

SURFACE MODIFICATION OF OXIDIZED COAL BY METHANOL VAPOR

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ABSTRACT

A bituminous coal was oxidized at 125°C for times varying from 0 to 48 hours and then chemically treated with a gaseous mixture of nitrogen, methanol, and an acid catalyst at 190°C for one hour. The differences between oxidized and methanol-treated coal surfaces were characterized by zeta potential, induction time, and contact angle measurements. Methanol-treated coals had more positive zeta potentials, lower induction times, and higher contact angles indicating a significant increase in the hydrophobicity of the treated coal surfaces. Using C¹³ labeled methanol for tracing the reaction products, NMR analysis indicated between 0.5 - 1.2 carbons are added per 1000 carbons of coal as a result of the treatment.

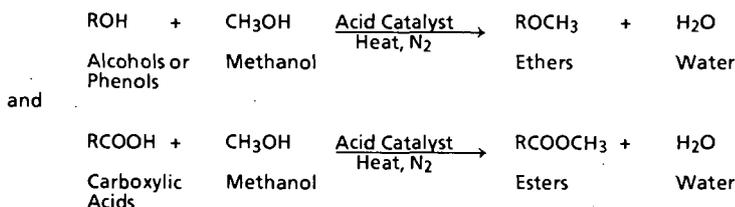
INTRODUCTION

In fine coal processing, the product quality depends largely on the surface properties of the feed coal. Processes that rely on surface properties of coal and its associated mineral matter include flotation [1-3], selective agglomeration [4-6], selective flocculation [7,8], and electrostatic separation [9,10]. The rheology of coal-water and coal-oil slurries is also dependent on the surface properties of the coal and its associated mineral matter [11-13]. Therefore, in handling or processing fine coals, we must understand the relationship between their surface properties and beneficiation response.

The hydrophobicity of the coal surface varies with rank, the extent of oxidation, and the nature and amount of inorganics. During mining, stockpiling, and processing of coal, oxidation of the coal occurs. Such oxidation can dramatically influence the wettability of the coal particles resulting in poor recoveries in surface-dependent coal beneficiation processes.

Both fresh and oxidized coals contain a variety of functional groups containing oxygen, nitrogen, and sulfur. Due to their abundance and polarity, oxygen containing functional groups contribute more to the chemical behavior of the coal surface than do those containing nitrogen and sulfur. Analyses of coals indicate that the major oxygen functional groups are phenols, ethers, and carbonyls [14-19]. The presence of polar oxygenate functional groups, such as phenols and carbonyl containing groups, is assumed to result in increased hydrophilicity of the coal surface.

Capping of polar oxygenate functional groups through methylation is expected to increase the hydrophobicity of the coal surfaces. A method for the methylation of coal surfaces has been reported [20]. This method consists of treating fine coal particles with a gaseous mixture of nitrogen, methanol vapor, and an acid catalyst (SO₂ or HCl) at temperatures of 150 - 190°C for one hour. It is proposed that the polar coal hydroxyl groups (ROH) are converted to ethers, while the carboxylic groups (RCOOH), if present, are esterified. The following chemical reactions were proposed:



The resulting ethers and esters are less hydrophilic than the original phenolic and carboxylic groups and have less hydrogen bonding potential. After this treatment, the coal particle surface becomes more hydrophobic and should respond better in conventional beneficiation processes.

In this investigation, a Pittsburgh seam bituminous coal was air oxidized at 125°C for various times up to 48 hours, and some of these oxidized samples were treated with methanol as described above. The oxidized and methanol-treated coal surfaces were characterized by measurement of zeta potential, induction time, and contact angle. The determination of the degree of methylation was achieved by reacting the coal with C13 labeled methanol in the presence of an acid catalyst followed by NMR analysis of the incorporated C13 label. The goal of this investigation was to clarify the chemistry of this surface modification method.

EXPERIMENTAL PROCEDURES

Sample Preparation:

The ultimate analysis of the Pittsburgh seam bituminous coal is shown in Table 1. Both 100 X 325 mesh coal powders and 1cm x2cm x3cm coal chunks were examined. The powdered coals were prepared by passing a 1/4 inch X 0 size fraction through a jaw crusher followed by hammer milling to yield a 28 X 0 mesh sample. This coal sample was then dry screened to obtain the 100 X 325 mesh size fraction. The coal chunks were machined and wet ground to the desired size. One side of the chunk was polished with emery cloth and alumina powder to obtain a smooth surface. Both the powdered coal samples and the coal chunks were stored under an argon atmosphere to reduce air oxidation.

Accelerated Oxidation:

The coal samples were placed in an oven at 125°C for 2, 4, 8, 24, and 48 hours. The bed thickness for the coal powders during this oven oxidation was approximately 1/8 inch. All of the oxidized coals were stored under argon after treatment.

Methanol Treatment:

As described by Attar [21], the oxidized coal samples were exposed to a gaseous mixture of nitrogen, methanol, and either SO₂ or anhydrous HCL at a temperature of 190°C for one hour. Twenty-gram samples of powdered coal were poured into a fritted one-inch diameter VYCOR tube 18 inches long with glass wool on both sides to maintain the uniform solid core packing. The coal chunk was placed in the same

tube and the chunk was also centered using glass wool. The methanol saturated nitrogen gas flow during these runs was approximately 680 ml/min with 7.0 volume percent of the flow being the acid catalyst (SO₂ or HCl). After treatment, samples were cooled to room temperature and stored under argon.

Zeta Potential Measurements:

Zeta potentials of these oxidized and treated fine coals were measured using the PEN KEM LASER ZEE MODEL 501 instrument. Coal particles (0.30g) were placed in 100 ml of 10⁻³ M potassium nitrate solution and sonified for one minute. The proper pH was achieved by addition of dilute nitric acid or sodium hydroxide solutions and the zeta potentials were measured in the pH range of 2.0 - 11.0.

Induction Time Measurements:

The attachment of a particle to an air bubble is the requirement for successful flotation. This phenomenon involves the thinning and rupture of the wetting film between colliding bubble and particles. Induction time [22-23] is defined as the contact time required to thin the disjoining film between coal particle and air bubbles and establish a three-phase contact. This important parameter is closely related to flotation processes and is useful in determining flotation kinetics as well as in predicting flotation recoveries of fine coal particles.

Using accepted procedures [23] for obtaining consistent induction time measurements, one gram of fine coal particles was agitated in 100 ml of distilled water for two minutes. After the formation of a uniform coal slurry, approximately 20 ml was transferred into a rectangular optical PLEXIGLASS cell to form a bed of particles. The cell was placed on the moving stage of the microscope for measurements. Inside the cell, a microsyringe was used to form an air bubble 2mm in diameter at the tip of the glass tube and let stand for one minute to reach equilibrium before making contact with the particle bed. The contact time was gradually increased from short times to determine the minimum time for the particle to adhere to the surface of the bubble. The contact time was then preset and ten measurements were taken at different regions of the particle bed to yield the average induction time.

Contact Angle Measurements:

Contact angle has been widely used to evaluate the hydrophobic nature of coal, first by Brady and Gauger [24], who showed that the hydrophobicity varied with rank. Later, Horsely and Smith [25], Sun [26], and Aplan [27] have investigated in detail the relationship between the contact angle and rank and have related the contact angle to coal floatability.

The contact angles in this work were measured using the captive bubble method [28]. The polished coal chunks were mounted and placed into distilled water in a PLEXIGLASS cell. The air bubble was attached to the oxidized and treated coal surfaces by using a screw-type microsyringe equipped with an inverted 22 gauge needle. The air bubble was allowed to reach equilibrium for 20 minutes and the contact angle measurement was taken on both sides of the bubble by a Gartner Scientific goniometer at ten different areas over the polished surface.

Surface Treatment using C13 Labeled Methanol :

To obtain a better understanding of the proposed chemical reactions, C13 labeled methanol was reacted with coal particles to determine the degree of methylation. A 250 ml three-necked round bottom flask was charged with 700 mg of untreated Pittsburgh seam coal and then flushed with nitrogen. The flask was heated to 190°C with a heating mantle and was allowed to equilibrate (190 +/- 5°C). After equilibration, the pure nitrogen atmosphere was replaced with nitrogen containing 7 percent acid catalyst. The C13 labeled methanol from the Aldrich Chemical Co. (99 atom %) was added from a microsyringe, through a MININERT valve into a small suspended beaker for the saturation of the reaction atmosphere. To assure that saturation was achieved, the labeled methanol was added until droplets were observed condensing on the walls of the flask. The coal sample was exposed to this gaseous mixture for one hour. Following reaction, the flask was swept with nitrogen and cooled to room temperature. To assure that physically adsorbed reagents were removed, the treated coal samples were vacuum dried for 24 hours and stored under argon.

The methylated coal samples were analyzed by a Bruker CXP-100 nuclear magnetic resonance spectrometer. The spectra were acquired by spinning at the magic angle, using a cross-polarization contact time of 1.0 ms, 3.5 µm -90 degree pulse width and a 2.0 second recycle time. The spectrometer was operated at 25.18 MHz and the aromatic carbon resonance was assigned a chemical shift of 129 ppm.

RESULTS AND DISCUSSION

Air oxidation of the coal under either ambient temperature conditions or under accelerated conditions can result in the uptake of oxygen and the conversion of hydrocarbon constituents into oxygen containing functional groups [29-32].

Accelerated oxidation of the Pittsburgh seam coal indicates that at long exposure times there was a significant increase in the oxygen content determined by difference. The results of the oxidation of this coal are summarized in Table 2.

As expected, the oxygen content increased with the oxidation time. The apparent increase in the oxygen content shown in Table 2 is a measure of total oxidation and should not be interpreted directly as increase in oxygen functionality on particle surfaces. Increasing the number of polar groups on the coal surface is expected to cause the coal to become more hydrophilic. The increase in the hydrophilicity of the oxidized coals can be attributed to increased interfacial attractive forces between polar oxygenate functionality on the coal surface and liquid water.

The surface potential of particles in an aqueous solution can be determined by electrophoresis, in which electrophoretic mobilities (μ) are measured in an applied electric field. The zeta potential (ζ) for a particle in an aqueous solution can be calculated by the von Smoluchowski equation (1):

$$\zeta = \mu\eta / (\epsilon_T \epsilon_0)$$

where η is the viscosity of the aqueous solution, ϵ_T is its dielectric constant, and ϵ_0 is the permittivity of free space.

Figure 1 shows the zeta potentials in aqueous solutions of pH 2 to 11 for fresh and oxidized coals. The negative potentials observed at high pH are assumed to result from the adsorption of hydroxyl ions and/or the deprotonation of acid sites, and the positive potentials observed at low pH result from the adsorption of hydrogen ions

on basic sites. Comparison of the zeta potentials between the fresh and oxidized Pittsburgh seam coals over the pH range of 2 to 11 reveals that the zeta potentials of the oxidized coal are approximately 30 mV more negative than the fresh coal in the entire pH range. Furthermore, the curve of the zeta potentials of the oxidized coal does not have an isoelectric point (point of zero charge) while the fresh coal has an isoelectric point at the pH of 5.0. Since these zeta potentials are measures of the average distribution of surface potential, it is apparent that the oxidized coal surfaces are dominated by acidic sites while the fresh coal has a mixture of basic and acidic sites. This increase in acidic sites on the oxidized coal surface is also supported by the observed increase in the oxygen content shown in Table 2. It is assumed that the presence of more oxygen containing functional groups (i.e., phenols or carboxylic acids) on the interface between the coal particle and the aqueous phase will cause the coal to be more hydrophilic.

Both the induction time and contact angle measurements in Figures 2 and 3 indicate that the coal surface becomes more hydrophilic with longer oxidation times. The fresh Pittsburgh seam coal had an induction time of 1350 microseconds. After 48 hours of oxidation, this value increased to 2200 microseconds. Fresh Pittsburgh seam coal had a contact angle of 45 degrees, which decreased to 21 degrees after 48 hours oxidation. The increase in induction time and the decrease in the contact angle indicate that a more hydrophilic surface results from oxidation.

Following oxidation, 20 gram samples of oxidized coal were treated with the gaseous mixture of nitrogen, methanol, and 7% sulfur dioxide at 190°C for one hour to investigate restoration of the hydrophilicity of the coal surface. In Figure 4, it is apparent that the zeta potentials of the methanol-treated oxidized coal powder show a significant increase of approximately 20 mV as a result of treatment. This suggests a reduction in the acidic sites of the treated coal surface indicating a higher level of hydrophobicity. Comparison of the treated coal (Figure 4) with the fresh coal (Figure 1) shows that the isoelectric point was only slightly lower (pH of 4.2 versus 5.0) for the treated coal, suggesting that the oxidized coal surface was restored to nearly its original hydrophobicity.

Consistent with the zeta potential changes observed, the methanol treatment also reduced the induction time and increased the contact angles of the oxidized coals. Both results, presented in Figures 2 and 3, indicate increasing hydrophobicity of the oxidized coal surface as a result of the treatment.

To determine the effectiveness of the acid catalyst, a comparison study was performed using C13 labeled methanol. Pittsburgh seam coal was reacted on a small scale, as described in the experimental section, with the C13 labeled methanol with and without acid catalyst (SO₂ or anhydrous HCl). These C13 labeled coal samples were then analyzed by NMR to determine the amount of methylation.

The spectra from the treated samples are shown in Figure 5. The peak at 52 ppm indicates that methylation occurred; however, the labeled peak is enhanced by 100 fold due to the 99% C13 enrichment of the labeled methanol. The spectra indicate that the level of methylation was the highest when anhydrous HCl was used as the acid catalyst. The incorporation of the labeled methanol can be determined by the change in aromaticity during the treatment. The carbon aromaticity of the coal samples determined by the NMR analyses is summarized in Table 3.

The NMR results presented in Figure 5 and Table 3 can be used to estimate the degree of derivitization of the coal. The results are tabulated in the last column of

Table 3. The values are arrived at by assuming the chemistry is simple conversion of coal hydroxyl groups to methyl ethers:



The uncertainty in measurements of f_a (aromaticity of the coal) is substantial, but the data indicates little if any influence of gaseous SO_2 as an acid catalyst for the above reaction. However, the presence of gaseous HCl appears to increase the incorporation of label into the coal. In all cases the amount of apparent methylation is small (0.5-1.2 carbons/1000 carbons of coal) when expressed in terms of total carbon in the sample. This could be misleading if the derivitization reaction is limited to the coal surface, because only a very small fraction of the total sample carbon is present as exposed carbon on the particle surface. Unfortunately, the CP C13 NMR is not surface selective and yields only a measure of derivitization relative to the total carbon in the sample. Other chemical reactions could also result in the incorporation of label into the product coal to produce esters or silylethers.

The similarity of the methoxy chemical shifts of product structures is such that we cannot rule out the possibility that these mechanisms of incorporation are minor contributors to the C13 intensity in Figure 5.

SUMMARY

Accelerated oxidation of the Pittsburgh seam coal resulted in a more hydrophilic surface, which was indicated by more negative zeta potentials, higher induction times, and lower contact angles. However, upon treatment of these oxidized coals with gaseous nitrogen, vaporized methanol, and 7 percent SO_2 at 190°C for one hour, the apparent original hydrophobicity of the coal was restored.

NMR analysis of the C13 labeled coal indicates that anhydrous HCL is a more effective methylation catalyst than SO_2 and confirms that the proposed methylation reactions do occur. The NMR results indicate little if any enhancement of methoxy incorporation when SO_2 treatment is compared with simple treatment with no acid catalyst in the methanol saturated nitrogen.

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Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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TABLE 1: ULTIMATE ANALYSIS OF AS-RECEIVED PITTSBURGH SEAM COAL, GIVEN AS PERCENT BY WEIGHT

Moisture	1.3
Carbon	78.1
Hydrogen	4.9
Nitrogen	1.5
Sulfur	1.2
Ash	5.5
Oxygen (by difference)	8.1

TABLE 2 : OXIDATION OF PITTSBURGH SEAM COAL AT 125 C

<u>TIME (HRS.)</u>	<u>OXYGEN CONTENT (Wt.%)*</u>
0	8.1
4	8.5
8	8.5
24	9.9
48	10.8

* WEIGHT DIFFERENCE METHOD

TABLE 3 : EXPERIMENTAL RESULTS OF C13 LABELED METHANOL-TREATED COALS

<u>COAL SAMPLE</u>	<u>AROMATICITY (+/- 0.02)</u>	<u>C13/1000 CARBONS</u>
UNTREATED	0.71	----
NO ACID CATALYST *	0.68	0.5
7 % SO2 *	0.68	0.5
7 % HCL *	0.64	1.2

* ALL TREATMENTS PERFORMED IN THE PRESENCE OF C13 LABELED METHANOL AND NITROGEN AT 190°C FOR ONE HOUR

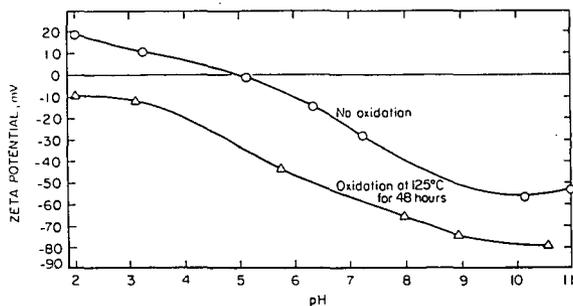


Figure 1. Effect of Oxidation on Zeta Potential of Pittsburgh Seam Coal.

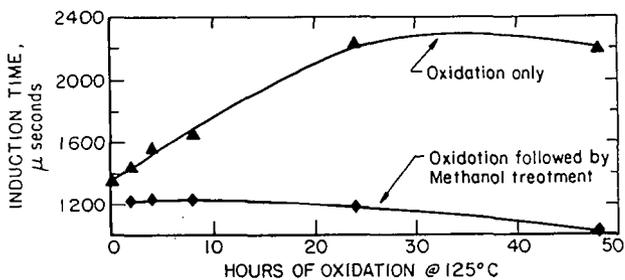


Figure 2. Effect of Oxidation and Methanol Treatment on Induction Time Measurements on Pittsburgh Seam Coal.

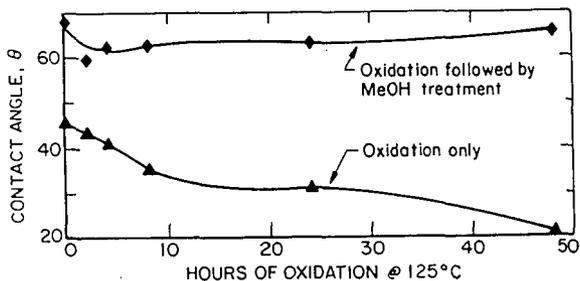


Figure 3. Effect of Methanol Treatment on the Contact Angles of Oxidized Pittsburgh Seam Coal.

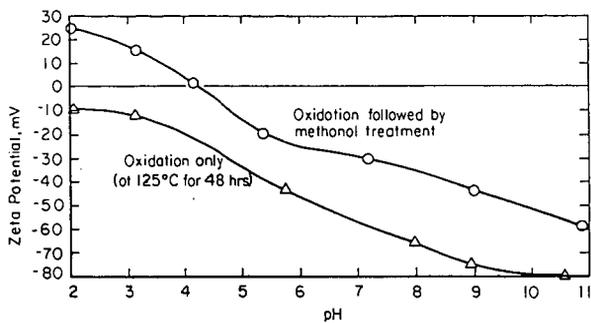


Figure 4. Effect of Methanol Treatment on Zeta Potential of Oxidized Pittsburgh Seam Coal.

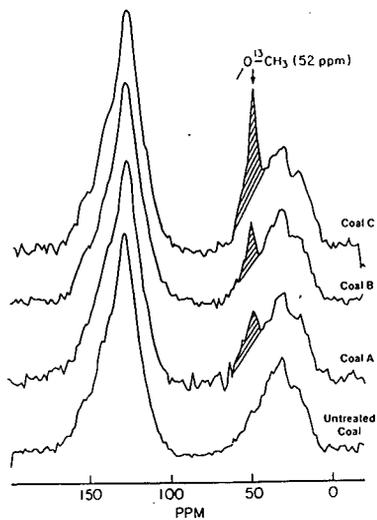


Figure 5. Comparison of Acid Catalysts for ^{13}C Methanol-Treated Pittsburgh Seam Coal
 Coal A - No Catalyst Presence
 Coal B - 7% SO_2
 Coal C - 7% Anhydrous HCL