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ADVANCED SPECTROSCOPIC ANALYSIS OF COAL SURFACES DURING BENEFICIATION

FOSSIL ENERGY QUARTERLY REPORT
October 1, 1988 - December 31, 1988

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ABSTRACT

Development work advanced on two new FTIR spectroscopic approaches for measuring coal surface oxidation and on-line infrared spectra of coal. The former FTIR/UV approach used UV induced oxidation to gauge the level of carbonyl forming species present in coal. The latter approach is called Transient Infrared Emission Spectroscopy (TIRES) and uses pulsed surface heating of coal to obtain an emission spectrum which is not distorted by excessive self absorption.

In the FTIR/UV work oven-oxidized coals were analyzed after 1, 3, and 6 days of exposure to oxygen at 100°C. Spectra of the oven and UV induced carbonyl formation overlapped but had somewhat different band shapes indicative of some differences in the two oxidation processes. These differences, however, still allowed the FTIR/UV method to monitor coal surface oxidation and to do so with higher surface specificity and without the use of a difficult to obtain "fresh coal" standard.

A TIRES apparatus was constructed using an argon ion laser, rotating sample stage, and FTIR spectrometer. A spectrum was measured of Illinois #6 coal moving at a velocity of 60 ft/min. which compared favorably with photoacoustic spectrum of the same coal.

ADVANCED SPECTROSCOPIC ANALYSIS OF COAL SURFACES DURING BENEFICIATION

J. F. McClelland and J. S. Oh

OBJECTIVE

This project's objective is to develop and test new Fourier transform infrared (FTIR) spectroscopic approaches from the perspective of measurement concepts, instrumentation for these measurements, and analytical methodologies to apply the measurements to coal analysis problems, especially as they pertain to the evaluation of advanced coal cleaning techniques.

INTRODUCTION

Work proceeded on two new approaches: FTIR analysis of coal surface oxidation with the use of UV irradiation to gauge the level of carbonyl-producing species present in the surface region, and Transient Infrared Emission Spectroscopy (TIRES) which exploits a laser-induced thermal transient in coal to obtain, for the first time, analytically useful FTIR spectra of coal streams in motion. This latter approach is being pursued with primary funding from the Center for New Industrial Materials at Iowa State University.

The conventional FTIR method for determining the surface oxidation of an aged coal is to measure the growth in the carbonyl band by subtracting a fresh coal spectrum from an aged coal spectrum. This method may suffer from the unavailability of fresh coal, from the inherent variability in the spectra of fresh coal samples, and from the relatively deep probe depth of infrared analysis in the carbonyl region of coal spectra. The fresh coal availability and variability problems make it difficult to obtain and to compare data from one laboratory to the next, whereas the probe depth in the carbonyl region of approximately 100 μm (assuming an absorption coefficient of 100 cm^{-1}) implies that the compositional information obtained is more related to the bulk than to the surface. Hence, an analytical method is needed for coal surface analysis that does not require a fresh coal standard and that is more surface-specific.

The new FTIR/UV method for coal surface analysis gauges the amount of carbonyl-forming species present at a given time in an aged coal sample rather

than how much carbonyl has been produced in the progression from a fresh to an aged surface condition. The method uses a calibrated dose of UV radiation to generate carbonyl in the near-surface region (approximately 100 Å deep) of the coal specimen being analyzed. Consequently, a spectral subtraction of "after" minus "before" UV irradiation produces a large carbonyl difference band for a fresh coal surface and a smaller band for a more aged surface. The method allows the analysis to be done using only the coal specimen to be measured and a calibrated UV source. The analysis depth is determined by the decay length of UV rather than IR photons (approximately 10^{-2} μm rather than 100 μm). Consequently, the FTIR/UV method is more surface specific.

The TIRES method is uniquely suited for measuring IR spectra of coal sweeping past a measurement point on a conveyor belt. Such spectra can be used to obtain of a wealth of information on coal composition and process performance properties. Therefore, coal spectra are of key interest in understanding how coal beneficiation processes work and for monitoring processing performance. In the past, on-line IR analysis of coal has not been practical due to the high optical density of coal and to instrumentation considerations. IR emission spectroscopy is a desirable method because it fits the single-ended measurement needs of remote on-line detection. However, K. H. Rhee and L. R. Cousins ("Infrared Interferometry - Emission Spectra in the Middle-Infrared Region," in Spectrometry of Fuels, edited by R. A. Friedel, Plenum Press, New York, 1970, p. 216) reported that: "Infrared emission spectra of solids and liquids are critically dependent on the thickness of samples. A discrete band spectrum is obtained provided the sample is thin enough so that the effect of self-absorption is minimal." Coal moving on a conveyor belt is not optically thin enough to meet the requirement reported by Rhee and Cousins. The TIRES method reduces the optical density (self absorption) problem to an acceptable level by generating an elevated temperature transient in a thin surface layer of coal by transient laser irradiation of the coal surface. The transient IR emission radiation is then focused into an FTIR spectrometer for analysis.

PROGRESS - FTIR/UV

Figure 1 shows the carbonyl-band-difference spectra for an Illinois #6 coal which was oxidized in an oven at 100°C for periods of 1, 3, and 6 days. The dAov spectra are "after" - "before" oven oxidation difference spectra going from 1 (lower) to 3 (middle) to 6 (upper) days in the oven. The dAuv spectra are "after" - "before" UV oxidation difference spectra of samples that had previously been oxidized in the oven for 1 (upper), 3 (middle), and 6 (lower) days. The ddAuv spectra are difference spectra generated by subtracting the dAuv spectra in the figure from the analogous dAuv spectrum of a fresh coal sample in order to make a direct comparison with the dAov spectra. The ddAuv and dAov spectra have the same top to bottom ordering. Note that the dAuv spectra have a different band shape and peak maxima position indicative of some differences between the UV and oven oxidation processes. Nevertheless, both UV and oven induced carbonyl bands have substantial overlaps, as required for this measurement approach.

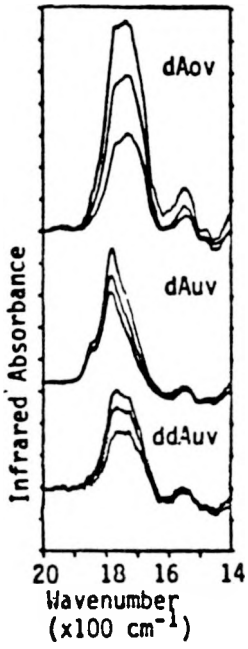

Figure 1. Carbonyl band difference spectra of Illinois #6 coal. dAov denotes difference spectra of "after" - "before" oven oxidation for 1 (lower), 3 (middle) and 6 (top) days in the oven. The dAov spectra are "after" - "before" UV oxidation difference spectra of samples that had been oxidized for 1 (top), 3 (middle) and 6 (lower) days.

The ddAuv spectra are difference spectra obtained by subtracting the dAuv spectra from a dAuv spectrum of fresh coal in order to make comparisons as shown in Fig. 2 to dAov spectra. The ddAuv and dAov spectra have the same ordering.

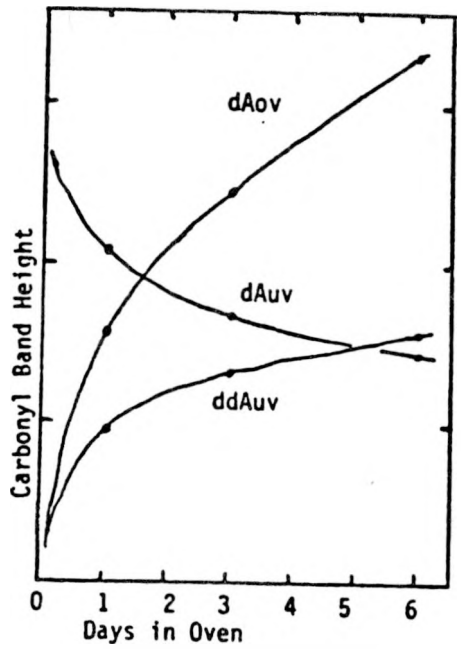

Figure 2. Changes in carbonyl band height versus oven oxidation time.

Figure 2 is a plot of the carbonyl band heights as a function of oxidation time for the three types of spectra using the same scaling for all spectra. Note that the ddAuv curve turns over more than the dAov curve, which is suggestive of a more rapid surface-region oxidation. The dAuv curve decreases with oxidation and demonstrates the possibility of monitoring coal surface oxidation by the FTIR/UV method.

Several data handling issues have been investigated preparatory to future measurements on a range of coals that will test the capabilities of the FTIR/UV method as a gauge of coal surface oxidation. Spectra need to be normalized to account for variations in the photoacoustic signal generation efficiencies of different coal samples. We propose to use the value of the area under coal spectra from 2000 to 2500 cm^{-1} to normalize all coal spectra because this spectral region shows very little change as a function of oxidation. A second spectral processing routine was investigated which involves using spectral subtraction of water bands from coal spectra rather

than employing various sample drying processes. Such processes run the risk of causing additional surface oxidation. The spectral subtraction approach was found to be effective in removing moisture band spectral interference in the carbonyl region.

The changes in coal spectra induced by UV irradiation were examined in terms of fresh versus oven oxidized samples, the C-H versus carbonyl stretch band regions, and using peak-height versus peak-area data analysis. It was found that UV irradiation of fresh coal caused growth (depletion) of the carbonyl (C-H) band with little difference between peak and area plots. UV irradiation, also caused growth of the carbonyl band in oven oxidized samples but little change was observed in the C-H band. The conclusion is that the peak height changes of the carbonyl band are the best gauges of coal surface oxidation with the FTIR/UV method.

PROGRESS - TIRES

A preliminary TIRES measurement was made on Illinois #6 coal chunks mounted on a rotating disk to simulate a conveyor belt moving at 60 ft/min. An argon ion laser operating at 3 W was focused on the coal with a focal spot size of approximately 1 mm in diameter. The emission spectrum was measured with a Perkin-Elmer Model 1800 FTIR fitted with a wide-band MCT detector. Figure 3 shows the experimental setup.

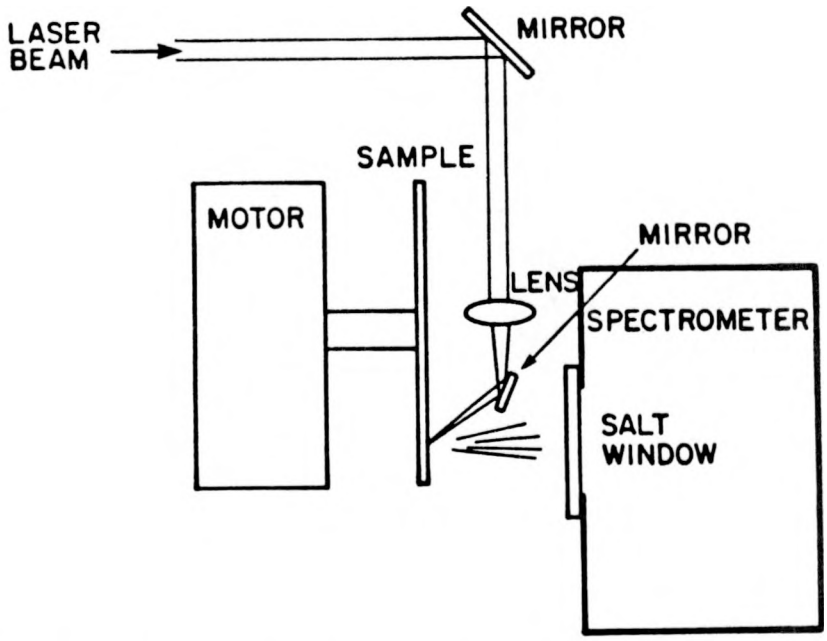

Figure 3. Experimental apparatus for TIRES measurement.

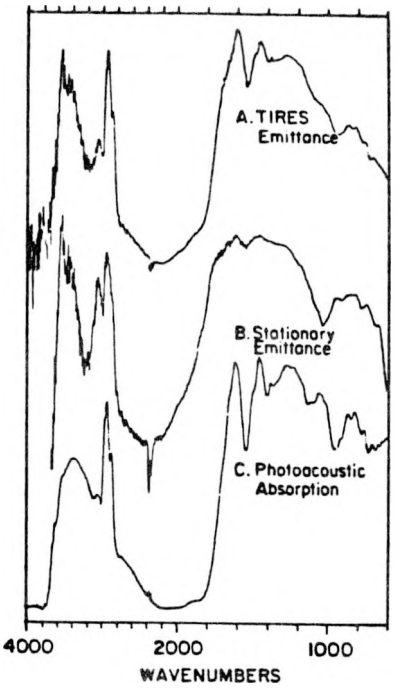

Figure 4. Spectra of Illinois #6 coal measured by TIRES, stationary emission, and photoacoustic detection.

The IR spectra of Illinois #6 coal are shown in Figure 4 measured by TIRES, stationary emission, and photoacoustic detection for comparison. The emission spectra have been normalized with a black body spectrum and the photoacoustic with a carbon black spectrum. Note that the TIRES spectrum compares favorably with the photoacoustic spectrum whereas the stationary emission spectrum is distorted by self-absorption to the point of limited usefulness.

We think that the TIRES spectrum in Fig. 4 is the first infrared spectrum measured for coal in chunk form (5 mm thick) in rapid motion past an observation point. The TIRES on-line method has the potential of allowing a comprehensive monitoring of the compositional and performance properties of feed stock and processed coal from beneficiation processes. The properties information would be obtained by inputting the TIRES spectral data into a factor analysis program. The properties information would allow process parameters to be adjusted to optimize the quality of the processed coal.

Alternatively, the TIRES method could also be used to optimize other coal utilization processes, such as combustion or coking.

It is important to note that the TIRES on-line method should allow the efficiencies of many coal beneficiation and utilization processes to be optimized during plant operation. Previously, individual samples had to be taken to a laboratory for analysis. This made infrared spectroscopic monitoring of processes in real-time impossible because the number of samples required could not be analyzed fast enough.

FUTURE WORK

The FTIR-UV and TIRES results indicate unique possibilities for these new spectroscopic methods. The FTIR-UV method will continue to be developed as a means of increasing the surface sensitivity of coal oxidation analyses without the need of a fresh coal standard. Tests will be made on coals of different particle size and types to determine how these factors influence results. An effort will be made to better understand the differences between the UV and other coal oxidation processes and how differences may influence FTIR-UV results. The influence on the UV irradiation process of moisture in coal will also be explored.

The TIRES work on coal will not be pursued until the FTIR-UV task has advanced more. Important future research topics to be advanced include how the relative band strengths of different coal components vary in TIRES versus other IR spectra of coal and how well TIRES spectra can predict coal performance in processing by factor analysis programs.

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