Gaikwad, R. P. Fuel 1986, 65, 1254.
(32) Huffman, G. P.; Huggins, F. E.; Dunmyre, G. R.; Picnocco, A. J.; Lin, M. C. Fuel 1985, 64, 849.

⁽³³⁾ Kubelka, P.; Munk, F. Z. Tech. Phyc. 1931, 12, 593. (34) Krevelen, V. D. Fuel 1950, 29, 269.



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



Time of oxidation (h)

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



WAVENUMBER

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

first points in Figure 1 and the first 9 h in Figure 2). During this period, the elemental composition of the organic part of the lignite was not affected by the oxidation process. The second stage of the oxidation persisted from 9 to 24 h during which period there was a fast increase in oxygen content whereas the loss of hydrogen was slow (Figures 1 and 2). During the last stage, the H/C atomic ratio decreased rapidly but the increase of the O/C atomic ratio was much slower than that in the second stage (Figure 1). The increase in O/H atomic ratio was faster during the second stage of the oxidation than during the last stage.

Structural Analysis. Figure 3 presents the difference spectra, which were obtained by subtracting the spectra of the oxidized Beypazarı lignite samples from that of the original lignite. As the oxidation time increased, major



Figure 4. Plot of the change in intensity of the CH_2 2926-cm⁻¹ band and CH_3 2872-cm⁻¹ band relative to the 1610-cm⁻¹ band versus time of oxidation at 150 °C.

changes in the spectra were observed in the 3000-2500, 2000-1600, and 1200-800-cm⁻¹ regions. The bands corresponding to 2926 and 2872 cm⁻¹ wavenumbers are due to C-H stretching vibrations of CH₂ and CH₃ groups. As pointed out above, the oxidation of Beypazarı lignite proceeded in three consecutive stages in which both the elemental analysis of oxidized coals and the relative intensities of aliphatic CH2 and CH3 groups followed the same trends with respect to the duration of oxidation. Figure 4 presents the intensities of aliphatic C-H stretching of both CH_2 and CH_3 groups relative to the intensity of the 1610-cm⁻¹ absorption by aromatic stretching vibrations as a function of the duration of oxidation. It appears that, up to, approximately, 25 h of oxidation there was no significant change in the intensity of aliphatic CH₂ and CH_3 groups even though it is claimed that they are the first groups to react with oxygen during the initial stages of oxidation of some other coals.^{20,27-29} The characteristic bands near 1090 and 980 cm^{-1} in the spectra shown in Figure 3 are due to iron(II) sulfate.³¹ Iron(II) sulfate must be considered as the main oxidation product of pyrites present in coals.³² It seems that, as the alkyl groups remained unoxidized during the first 25 h of oxidation, iron(II) sulfate was the main oxidation product during this time. In other words, it may be claimed that the formation of iron(II) sulfate in the Beypazari lignite was much faster than the oxidation of alkyl groups. The activation energies for both the formation of oxycoal and the combustion of coal have been estimated as 66.94 and 104.6-146.44 kJ/mol respectively.35 Comparison of these values with the activation energy of the combustion of iron sulfide,³⁶ 39 kJ/mol, which forms iron(II) sulfate by oxidation,³² makes it quite understandable that iron(II) sulfate is formed more rapidly than the oxidation of the organic part of the coal at 150 °C. Figure 5 shows the change in the intensity of iron(II) sulfate bands produced by the oxidation in Bevpazarı lignite with respect to oxidation time. It seems clear that the formation of iron-(II) sulfate was the preferred reaction throughout the first 25 h. As is seen in Figure 5, the rate of oxidation of alkyl groups increased after the first 24 h and the rate of formation of iron(II) sulfate remained constant after the first 25 h till the end of oxidation.

The classes of carbonyl-containing functionalities, aryl esters (1771 cm^{-1}) , diaryl ketones (1655 cm^{-1}) , carboxylate

 ⁽³⁵⁾ Cavalieri, R. P.; Thomson, W. J. Fuel 1990, 69, 334.
 (36) van Krevelen, D. W. Coal; Elsevier: Amsterdam, 1961; Chapter



Figure 5. Plot of the change in K-M units of 1090 cm⁻¹; $FeSO_4$ ·H₂O versus time of oxidation.



Time of oxidation (h)

Figure 6. Plot of the change in K-M units of 1771 cm⁻¹; aryl ester band versus time of oxidation at 150 °C.

anions (1540 cm⁻¹), and anhydrides (1843 cm⁻¹), observed previously by other authors,^{25,27,28,37-41} during the oxidation of coals were also identified in the present work. The major products were aryl esters, and their formation was observed in four stages from 4 h of the start of the oxidation as shown in Figure 6. During the first stage, there was a fast but slight increase in the intensity of aryl esters bands. In this stage, the formation of aryl esters can be explained by the reaction between carboxylic acids and hydroxyl groups already existing in the lignite. The intensity of aryl esters band was almost constant in the second stage which was between 10 and 24 h of oxidation. After 24 h, the aryl ester formation started again, up to approximately 96 h of oxidation. The intensity of aliphatic CH_2 and CH_3 groups decreased between 24 and 96 h of oxidation, as explained above in Figure 4. It was thought that the aliphatic CH₂ and CH₃ groups started to react with oxygen to form carboxyl-containing functional groups during this period. There was almost no change in the intensity of the aryl esters band after 96 h of oxidation. The oxygencontaining functionalities were also observed in solid-state ¹³C NMR spectra. The absorption at 155 ppm in Beypazarı lignite can be attributed to phenols which is consistent with the absorption of a peak at m/z 105 in the Py-MS spectrum in Figure 7. Carboxylic acids, esters, and lactones



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

generally absorb around 177 ppm in low-rank coals.⁴² Thus, the bands which were observed in Beypazarı lignite at 170 and 177 ppm can be respectively attributed to carboxylic acids and esters. The intensity of the ester band at 177 ppm increased as oxidation proceeded and the significance of the phenol band at 155 ppm almost disappeared, becoming merely a small shoulder during the same oxidation period. Absorption at lower fields around 200 ppm can be attributed to such carbonyl-containing functional groups as ketones and aldehydes, but the intensity of these bands was less than that of the other that have been discussed.

The aromatic structure was not affected during oxidation at 150 °C. The concentrations of aromatic rings such as benzene (m/z 78), phenol (m/z 94) and naphthalene (m/z128) in Py-MS products remained almost unaffected by oxidation (Figure 8). Similarly, the intensity of the IR band at 1610 cm⁻¹ corresponding to aromatic structures was not changed significantly by oxidation of Beypazarı lignite. Although the DRIFT and Py-MS analysis, as explained above, showed little change of aromatic structure during oxidation, a slight increase of aromaticity factor was observed by solid-state ¹³C NMR (Table II). As the duration of oxidation increased there was a decrease in

⁽³⁷⁾ Bellamy, L. J. The Infrared Spectra of Complex Molecules;
Chapman and Hall: London, 1975; Vol. 1.
(38) Kuehn, C. W.; Davis, A.; Painter, P. C. Int. Conf. Coal Sci. 1983,

⁽³⁸⁾ Kuehn, C. W.; Davis, A.; Painter, P. C. Int. Conf. Coal Sci. 1983 304.

⁽³⁹⁾ Kister, J.; Guiliano, M.; Mille, G.; Dou, H. Fuel 1988, 67, 1076.
(40) Gaines, A. F. In New Trends in Coal Science; Yürüm, Y., Ed.; NATO ASI SEries C 244; Kluwer Academic Publishers: Dordrecht, 1988; p 197.

⁽⁴¹⁾ Fuller, M. P.; Hamadeh, I. M.; Griffiths, P. R.; Lowenhaupt, D. E. Fuel 1982, 61, 529.

⁽⁴²⁾ Axelson, D. E. Solid-State Nuclear Magnetic Resonance of Fossil Fuels: An Experimental Approach; Multiscience Publications: Canada, 1985, 202.



m/z



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

<i>t</i> (h)	fa	$f_{ m al}$	<i>t</i> (h)	fa	$f_{ m al}$		
0	0.51	0.40	48	0.51	0.29		
12	0.47	0.29	120	0.55	0.27		
24	0.52	0.30					

the aliphatic factor from 0.40 to 0.27 but the aromaticity factor increased only from 0.51 to 0.55. O-substituted aromatic carbon in phenols, aromatic ethers, and anhydrides gives peaks between 164 and 148 ppm,⁴³ and the presence of mineral matter, particularly the incorporation of carbonates which interfere with the aromatic region may increase the aromaticity factor.44 The observed increase in aromaticity may be due to both the mineral matter in Beypazarı lignite in which the ash content was 24.3% and the formation of anhydride during oxidation. In this study, an anhydride band was observed both in the FT-IR difference spectra of the oxidized samples at 1843 cm⁻¹ (Figure 3) and in the solid-state ¹³C NMR spectra at 164 ppm (Figure 9). The decrease in the concentration of the aliphatic groups (Table II) demonstrates that the aliphatics were more readily oxidized active to oxidation to carboxylate- and carbonyl-containing functional groups than the aromatics in Beypazarı lignite. These results are consistent with some of the literature, 43 but other authors 30 show that the $C_{\rm Ar}/C_{\rm Al}$ ratio increases as a function of time of oxidation at 105 °C.

The overall change of the oxidation on the structure of Beypazarı lignite was also studied by Py-MS spectroscopy. Figure 5 presents the low-voltage pyrolysis mass spectra of fresh and 120-h-oxidized Beypazarı lignite samples. In order to explain the changes in chemical composition of the lignite pyrolysates, both quantitatively and qualitatively, the peak intensities of major molecular ion series were calculated by multiplying the peak height with the maximum intensity. The differences between the intensities of the molecular ion series of oxidized and fresh pyrolysates are plotted versus the mass number of the



Figure 9. CP/MAS/TOSS ¹³C NMR spectra of fresh and oxidized Beypazarı lignite samples (120 h at 150 °C): (A) fresh; (B) 48 h; (C) 120 h.

molecular ion series in Figure 8. The most prominent ion series which were affected by the oxidation process were respectively m/z 94, 108, 122, 136 (alkylphenols); m/z 110, 124, 128 (dihydroxybenzenes); m/z 78, 92, 106, 120, 134 (alkybenzenes); m/z 43, 57, 71, 85 (alkyl groups); m/z 42, 56, 70, 84, 98, 112 (alkenes), and m/z 128, 142, 156, 170 (alkylnaphthalenes). However, m/z 108 C₁-alkylphenol, m/z 170 C₃ alkylnaphthalene, m/z 106 C₂-alkybenzene, and m/z 124 C₁-alkyldihydroxybenzene molecular ions were more affected by oxidation than the other homologs in each of the molecular ion series. The formation of an alkene series was due to breaking of the alkyl groups next

⁽⁴³⁾ Dereppe, J. M.; Moreaux, C. Landais, P.; Monthioux, M. Fuel 1987, 66, 594.

⁽⁴⁴⁾ Axelson, D. E. Solid-State Nuclear Magnetic Resonance of Fossil Fuels: An Experimental Approach; Multiscience Publications: Canada, 1985; p 73.

to aromatic rings during pyrolysis.²⁶ The significant change in the concentration of alkyl groups has been claimed to show that these groups are mostly the substituents of aromatic rings such as in alkylphenols, alkylbenzenes, alkylnaphthalenes, and alkyldihydroxybenzenes in the organic structure of Beypazarı lignite. These alkyl groups were also identified by ¹³C NMR spectroscopy. Alkyls next to aromatic rings, such as α methylene Ar-*(CH₂)-CH₃ and methyl Ar-*CH₃, appeared respectively at 33 and 26 ppm in the aliphatic region of the spectrum of fresh Beypazari lignite and the band corresponding to terminal methyl groups $Ar-(CH_2)-*CH_3$ appeared at ≈ 14 ppm as a shoulder (Figure 9). The presence of the 14-ppm band also supports the presence of methylene groups in alkyl chains next to aromatic rings at 33 ppm. Oxidation of alkyl groups gave the carbonyl and the carboxyl functionalities and the pyrolysis of those groups gave CO_2^+ (m/z 44), CO^+ (m/z 28), and CH_3COOH^+ (m/z 60) molecular ions in Py-MS experiments in concentrations which increased after 120 h of oxidation (Figure 8). The effect of the oxidation on alkynaphthalenes and alkylbenzenes was less than the effect on alkylphenols and alkyldihydroxybenzenes because of the absence of electron-withdrawing groups such as hydroxyl. Such groups make the oxidation of the alkyl substituents easier.

In addition to the oxygen-containing molecular ions, there were some sulfur-containing major molecular ion peaks at low mass numbers. These molecular ion series have been reported previously.^{26,45-48} Both fresh and oxidized Beypazarı lignite pyrolysates gave signals at m/z34 (H_2S^+) and 64 (SO_2^+) . The changes in the intensity of these molecular ions, during the oxidation process at 150 °C are presented in Figure 8. The negative value intensity of the m/z 34 H₂S⁺ molecular ion, after the pyrolysis, is due to the oxidation of sulfur-containing functional groups such as disulfur, thiophenes, or thiols which are converted to sulfones, thiosulfones, thiosulfoxides, and sulfonic acids. as observed in the study of Attar.⁴⁹ There was an increase of SO_2^+ formation after the oxidation process but, since there were already oxidized sulfur moieties in fresh lignite, the oxidation did not affect the organic sulfur greatly (Figure 8). Experiments indicate that carbon monoxide is a pyrolysis product of ethers, quinones, and benzofurans and carbon dioxide is formed from the pyrolysis of carboxylates, carboxylic acids, anhydrides, and esters.⁴⁸⁻⁵⁰ The formation of carbon dioxide, carbon monoxide, and

(49) Attar, A. Fuel 1978, 57, 201.

acetic acid from the fresh lignite indicated that before the oxidation there were significant amounts of carbonyl and carboxyl groups in the lignite. After the oxidation, there was an increase in the formation of these molecular ions, as shown in Figure 8; in particular, m/z 44 (CO₂⁺) was much more than m/z 28 (CO⁺) and 60 (CH₃COOH⁺). This indicates that the formation of carboxyl functional groups by oxidation exceeded the formation of carbonyl groups.

Conclusions

The present work investigated the effects of air oxidation at 150 °C on the structural characteristics of Beypazari lignite. It was observed that the formation of iron(II) sulfate had an important role in controlling the oxidation of the organic structure, particularly during early times of the process. The formation of iron(II) sulfate prevented the oxidation of aliphatic CH₂ and CH₃ groups for up to 24 h. After that time, these groups started to react with molecular oxygen to yield carboxyl-containing functional groups. Aliphatic CH_2 and CH_3 groups which were adjacent to aromatic rings as in alklyphenols, alkylbenzenes, and alkylnaphthalenes oxidized during the process. m/z 108 C₁-alkylphenol, m/z 170 C₃-alkylnaphthalene, m/z106 C₂-alklybenzene, and m/z 124 C₁-alkyldihydroxybenzene molecular ions were affected more than the other homologs in each of the molecular ion series by oxidation. The major oxidation product was aryl esters. DRIFT and Py-MS analysis showed that aromatic structures were little changed during the oxidations but solid-state ¹³C NMR indicated a slight increase in aromaticity from 0.51 to 0.59. This increase was due to the formation of anhydride as oxidation proceeded and also due to the presence of much mineral matter in Beypazarı lignite. It was concluded that the interference of the anhydride band and particularly of the carbonates in the mineral matter with the NMR absorption by aromatic carbons increased the aromaticity factor by Beypazarı lignite. There was a decrease of aliphatic groups between 24 and 96 h of oxidation, the most effective for the oxidation period of organic structure, and the O/H atomic ratio also increased during this period. After 96 h of oxidation, there were no further changes to either the organic structure or the inorganic matrix.

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⁽⁴⁵⁾ Nip, M.; Leeuw, J. W.; Schenck, P. A. Geochim. Cosmochim. Acta 1988, 52, 637.

⁽⁴⁶⁾ Harper, M. A.; Meuzelaar, H. L. C.; Given, H. H. Fuel 1984, 63, 793.

 ⁽⁴⁷⁾ Tromp, P. J. J.; Moulijn, J. A.; Boon, J. J., Fuel 1986, 65, 960.
 (48) Meuzelaar, H. L. C.; Harper, A. M.; Hill, G. R.; Given, P. H. Fuel 1984, 63, 640.

⁽⁵⁰⁾ Campbell, J. H. Fuel 1978, 57, 217.