Air Oxidation of Turkish Beypazarı Lignite. 3. Change in the Structural Characteristics of the Residue in Oxidation Reactions at 150 °C

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Beypazarı lignite was subsequently demineralized with HCl/HF and extracted by pyridine under supercritical conditions. The extracted residue was oxidized in air at 150 °C for up to 120 h in a ventilated oven. Elemental analysis, diffuse reflectance Fourier transform infrared (DRIFT), solid-state ^{13}C CP/MAS/TOSS NMR, and pyrolysis mass (Py-MS) spectroscopic techniques were used for the structural characterization of the oxidized and unoxidized samples. It was found that the oxidation of the extracted residue proceeded in two consecutive stages. The rate of oxidation, as measured by changes in the concentrations of carboxyl and aliphatic CH_2 and CH_3 groups and in the O/H atomic ratio, was much faster in the initial than in the second stage. The removal of 90.1% of the mineral matter and 39.7% of the soluble material from the parent lignite facilitated the access of oxygen to the network structure which was relatively enriched in aromatic units by the supercritical fluid extraction. It was therefore easier to form aryl esters, alkyl esters, and anhydrides. Since aliphatic structures were relatively less in concentrations than aromatics, there was little change in the intensities of alkylbenzenes, alkylnaphthalenes, alkyldihydroxybenzenes, alkylphenols, and alkanes during oxidation. The higher intensities of CO_2^+ (*m/z* 44) and CH_3COOH^+ (*m/z* 60) molecular ions observed in Py-MS than CO^+ (*m/z* 28) molecule ion indicated that more carboxyl-containing functional groups were formed by oxidation than carbonyl-containing groups. Aromatic structures in the organic network were not affected during oxidation. The oxidation pathway of the extracted residue was considered to lie between of the oxidation pathways of the parent and the demineralized Beypazarı lignites.

Introduction

It is generally accepted that low-temperature air oxidation alters the organic and the inorganic composition of coals and these changes have important impacts on both physical and chemical properties.[1–13] The reaction pathway and the oxidation products of the organic material vary depending on the rank of the coals and the temperature of oxidation, in particular, low-rank coals are the most sensitive to oxidation.[14–29]

In the previous papers of this series, the oxidation pathway and the structural characteristics of the parent lignite and of the demineralized lignite were studied at 150 °C.[30,31] It was found that air oxidation proceeded in three consecutive stages in the parent lignite whereas the

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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%

demineralized lignite was oxidized in a single stage by a diffusion-controlled mechanism. It was also observed that during the oxidation of both lignites the aliphatic groups were more susceptible to attack than the aromatic structures.

Although most studies suggest that air oxidation under mild conditions has a significant effect on the aliphatic structure of coals,[32-35] there are conflicting results suggesting that the aromatic units are affected more than the aliphatics. Thus, it has been reported that the ratio of aromatic to aliphatic carbon in air at 105 °C increased with the time of oxidation.[36] A South African coal and its pyridine-extracted products were oxidized at 150 °C. The FT-IR characterization of this coal, its extract, and residue showed decreases in the intensities of both the aromatic (3100–2992 cm^{-1}) and the aliphatic (2992–2795 cm^{-1}) C–H stretching regions as the time of oxidation increased.[37] Kalema and Galavas observed that air oxidation at 200 and 250 °C affected aliphatic carbons more than aromatics in the ratios of 3–4/1.[38] Studies combining ^{13}C CP/MAS NMR and FT-IR spectroscopic techniques revealed the aliphatic moities to be more active than the aromatics.[39,40] Khan et al. studied the influence of air oxidation on the structure of Pittsburgh No. 8 coal and its pyridine-soluble and -insoluble parts at 150 °C using ESR and ^{13}C NMR spectroscopies and concluded that the extract, which had relatively high hydrogen content, was affected more than the hydrogen poor residue and that the percentage of aromatic carbons was not changed significantly during oxidation.[41]

The objective of the present study was to investigate the effect of air oxidation on the structural characteristics of the extracted residue which was relatively enriched by aromatic structures with regard to aliphatics after supercritical fluid extraction.

Experimental Section

The elemental analysis of Beypazarı lignite used in this study is shown in Table 1. Beypazarı lignite was subsequently demineralized with HCl/HF and extracted in the presence of pyridine under supercritical conditions. Sample preparation, demineralization, and the method of oxidation of the extracted residue have been described previously.[30,31] The extracted residue was subjected to oxidation at 150 °C for up to 120 h. The samples were characterized by elemental analysis, diffuse reflectance Fourier transform infrared (DRIFT), solid-state ^{13}C CP/MAS/TOSS NMR, and pyrolysis mass (Py-MS) spectroscopies. The procedures for these techniques have also been described in detail.[30]

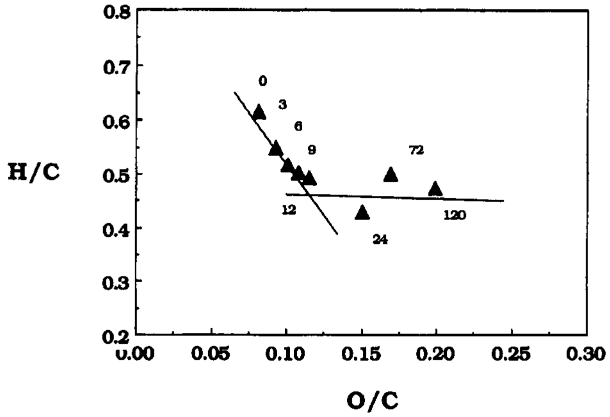

Figure 1. van Krevelen diagram of fresh and oxidized residue (the numbers on the graph show the time of oxidation in hours).

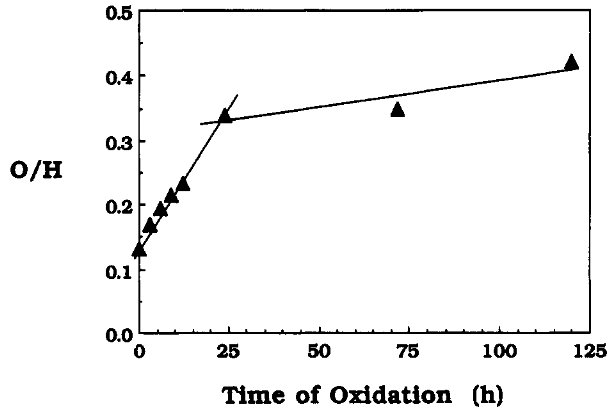

Figure 2. Change of O/H atomic ratio of fresh and oxidized residues versus time of oxidation at 150 °C.

Supercritical Fluid Extraction. Demineralized Beypazarı lignite was extracted by supercritical pyridine. The extractor was built entirely of stainless steel, and hydrostatically tested to 330 atm. A 60-g sample of moisture-free, demineralized Beypazarı lignite was swollen in 200 mL of pyridine. This preswollen sample was poured into a cellulose thimble and placed in the extractor; 200 mL more of pyridine was added to the system which was then repeatedly (3 times) pressurized with nitrogen to 170 atm and evacuated. On heating, the temperature and the pressure within the extractor rose to 347 °C and 75 atm in 1 h. After 2 h of extraction, coolant water was passed through the condenser and the system was thus cooled to ambient temperatures to permit the pressure within the extractor to drop to atmospheric level. This procedure was repeated until the extracted solution was colorless and transparent. The residue was washed successively with dilute HCl, distilled water and acetone to remove the pyridine remaining inside the pores; it was then dried to a constant weight at 110 °C under vacuum.

Results and Discussion

Elemental Composition. Figure 1 presents the elemental analysis of fresh residue and of its oxidized products plotted on a van Krevelen diagram (H/C vs O/C). The O/H atomic ratios of the fresh and oxidized samples were also plotted with respect to the time of oxidation (Figure 2). It will be seen that the oxidation pathway of the extracted residue can be divided into two consecutive stages. In the initial stage, for up to 24 h, the fast decrease of the H/C and the slow increase of the O/C atomic ratios indicated the elimination of water from the organic

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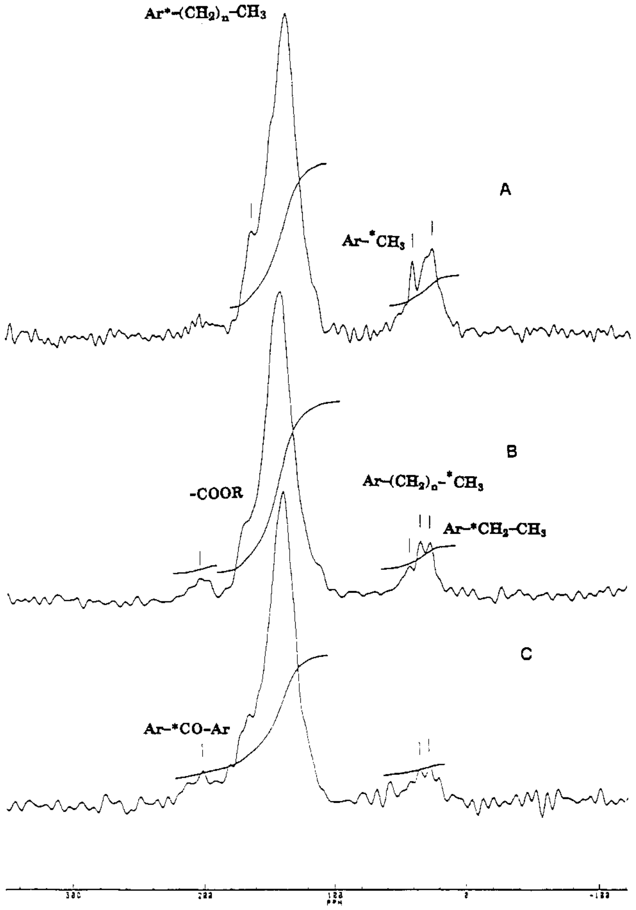

Figure 3. CP/MAS/TOSS ^{13}C NMR spectra of fresh and oxidized (at 150 °C) residues: (A) fresh; (B) 48 h; (C) 120 h.

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

t (h)	f_a	f_{al}
0	0.82	0.18
12	0.85	0.12
120	0.85	0.08

structure and, in fact the slope of the initial H/C vs O/C graph is close to 2. This behavior was also observed in the third stage of the oxidation of the parent lignite[30] and throughout the whole oxidation period of the demineralized Beypazarı lignite.[31] During the second stage of the oxidation of the extracted residue, persisting from 24 to 120 h, the gain of oxygen was much more significant than the change in hydrogen concentration. It appears that the oxidation pathway of the extracted residue was intermediate between the oxidation pathways of the parent and the demineralized Beypazarı lignites.

Structural Analysis. The extracted residue from demineralized Beypazarı lignite differed very significantly from both the parent lignite and the demineralized. Thus, whereas the parent lignite possessed H/C and O/C atomic ratios of 1.08 and 0.31, these ratios were only 0.62 and 0.08 in the extracted residue. ^{13}C NMR spectra (Figure 3, Table 2) showed the extracted residue to possess increased proportions of aromatic structures, its aromaticity being increased from 0.51 to 0.82. Clearly, the structure of the extracted residue resembles that of a coal. In order to observe the changes in the low quantity of aliphatic CH_2 and CH_3 groups in the extracted residue during oxidation, all DRIFT spectra were expanded in the 4000 and 2000-cm^{-1} region (Figure 4). The bands at 2962, 2926, 2872, and 2853 cm^{-1} were due to the C–H stretching of aliphatic CH_3 (asym), CH_2 (sym), CH_3 (sym), and CH_2 (asym) groups, respectively. The symmetric C–H stretching of aliphatic CH_2 and CH_3 intensities relative to the 1610-cm^{-1} aromatic stretching band were plotted with respect to the duration of oxidation (Figure 5). These ratios suggest that the air oxidation of the extracted residue proceeded in two consecutive stages as was observed from the elemental analysis (Figures 1 and 2). It appears that the loss of aliphatic CH_2 and CH_3 groups was significant at the initial stage for up to approximately 24 h of oxidation as was observed for the oxidation of demineralized Beypazarı lignite.[31] The formation of iron(II) sulfate prevented the oxidation of the organic structure of the parent lignite during the first 24 h.[30] After the first 24 h, there was almost no change in the intensity of methylenes and methyl groups till the end of oxidation of the extracted residue. The loss of aliphatic CH_2 and CH_3 groups was consistent with the formation of carboxyl-containing functionalities: aryl esters (1771 cm^{-1}), alkyl esters (1741 cm^{-1}), and anhydrides (1843 cm^{-1}) which became apparent in the difference DRIFT spectra as the duration of oxidation increased. The expanded difference spectra in the carbonyl- and carboxyl-containing region are presented in Figure 6. Bands corresponding to carboxylic acids (1683 cm^{-1}) and carboxylate anions (1588 cm^{-1}) also appeared in the difference spectra but the intensities of these groups decreased as the time of oxidation increased. This decrease may imply that esters and anhydrides were formed through carboxylic acids and carboxylate anions. As is seen clearly from Figure 7, the oxidation reaction also proceeded in two consecutive stages in terms of carboxyl-containing functional groups. The rates of formation of aryl esters and alkyl esters were greater at the initial stage of oxidation whereas between 24 and 120 h the intensity of these groups remained almost constant.

The results so far are consistent with the literature,[37–41] however, these observations of the oxidation of the extracted residue differed from those of some other studies[20,42] and also from observations of the oxidation of the parent and the demineralized Beypazarı lignite.[30,31] The rates of loss of aliphatic CH_2 and CH_3 groups on oxidation and the rates of formation of carboxyl-containing functional groups were much greater at 150 °C, and particularly at higher temperatures than 150 °C.[33,34] We have observed that the intensity of aliphatic CH_2 and CH_3 groups decreased sharply in the first 5 h of oxidation of the extracted residue (Figure 5) and that rate of formation of the aryl and alkyl esters was similar during the same time interval (Figure 7).

Oxidation of the extracted residue indicated that the rate of loss of aliphatic CH_2 and CH_3 groups and the rate of formation of aryl and alkyl esters and the changes in O/H atomic ratio at the initial stage of oxidation were greater than in the oxidation of either the parent[30] or the demineralized Beypazarı lignite.[31] The organic structure of the parent lignite was particularly stable at that stage due to the formation of iron(II) sulfate.[30] It was considered that the removal of 90.1% mineral matter and 39.7% of soluble materials from the Beypazarı lignite facilitated the access of oxygen to the coal structure. Moreover, the enrichment of the concentration of aromatic groups, as a consequence of the higher aromaticity caused by supercritical fluid extraction and the more relaxed macromo-

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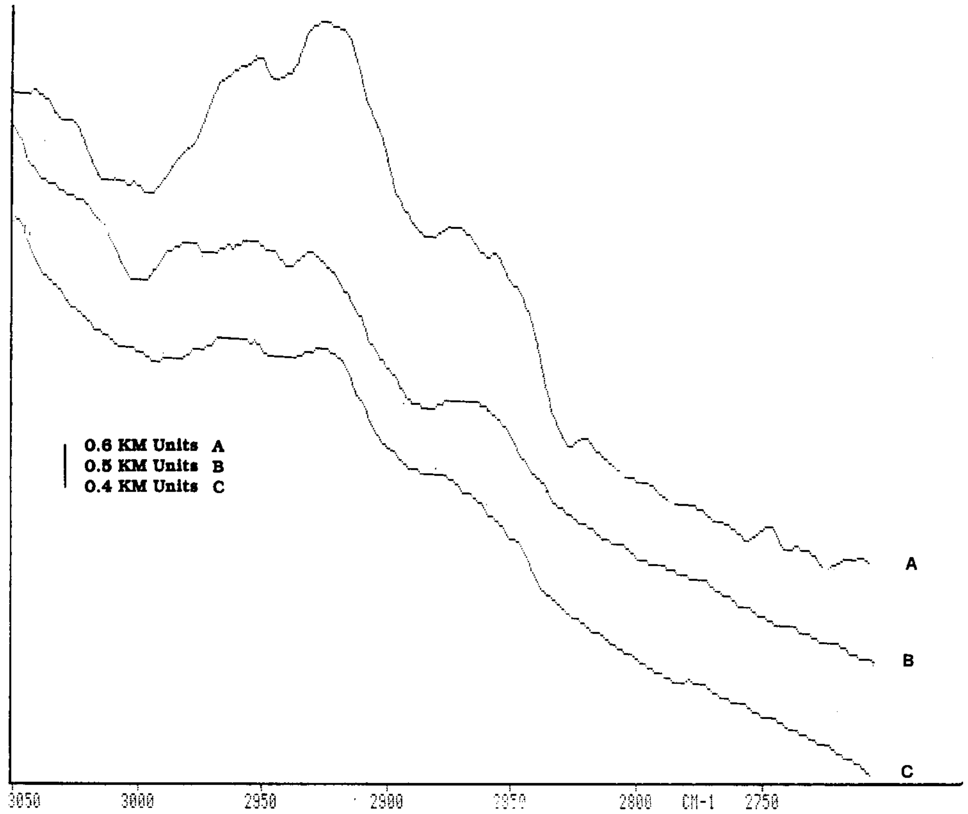

Figure 4. DRIFT spectra of fresh and oxidized (at 150 °C) residues between 4000 and 2700 cm^{-1}: (A) fresh; (B) 72 h; (C) 120 h.

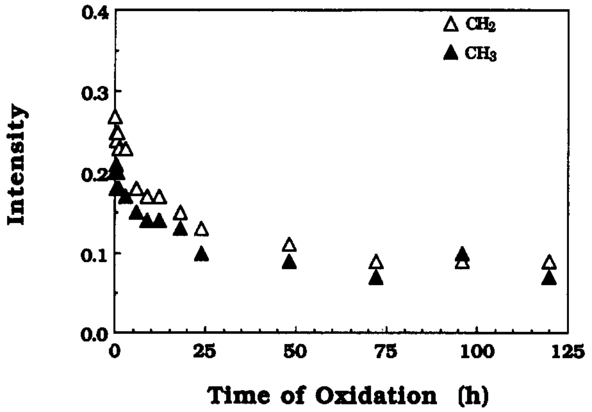

Figure 5. Change in intensity of the CH_2 2926-cm^{-1} and CH_3 2872-cm^{-1} bands relative to the 1610-cm^{-1} band versus time of oxidation at 150 °C.

lecular structure of residue, greatly increased the rate of oxidation of methylenes and methyls.

The bands at 20 and 29 ppm in solid-state ^{13}C NMR spectra can be assigned to α-methyl groups Ar–$^*CH_3$ and α-methylenes Ar–$^*CH_2$–CH_3, respectively.[43] Terminal methyl groups Ar–$(CH_2)_n$–$^*CH_3$ appeared at 14 ppm (Figure 3). These bands apparent in the spectra are consistent with the literature.[25,30,31,40,44] As the time of oxidation increased, the intensities of these groups decreased significantly (Figure 3) and the aliphaticity changed from 0.18 to 0.08 (Table 2). Aromatic carbons gave the band around 140 ppm and aryl esters which were the major oxidation product, appeared at approximately 168 ppm. The band which appeared at approximately 200 ppm can be assigned to ketones, and its intensity remained almost constant during oxidation.[43] DRIFT measurements were consistent with this result in that there was no absorption band of ketone in the difference spectra

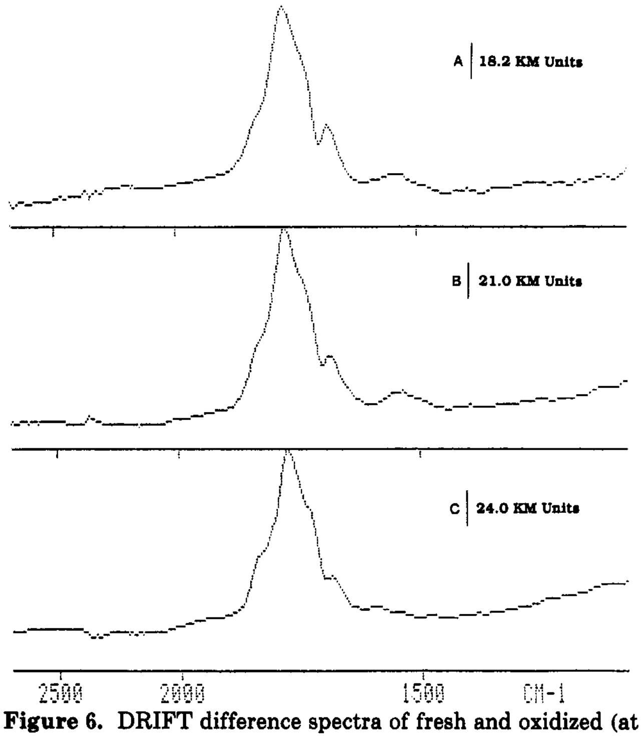

Figure 6. DRIFT difference spectra of fresh and oxidized (at 150 °C) residues between 2500 and 1500 cm^{-1}: (A) 24 h; (B) 72 h; (C) 120 h.

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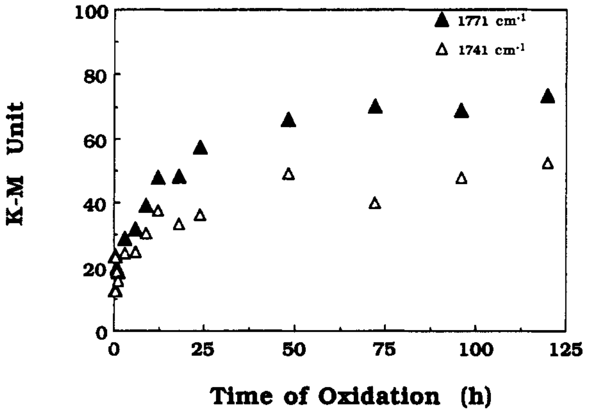

Figure 7. Change in K-M unit of the 1771-cm^{-1} aryl ester band and the 1741-cm^{-1} alkyl ester band versus time of oxidation.

of the extracted residue as the time of oxidation increased. Although the formation of ketones was observed during the oxidation of the parent lignite,[30] carbonyl-containing functionalities were not observed during oxidation of the demineralized Beypazarı lignite at 150 °C.[31]

Aromatic structures were not affected significantly by air oxidation at 150 °C. The aromaticity changed from 0.82 to 0.85 and neither a positive nor a negative band due to aromatic structures could be observed at 1610 cm^{-1} in the difference DRIFT spectra during oxidation (Figure 6). Oxidation of the parent[30] and the demineralized Beypazarı lignite[31] also indicated the stability of the aromatic structures to air oxidation. However, the slight increase in the aromaticity of those samples was due to the formation of anhydrides and the presence of minerals, particularly in the parent lignite.[30] The aromatic structure of Pocahontas No. 3 coal which has a similar aromaticity value to the present extracted residue seems quite stable during oxidation at 100 °C, whereas other Argonne Premium coal samples show a slight increase in aromaticity at that temperature.[44] The pyridine residue from Pittsburgh No. 8 coal also retains its the aromaticity at 0.78 during oxidation at 150 °C.[41]

Alterations in the organic structure of the oxidized and unoxidized residues were also observed by low-voltage Py-MS spectroscopy which indicated that the pyrolysis products were similar (Figure 8) though the intensities of the products were different from the parent[30] and the demineralized Beypazarı lignite[31] (Figure 9). Molecular ion series were observed which demonstrated the presence of aliphatic substituents adjacent to aromatic structures, namely alkylphenols, m/z 94, 108, 122, and 136; alkyldihydroxybenzenes, m/z 110, 124, and 128; alkylbenzenes, m/z 92, 106, 120, and 134; and alkylnaphthalenes, m/z 142, 156, and 170. The changes in the intensities of the Py-MS spectra were calculated as was described previously.[30] In addition to these molecular ion series, alkyl groups, m/z 43, 57, and 71 were also seen to be affected by oxidation, particularly those aliphatic methylenes and methyls which were α substituents of aromatic rings were readily oxidized to form such carboxyl containing functionalities as esters. The intensities of the molecular ions of m/z 108 C_1-alkylphenol, m/z 142, 156, and 170 C_1, C_2, C_3-alkylnaphthalenes, m/z 106 C_2-alkylbenzene, and m/z 124 C_1-alkyldihydroxybenzene were affected much more than the intensities of other ions of the homologous series during oxidation of the extracted residue. One suggests that the CO_2^+ (m/z 44) and CH_3COOH^+ (m/z 60) molecular ions that were observed were formed by the pyrolysis of esters, these being the major oxidation products. The formation of CO^+ (m/z 28) molecule ion was probably due to the pyrolysis of the ketones which were observed in ^{13}C NMR spectra. Jakab et al. showed carbonyl and carboxyl groups of a high-volatile A bituminous coal to be the major products of the oxidation at 100 °C. In addition, the concentrations of alkylnaphthalenes and alkylphenols decreased during the oxidation of that coal.[27] The increase in the intensities of the CO_2^+ (m/z 44) and CH_3COOH^+ (m/z 60) molecular ions corresponded approximately to the decrease in the intensities of the molecular ion series of alkylphenols, alkyldihydroxybenzenes, alkylbenzenes, alkylnaphthalenes, and alkyls. Although the oxidation pathways of the parent[30] and the demineralized Beypazarı lignite[31] and the extracted residue differed in each case, the more carboxyl-containing functional groups were formed by oxidation than carbonyl functionalities, as is seen from Figure 9. The peak m/z 79 was due to pyridine which could not be removed from the organic structure either under vacuum at 110 °C or by oxidation at 150 °C for 120 h. There is no evidence as to whether the remaining pyridine affects the oxidation reactions of the extracted residue at 150 °C.

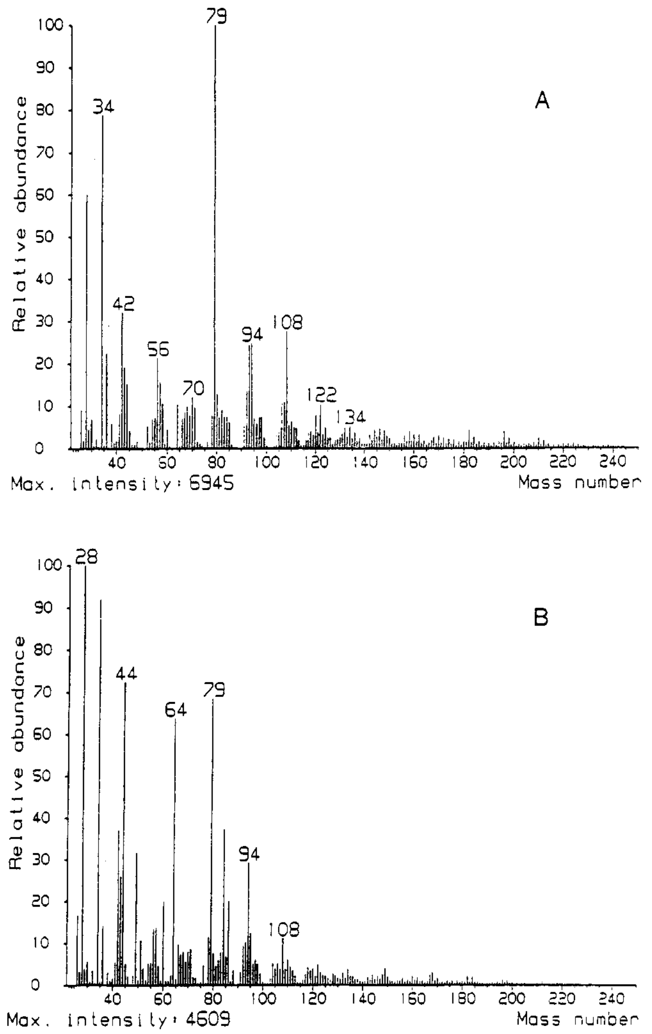

Figure 8. Low-voltage pyrolysis mass spectra of fresh and oxidized residues: (A) fresh; (B) oxidized residue (120 h at 150 °C).

Conclusions

In the present study, the effect of air on the structural characteristics of the extracted residue at 150 °C have

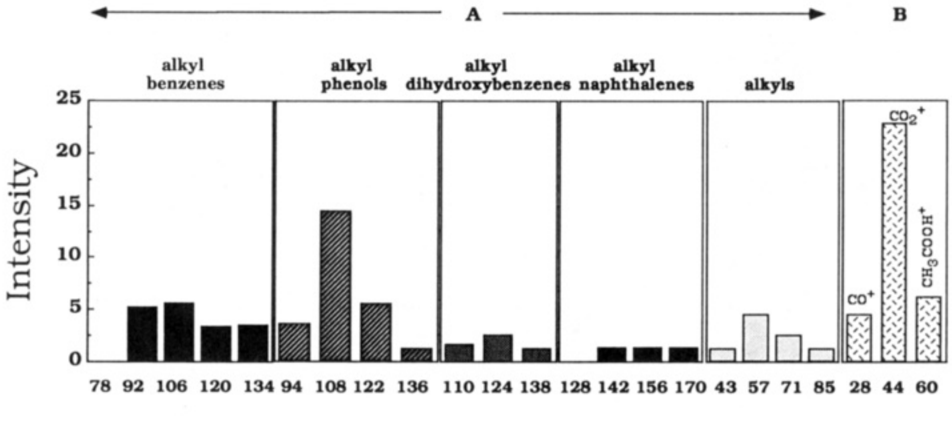

Figure 9. (A) Positive difference ion peak intensities of molecular ion series between pyrolysates of oxidized (120 h at 150 °C) and fresh residues versus mass numbers (showing a negative trend). (B) Intensities of the molecular ions versus mass numbers.

been presented with respect to the time of oxidation. Demineralization and supercritical pyridine extraction of Beypazarı lignite left an aromatic (f_a = 0.82 instead of 0.51[30]) and apparently open residue. Air at 150 °C oxidized similar chemical sites to those attacked in the parent and demineralized lignite.[30,31] The van Krevelen diagram (H/C vs O/C), the change of the O/H atomic ratio, the loss of aliphatic CH_2 and CH_3 groups, and the formation of aryl ester and alkyl ester showed that the oxidation reaction of the residue proceeded in two consecutive stages. During the first 24 h of oxidation, the rates of loss of aliphatic methyls and methylenes and the rate of formation of carboxyl-containing functional groups were quite fast. Subsequently, there were almost no significant changes in the intensity of any functional groups. However, oxidation was not effective for the organic structure of the parent lignite[30] as was observed for the demineralized[31] and for the extracted residue at the initial stage. The removal of 90.1% mineral matter and 39.7% of solubles from the parent lignite facilitated the access of oxygen to the network; in which supercritical fluid extraction had enriched the concentration of aromatic units and made it easier to form aryl esters, alkyl esters and anhydrides. The rate of the oxidation exceeded that of the demineralized lignite[31] under the same conditions and was no longer restricted by the rate of diffusion through the pores system. The molecular ion series of alkylphenol, *m/z* 94, 108, 122, and 136; alkyldihydroxybenzene, *m/z* 110, 124, and 128; alkylbenzene, *m/z* 92, 106, 120, and 134; alkylnaphthalene, *m/z* 142, 156, and 170; and alkyl, *m/z* 43, 57, and 71 decreased and the molecular ions of CO_2^+ (*m/z* 44), CH_3COOH^+ (*m/z* 60), and CO^+ (*m/z* 28) increased. However, the changes in the intensities of these molecular ion series were much less than the similar changes observed after oxidation of the parent and the demineralized Beypazarı lignite.[30,31] The aliphatic units which were relatively lower in concentration than the aromatics and generally comprised the substituents of aromatic structures were readily oxidized particularly during the initial stage of oxidation. Aromatic structures were not affected significantly during oxidation.

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