INTERACTION OF COALS WITH OXYGEN AT TEMPERATURES UP TO 600°C

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ABSTRACT

Coking and combustion properties of coals alter on oxidation. The carbonyl or ether groups which are formed during oxidation apparently cause these changes or are transient oxidation intermediates. In the present work we investigated the oxidation of six coals, ranking from lignite to anthracite, in molecular oxygen at temperatures up to 600°C. The original coals and coals extracted with benzene–alcohol or pyridine were examined. A differential scanning calorimetry system (DSC) was utilized to determine the oxidation thermograms of the coals. The residual material obtained after the DSC experiments was further investigated by Fourier transform infrared spectroscopy (FTIR) to determine the structural changes which had occurred. We found that coals contained relatively few structural groups which indicated different oxidation temperatures. The oxidation temperatures of similar structures in different coals increased with increasing rank. Extraction of coals with simple solvents, i.e., benzene–alcohol or pyridine, rendered coals more susceptible to oxidation. The resistance of coals to oxidation increased as the rank of the coal was increased. At oxidation temperatures up to 350°C both carbonyl and ether groups formed in the coal structure. As the temperature of oxidation was raised to 600°C, i.e., low-temperature controlled combustion, the carbonyl groups disappeared and generally the ether groups dominated in the oxidized product.

INTRODUCTION

The combustion of coal is a complex process involving a progressive series of reactions. The mechanism and sequence of reactions occurring at temperatures above 600°C has been intensively examined [1–3]. Several general pathways have also been proposed for the action of oxygen on coal constituents at temperatures below 200°C [4–11]. The temperature range between 200 and 600°C has not been studied in detail in terms of oxidative reactions; this range is considered as slightly high for oxidation studies and low for combustion processes. The present work investigates the course of oxidation reactions in the early stages of combustion of six coals of different rank by molecular oxygen at temperatures up to 600°C.

It is well established that both coking and combustion properties are altered during oxidation [4,5]. Wachowska et al. [4] suggested that during the

initial stages of oxidation a carbon–oxygen complex of the peroxygen type was produced. These peroxy radicals form peroxides and hyperoxides at a later stage of oxidation. However, these compounds are unstable and decompose at relatively low temperatures to produce various molecules containing different oxygen functional groups. Ignasiak et al. [6] observed an increase in the concentration of the reactive oxygen groups (OH, COOH and C=O) during low-temperature oxidation. Wachowska and Angelova [7], Ignasiak et al. [8] and Wachowska et al. [4] attributed the loss of the swelling properties of coals to the formation of ether cross-links, which created a three-dimensional aggregate that offered resistance to swelling on pyrolysis.

In contrast to these results, in an FTIR study, Painter et al. [9,10] demonstrated that carbonyl and carboxyl groups were formed during the early stages of oxidation of coal. Rhoads et al. [11] indicated that the products of oxidation detected by FTIR spectroscopy at 60 and 140°C were identical, although the appearance or loss of functional groups occurred at different rates. Thus, there was no support for the contention that the mechanism of oxidation at 60°C differed from that at 140°C, although it was possible that there was a different distribution of the detectable products, due to the relatively high stability of peroxides at lower temperatures. There was also no evidence for the formation of ether cross-links in the early stages of coal oxidation, although this may have been due to the masking of the bands of the ether groups by the overlapping C–O stretching and OH bending modes of hydroxyl and carboxylic acid groups. Thus the loss of plasticity could be attributed to the loss of aliphatic C–H groups that served as a source of transferrable hydrogen and thermally cleavable bridges. Grint and Perry studied the effect of oxidation on the fluid properties of coking coals by X-ray photoelectron and infrared spectroscopies [12]. It was found that oxidation in air at 100°C destroyed the fluid properties of coal within 48 h, resulting from oxygen incorporation as OH into the coal surface. Fluidity inhibition was therefore caused by a surface cross-linking reaction which occurred during pyrolysis of the oxidized coals [12].

DSC combined with FTIR spectroscopy can be a very powerful tool for the study of the oxidation reaction of coals. Historically, differential thermal analysis (DTA) methods were used extensively in the study of the decomposition of coal in an inert atmosphere. The thermograms obtained were characteristic of the coal studied [13] and various investigators observed similar qualitative results for coals of the same rank [14]. More quantitative results were obtained with the introduction of DSC techniques [15–17]. Since DSC permits the study of the decomposition reactions of coals in reductive or oxidative atmospheres as well as in an inert atmosphere, the effects of reactive and unreactive atmospheric conditions may be compared simultaneously. In the present work a DSC system was used to follow the oxidation of six coals ranking from lignite to anthracite at temperatures up to 600°C. The reaction residues obtained after the DSC experiments were

further investigated with FTIR spectroscopy to determine the structural changes which occurred.

The coals contained few structural groups which oxidized at different temperatures. Carbonyl and ether groups were formed at temperatures below 350°C. At higher temperatures, the carbonyl groups disappeared; ether groups remained, possibly forming cross-links between the structural units of the coal.

EXPERIMENTAL

The coals used in this work were obtained from the Penn State Coal Sample Bank. The analyses of the coals used and their ranks are presented in Table 1. Coals were ground to 0.125 mm size (-120 U.S. standard sieve) in a nitrogen atmosphere. Coal samples were exhaustively extracted with benzene–ethanol (50:50 v/v) or with pyridine in Soxhlet extractors under nitrogen. Extracted coals were washed with ethanol and dried in a nitrogen atmosphere at 100°C and stored under nitrogen.

A Mettler TA 3000 thermal analysis system with a Mettler DSC 30 cell were used for the DSC experiments. Open aluminium pans of 40 μl volume were employed in the DSC cell. An oxygen flow of 50 ml min^{-1} was maintained through the cell. Sample sizes of 5–10 mg were used in all the experiments. The samples were heated at a rate of 10°C min^{-1} from 30 to 600°C. After obtaining the overall oxidation thermograms, the experiments were repeated to collect samples of the solid residues. These experiments were stopped at specific temperatures selected by reference to the initial thermograms. Samples collected in this way were immediately quenched by immersion in liquid nitrogen within a glass vial to prevent further oxidation of the sample. These samples were stored under a nitrogen atmosphere for FTIR analysis. The temperature calibration of the thermal analysis system

TABLE 1

Elemental analyses and ranks of coals used

Seam name	PSOC No.	Rank	Content (%) (dry, mineral matter free basis)						
			C	H	N	S(org)	Cl	O(diff)	Mineral matter (dry)
Noonan	247	Lignite	75.53	4.84	1.51	0.50	0.01	17.61	12.77
Adaville	474	Sub.Bit.B	79.21	4.07	1.24	0.84	0.02	14.64	5.40
Ill. No. 6	1098	Hv.Bit.A	83.01	5.64	1.51	1.91	–	7.93	18.99
L. Kittaning	1139	Mv.Bit.	87.47	5.18	1.64	0.74	0.12	4.86	7.98
L. Freeport	317	Lv.Bit.	90.43	4.44	1.64	0.58	0.08	2.85	17.40
Primrose	867	Anthracite	96.92	1.04	0.78	0.55	0.03	0.68	15.75

was shown to be correct within the specifications of the instrument; the heat flow was calibrated using the heat of fusion of a precise quantity of indium.

Infrared spectra were obtained with a Nicolet X-1 FTIR spectrometer. KBr pellets were prepared by grinding 2.5 mg of coal with 200 mg of KBr in a grinder for 20 min. Pellets, 13 mm in diameter, were pressed in an evacuated die from a ~ 60 mg mixture of KBr and sample under 15 tons pressure for 1 min and dried at 110°C for 72 h in a nitrogen atmosphere to remove water. Spectra were obtained at a resolution of 2 cm^{-1}. The thickness of the pellets was identical for all samples and the reproducibility for identically prepared samples was well within 5%. Therefore, the intensity of the bands due to the same functional groups in consecutive FTIR spectra depended only on the reaction conditions and they can be used for comparison on a qualitative basis.

RESULTS AND DISCUSSION

Oxidation thermograms of original and extracted coals

Figure 1 shows the oxidation thermograms of the original and solvent-extracted coals obtained with a differential scanning calorimeter at tempera-
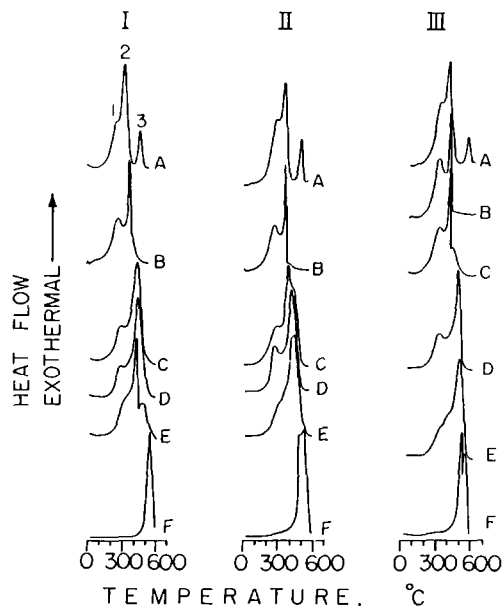

Fig. 1. Oxidation thermograms of I. original coals, II. benzene–alcohol-extracted coals, III. pyridine-extracted coals. (A) Lignite; (B) Sub.Bit.B. coal; (C) Hv.Bit.A. coal; (D) Mv.Bit. coal; (E) Lv.Bit. coal; (F) Anthracite.

TABLE 2

Temperature at which the first oxidation peak appeared in original and extracted coals

PSOC No.	Oxidation temperature (°C)		
	Original coal	Benzene–alcohol-extracted coal	Pyridine-extracted coal
247	310	295	300
474	305	295	295
1098	310	300	295
1139	310	300	300
317	320	320	315
867	–	300	300

tures between 30 and 600°C with a moderate heating rate of 10°C min^{-1} under a dynamic oxygen atmosphere. These thermograms indicate that the oxidation of coals at temperatures up to 600°C is a complex, multistage phenomenon. The most complex oxidation thermograms were seen for the lignite sample. Three peaks dominated the oxidation thermograms. For convenience we identified these peaks as the first, second and third oxidation peaks (Fig. 1). The first oxidation peak was absent only in the thermogram of the anthracite sample. The second oxidation peak was observed for all the coals. The third oxidation peak was present only in the thermograms of the lignite sample. The occurrence of these oxidation peaks suggests the existence of different types of structure which oxidize at various temperatures. Eventually, upon oxidative heating, as our FTIR studies revealed, conversion of some functional groups attached to these structural units took place. The temperatures at which oxidation peaks appeared differed according to the rank of the coal. Table 2 presents the temperatures at which the first peaks occurred in the original and extracted coals. In the original coals the first oxidation peaks appeared at ~ 310°C. It is remarkable that all types of coal except the anthracite started to interact with oxygen at this temperature. This suggests that similar structural units are present in coals of different ranks and that it is the interaction of these units with oxygen which is the reason for the appearance of these oxidation peaks.

The insoluble matrix remaining after the extraction of coal with simple solvents displays altered physical and chemical properties [18,19]. Thus, it was conjectured that the material extracted by simple solvent systems, such as benzene–alcohol or by a more effective solvent such as pyridine, would affect the oxidation processes of a coal. In fact, extraction of the coals decreased the temperature at which the first oxidation peaks occurred by about 10°C compared with that of the original coals. Extraction also caused an unresolved shoulder to appear at 300°C for the anthracite sample. This phenomenon needs further investigation.

TABLE 3

Temperature at which the second (major) peak appeared in original and extracted coals

PSOC No.	Oxidation temperature (°C)		
	Original coal	Benzene–alcohol-extracted coal	Pyridine-extracted coal
247	390	365	370
474	420	410	400
1098	465	420	390
1139	470	475	475
317	450	495	490
867	550	550	510, 545

Table 3 presents the temperatures at which the second oxidation peaks appeared. These peaks were observed in the oxidation thermograms of all of the coals of different ranks examined in the present work. The temperatures at which the second oxidation peaks were observed increased with increasing rank. In lignite this major oxidation peak occurred at 390°C while in anthracite it appeared at 550°C. An immediate conclusion drawn from these results is that as the rank of the coal increased the resistance of the coal to oxidation reactions also increased. It is suggested that the increase of the temperature of the second oxidation peaks in the direction of increasing rank was primarily due to the interaction of different structures existing in coals of different ranks with oxygen. The most probable candidates for this interaction are the polyaromatic structural units of coals. Coal is generally represented as being composed of aromatic and hydroaromatic units with functional groups which form cross-links between the units [20]. The lower rank coals [< 90% C, mmf (mineral matter free)] contain 4–5 rings per unit structure while high rank coals (90–95% C, mmf) contain 6–20 rings per unit structure [13]. In an electrochemical study Peover and White [21] showed that the standard oxidation potentials of RH to RH^+ increase as the number of rings of the polycyclic compounds increases. The driving force for the reaction in terms of electrode potentials for anthracene, benz(a)anthracene, pyrene, chrysene and triphenylene are reported as 0.99, 1.07, 1.12, 1.29 and 1.50 V, respectively. Similar results for a longer series of polycyclic compounds were reported in terms of standard potentials of oxidation of R^- to R by Perichon [22]. In the present work, the driving force for the oxidation reactions is the temperature drop across the solid coal particles. Therefore, the higher temperature required to initiate the reaction is an indication of the need for a higher activation energy and demonstrates a higher resistance to the progress of the reaction. Conclusions reached from studies on pure compounds may lead to erroneous deductions when carried over to naturally occurring "impure" materials like coal where there are numerous factors, some known and some still to be elucidated, which affect

TABLE 4

Temperature at which the third oxidation peak appeared in original and extracted coals

PSOC No.	Oxidation temperature (°C)		
	Original coal	Benzene–alcohol-extracted coal	Pyridine-extracted coal
247	500	515	525
474	–	410	410
1098	–	440	400
1139	–	–	–
317	480	–	–
867	–	–	–

the progress of the reactions. Thus the resistance of pure polyaromatic compounds to oxidation may not be analogous to that of high rank coals. However, our findings on the shift towards higher temperatures at which the second oxidation peak occurred in high rank coals give satisfactory evidence for the tendency of coals towards oxidation reactions.

Benzene–alcohol and pyridine extraction lowered the temperature at which the second oxidation peak occurred in lignite, subbituminous and high volatile bituminous coals. The temperature at which the second oxidation peak occurs in the medium and high volatile bituminous coals and anthracite was not affected by the extractions. For lower rank coals this extraction probably made sites in the coal matrix susceptible to oxidation which had previously been covered with material resistant to oxidation at that temperature. Pyridine extraction of the anthracite also resulted in reduction of the oxidation temperature by 40°C and resolved the main peak into two peaks at 510 and 545°C. These peaks probably indicate the presence of two different structures in the anthracite which oxidize at these temperatures.

Table 4 presents the temperatures at which the third oxidation peak occurred in the thermograms of the original and extracted coals. Out of the original coals, the third peak appeared only for the lignite sample. For the subbituminous and the high volatile bituminous coals utilized in the present work, benzene–alcohol and pyridine extraction allowed the development of the third oxidation peak. The third oxidation peak occurred at higher temperatures in extracted lignites than in the original lignite.

The results of the oxidation experiments performed in the DSC in an atmosphere of molecular oxygen disclosed the presence of two types of structure in coals (three in the lignite and one in the unextracted anthracite) having oxidation temperatures increasing with rank. Extraction of the coals with benzene–alcohol or pyridine decreased the oxidation temperatures of the low rank coals.

TABLE 5

Percentage of organic residual material (dmmf) after oxidation of the original coals

PSOC No.	Oxidation temperature (°C)		
	30–350	30–450	30–600
247	64	15	12
474	65	–	7
1098	63	–	21
1139	74	–	13
317	–	56	8
867	–	–	15

In order to study the composition of the material remaining after each oxidation stage, observed as a peak in the thermograms, oxidation experiments were repeated at the same heating rate. They were halted abruptly when the temperature reached 350 or 450°C and samples were immediately immersed in liquid nitrogen. The residual material was weighed and its FTIR spectrum determined.

Table 5 presents the percentage of the residual organic material remaining after oxidation. Experiments run to 600°C produced 7–21% of residual organic material in coals ranking from lignite to anthracite. There seemed to be no simple correlation between these values and the ranks of the coals. In the oxidation experiments stopped at 350°C, 63–74% of the residual organic matter remained. The residual material increased in the order of rank from lignite to medium volatile bituminous coal. In the oxidation experiments run to 600°C, only the lignite and low volatile bituminous coal showed peaks at ~ 400°C in addition to the other oxidation peaks. Therefore, for these two cases oxidation experiments were repeated under the same conditions and halted at 450°C to obtain the residual material after the third oxidation peak in the thermogram. 15 and 56% material remained in the lignite and low volatile bituminous coal, respectively.

FTIR spectra of oxidized coals

Figure 2 shows the FTIR spectra, plotted as absorbance, of the lignite sample in oxidation experiments which were stopped at 350, 450 and 600°C (Fig. 2.I) and of the subbituminous coal after experiments stopped at 350 and 600°C (Fig. 2.II). The band near 1707 cm^{-1} was due to C=O stretching of carbonyl [23] and/or carboxyl [24] groups. This band, although quite strong in the spectrum of lignite oxidized at 350°C, was not observed in the spectra of the products of high-temperature oxidation. Related to this band were two significant bands at 1114 and 1030 cm^{-1}. These are assigned to C–O–C stretching vibrations; the 1114 cm^{-1} band being due to asymmetric [25,26] and the 1030 cm^{-1} band symmetric vibrations of ether groups [25].
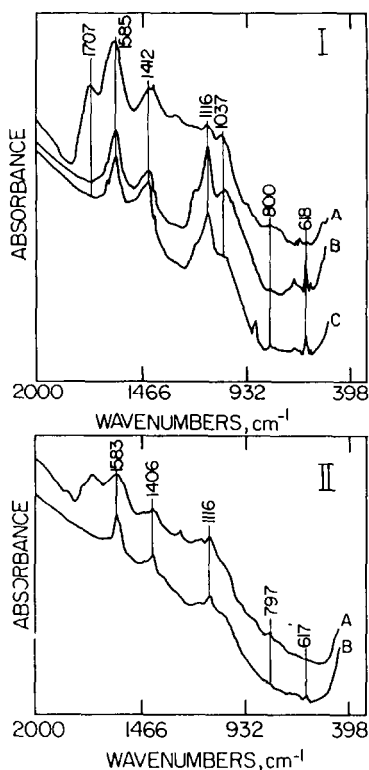
Fig. 2. FTIR spectra of oxidized coals. I. Lignite: (A) 350°C; (B) 450°C; (C) 600°C. II. Sub.Bit.B. coal: (A) 350°C; (B) 600°C.

The 1030 cm^{-1} absorption is claimed to be due to the presence of clay minerals in coals [9,11]. We observed bands due to clay minerals in the 1032–1037 cm^{-1} region in all ranks of coals. In the original coals we identified absorption bands due to ether groups within the 1096–1109 cm^{-1} region in all ranks of coals. In addition to the initial etheric absorption bands a new absorption band near 1116 cm^{-1} (1136 cm^{-1} in medium volatile bituminous coal) developed in the oxidized products (Fig. 3). This band is characteristic of aliphatic ethers. Mashiko [27] and Snyder and Zerbi [28] assigned the main C–O band of alkyl ethers to the 1120 cm^{-1} region with slight variations due to structural and conformational effects. Studies of alkylethers by Perchard [29] established the antisymmetric C–O–C band to be located at 1120 cm^{-1}. We observed this band in the FTIR spectra of all of the oxidized coal products. Apparently, in addition to the ether groups pre-existing in the coal structure, additional ether groups developed in the structure as a result of oxidation reactions. Thus far, evidence for the presence of ether groups has been obtained only with FTIR measurements; hopefully future confirmation will be obtained from other spectroscopic
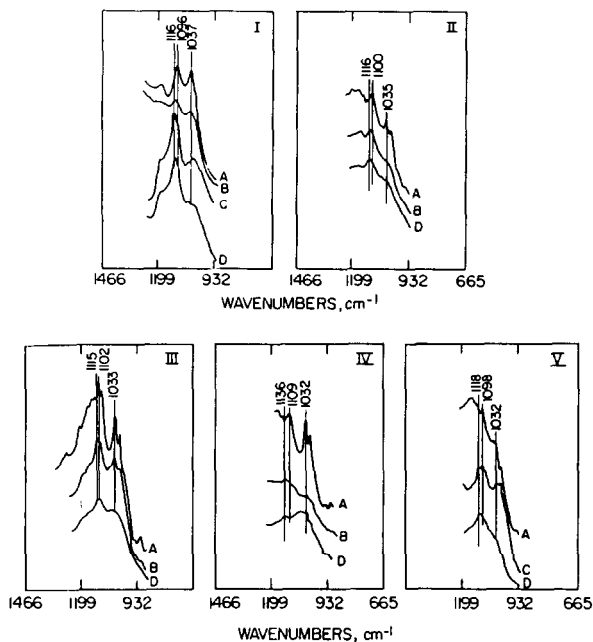
Fig. 3. FTIR spectra of the original and oxidized coals for the expanded 1199–932 cm^{-1} region. I. Lignite; II. Sub.Bit.B. coal; III. Hv.Bit.A. coal; IV. Mv.Bit. coal; V. Lv.Bit. coal; VI. Anthracite. (A) Original; oxidized at (B) 350°C, (C) 450°C, and (D) 600°C.

techniques, viz. solid-state NMR spectroscopy. Our evidence for the development of ether groups within a coal structure during oxidation tends to confirm the school which proposes the existence of ether groups rather than carbonyl groups in oxidized coals [4,7,8].

In the FTIR spectra of oxidized coals we observed that at temperatures higher than 350°C carbonyl groups started to disappear. In Table 6, intensities of the carbonyl and of the newly formed ether absorption bands in the coals oxidized at different temperatures are presented relative to the intensities of clay minerals. The intensity of the etheric band in the lignite spectra increased as the temperature of the oxidation reaction increased. The same phenomenon was observed in the spectra of subbituminous coal. The intensity of the carbonyl absorption decreased to zero in the spectra of both lignite and subbituminous coals as the temperature was raised. Our results are in accord with the observations of Ignasiak et al. [8] and Wachowska et al. [4]. These workers attributed the loss of the swelling properties of coals upon oxidation to the formation of ether cross-links which created a three-dimensional aggregate that offered resistance to swelling on pyrolysis. Our results indicate that although during the early stages of low-temperature oxidation both C=O and C–O–C groups were formed, subsequently during oxidation at higher temperatures the carbonyls disappeared and ether groups dominated in the oxidized coal products.

TABLE 6

Intensities of C=O (1707 cm^{-1}) and C–O–C (1115 cm^{-1}) absorption bands relative to the clay mineral absorption band (1030 cm^{-1}) in the coals oxidized at different temperatures (°C)

PSOC No.	$I(1707\ cm^{-1})/I(1030\ cm^{-1})$ at			$I(1115\ cm^{-1})/I(1030\ cm^{-1})$ at		
	350°C	450°C	600°C	350°C	450°C	600°C
247	1.0	0	0	1.1	1.4	1.6
474	0.8	–	0	1.2	–	1.3
1098	0.4	–	0	1.1	–	1.1
1139	0.9	–	0	1.2	–	1.0
317	–	0.4	0	–	1.1	1.2
867	–	–	0	–	–	0.5

The band near 1600 cm^{-1} is due to aromatic ring stretching vibration and probably also C=O stretching of quinones bridged to acidic hydroxyl. Recent work by Painter et al. [30] supports the assignment of this band to an aromatic stretching mode in coal. The intensity of this band decreased as the temperature was gradually raised to 600°C. This might be due to oxidation of some aromatic material, or, if C=O groups of quinones contributed to the intensity of this band, it would be due to the loss of carbonyl groups by oxidation.

The 900–700 cm^{-1} region in the spectra contained bands assigned to aromatic CH out-of-plane bending vibrations. The bands at 875 and 800 cm^{-1} might be due to trisubstituted aromatic vibrations [29] and the band at 780 cm^{-1} might be due to monosubstituted aromatic vibrations [31]. The presence of weak bands near 1276 and 1182 cm^{-1}, which might be due to *para*-substituted aromatics [31], confirmed the previous assignments.

The absorption within the region 700–600 cm^{-1} was most probably due to N=O stretching vibrations [31] and the intensity of these bands increased as the temperature was raised to 600°C.

Figure 4 shows the FTIR spectra of high volatile (Fig. 4.I) and medium volatile bituminous coals (Fig. 4.II). In these spectra the change in the intensity of C=O and C–O–C bands paralleled those previously described for the lignite and subbituminous coal. The intensity of the ether absorption bands near 1103 cm^{-1} was much stronger in the 350°C oxidation product of the high volatile bituminous coal than the C=O absorption near 1700 cm^{-1}. As the oxidation temperature was increased the carbonyl band disappeared; the intensity of the ether bands remained constant (Table 6). In the case of the medium volatile coal, although the spectrum for the 350°C experiment was not well resolved, the presence of both carbonyl and ether bands was observed. As the temperature of oxidation was raised to 600°C the carbonyl bands were eliminated; there was but a slight decrease in the intensity of the ether absorption.
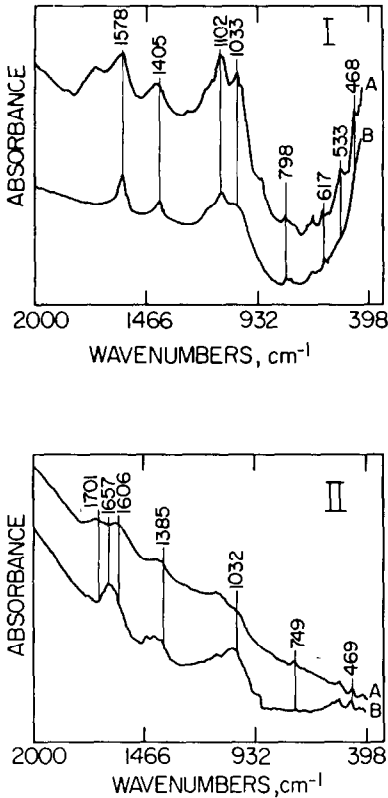
Fig. 4. FTIR spectra of oxidized coals. I. Hv.Bit.A. coal: (A) 350°C, (B) 600°C. II. Mv.Bit. coal: (A) 350°C, (B) 600°C.

Figure 5 shows the FTIR spectra of the oxidized low volatile bituminous coal (Fig. 5.I) and the oxidized anthracite (Fig. 5.II). Carbonyl and ether bands were also observed in the spectra of the oxidized low volatile bituminous coal. Absorption bands due to aromatic ring stretching and to methyl and methylene group vibrations were near 1600 and 1400 cm^{-1}, respectively. As the oxidation temperature was raised to 600°C (Fig. 5.I.B), carbonyl absorption disappeared but the intensity of the bands in the ether group absorption region increased. Since the thermograms of the anthracite sample contained only one peak it was not possible to observe the effect of rising temperature. The spectrum shown in Fig. 5.II is of the product obtained at 600°C. The carbonyl band near 1700 cm^{-1} was absent and there was weak absorption due to ether vibrations. The aromatic ring stretching vibration near 1600 cm^{-1} and methyl and methylene group vibrations near 1400 cm^{-1} were also present in this spectrum.

Table 6 indicates the relationship between coal rank and resistance to oxidation. As previously stated in the DSC section of this report, resistance
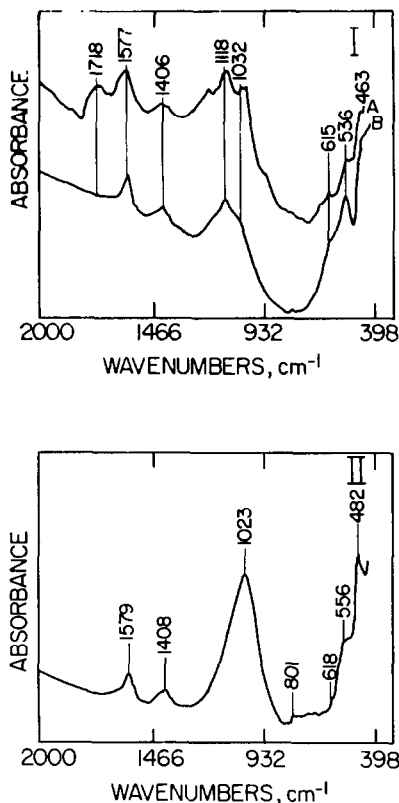
Fig. 5. FTIR spectra of oxidized coals. I. Lv.Bit. coal: (A) 450°C, (B) 600°C. II. Anthracite at 600°C.

to oxidation increases as the rank of the coal increases. In Table 6 it can be seen that the relative intensity of the ether absorption decreased from 1.6 in lignite to 0.5 in anthracite. This may be interpreted in the following manner: in lower rank coals quantitatively more oxidation products are formed, while fewer oxidation products are produced in the higher rank coals due to resistance to the oxidation processes.

As observed in other studies [4–11,24,26] the increase in both carbonyl and ether groups probably is directly related to the loss of coking and combustion properties in coals oxidized at temperatures below 300°C. There remains a controversy as to whether the carbonyl or the ether groups bear the main responsibility for the loss of the swelling properties in coal during oxidation. We observed the presence of both functional groups during oxidation reactions performed up to 350°C. As the temperature of oxidation increased, the ether group content rose while the carbonyl content decreased. At higher temperatures carbonyl groups started to disappear while the ether groups remained the dominant oxidation product; probably in the

form of cross-links between coal structural units. The rank of the coal seemed not to have an effect on this process.

CONCLUSIONS

(1) Coals contain relatively few structures having different oxidation temperatures. The oxidation temperatures of similar structures in different coals increased with rank.

(2) As the rank of coal increased the resistance of coals to oxidation also increased.

(3) Extraction of coals with benzene-alcohol or pyridine rendered the coals more susceptible to oxidation.

(4) It was observed that during oxidation of coals at temperatures below 350°C both carbonyl and ether groups were formed. As the temperature of oxidation was increased to 600°C, the carbonyl groups disappeared and ether groups predominated in the oxidized product.

ACKNOWLEDGEMENTS

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