

COMPARISON OF FOURIER TRANSFORM INFRARED-PHOTOACOUSTIC SPECTROSCOPY (FTIR-PAS) AND CONVENTIONAL METHODS FOR ANALYSIS OF COAL OXIDATION

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ABSTRACT

Fourier Transform Infrared-Photoacoustic Spectroscopy (FTIR-PAS) has been used to study variations in coal oxidation produced under laboratory-controlled conditions (temperatures of 140 and 150°C and exposure times up to 72 hours). Prominent oxidation-induced spectral changes were monitored by the peak heights of carbonyl (1690 cm^{-1}) and carboxylate (1575 cm^{-1}) bands. Changes in these peak heights have been plotted against conventional test data which are sensitive to the oxidation level of coal. Good linearity was observed for comparisons with the U.S. Steel oxidation test by alkali extraction and with measurements of the heating value. Advantages demonstrated for the FTIR-PAS method of monitoring coal oxidation include speed of analysis (several minutes), non-destructive character, minimal sample preparation (coarse powder), insensitivity to sample mass, and flat spectral baselines without hydroxyl band interference common to KBr-pellet IR transmission spectroscopy.

INTRODUCTION

It is well known that exposure of fresh coal to air will deteriorate its coking propensity as well as heating value, floatability, and other properties. The oxidation of coal begins with adsorption (physical adsorption and chemisorption) of oxygen on accessible aromatic and aliphatic surface sites to form acidic functional groups, in particular, $-\text{COOH}$, $=\text{CO}$, and phenolic $-\text{OH}$ (1). If moisture is generated from chemically combined hydrogen in coal, some chemisorbed oxygen will produce peroxide or hydroperoxide complexes. The breaking down of these hydroperoxide groups at higher oxidation temperature (140°C) is responsible for the loss of CH groups (2). At later stages of oxidation, the acids produced combine with phenol to generate esters or anhydrides (2,3,4). Conventional oxidation testing methods (including free swelling, Gieseler plasticity, U. S. Steel oxidation transmission, and heating values) not only need a considerable time to complete a single measurement but also offer no information about the detailed chemical changes of coal. For instance, the U. S. Steel oxidation transmission test can only indicate whether or not coal is good for metallurgical use (5) while heating values provide only caloric data.

Methods based on diffuse reflectance (4,7,8), transmission (2,3,6), and photoacoustic (7,8) Fourier Transform Infrared (FTIR) spectroscopy have been used extensively in recent years in studies of oxidation associated coal beneficiation products. These methods can help reveal the detailed mechanisms of coal oxidation. Painter *et al.* (2,3,6) applied the transmission FTIR method to study oxidation mechanisms. They attributed the formation of ester links as responsible for the loss of free swelling characteristics and suggested that loss of aliphatic CH groups during oxidation is responsible for reduction of Gieseler plasticity. The groups of Hamza (7) and Lynch (8) have deduced that coal oxidation is initiated at aliphatic carbon adjacent to aromatic rings and that the initial generation of hydroperoxides and cyclic peroxides precedes the formation of carbonyl functionality which can reduce the hydrophobicity of coal surfaces, resulting in decreased floatability. On the contrary, Spitzer (9) believes that the decrease of floatability of coal after oxidation is associated with decreasing alkyl content and not with increasing oxygen content.

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Although there are controversies in explaining the oxidation results characterized by FTIR methods, the information provided enables insights into detailed reaction mechanisms. However, there are several inherent disadvantages in diffuse reflectance and transmission methods including difficulty in obtaining a suitable reference spectrum in diffuse reflectance measurements, variable moisture content in KBr-pellet transmission spectroscopy, tedious sample preparation, severe background scattering, difficulty in selection of correct scaling factors for spectral subtraction, and uncertainty of pressure effects in making KBr pellets. The FTIR-PAS method is able to provide the same quality of results as the other FTIR methods in analyzing coal beneficiation products but with fewer problems. In this paper, capabilities of the FTIR-PAS method for characterizing coal oxidation are demonstrated with comparisons of FTIR-PAS results to those of conventional coal analysis data.

EXPERIMENTAL

FTIR-PAS spectra were measured with an IBM Instruments IR-98 FTIR system (8 cm⁻¹ resolution, 128 scans) and a photoacoustic cell designed and constructed at the Ames Laboratory. The cell sample cup volume was less than 0.1 cm³ and contained helium gas during measurements to enhance the signal amplitude. The photoacoustic interferogram signal was detected in the frequency range 90 to 900 Hz by a model 4176 pre-polarized Bruel and Kjaer microphone with 50 mV/Pa sensitivity. Signals were amplified by a thousand gain preamplifier before being fed into the FTIR instrument for processing. After the interferogram was Fourier transformed, spectra were subtracted using the IR-98 software and difference spectra plotted, usually without spectral smoothing.

The Illinois No. 6 coal used in this oxidation study was obtained from the Ames Laboratory Coal Library (11). It came from the Captain Mine in Randolph County, IL. The description of the coal is given in Table 1.

Table 1. Analysis of Illinois No. 6 Coal Performed at Ames Laboratory

Proximate Analysis, (%)	Moisture	Volatile Matter	Ash	Sulfur Forms (dry)				Heating Value (Btu/lb) Dry
				Total Sulfur	Pyritic Sulfur	Sulfate Sulfur	Organic Sulfur (by diff.)	
	8.14	33.65	13.12	3.45	2.03	0.14	1.28	12,189
Ultimate Analysis, (%)		C	H	S(total)	N	O(by diff.)		
		62.17	4.13	3.45	1.60	15.53		

Controlled oxidation of the Illinois coal was performed at Ames Laboratory by placing samples in an oven at either 140 or 150°C for varying times up to 72 hours with an air flow rate of 42 ml per second. The particle size ranged from 44 to 125 micrometers (120 to 325 mesh). FTIR-PAS spectra, heating value measurements, and U. S. Steel oxidation transmission tests on the Illinois #6 coal were also completed in this Laboratory. The amount of sample needed for acquiring FTIR-PAS spectra was roughly 15 mg. No sample preparation after sieving was required for this measurement. Raw or oxidized coal was poured directly into the photoacoustic cell's sample holder and the spectra were measured. Since the photoacoustic signal is rather insensitive to the amount of sample used for measurements, volume sampling is adequate.

and it is unnecessary either to weigh out samples for analysis or to adjust the spectrum weighting factor during spectral subtraction. The FTIR-PAS spectral acquisition time is typically three minutes (128 scans) per sample. The degree of oxidation as characterized by this method is determined by the changes in peak heights of carbonyl (1690 cm^{-1}) and ionized carboxyl (1575 cm^{-1}) bands which can be quantitatively measured by spectral subtraction.

Measurements for the U. S. Steel oxidation transmission test (5) were performed by: adding 1g of coal sample to 100 ml of 1 N NaOH; adding one drop of Tergitol to the caustic-coal slurry; boiling the caustic-coal slurry for 3 minutes; cooling and filtering the slurry through a 45 micrometer Whatman filter paper; diluting the filtrate with distilled water to a total volume of 80 ml; and measuring the percent transmission of the solution with a spectrophotometer set at 520 nm. The heating values were determined using the standard ASTM method (D2015).

RESULTS AND DISCUSSION

Spectra 1a and 1b of Figure 1 are for raw Illinois #6 coal acquired by conventional transmission FTIR and FTIR-PAS methods, respectively. Besides the problems of background scattering and uncertainty of hydroxyl bonds (1600 and 3400 cm^{-1}) in spectrum 1a, these two methods give qualitatively similar results. Spectrum 1c was acquired by the FTIR-PAS method on the same Illinois #6 coal after oxidation in air at 140°C for 24 hours. Spectrum 1d shows the spectral differences between the oxidized and the raw coal after spectral subtraction. No weighting factor adjustment was used or was necessary because scaling of the FTIR-PAS spectrum is insensitive to sample mass.

Besides the increases of carbonyl (1690 cm^{-1}) and carboxylate (1575 cm^{-1}) bands as well as the decrease of aliphatic CH groups ($\sim 2900\text{ cm}^{-1}$), there also appear to be slight losses in aromatic CH ($\sim 3050\text{ cm}^{-1}$) and in hydroxyl OH ($\sim 3550\text{ cm}^{-1}$) groups. The observations at 1690 , 1575 , and 2900 cm^{-1} are consistent with Painter's results (3,6), while all of the features observed are in agreement with Smyrl's results (4). Apparently Painter's failure to see the features near 3050 and 3550 cm^{-1} is due to the moisture interference and subtraction factor selection problems associated with transmission. Smyrl applied an in-situ diffuse reflectance method to characterize coal oxidation which, like the present work, is free from worries of moisture interference and subtraction factor selection.

Although there is controversy about which portions of coal are consumed during oxidation, the carbonyl, carboxylate and ester groups produced by the reaction have never been doubted. Therefore, these functional groups were selected to correlate with the results from conventional characterization methods. For instance, Figure 2 shows the increase of carbonyl and ionized carboxyl peak heights measured by the FTIR-PAS method and the variations of percent transmission measured by the U. S. Steel oxidation transmission test versus time of oxidation for Illinois #6 coal samples at 140°C . Similar saturation trends for FTIR-PAS and U. S. Steel tests are evident for oxidation conducted at both 140 and 150°C , resulting in the asymptotic behavior of carbonyl and carboxylate group changes. Figure 3 shows that the FTIR-PAS and U. S. Steel test data are linearly correlated. Data for coal oxidized at 140°C and 150°C are plotted in this figure to show that linearity is maintained for two different oxidation conditions. The linear correlation was found for both temperatures to better than 6% transmission units.

Two hypotheses regarding coal oxidation behavior are suggested by the linear correlation observed. First, the loss of coking properties of coal during oxidation is due to the formation of oxygen functional groups. Since the U. S. Steel test is a measurement of coking properties, the linear relationship of these two methods

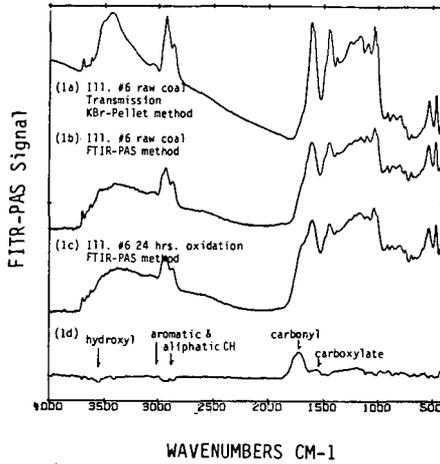


Figure 1. Comparison of Illinois #6 coal spectra, measured by transmission and photoacoustic methods and an example of a spectral subtraction result using photoacoustic spectra to show oxidation induced spectra changes.

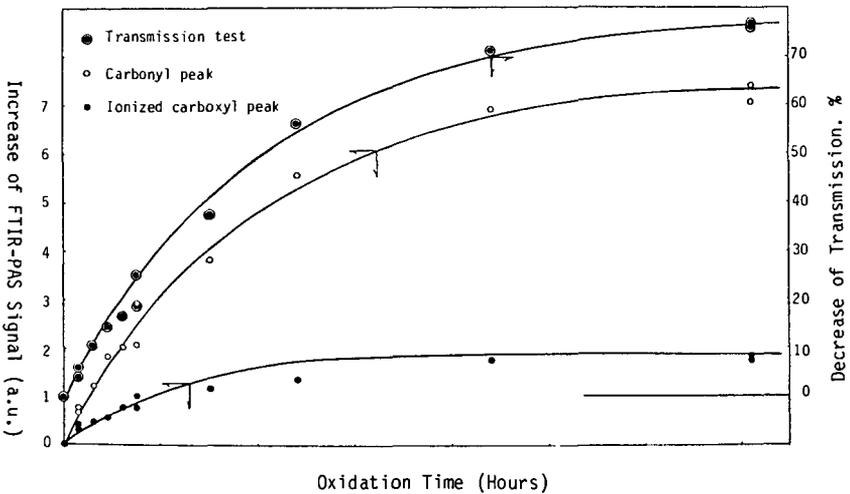


Figure 2. Progress of oxidation measured by the FTIR-PAS method and U. S. Steel alkali extraction transmission test (a.u.=arbitrary units).

suggests that both the degradation of coal in coking ability and the U. S. Steel transmission value are due to the formation of oxygen functional groups. Second, the coal particles in the size range explored appear to be oxidizing uniformly throughout their volume rather than to a decreasing degree with depth as would be the case for a diffusion limited process. The hypothesis is based on the fact that for this size coal sample, particles are opaque and the FTIR-PAS measurement senses a surface layer whereas the U. S. Steel test is a bulk determination. Since the data of the two methods have a linear correlation, the surface and bulk regions appear to be uniformly oxidized. To test this hypothesis further, the coal samples oxidized at 140°C were ground to the micrometer size range to permit the FTIR-PAS measurement of the bulk material oxidation changes since the particles are no longer opaque. To prevent additional coal oxidation during the grinding process, the grinder capsule which contained coal was cooled by liquid nitrogen. The results obtained from the FTIR-PAS spectra of ground, oxidized coal are plotted in Figure 4 against the results before grinding. The linear relation found in this plot indicates the same time evolution for oxidation of surface and bulk regions of the samples. Hence, the oxidation processes do not appear to be either separate surface-bulk processes or diffusion-limited processes but rather processes occurring uniformly throughout the bulk for the experimental conditions used.

There are two heating value estimating formulas available for coal, the Dulong and the Dulong-Berthelot formulas (Ref. 1, p. 35). In these two formulas the heating value decreases linearly with increasing oxygen content of coal. This implies that the decrease of heating value during oxidation can be correlated linearly with the amount of oxygen functional groups produced. Figure 5 is a plot of the decrease in the ASTM heating value versus increase in coal oxidation as monitored by changes in the sum of peak amplitudes associated with carbonyl and carboxylate bands of Illinois #6 coal. A common linear relation was found between these two methods for both 140 and 150°C oxidation conditions. This linear relationship between heating value degradation and FTIR-PAS data may enable optimization of coal beneficiation processes when coal oxidation occurs during the process. Since the beneficiation process includes demineralization, the decrease of mineral contents of coal can also be monitored by the same FTIR-PAS spectrum. Hence, the trade-off between mineral removal and loss of heating value can be evaluated based on one sample and a single data acquisition effort. Furthermore, the correlation between the U. S. Steel test and FTIR-PAS data can also be used to determine whether or not demineralized coal still has coking properties for metallurgical use.

Samples of coal oxidized by natural weathering, which were provided by the Koppers Company, were also studied and the FTIR-PAS spectra were measured. Linear correlations were found between our FTIR-PAS results and results obtained previously (10) for the U. S. Steel oxidation transmission, free swelling index, and Gieseler plasticity tests. These findings, which will be reported fully elsewhere, suggest that FTIR-PAS data can be correlated and substituted for data from these conventional coal tests which demand more time.

In the above discussions, only spectral changes of oxygen-containing functional groups generated during oxidation of coal were used to correlate with conventional testing method results. If the other features of FTIR-PAS subtraction spectrum 1d (as shown in Figure 1) are also involved in the data manipulation, more relations may be found that will provide a better understanding of the oxidation process.

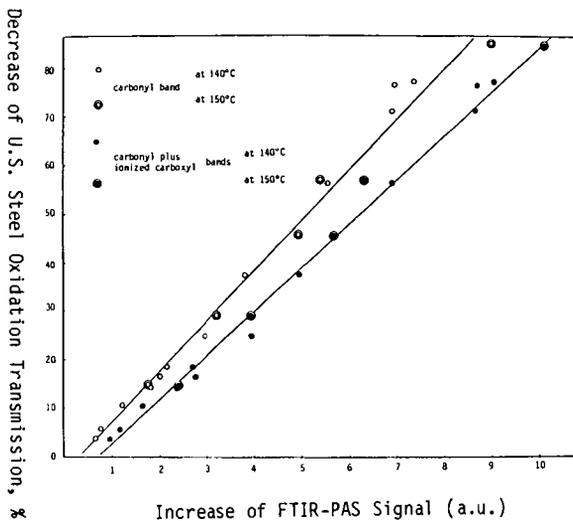


Figure 3. Comparison of FTIR-PAS signal to U. S. Steel oxidation transmission tests at the oxidation temperatures of 140 and 150°C (a.u.=arbitrary units).

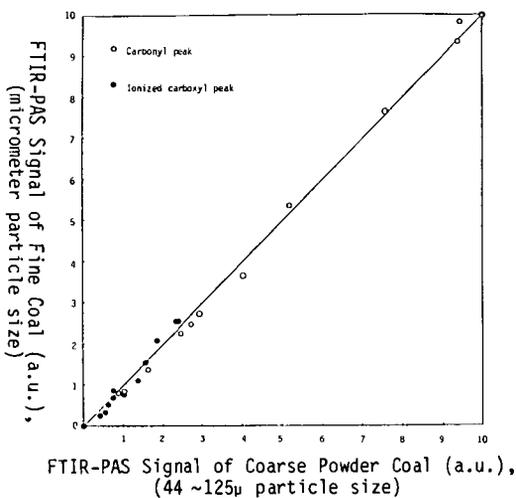


Figure 4. Plot of the photoacoustic signal for coarse opaque versus signal for fine non-opaque coal powders showing that oxidation has occurred uniformly through the coarse powder volume (a.u.=arbitrary units).

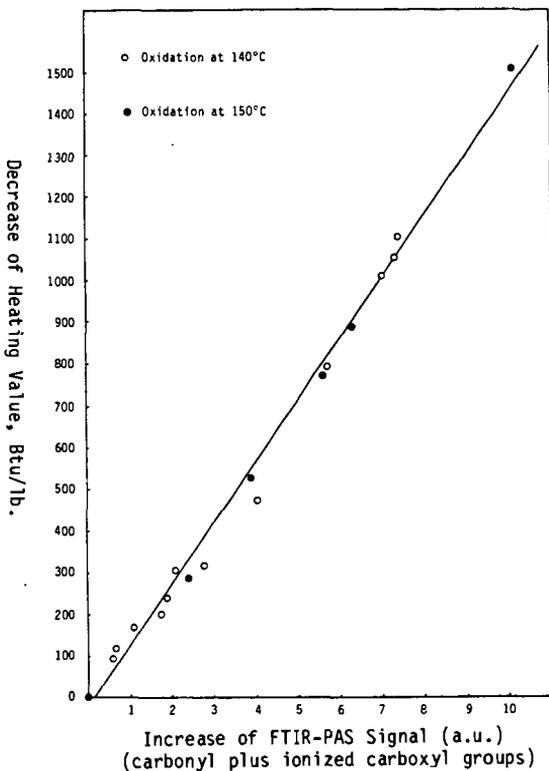


Figure 5. Comparison of FTIR-PAS signal to heating value measurement at the oxidation temperatures of 140 and 150°C (a.u.=arbitrary units).

CONCLUSIONS

FTIR-PAS spectral changes induced by coal oxidation have been found to correlate linearly with results of conventional coal analysis methods that are sensitive to coal oxidation. Advantages demonstrated for the FTIR-PAS method of monitoring coal oxidation include speed of analysis (several minutes), non-destructive character, minimal sample preparation (coarse powder), insensitivity to sample mass, and flat spectral baselines without hydroxyl band interference common to KBr-pellet IR transmission spectroscopy.

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