

FTIR STUDIES OF SARAN CHARs

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Abstract—FTIR spectroscopy has been applied to a study of oxidized Saran chars. A pregrind technique is applied during KBr pellet preparation which, along with inherent advantages of FTIR, produces much higher quality spectra than could previously be obtained. Bands occurring in the spectra of the oxidized carbons at 1720 and 1585 cm^{-1} are assigned to carbonyl vibrations in COOH groups and to aromatic ring stretching modes, enhanced in intensity by oxygen containing functional groups, respectively. The intensity of the 1720 cm^{-1} band is found to vary linearly with % burn-off in the carbon sample. It is suggested that the activity of the 1585 cm^{-1} band which is found to increase in intensity as a function of % burn-off, is caused mainly by an increase in oxygen containing functional groups at advancing levels of burn-off. A mechanism is postulated for the formation of surface anhydrides based on IR results. This involves early formation of anhydride structures followed by conversion of anhydrides to acidic groups via hydrolysis with atmospheric moisture.

1. INTRODUCTION

Coal chars have found extensive commercial application in the past century, particularly in areas such as water purification. However, relatively little is known concerning the overall chemistry of these substances, which in many cases are formed via oxidation of carbonization products of coals. The Saran chars to be used in this particular study are no exception, and it is hoped that through the use of FTIR spectroscopy as part of a more wide-ranging characterization study reported elsewhere [1], more insight may be gained into the chemistry of the gasification process in these materials.

Studies of carbon oxidation extend as far back as 1863 [2] and a variety of chemical [3-6] and spectroscopic [7, 8] methods have been applied to the problem. In principle, IR spectroscopy should be a particularly useful technique in such studies, allowing the observation of changes in individual functional groups as a function of degree of oxidation. Unfortunately, IR studies of carbon present a number of intractable problems. The most severe of these is the presence of an intense background absorption. In part, this background is due to particle scatter. However, in carbonaceous materials the wings of electronic absorption bands extend into the IR region of the electromagnetic spectrum and make an additional contribution to the background.

The particle size distribution and related IR scattering problem has been overcome to some degree by Ishizaki *et al.* [7], who used a multiple-grind technique in forming KBr pellets of dry oxidized carbons. Although the IR spectra obtained were still not of outstanding quality, Ishizaki was able to propose a mechanism for the dry oxidation of carbon which favors formation of carboxylates, lactones, quinones and phenols. An oxidation mechanism including formation of carboxylo-carbonate structures was also proposed by Zawadzki [8] based on IR analysis of oxidized carbon films.

While the above work made some progress in the

study of carbon using IR spectroscopy, it must be kept in mind that only conventional (dispersive) IR techniques were employed. The recent development of computerized Fourier Transform (FTIR) spectroscopy offers several advantages over dispersive instruments, discussed in detail in a number of articles [9-11]. Essentially, the use of an interferometer rather than a system of gratings and slits results in a higher energy throughput to the detector. This, along with the ability of such internally calibrated computer systems to co-add a large number of interferograms, results in markedly superior spectra. Consequently, it should be useful to undertake a study of carbon and its oxidation products using FTIR spectroscopy on the premise that better quality spectra should lead to more information concerning the oxidation process.

2. EXPERIMENTAL

The carbon char used in this study was produced from a Saran copolymer (9:1 molar ratio vinylidene chloride:vinyl chloride). The polymer, supplied by the Dow Chemical Co., was carbonized in Ar at 1173 K. Saran char samples (70 \times 100 mesh) were placed in a tube furnace and heated in N_2 to 1223 K for 4 hr. They were then cooled to 648 K and reacted with air (1 atm) to the desired level of burn off [1]. Besides the original char, the five samples listed in Table 1, ranging from 8.9 to 21.9 wt.% oxygen, were examined.

FTIR spectra were recorded on a Digilab 15B FTS systems. Spectra were generated by co-adding four hundred "scans" (interferograms) at 2 cm^{-1} resolution. Preparation of suitable KBr pellets for IR examination presented a study in itself, due mainly to the difficulty in grinding the carbon samples finely enough to minimize scatter in the spectra. Initially the carbon samples were ground alone in a Perkin Elmer Wig-L-bug. Then, approx. 0.8 mg of any sample of 18.4 wt.% oxygen or higher, or approx. 0.4 mg of any sample below 18.4 wt.% oxygen was ground for 30 sec along with 300 mg potas-

Table 1. Surface areas and oxygen contents of chars gasified to various burn-offs

SAMPLE BURN-OFF %	SURFACE AREA		OXYGEN ON CHAR WT. %	CO/CO ₂ OF DESORPTION PRODUCTS
	H ₂ m ² /g	CO ₂ m ² /g		
16.5	1,145	1,366	8.9	8.7
35.2	1,375	1,067	16.0	7.2
50.4	976	955	18.7	5.6
71.6	462	414	21.9	3.7
89.1	246	249	21.6	3.7

sium bromide. Less sample is used in the cases of less oxidized samples in order to overcome problems with high background absorption and scatter in the spectra of these chars. A pellet was then pressed under vacuum for approx. 10 min at 68 MPa. Typical spectra resulting from KBr pellets of samples of 16.5 and 89.1% burn-off (BO) are shown at the bottom of Figs. 1 and 2, respectively. It should be noted here that all spectra shown in

this study have been scale expanded to more clearly display details, thus making the ordinate scale arbitrary. Initial examination of the spectra reveals a low signal to noise ratio, along with an intense scattering peak around 850 cm⁻¹ in the 16.5% BO sample. This band also appears in the spectrum of the 89.1% BO sample, though to a lesser degree. Also appearing in the 89.1% BO spectrum are bands near 1720, 1585 and 1250 cm⁻¹. Peaks

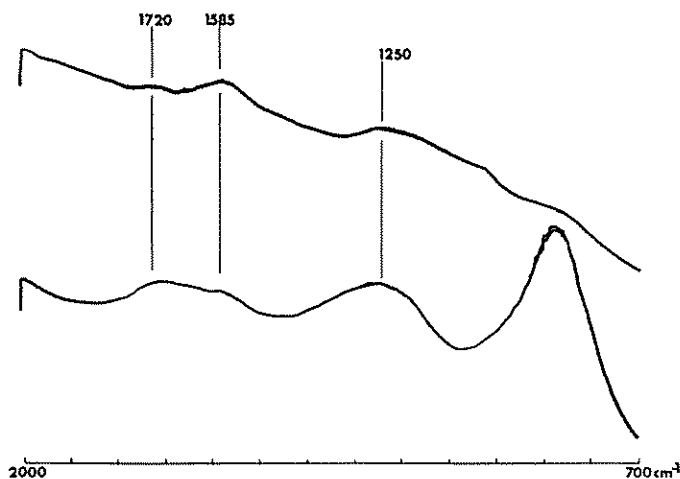


Fig. 1. Bottom, FTIR spectrum from 2000 to 700 cm⁻¹ of Saran char after 16.5% burn off, no pregrind in KBr pellet preparation; top, FTIR spectrum of same sample using pregrind method in KBr pellet preparation.

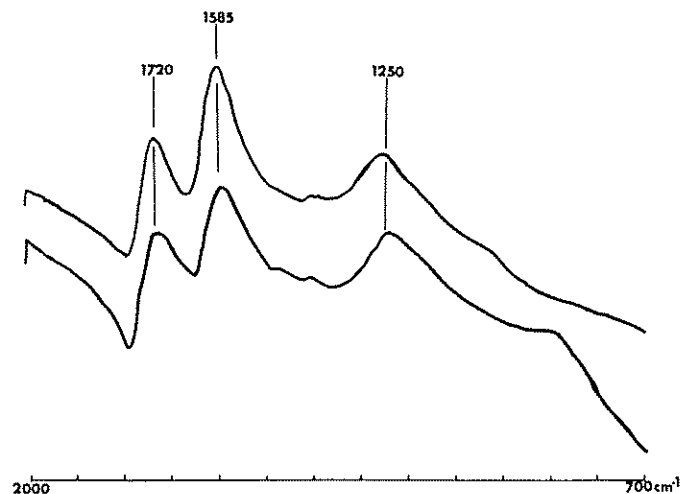


Fig. 2. Bottom, FTIR spectrum from 2000 to 700 cm⁻¹ of Saran char after 89.1% burn off, no pregrind in KBr pellet preparation; top, FTIR spectrum of same sample using pregrind method in KBr pellet preparation.

also appear in very much the same positions in the 16.5% BO spectrum, although they are not nearly as intense as in the more highly oxidized sample.

The presence of an intense background together with an individual scattering peak suggests that the samples have not been ground sufficiently. We have examined this problem in terms of the analysis of mineral matter in coal[12-14] and one solution, originally proposed by Elliott *et al.*[†] involves a two-stage method of grinding mineral samples. Initially, a given amount of sample is preground along with 25 mg of KBr for 30 sec. Then, 275 mg of KBr is added, and the mixture is ground a further 30 sec before pressing as described earlier. It should be noted that grinding times refer to our individual equipment. We have found that required grinding times vary from grinder to grinder.

Spectra resulting from the application of this method to the 16.5 and 89.1% BO carbon samples are shown at the top of Figs. 1 and 2, respectively. It is immediately apparent that there is a considerable improvement in the signal to noise ratio and the peak near 850 cm^{-1} has been eliminated in the spectra of both samples, thus demonstrating that this peak is due to scatter that is a direct result of insufficient initial grinding.

3. RESULTS AND DISCUSSION

FTIR spectra of the original Saran char, along with samples after 16.5, 50.4 and 89.1% burn-off are compared in Fig. 3. As oxidation increases, the development of a much higher signal to noise ratio (due to increased grindability) along with three bands at 1720, 1585 and 1250 cm^{-1} is apparent. The increase in intensity of these three bands as a function of oxidation, especially those at 1720 and 1250 cm^{-1} , is quite similar to the behavior of the spectra of oxidized coal samples[15]. The 1720 cm^{-1} band is characteristic of a carbonyl group and we will present evidence demonstrating that this band is predominantly due to carboxylic acid groups. It will follow

from this argument that the 1250 cm^{-1} band is partly associated with C-O stretching and OH bending modes in this functional group.

The assignment of the 1585 cm^{-1} band is more interesting, partly due to a correspondence with the controversy concerning the assignment of the 1600 cm^{-1} band in the spectra of coals. There are essentially three possible assignments, first, to an aromatic ring stretching mode. A strong Raman line appears in the spectrum of graphite near 1580 cm^{-1} , but this mode is IR inactive in well ordered structures. If we are to make such an assignment the activity and intensity of this band has to be explained.

The second assignment, and one most frequently invoked in IR spectroscopic studies of carbonaceous materials, is to a highly conjugated hydrogen-bonded carbonyl, analogous to the structure of acetyl acetone[16, 17]. Finally, if -COOH groups are formed during oxidation they can exchange to give COO⁻ salts in the presence of suitable minerals (e.g. KBr). The COO⁻ group absorbs near 1580 cm^{-1} .

The questions concerning the band assignments were resolved by FTIR examination of samples after two types of treatment, acetylation to determine (reactive) hydroxyl groups, and successive base-acid washing, which allows us to discriminate between -COOH groups and other types of carbonyl functional groups. The O-H stretching mode of hydroxyl functional groups appears near 3400 cm^{-1} , but even in dried KBr pellets there is residual absorption in this region due to water adsorbed into the KBr during grinding[18]. In the spectra of the chars there was only weak absorption in this region, indicating little or no hydroxyl groups are present. Acetylation, using the method of Blom *et al.*[19], is a well known and widely applied method of measuring hydroxyl-functional groups, especially in coal, through the formation of esters. Acetylation of coal samples produces an intense band in the spectrum near 1770 cm^{-1} . Acetylation of the Saran 50.4% BO sample produced no evidence of such a band, ruling out the presence of any appreciable concentration of hydroxyl

[†]Private communication.

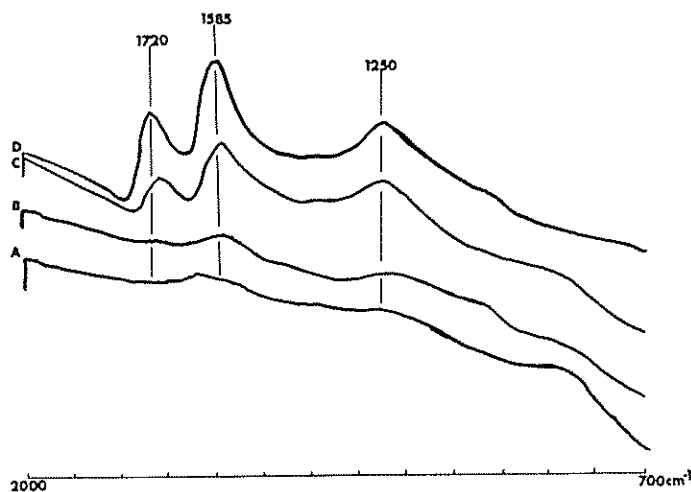
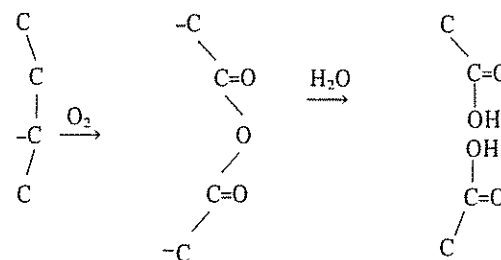


Fig. 3. (a) FTIR spectrum of "as received" Saran char. (b) FTIR spectrum of Saran char after 16.5% burn off. (c) FTIR spectrum of Saran char after 50.4% burn off. (d) FTIR spectrum of Saran char after 89.1% burn off.

groups in the oxidized samples. As a result the 1585 cm^{-1} band cannot be assigned to a hydrogen bonded conjugated carbonyl. Upon acetylation of the OH groups involved we should anticipate a shift in the frequency of the 1580 cm^{-1} band to higher frequency. As we detected no hydroxyl groups we naturally did not observe a shift in the frequency of this band upon acetylation.

The assignment of the 1720 cm^{-1} band follows from an examination of the affect of alkali washing. As mentioned before, the 1720 cm^{-1} band of carboxylic acids shifts to around 1580 cm^{-1} when they are in the salt form, COO^- . Thus, replacement of the hydrogen with an exchangeable cation, such as Na^+ , should result in the disappearance of the 1720 cm^{-1} band in the spectrum. The FTIR spectrum of the 89.1% BO Saran sample after sitting about two weeks in a 0.1 N NaOH solution is compared to the spectrum of the original sample in Fig. 4. It can be seen that the 1720 cm^{-1} band has completely disappeared, leaving a weak band near 1690 cm^{-1} , while a band at approx. 1570 cm^{-1} is now superimposed upon the 1585 cm^{-1} vibration. Based on this evidence we can only conclude that the 1720 cm^{-1} band is due to COOH groups. We will discuss the origin of the 1690 cm^{-1} band below. However, it is important to note that there is no evidence for the formation of lactones, which absorb in the region $1750\text{--}1790\text{ cm}^{-1}$ [16, 17]. Barton and Harrison [20] suggested that such groups are formed on carbon surfaces. In addition, the --COOH groups have to be present in the form of hydrogen bonded pairs, since lone --COOH groups have bands at higher frequencies (near 1750 cm^{-1}). This latter observation suggests a mechanism of formation of such groups, since hydrogen is not present during the oxidation. We propose that anhydrides are initially formed and these groups are hydrolyzed by atmospheric water to form carboxylic acids.



There is a direct relationship between the formation of the acid groups and the degree of oxidation as shown from a plot of the intensity of the 1720 cm^{-1} band (adjusted for amount of sample present in the KBr pellet) vs the percent burn off, as shown in Fig. 5. The plot obtained is linear and passes through the origin.

We can now address the question of the origin of the 1585 cm^{-1} band and whether it is caused by COO^- structures of C-C aromatic ring stretching vibrations, having eliminated an assignment to a hydrogen bonded conjugated carbonyl. If COOH structures can be exchanged to $\text{COO}^- \text{Na}^+$ with accompanying band shifts in the IR spectrum, then the opposite should be true of $\text{COO}^- \text{X}^+$ structures when exchanged with H^+ ions. Thus, any structures of this type in the carbon samples should, when treated with an acid, become COOH type structures and be shifted to around 1720 cm^{-1} in the IR spectrum together with corresponding decrease in the intensity of the 1585 cm^{-1} band. To that end, a portion of the NaOH treated 89.1% BO Saran sample was soaked for 24 hr in 1N HCl. The spectrum is also compared to the original 89.1% BO sample and the NaOH soaked sample in Fig. 4. It can be seen that the 1570 cm^{-1} band has shifted back to 1720 cm^{-1} in the HCl treated sample but the 1585 cm^{-1} band remains unaltered. The fact that this band did not shift upon acid treatment suggests that

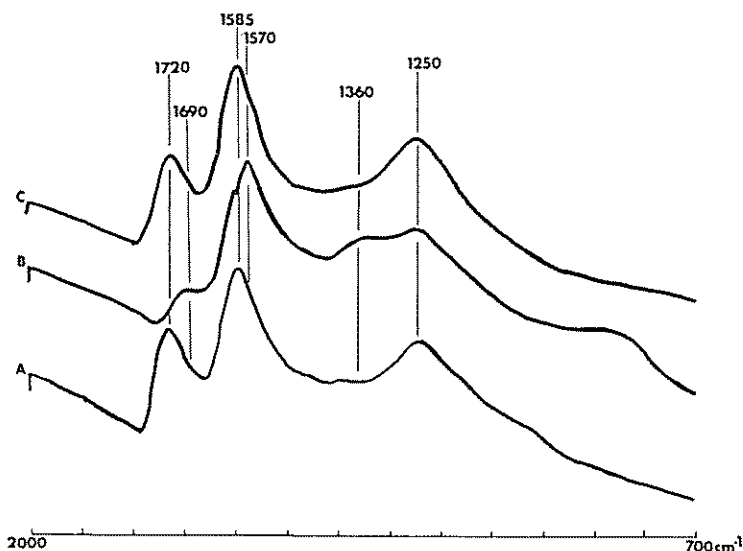


Fig. 4. (a) FTIR spectrum of Saran char, 89.1% BO. (b) Spectrum of same sample after sitting 2 weeks in a 0.1N NaOH solution. (c) Spectrum of same sample after NaOH soaking followed by soaking 24 hr in 1N HCl solution.

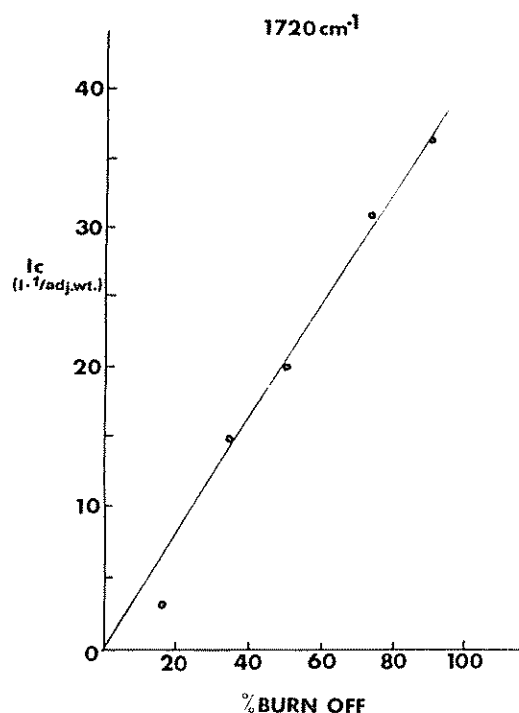


Fig. 5. Plot of intensity of the 1720 cm^{-1} band (adjusted for amount of sample present in the KBr pellet) vs % burn-off in the Saran char.

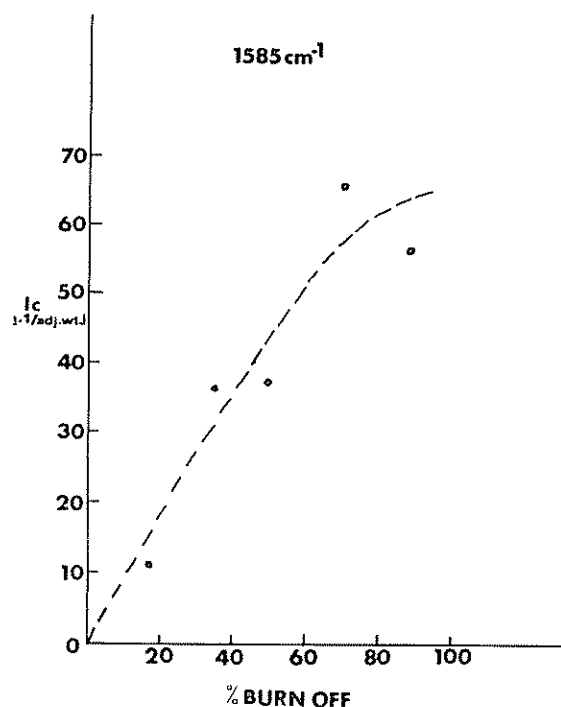


Fig. 6. Plot of intensity of the 1585 cm^{-1} band (adjusted for amount of sample present in the KBr pellet) vs % burn-off in the Saran char.

it can be assigned to a C-C ring stretching mode. Nevertheless, the intensity of this band is affected by the presence of oxygen containing functional groups, presumably at the edge of the graphite-like structures. Evidence for such intensity enhancement may be seen in Fig. 6, which plots the absolute intensity of the 1585 cm^{-1} band vs % burn-off. The general rise in intensity up to about 70% burn-off (21.9 wt.% oxygen) indicates increasing contribution by functional groups which are products of the oxidation process. However, the intensity of this band apparently levels off. This is the type of behavior we would anticipate if this mode were an aromatic ring stretching mode. In the original carbon this mode is inactive or weak in the IR, but has a strong Raman line at this frequency. The introduction of oxygen containing functional groups, which usually have a significant dipole moment, not only could allow a previously inactive mode to become active due to a breakdown in symmetry selection rules, but also lead to significant intensity enhancement due to a larger change in dipole moment during the ring stretching molecular vibration. Naturally, we would expect a levelling off in this effect after a certain number of groups had been introduced into the carbon. The same general trend, i.e. gradual increase followed by a levelling off may be observed in wt.% oxygen on char (Table I). This suggests that intensity of the 1585 cm^{-1} may be directly related to the amount of oxygen containing functional groups present even though it can be assigned to a ring stretching mode.

So far, we have been able to conclude that there is a negligible concentration of hydroxyl groups present in

the oxidized chars, but an appreciable concentration of carboxylic acid groups. However, thermal desorption experiments [11] gave a product ratio of CO to CO₂ of at least 4:1, depending upon the char (Table I). Simple thermal desorption of -COOH groups would be expected to give H₂O and equal proportions of CO and CO₂. Consequently, there must be other oxygen containing functional groups present. There is considerable evidence for such groups in the spectrum. The band near 1690 cm^{-1} in the spectrum of the char exchanged with NaOH is probably not a -COOH type structure, which absorbs near 1720 cm^{-1} . It is more likely a ketone [16] which would be expected to give CO upon thermal desorption. However, the intensity of this band is weak and it would take an enormous difference in the extinction coefficients of ketones relative to carboxylic acids to account for the CO formed upon desorption. This seems highly unlikely to us based on our previous experience of IR studies of materials such as coals [15, 18] and reviews of group frequencies and intensities [16]. Fortunately, we do not have to search too far for a more likely origin for the preponderance of CO groups evolved during thermal desorption. It was mentioned above that the 1250 cm^{-1} band is due to C-O groups. In carboxylic acids the single bond C-O stretching vibration is coupled to the O-H bending mode to give an absorption near 1250 cm^{-1} . However, upon ion exchange to form COO⁻ groups this band should disappear to give asymmetric and symmetric $\begin{array}{c} \text{C}-\text{O} \\ | \\ \text{O} \end{array}$ stretching modes near 1570 and 1360 cm^{-1} , respectively, as observed. However, Fig. 4 demonstrates that upon exchange with NaOH the broad band near

1250 cm^{-1} is somewhat reduced in intensity but still prominent. Since this region of the spectrum is characteristic of C-O single bonds and there is no evidence of the presence of significant amounts of hydroxyl groups, we conclude that in the spectrum of the exchanged material this band is principally due to ether type structures. Upon thermal desorption we would anticipate that these groups would give CO. Furthermore, ether groups absorb weakly in the IR spectrum relative to carbonyls, so the relative proportion of gaseous products is not unreasonable in terms of this interpretation.

4. CONCLUSIONS AND SUMMARY

FTIR spectroscopy has proved to be a useful tool in studying a series of Saran carbons oxidized to various levels. In order to obtain quality spectra, problems with particle scatter had to be overcome through the use of modified grinding techniques. Once suitable spectra were obtained, band assignments could be made. It was found that carboxylic acid structures were present in the oxidized products, and these structures increased in numbers linearly with degree of oxidation (% burn-off). The characteristic 1580 cm^{-1} band observed in a number of studies of carbonaceous materials has been assigned to an aromatic ring stretching mode that is intensity enhanced by the presence of oxygen containing functional groups formed during the burn-off process. A mechanism was postulated involving the formation of surface anhydrides, which are converted to acidic groups by hydrolysis with atmospheric moisture. Finally, a band due to ethers and also a weak band due to ketones are identified.

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