

AGING STUDIES OF BITUMINOUS COAL BY ESCA AND FTIR

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ABSTRACT

Electron Spectroscopy for Chemical Analysis (ESCA or XPS) and transmission Fourier Transform Infrared Spectroscopy (FTIR) were used to examine aged bituminous coals. The coals were obtained from the Illinois #6, Kentucky #9, Pittsburgh and Upper Freeport seams. The coals were stored under either ambient air, mine site tap water or nitrogen as they were exposed first to cold weather (10 C), warm weather (25 C) and the following cold season. Samples over the time periods were analyzed as raw, milled and processed coals. Emphasis was placed on changes in C, O, N and S functionalities on the surface by ESCA analysis, and in the bulk by transmission FTIR.

INTRODUCTION

The aging of coal is of interest both to the fuel and coking industry due to the physical and chemical changes aging causes. The changes can affect the behavior and properties of coal, and therefore affect the coal as it is processed and utilized. In the majority of cases, the effects are negative. Oxidation, a major mechanism in the aging process, can decrease the fuel value of coal. Processing can become more problematic as aging occurs. (1-3)

Storage of coal is where significant oxidation can occur as coal ages. (1,2) Coal is commonly stored in large stockpiles open to weather conditions. In this study, storage conditions were modified to investigate what effects they may have on controlling or inhibiting aging. (4) Samples were stored under nitrogen gas, tap water or ambient air.

EXPERIMENTAL

Coal samples, obtained by Otisca Industries, Ltd., were collected as they were brought up out of the mine. Coal was collected from the Illinois #6, Kentucky #9, Pittsburgh and Upper Freeport seams. The coal was placed under one of three atmospheres upon collection: nitrogen, ambient air or local mine site tap water.

Upon arrival at Otisca, the samples were riffled and crushed to 30m x 0 following ASTM methods, and returned to their respective environments. The coal was stored in 5 gallon pails holding approximately 17 lbs. each, and exposed to local weather during cold weather (10 C), the following

warm season (25 C) and another cold season. Individual samples were taken after each weather extreme. Samples were analyzed as raw samples, milled samples, and milled and processed samples. Raw coal was reduced to 60m x 0. Milled samples were ball milled to 15 m x 0. Processed samples were first milled and then agglomerated using pentane. At this point mineral matter was removed.

Initially a set of samples from each seam was analyzed before exposure to weather to establish a baseline for the aging study. The handling, analysis, and results of these analyses were presented in a previous preprint.(5)

The samples received from Otisca were handled as previously described (5). Analysis was done using a Perkin - Elmer Physical Electronics 5100 ESCA spectrometer using a non - monochromatized Mg K α X - ray source under the conditions 300W, 20mA and 15kV. Transmission FTIR spectra were collected on a Nicolet 7199A FTIR spectrometer with an MCT detector, taking 1000 scans, and a Mattson Alpha Centauri FTIR spectrometer with DTGS detector, taking 32 scans.

RESULTS AND DISCUSSION

In the previous study (5), the baseline samples were analyzed to establish what information can be obtained from the ESCA and FTIR analyses. In that study it was shown that as the samples went from raw to milled to processed there was a decrease in mineral matter. In the milled samples, mineral surfaces were generally covered by a thin film of organic matter. In the processed samples, most mineral matter was separated from the coal during agglomeration. It was also shown there was no significant difference in the baseline samples due to differing storage conditions.

In this study, the trends from raw to milled to processed coal were observed throughout the storage period, as would be expected. No major differences due to storage conditions were observed, but some difference was seen in the nitrogen stored samples.

As the coal aged (see Table 1), changes in the surface percent atomic concentration (%AC), oxygen to carbon ratios (O/C), and peak shape changes were examined. Changes in %AC carbon and oxygen would be an indication of oxidation, as would peak shape changes. Peak shape changes were examined in the FTIR spectra.

As the coal aged, trends were investigated in percent atomic concentrations. The inorganic elements such as Al and Si showed no notable changes over the storage period. Sulfur also remained consistent throughout aging, and nitrogen exhibited only minor fluctuations over the aging period. The largest change was seen in %AC carbon of the raw samples. There was an increase of up to 10 %AC between the baseline and first aged samples in all 4 seams. See Figure 1. There were slight variations through to the 7th batch, with only Illinois showing a significant decrease in %AC C. See Figure 2.

The milled samples showed a slight decrease in %AC from

the baseline to 1st aged sample. Slight decreases were seen in batch 4 or 5 in all seams, with the largest seen in the Pittsburgh samples.

In the processed samples, The %AC C was consistent through batch 1 - 7 except for the Kentucky seam, where a decrease was seen over batch 4 - 6, with an increase in the 7th batch.

Looking at what effect the storage conditions had, very little change was observed. In all four seams, no significant change in %AC C was seen in the air or water stored. Differences due to nitrogen storage was only significant in the Upper Freeport seam.

The trend in %AC total oxygen decreased through the processed samples due to the removal of minerals. Surface organic oxygen was calculated using the method of Perry and Grint (3), by subtracting oxygen as SiO_2 and Al_2O_3 . There were fluctuations in %AC surface organic oxygen as the samples aged. The least fluctuation was seen in the Pittsburgh seam, the most in the Upper Freeport seam.

The calculated %AC surface organic oxygen was used to calculate O/C ratios. An increase in this ratio would indicate oxidation of the coal was occurring. The largest difference in O/C ratio between treatments was seen in the Illinois and Upper Freeport seams, the least in Kentucky and Pittsburgh. No trend of increasing O/C ratio was seen except in Illinois raw samples. See Figure 3.

Peak shape changes were only notable for C, O, N and S. The C 1s envelope exhibited no gross changes as the samples aged. Slight increases in the shoulder and tailing towards the high binding energy side were observed over all treatments through batch 7. This would indicate a slight increase in the oxidized carbon functionalities and possibly a slight increase in aromatic carbon. See Figure 4.

The O 1s envelope has contributions from both organic and inorganic species. It is a broad slightly asymmetric peak. As the coal aged, a more distinct shoulder was seen towards low binding energy. The most severe case was seen in the processed samples. The inorganic matter was largely removed at this point. The shoulder was due to organic (carbon - bound) oxygen. See Figure 5.

The S 2p peak shape didn't vary much over the storage period. The presence of one or two peaks and the relative intensities of these two peaks varied. No solid trends were seen between the seams. In the Kentucky seam raw samples, there was one peak in the water stored sample and baseline nitrogen stored, but two peaks in the air stored and last nitrogen stored. The relative intensity of these two peaks varied as well. In the water stored milled baseline samples, the inorganic/oxidized organic species peak (5) was more intense than the organic species peak. In the 3rd batch sample, the relative intensities were reversed. See Figure 6. In the Upper Freeport samples, the trend was reversed for the respective samples. No definite trend was seen in or

between the seams.

The infrared results reflected the removal of the mineral matter with decreases in intensity of inorganic peaks. There was little difference between raw and milled samples, but there was significant difference between raw and processed samples. There were some differences in general between the seams, particularly in the 1400 - 700 cm^{-1} region where bands corresponding to clay mineral matter appears. Kentucky and Pittsburgh had less of this matter than Illinois and Upper Freeport. This was most evident in the raw and milled samples.

No major changes were obvious from the infrared spectra. Over the four seams there was one trend in the 1800 - 1650 cm^{-1} region. In the early samples there was a small peak at approximately 1730 cm^{-1} or a shoulder between 1800 - 1650 cm^{-1} . As the coal aged this small peak became less intense or the shoulder less prominent. This indicates there may be a decrease in carbonyl as the coal aged. See Figure 7.

CONCLUSIONS

This study shows that no major oxidation, either in the bulk or at the surface, was evidenced in these studies over the time period and temperature range they were stored at based on these analyses.

ACKNOWLEDGEMENTS

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Batch #	Storage History
1	baseline
2,3	1st cold season
4,5	warm season
6,7	2nd cold season

FIGURE 1

KENTUCKY #9 (AIR) - ALL TREATMENTS
SURFACE CARBON AS COAL AGED

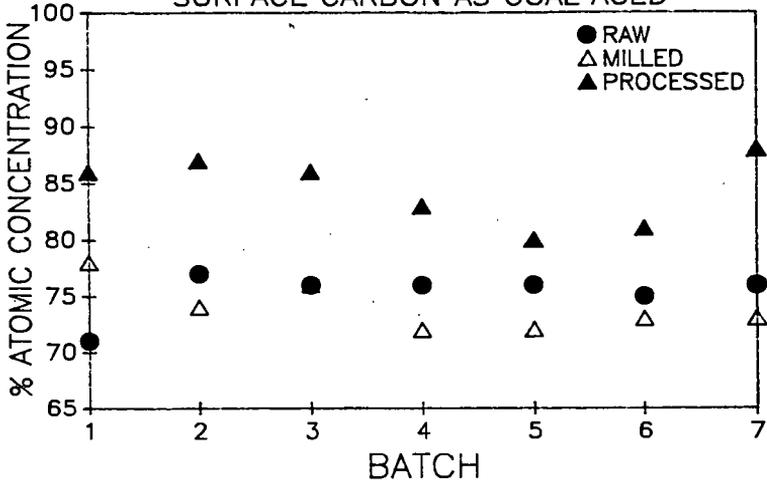


FIGURE 2

ILLINOIS #6 (AIR) - ALL TREATMENTS
SURFACE CARBON AS COAL AGED

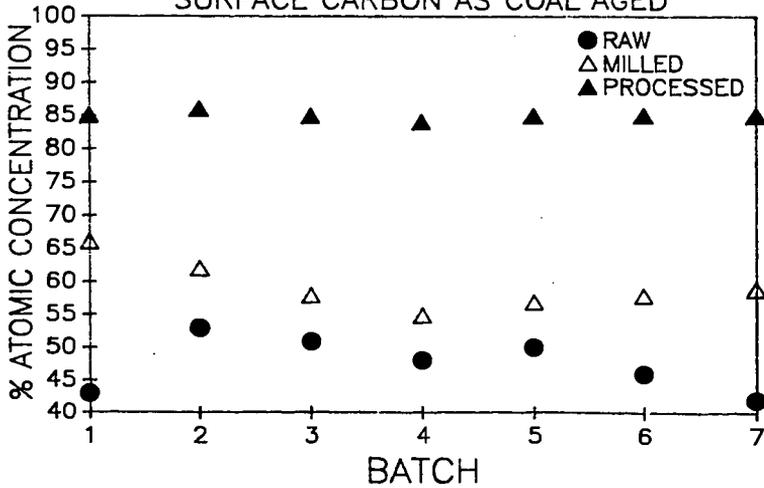


FIGURE 3

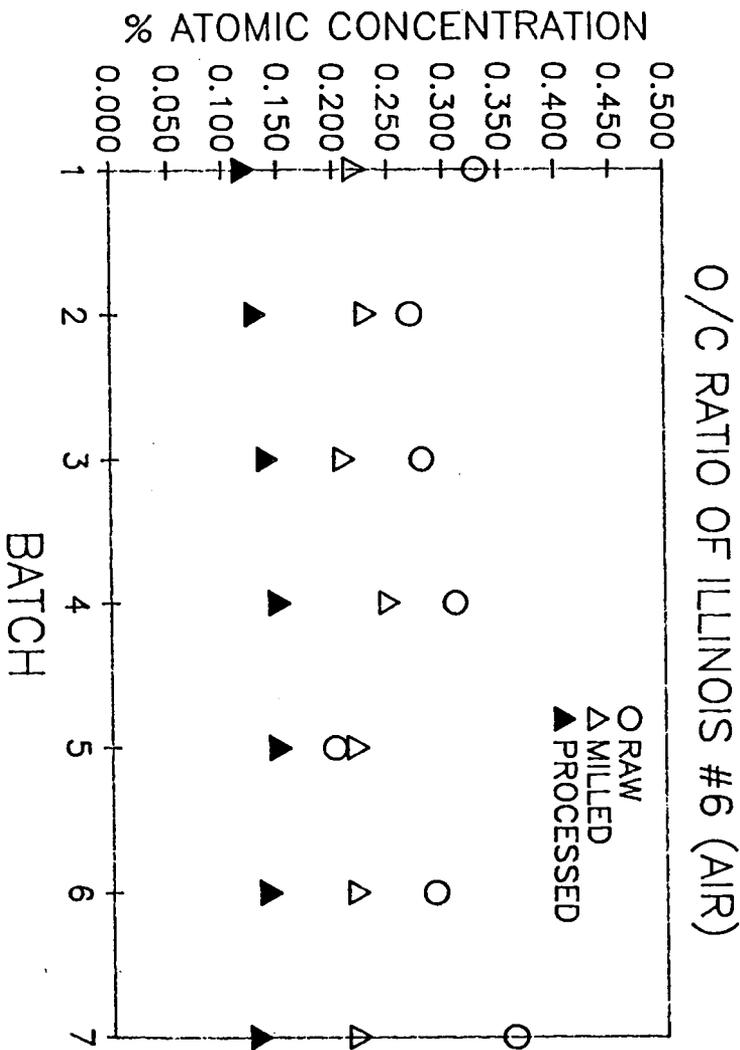


FIGURE 4

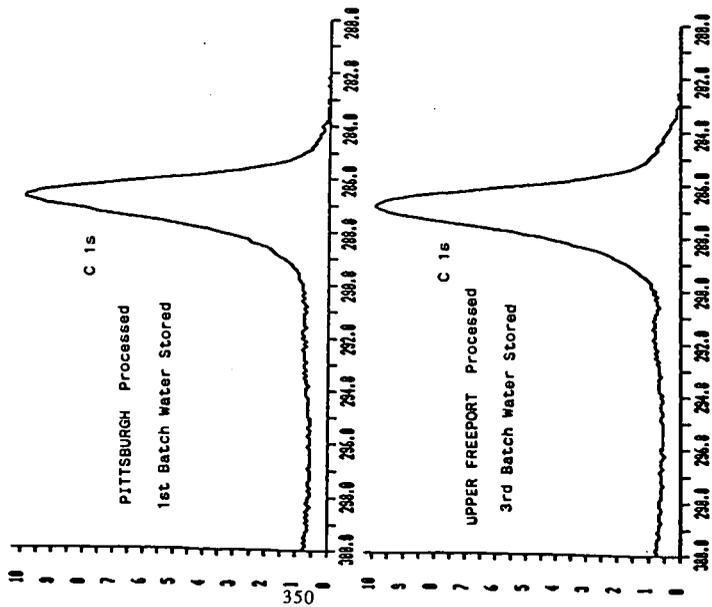


FIGURE 5

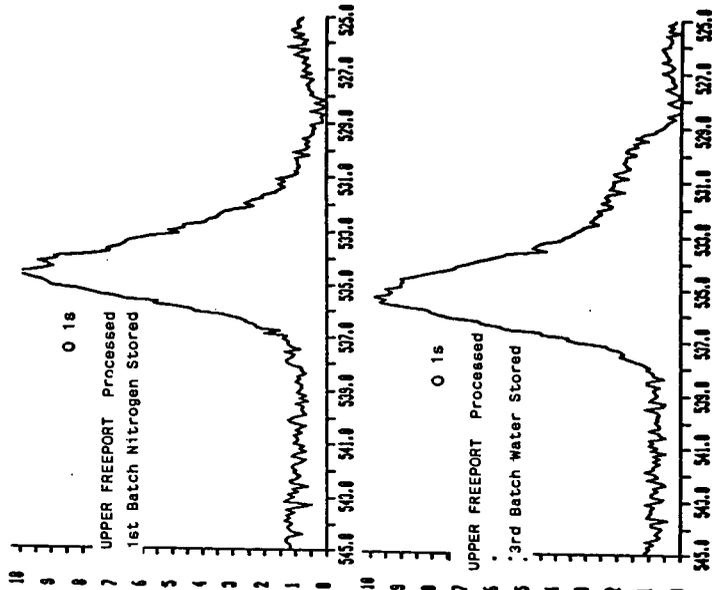


FIGURE 7

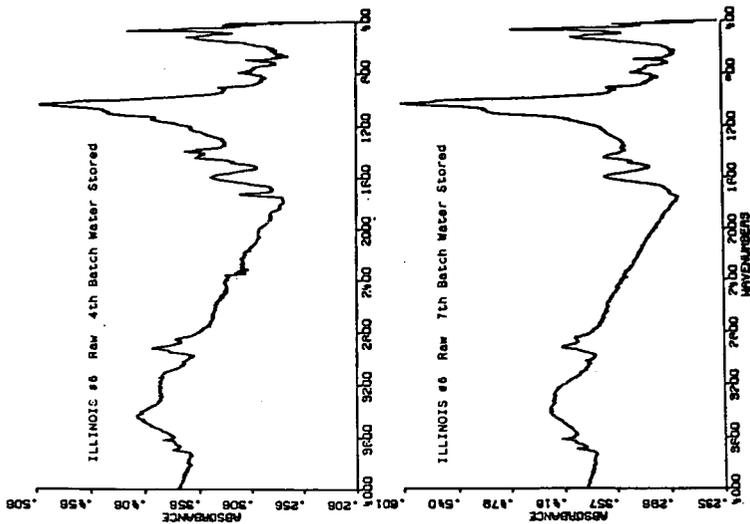


FIGURE 6

