

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.

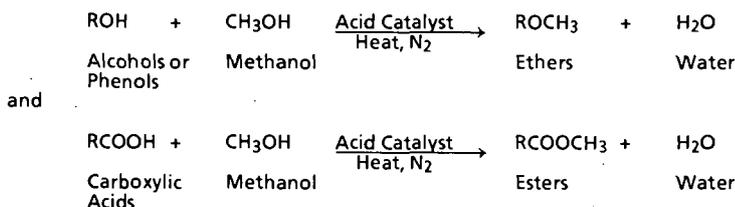
INTRODUCTION

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 (SO_2 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 μ m -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.

REFERENCES

1. Brown, D.J., "Coal Flotation," Froth Flotation - 50th Anniversary Volume, Fuerstenau, D.W., ed., AIME, New York, pp. 518-538 (1962).
2. Zimmerman, R.E., "Froth Flotation," Coal Preparation, 3rd ed., Leonard, J.W. and Mitchell, D.R., eds., AIME, New York, pp. 10-66 - 10-90 (1968).

3. Baker, A.F., Miller K.J. and Deurbrouck, A.W., "Two-Stage Flotation Selectively Floats Pyrite from Coal," *Coal Mining and Processing*, pp. 44-46 and 56 (August 1973).
4. Mehrotra, V.P., Sastry, K.V.S. and Morey, B.W., "Review of Oil Agglomeration Techniques for Processing of Fine Coals," *Int. J. Min. Proc.*, Vol. 11., pp. 175-201 (1983).
5. Keller, D.V., "The Otisca Process of Preparation and Dewatering of Fine Coal," *Proceedings of the Consolidation and Dewatering of Fine Particles Conference*, University of Alabama, pp. 152-71 (August 10-12, 1982).
6. Chiang, S.H. and Klinzing, G.E., "Process of Removing Mineral Matter from Coal," U.S. Patent Number 4,613,429 (September 23, 1986).
7. Attia, Y.A., Conkle, H.N. and Krishnan, S.V., "Selective Flocculation Coal Cleaning for Coal Slurring Preparation," in *Proc. 6th Int. Symp. Coal Slurry Combust.*, pp. 582-97 (1984).
8. Attia, Y.A., "Cleaning and Desulfurization of Ultrafine Coal Suspensions by Selective Flocculation," *Processing and Utilization of High Sulfur Coals*, Attia, Y.A. ed., Elsevier (1985).
9. Incullet, I.L., "Electrostatic Mineral Separation," *Research Studies Press*, John Wiley and Sons, Inc., N.Y. (1984).
10. Advanced Energy Dynamics, Inc., "Dry Electrostatic Cleaning of Ohio Coals," Final Report, Grant No. 10-85-016, Ohio Coal Development Office of the Ohio Department of Development (March 1987).
11. Chiang, S.H. and Venkatadri, R. "Effect of Surface Property on Fine Particle Dewatering," *Proc. 4th World Congress on Filtration*, Ostend, Belgium (April 20-24, 1986).
12. Dinger, D.R., Funk, J.E. Jr., and Funk, J.E. Sr., "Rheology of a High Solids Coal Water Mixture: Co-Al," *Proc. Fourth International Symposium on Coal Slurry Combustion*, Orlando, FL., Pittsburgh Energy Technology Center, Pittsburgh, PA (1982).
13. Tsai, S.C. and Knell, E.W., "Rheology and Its Effects on Atomization of Coal Water Slurry," *First Annual Pittsburgh Coal Conference*, Pittsburgh, PA, September 17-21 (1984).
14. Rosenbaum, J.M., Ph.D. Thesis, U.C. Berkeley (1981).
15. Abdel-Baset, Z., Given, P.H. and Yarzab, R.F., *Fuel* Vol. 57, p. 95 (1978).
16. Teo, K.C., Finora, S. and Leja, J., *Fuel* Vol. 61, p. 71 (1982).
17. Schafer, H.N.S., *Fuel* Vol. 49, p. 271 (1970).
18. Lyengar, M.S. and Lahiri, A., *Fuel* 36 (3), p. 286 (1957).
19. Ruberto, R.G. and Cronauer, D.C., in: *Organic Chemistry of Coal*, (J.W. Larsen, ed.), ACS Symposium Series, 71, p. 50 (1978).
20. Attar, J., "Coal Demineralization and Depyritization Process," U.S. Patent 4,597,769 (1986).
21. Attar, J., "Coal Demineralization and Depyritization Process," U.S. Patent 4,597,769 (1986).
22. Sven-Nilsson, I., "Effect of Contact Time Between Mineral and Gravitational Collision Efficiencies for Single Collectors at Intermediate Reynolds Numbers," *J. Colloid and Interface Sci.*, Vol 94, No. 2, pp. 328-335 (1983).
23. Eigeles, M.A. and Volova, M.L., "Kinetic Investigation of Effects of Contact Time Temperature and Surface Condition on the Adhesion of Bubbles to Mineral Surfaces," in *Proc. 5th International Mineral Processing Congress*, IMM, London, pp. 271-284 (1960).
24. Brady, G.A. and Gauger, A.W., "Properties of Coal Surfaces," *Ind. Eng. Chem.*, Vol 32, p. 1599 (1940).
25. Horsley, R.M. and Smith, H.G., *Fuel* Vol. 30, p. 54 (1951).
26. Sun, S.C., *Trans AIME*, Vol. 199, p. 67 (1954).

27. Aplan, F.F., "Examining The Floatability of Western Coals," Geology, Mining, Extraction and the Environment, AIME, New York, NY, pp. 380 (1983).
28. Wark, I.W. and Cox, A.B., Trans. AIME, Vol 112, p. 189 (1934).
29. Bouwman, R., and Ivo L.C. Freriks, "Low Temperature Oxidation of a Bituminous Coal. Infrared Spectroscopic Study of Samples from a Coal Pile," Fuel, Vol. 59, pp. 315-322 (May 1980).
30. Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A. and Painter, P.C., "Further Studies of Coal Oxidation," Fuel, Vol. 62, pp. 1387-1392 (Dec. 1983).
31. Gethner, J.S., "Thermal and Oxidation Chemistry of Coal at Low Temperatures," Fuel Vol. 64, pp. 1443-1446 (Oct. 1985).
32. Huffman, G.P., Huggins, F.E., Dunmyre, G.R., Pignocco, A.J. and Lin, M.C., "Comparative Sensitivity of Various Analytical Techniques to the Low-Temperature Oxidation of Coal," Fuel, Vol. 64, , pp. 849-856 (June 1985).

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

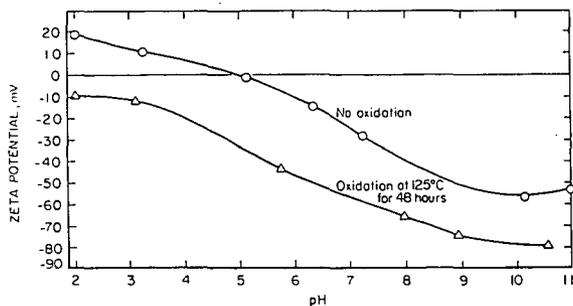


Figure 1. Effect of Oxidation on Zeta Potential of Pittsburgh Seam Coal.

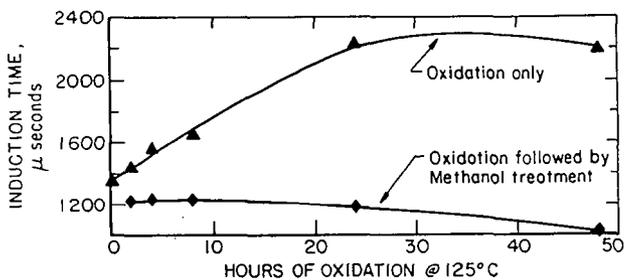


Figure 2. Effect of Oxidation and Methanol Treatment on Induction Time Measurements on Pittsburgh Seam Coal.

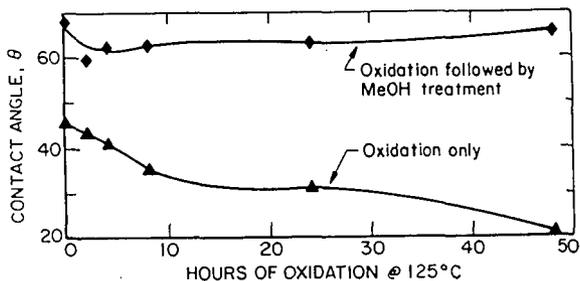


Figure 3. Effect of Methanol Treatment on the Contact Angles of Oxidized Pittsburgh Seam Coal.

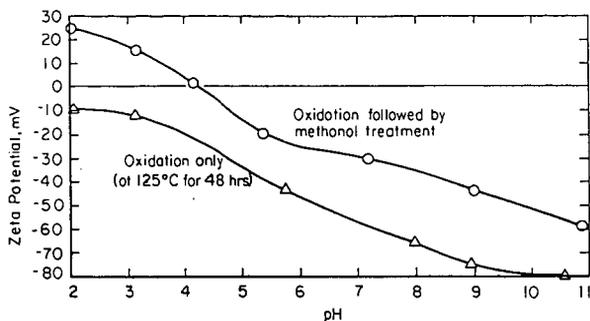


Figure 4. Effect of Methanol Treatment on Zeta Potential of Oxidized Pittsburgh Seam Coal.

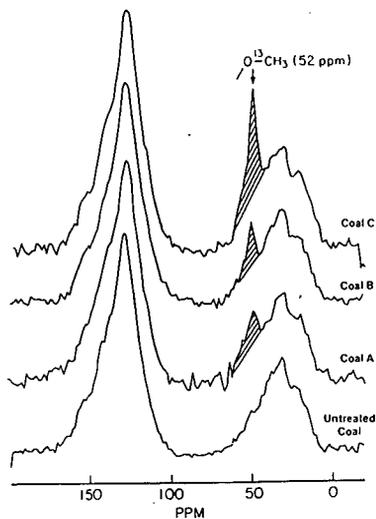


Figure 5. Comparison of Acid Catalysts for ^{13}C Methanol-Treated Pittsburgh Seam Coal
 Coal A - No Catalyst Presence
 Coal B - 7% SO_2
 Coal C - 7% Anhydrous HCL

GLASS TRANSITION TEMPERATURE OF MODIFIED COALS

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INTRODUCTION

Coals are macromolecular solids (1). Although they are not polymers in the sense they possess a repeat unit, they do possess several properties typical of synthetic crosslinked macromolecular networks (2). The crosslinks are thought to be covalent in nature. Hydrogen bonds (3,4) and intermolecular polarization forces (5,6) can be important associative forces as well.

Coals behave as glassy materials at room temperature (2). In the glassy state, macromolecular motion is impeded and only short segmental motion of the polymer chain is possible. The glassy state of a material is characterized by its glass transition temperature, T_g , the temperature at which the polymer changes from a glass to a rubber. A rubber is characterized by significant macromolecular mobility compared to the glassy state. The practical utility of polymers and their different properties depend heavily on their glass transition temperatures. Thus, an important area of research is to understand how different molecular features affect the glass transition temperature.

This research is based on the premise that the glass transition temperature is a fundamental property of coals as well, and that it may have an important relation to several other coal properties. For example, the diffusivity of organic solvents in polymers increases by several orders of magnitude at the glass transition temperature (7). If the same concept can be applied to coal, the advantages of lowering the glass transition temperature of coal to enhance coal reactivity are obvious, particularly if the reaction is thought to be diffusion-controlled. Peppas *et al.* have demonstrated that coals swollen with pyridine exhibited lower glass transition temperatures than unswollen coals (8). In this research, we are primarily concerned with the impact of the network of hydrogen bonds in coals on their glass transition temperatures. Both differential scanning calorimetry (DSC) and thermomechanical analysis (TMA) were utilized to establish the importance of hydrogen bonding to T_g for two Argonne premium coals.

EXPERIMENTAL

Sample Preparation. Argonne premium Illinois and Wyodak coals were obtained in sealed ampoules from Argonne National Laboratory. Both coals were dried overnight under vacuum at 105°C. Analysis found: Illinois #6; C, 65.6%; H, 4.7%; N, 1.2%; Wyodak; C, 67.5%; H, 4.99%; N, 0.84%. The coals were alkylated according to the method of Liotta (3) using tetra-*n*-butylammonium hydroxide and the appropriate alkyl iodide in THF. One sample was exposed to THF

with no alkylating agent and is identified as the THF blank. Both elemental and IR analysis confirmed that alkylation had occurred.

Differential Scanning Calorimetry (DSC). The DuPont 910 DSC was used to measure the glass transition temperatures of the samples. Samples were heated from ambient to 600°C at a heating rate of 10°C/min. The system was purged with nitrogen at a rate of 100 mL/min to provide an inert atmosphere. Sample sizes of 5 mg or less were used. The DuPont 2000 Thermal Analysis System was used to analyze the data. Heat flow was plotted as a function of temperature. The glass transition temperature is indicated by a change in the baseline curve in a negative direction. The analysis package identified the inflection point of the change in the curve and this inflection was reported as T_g .

Thermal gravimetric analysis (TGA). The Shimadzu HT 50 TGA was used to monitor weight loss as a function of temperature. The samples were run under nitrogen at a flow rate of 100 mL/min and heated from ambient to 550°C at a heating rate of 10°C/min.

Thermomechanical Analysis (TMA). The DuPont 943 TMA was employed to assess the softening characteristics of the coals. The TMA uses a weighted probe that will penetrate the sample due to the softening which indicates the onset of the glass transition. Probe displacement is plotted as a function of temperature and the softening point is indicated by a negative probe displacement. The macroexpansion probe was used on the TMA. The coal samples were obtained in powdered form. Flat-bottom aluminum DSC pans were used to hold the samples. The coal powder was packed into the pans to a thickness of about 2-3 mm. Typical sample weights were about 20 mg. The pans were then placed in the TMA under a 100 g weight load. This was done to ensure that settling of the sample would be complete. Probe displacement was monitored as a function of time at ambient temperature to insure that the sample was well-packed into a pellet. A 10 g weight was then applied and the cell was purged with nitrogen at a rate of 300 mL/min to obtain an inert environment. The sample was heated at a rate of 10°C/min to a temperature just below the temperature of significant weight loss as indicated by the TG curves.

RESULTS

Elemental Analysis. The O-alkylated coals were analyzed for carbon, hydrogen, and nitrogen. The hydrogen/carbon ratios for the various coals were consistent with the addition of approximately 6 alkyl groups per 100 carbons for the Illinois #6 coal. For the Wyodak coal, elemental analysis indicated addition of approximately 8 methyl groups per 100 carbon. FT-IR analysis of the O-alkylated coals indicated reaction had occurred as evidenced by the increased C-H absorption at 2900 cm^{-1} , reduction of the O-H absorption at 3300-3600 cm^{-1} , and the appearance of an absorption at 1700 cm^{-1} which is attributable to the C=O of esters formed from carboxylic acids.

DSC Results. A typical DSC thermogram obtained using the dry, whole Illinois #6 coal is presented in Figure 1. Note that there

is an increasing negative heat flow into the sample relative to the aluminum oxide reference. The glass transition is identified by the slope shift that occurs near 300°C. Its onset temperature of 295°C was reported as T_g . These results are consistent with those of Peppas *et al.* for a coal of similar rank (8).

The results for both coals and their alkylated derivatives are summarized in Table I. For the Illinois #6 coals, all reported values are the average of at least five measurements, except for the THF blank (no alkylating agent), which is the average of only two measurements. For the Wyodak coals, only three measurements were made. The effect of O-methylation is to decrease T_g by 100°C for the Illinois #6 coal and 75°C for the Wyodak coal. The effect of the alkyl chain length is not significant for the Illinois #6 coal, although there is clear trend of decreasing T_g with increasing chain length. Exposure of the Illinois #6 coal to THF solvent results in a lower T_g by 50°C.

TG Results. The percent weight loss versus temperature curves for the Illinois #6 coals are presented in Figure 2. Weight loss for the dry, whole coal and the THF blank (no alkylating agent) is not significant until nearly 400°C, which is significantly above the reported T_g 's for these coals. This result indicates that no major thermal degradation of the coal occurred before T_g , consistent with the results of Peppas *et al.* (8).

Initial weight loss for the O-alkylated coals occurs at much lower temperatures than the whole coal. Approximately 5-10% of the weight loss occurs in the range of 200-350°C for these coals. An additional 15-25% weight loss occurs in the region of 350-550°C. These coals are clearly much more volatile than the whole coal, which is consistent with other studies (3). It appears that these coals are in a rubbery state, however, before any significant weight loss occurs, since their T_g 's are all near 200°C as measured by DSC.

TMA Results. The whole and O-methylated coals were analyzed by TMA in order to assess their softening characteristics. The DSC results indicated that the O-methylated coal should soften at a much lower temperature than the whole coal. This expectation was confirmed. The results on the Illinois #6 coals are shown in Figure 3, where the probe displacement (dimensional change) is plotted against temperature. Note that the O-methylated coal softens at a much lower temperature than the whole coal. Similar results were obtained on the corresponding Wyodak coals.

DISCUSSION

The lowering of T_g by O-methylation of the coal is most probably attributed to the disruption of the hydrogen bond network known to exist in these coals. The hydrogen bonds serve as crosslinks between macromolecular chains and represent an important attractive force that should restrict chain mobility. That their disruption by O-alkylation lowers T_g of the coal is therefore not surprising. The effect of THF solvation on T_g is also substantial, although not as large as O-alkylation. This effect might be attributed to a

partial disruption of the hydrogen bond network by THF, which is a known hydrogen bond acceptor. THF is also expected to swell the coal substantially. When the THF is removed, not all of the disrupted hydrogen bonds are expected to reform.

The length of the added alkyl group appears to have only a small effect on T_g , contrary to our expectations. We believed that the addition of longer alkyl groups might disrupt noncovalent interactions other than hydrogen bonding that might exist between the macromolecular chains, thereby lowering T_g even more. Either these interactions are not important or O-alkylation fails to disrupt them. In the future, we plan to examine the effects of C-alkylation (5) on the glass transition temperatures of coals to explore this aspect more fully.

REFERENCES

1. Green, T.; Kovac, J.; Brenner, D.; Larsen, J. W. in "Coal Structure," Meyer, R. A., Ed.; Academic Press, New York, 1982, p 199.
2. Treloar, L. R. G. "The Physics of Rubber Elasticity," Clarendon Press, Oxford, 1975.
3. Liotta, R.; Rose, K.; Hippo, E.; J. Org. Chem. 1981, 46, 277-283.
4. Larsen, J. W.; Green, T. K.; Kovac, J. J. Org. Chem. 1985, 50, 4729.
5. Miyahe, M.; Stock, L. M. Energy Fuels 1988, 2, 815.
6. Quinga, E. M. Y.; Larsen, J. W. Energy Fuels 1987, 1, 300-304.
7. Crank, J.; Park, S. J. "Diffusion in Polymers," Academic Press, London, 1968.
8. Lucht, L. M.; Larsen, J. M.; Peppas, N. A. Energy Fuels 1987, 1, 56-58.

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TABLE I

Glass Transition Temperatures of Modified Coals

Coal	T_g , °C	
	Illinois #6	Wyodak
Whole	300±5	276
THF Blank	247	---
O-Methylated	198±13	203
O-Butylated	185±7	---
O-Octylated	178±14	---

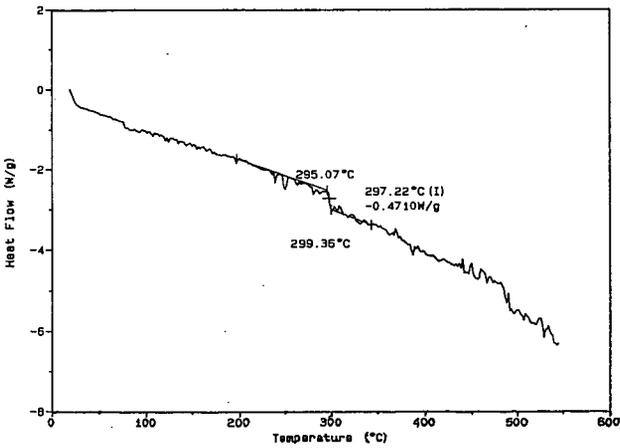


Figure 1. DSC Curve of Dry, Whole Illinois #6 Coal.

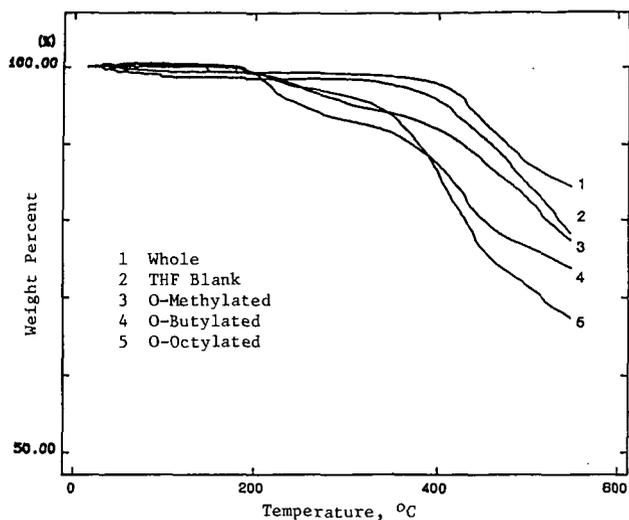


Figure 2. TGA Curves of Illinois #6 Coals.

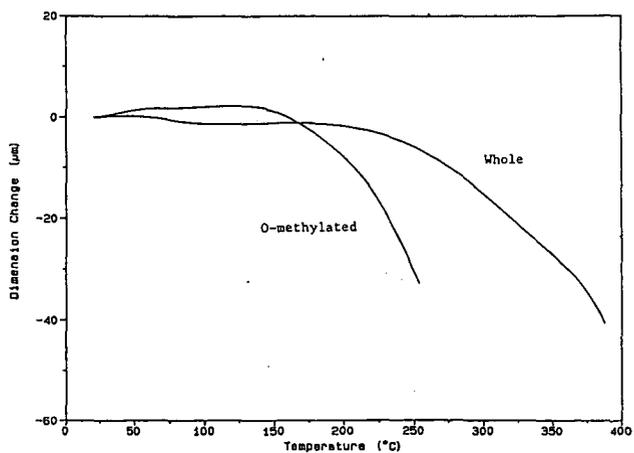


Figure 3. TMA Curves of Illinois #6 Coals

DISTRIBUTION OF ORGANIC SULFUR IN RAW AND SOLVENT EXTRACTED COALS

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INTRODUCTION

The removal of organic sulfur from coal presents the most serious challenge in coal desulfurization. Before efficient chemical processes can be developed for the removal of organic sulfur, information on the nature and distribution of sulfur-containing organic compounds in coal is needed.

The general nature of the organosulfur constituents known to exist in coal and coal-derived products have been briefly reviewed (1-4). Most of the literature about organosulfur compounds in coal is qualitative in nature. It is generally accepted that the predominant organic sulfur species present in coal are aromatic groups containing thiophenic sulfur. However, the percentages of thiophenic sulfur in various types of coals are not known. The presence of sulfur containing functional groups such as thiols and sulfides in various coals is also accepted by most coal scientists. However, the percentages of these groups in the various types or ranks of coal are not known. The presence of disulfide groups (R-S-S-R') in some coals is not generally accepted by coal scientists, although there is evidence that such groups may be present in coals (5). The quantitative determination of the various organic sulfur groups present in different types of coal is an area of coal research that has not received the attention it deserves.

Most of the work on characterizing the organic sulfur compounds in coal has been concentrated on studies of the thiophenic compounds, which are the most stable of the organic species present in coal. The thiophenic sulfur compounds are also the most difficult organosulfur compounds to remove from coal. Evidence in the literature and from our own work indicates that as much as 45% of the organosulfur compounds in mid-rank coals is aliphatic in nature, and contains various sulfidic and thiolic groups (5-10). Attar and coworkers used thermokinetic analysis to determine the proportions of thiolic, thiophenic, aliphatic sulfidic, aryl sulfidic, and thiophenic sulfur in five coals (2,3,6). These investigators estimated that 15-30% of the organic sulfur in coal is sulfidic, while 30-55% of the organic sulfur in lignite and 40-60% in bituminous coals is thiophenic. The remaining organic sulfur is assumed to be thiolic in nature. Yurovski used a classical approach to determine the types of organosulfur compounds in alcoholic solutions of phenol extracts of coal (5). In a study with a Russian coal Yurovski determined that about 48% of the organosulfur compounds in the coal were thiophenic in nature, while the remaining organosulfur compounds consisted of a mixture of thiols, sulfides, and maybe disulfides. George and Gorbaty used x-ray absorption near-edge structure (XANES) spectroscopy to study the distribution of sulfur groups in a Rasa lignite and an Illinois No. 6 bituminous coal (8-9). They concluded the lignite contained $30 \pm 10\%$ sulfidic and $70 \pm 10\%$ thiophenic sulfur (8), whereas the Illinois No. 6 coal contained $60 \pm 10\%$

sulfidic and $40 \pm 10\%$ thiophenic sulfur (9). Huffman and coworkers used x-ray absorption fine structure (XAFS) spectroscopy to examine the structures of sulfur groups in several bituminous coals (10). They concluded that the organic sulfur compounds in bituminous coals were predominantly thiophenic in nature. The results for bituminous coals reported by Gorbaty and Huffman differ significantly.

Many of the difficulties encountered in the investigations of solid coals are reduced in the analysis of extracts and reaction products of the coals. Tetrahydrofuran, pyridine, and dimethylformamide are quite useful solvents for the extraction of coals. Buchanan reported the sequential extraction of pristine Illinois No. 6 coal, APCSP-3, with toluene, tetrahydrofuran, dimethylformamide, and pyridine provided an extract that contained 28% (by weight) of the coal and 29% of the organic sulfur (11). Calkins and coworkers used other solvents for selective sulfur extraction. He found that tetrahydrofuran was superior to acetonitrile, ethylenediamine, and pyridine for the extraction of organic sulfur compounds from a Pittsburgh No. 8 bituminous coal (12-13). Buchanan and coworkers reported that hot perchloroethylene extracts elemental sulfur, formed in the oxidation of pyrite, from bituminous coals (14). They also reported that no appreciable amount of organic sulfur was extracted by perchloroethylene.

There is a considerable amount of information in the literature to indicate that organic sulfur compounds can be preferentially extracted from bituminous coals. In this paper we are reporting the differences between the organic sulfur content in 25 bituminous coals and residues of these coals after extraction with tetrahydrofuran and dimethylformamide.

EXPERIMENTAL

Most of the coals used in the study are from the western Kentucky (Illinois Basin) coal field. A list of the seams and ranks of the 25 coals are given in Table 1. Coal 82071 is from the eastern Kentucky (Appalachian region) coal field and coal 82074 is from the Indiana Lower Block seam, which is also part of the Illinois Basin. The coals were collected for a USDOE-sponsored project conducted at Western Kentucky University and stored under nitrogen after preparation (15). Most of the coals are clean products collected at preparation plants with coals 82071, 82073, and 82074 being run-of-mine samples.

The coals were subjected to standard analysis by ASTM methods (16), or methods with equivalent or better precision, as follows: proximate analysis using the LECO MAC-400 moisture, volatile matter, and ash analyzer (ASTM D 5142); ultimate analysis using the LECO CHN-600 carbon, hydrogen, and nitrogen analyzer and the LECO SC-132 sulfur analyzer (ASTM D 4239). Analytical data for the raw coals are given in Table 1 and data for extracted coals are given in Tables 2 and 3. Organic sulfur was determined by the direct determination method developed in this laboratory (17).

Solvent extractions of the coals were carried out using standard Soxhlet extraction assemblies at the atmospheric reflux temperatures of the two solvents employed, N,N-dimethylformamide (DMF) and tetrahydrofuran (THF). Prior to extraction, -60 mesh (250 μm) samples of each coal were vacuum dried at 60°C for six hours. Ten gram samples of dried coal in cellulose Soxhlet thimbles were then extracted for periods of 20-24 hours. The extracted coals were then rinsed with refluxing methanol in the Soxhlet apparatus for 5-6 hours and vacuum dried at 150°C until the samples reached a constant weight (6-10 hours). The extracted samples used in this study were prepared by Lloyd and coworkers (15). The averages of the percent coal extracted in triplicate runs on the 25 coals by the two solvents are given in Table 4.

RESULTS AND DISCUSSION

As shown in Table 1, the coals used in the study are predominantly high volatile bituminous C (hvCb) coals. All except coals 82071 and 82074 are from the western Kentucky coal fields (Illinois Basin) and all except coals 82071, 82073, and 82074 are washed coals. The total sulfur in the raw coals ranged from 1.35% to 3.65%, as reported on a dry basis.

Extraction of coals with organic solvents such as DMF and THF remove organic matter with subsequent increases in the percent mineral matter in the coal residues. The data in Tables 2 and 3 show increases in the ash contents of the coal residues which are in proportion to the coal extracted by the solvents. The general decreases in carbon, hydrogen, and volatile matter percentages is consistent with this trend. A comparison of the dry oxygen values in Table 1 with those for the extracted coals in Tables 2 and 3 show general increases in oxygen upon extraction with the organic solvents. This is likely due to the enrichment of oxygen-containing mineral matter in the extracted coals.

The total sulfur values for the extracted coals increase from the enrichment of mineral matter (pyritic and sulfatic sulfur forms) in the residues, as can be seen by comparing the total sulfur values for the raw coals in Table 1 with those for the residues in Tables 2 and 3. The increases in total sulfur are greater for the DMF-extracted coals than those for the THF-extracted coals. This is to be expected since the total material extracted by DMF (mean percent extracted = 24.8%) is greater than that extracted by THF (mean percent extracted = 14.0%). When the organic sulfur values for the raw coals are compared to the organic sulfur values for the DMF- and THF-extracted coals, one can see that there is a reduction of the organic sulfur in the extracted coals. The last two columns in Table 4 illustrate the magnitude of the reduction in the organic sulfur values for the DMF- and THF-extracted coals, respectively. The mean difference between the organic sulfur in the raw coal and that in the DMF-extracted coals is 0.19% (absolute). This mean difference for the THF-extracted coals is 0.16%.

Using the mean organic sulfur values in the raw coals, the mean organic sulfur values in the DMF- and THF-extracted coals, and the extraction percentages, a mean value for the organic sulfur in the coal extracts can be calculated. The mean value for the organic sulfur (daf basis) in the 25 coals is 1.63%. The mean value for the organic sulfur (daf basis) in the DMF-extracted coals is 1.45% and for the THF-extracted coals is 1.47%. With a mean extraction percentage of 24.8% for DMF this means the calculated mean organic sulfur value in the DMF extracts of the 25 coals is 2.18%. Likewise, the mean extraction percentage of 14.0 for THF can be used to calculate a mean organic sulfur value of 2.61% in the THF extracts of the 25 coals. The calculated organic sulfur values in the extracts of the 25 coals represent a 33.7% enrichment of organic sulfur in the DMF extracts and a 60.1% enrichment of organic sulfur in the THF extracts.

The lower percentage enrichment of organic sulfur in the DMF extracts compared to that for the THF extracts is consistent with the observations of other researchers. DMF extracts a greater percentage of the coals (24.8%) than THF (14.0%). The first material extracted from coal is richer in sulfur, and possibly oxygen and nitrogen, than the material removed as the extraction proceeds (18).

The data in Tables 1-4 were plotted in various ways in attempts to identify any trends in the rate of extraction of organic sulfur from the 25 coals. The only apparent relationships found were weak correlations between the organic sulfur extracted by the solvents and some of the other sulfur values for the coals. Figure 1 does indicate that the rate of extraction of organic sulfur from the coals using THF as the solvent may be dependent on the daf organic sulfur in

the raw coals. The correlation coefficient for this line is a moderate 0.56. However, as shown in Figure 2, the regression line between the daf organic sulfur in raw coals and the amount of organic sulfur extracted from the coals by DMF does not indicate a similar trend and gives a very low correlation coefficient. Also, as indicated by the other regression line in Figure 2, there does not seem to be any relationship between the percent of coal extracted and the amount of organic sulfur extracted from the coals. The data for the extractions with THF also indicated no such relationship.

The data in Table 4 strongly indicates that organic sulfur is removed from the 25 coals by the two solvents and enriched in the extracts. The organosulfur compounds that are the most likely to be extracted by the solvents are aliphatic in nature. Attempts to show a correlation between the amount of organic sulfur removed and changes in carbon and hydrogen values that would be consistent with the extraction of aliphatic compounds were unsuccessful. Work with the extracts themselves is necessary to establish any such relationship. Future experiments to study extracts of the coals are planned.

CONCLUSIONS

In conclusion, it can be stated that the data presented here indicate that organic sulfur is often enriched in the DMF and THF extracts of bituminous coals. The amount of organic sulfur preferentially extracted by the two solvents is weakly related to the sulfur contents of the coals. The average enrichment of organic sulfur in the THF extracts of the coals was calculated to be about 60%, whereas that for the DMF extracts was about 34%. The average percent of coal extracted by the solvents was 14% for THF and about 25% for DMF. It is likely that the organosulfur constituents extracted by the two solvents are aliphatic in nature, but no such conclusions can be drawn from the data presented in this paper.

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REFERENCES

1. Stock, L.M.; Wolny, R.; Balkrichna, B.; Energy & Fuels, 1989, **3**, 651-61.
2. Attar, A.; Corcoran, W.H.; Ind. Eng. Chem. Prod. Res. Dev., 1977, **16**, 168-170.
3. Attar, A.; "Sulfur Groups in Coal and Their Determinations," Chap. 56 in Analytical Methods for Coal and Coke Products, Vol. III, Karr, C.K., Ed., Academic: New York, 1979.
4. White, C.M.; in Handbook of Polycyclic Aromatic Hydrocarbons; Bjorseth, A.; Ed.; Marcel Dekker: New York, 1983, Chap. 13, 525-616.

5. Yurovskii, A.Z.: Sulfur in Coals, Published for the U.S. Department of the Interior, Bureau of Mines and the National Science Foundation, by the Indian National Scientific Documentation Centre, New Delhi, 1974, 56-62.
6. Attar, A.; Dupuis, F.; "Data on the Distribution of Organic Sulfur Functional Groups in Coals," in Coal Structure, Gorbaty, M.L., and Ouchi, D., Eds., Advances in Chemistry Series 192, American Chemical Society: Washington, D.C., 1981.
7. Riley, J.T., et al., "Removal of Aliphatic Sulfur and Chlorine Compounds from Coal," Technical Reports 1-3, Center for Research on Sulfur in Coal, Carterville, IL, 1990.
8. George, G.N.; Gorbaty, M.L.; J. Am. Chem. Soc., 1989, 111, 3182.
9. George, G.N.; Gorbaty, M.L.; Kelemen, S.R.; Prepr. Pap. - Am. Chem. Soc., Div. Fuel. Chem., 1989, 34(3), 738.
10. Huffman, G.P.; Huggins, F.E.; Mitra, S.; Shah, N.; Pugmire, R.J.; Davis, G.; Lytle, F.W.; Greeger, R.B.; Energy & Fuels, 1989, 3, 200.
11. Buchanan, D.H.; Osborne, K.R.; Warfel, L.C.; Wanping, M.; Lucas, D.; Energy & Fuels, 1988, 2, 163.
12. Calkins, W.H.; Energy & Fuels, 1987, 1, 59.
13. Calkins, W.H.; Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem., 1985, 30(4), 450.
14. Buchanan, D.H.; Chanen, C.; Puharich, K.; Warfel, L.C.; Hackley, K.C.; Kruse, C.W.; "Organic Sulfur Removal from Illinois Coal," Final Tech. Rept., Center for Research On Sulfur in Coal, Carterville, IL, October, 1990.
15. Lloyd, W.G.; Reasoner, J.W.; Hower, J.C.; Yates, L.P.; Clark, C.P.; Davis, E.; Fitzpatrick, A.; Irefin, A.; Jiminez, A.; Jones, T.M.; Reagles, C.L.; Sturgeon, L.P.; Whitt, J.M.; Wild, G.D.; Predictors of Plasticity in Bituminous Coal, " Final Rept., USDOE Contract No. DE-FG22-81PC40793, February, 1984.
16. Annual Book of ASTM Standards, Vol. 5.05, Amer. Soc. for Testing and Materials, Philadelphia, PA (published annually).
17. Riley, J.T.; Ruba, G.M.; Lee, C.C.; "Direct Determination of Total Organic Sulfur in Coal," in Geochemistry in Sulfur in Fossil Fuels, W.L. Orr and C.M. White, Eds., ACS Symposium Series No. 429, American Chemistry Society: Washington, D.C., 1990.
18. Buchanan, D.H.; Eastern Illinois University, Charleston, IL, private communication.

Table 1

Source and Characterization Data^a for Coals Used in the Study

Coal No.	Seam	Apparent Rank ^b	Moisture	Vol. Matt.	Ash	C	H	N	Total Sulfur	O (by diff.)
82074	IN L. Bl.	hVcB	10.46	35.0	8.77	73.42	5.03	1.51	1.72	9.56
82049	Elm Lick	hVcB	6.95	35.6	5.48	78.42	5.29	2.03	1.89	6.89
82048	KY #9	hVcB	8.73	37.1	9.21	72.49	4.88	1.64	3.17	8.61
82050	Bancroft	hVbB	2.81	39.8	5.95	75.97	5.11	1.36	3.12	8.49
82077	KY #11	hVcB	7.77	37.2	8.05	74.06	5.07	1.60	3.37	7.84
82060	KY #9	hVbB	7.06	36.6	7.86	73.80	4.97	1.64	2.87	8.87
82056	KY #9	hVcB	7.11	36.5	8.19	76.12	4.98	1.67	3.05	5.99
82080	KY #11	hVcB	8.40	38.1	6.38	74.78	5.10	1.62	3.35	8.78
82071	Mason	hVAb	3.24	34.3	7.07	78.37	5.01	1.61	1.35	6.59
82066	KY #11/12	hVcB	8.13	36.9	9.39	72.75	4.88	1.36	3.10	8.51
82051	Bancroft	hVbB	3.08	38.9	6.43	75.26	5.06	1.31	2.73	9.21
82067	KY #9	hVbB	2.83	36.1	8.85	72.87	5.05	1.56	2.86	8.81
82076	KY #9/11	hVcB	7.56	37.4	8.76	70.81	5.07	1.46	3.65	10.25
82063	KY #9	hVcB	7.92	36.3	8.30	73.74	4.95	1.63	3.37	8.02
82061	KY #9	hVcB	6.77	36.3	10.77	70.87	4.82	1.43	3.43	8.69
82064	KY #9	hVcB	7.49	36.5	7.95	76.31	4.81	1.64	3.12	6.17
82073	KY #9	hVAb	2.81	36.0	8.23	75.06	5.10	1.70	3.56	6.35
82062	KY #9	hVcB	5.96	36.8	8.51	72.94	4.86	1.60	3.09	9.00
82057	KY #14	hVcB	7.56	32.7	21.13	61.03	4.39	1.23	3.33	8.89
82069	KY #6	hVAb	2.74	35.3	8.78	76.02	4.96	1.62	2.59	6.02
82058	KY #14	hVcB	5.59	33.6	17.73	64.12	4.47	1.05	3.27	9.35
82052	Bancroft	hVcB	3.09	39.5	6.80	75.47	5.00	1.15	3.06	8.52
82059	KY #9	hVbB	6.38	36.5	9.15	74.33	4.92	1.75	3.39	6.46
82047	KY #9	hVcB	11.56	37.3	10.97	71.29	4.94	1.59	3.43	7.78
82054	KY #9	hVcB	8.30	37.5	8.15	74.73	5.07	1.68	3.30	7.07

^a Moisture is as-determined, other analytical values are on a dry basis. All values are percentage by weight.^b Apparent rank using as-determined moisture for calculation.

Table 2

Analytical Values^A for DMF-Extracted Coals

Coal No.	Vol. Matt.	Ash	C	H	N	Total Sulfur	O (by diff.)
82074	33.0	10.28	72.44	4.62	1.72	1.74	9.19
82049	33.5	6.90	74.50	4.76	7.70	2.14	4.00
82048	34.1	11.92	67.26	4.52	1.83	3.68	10.80
82050	37.6	7.74	72.22	4.75	2.14	3.54	9.61
82077	33.7	10.17	71.40	4.52	1.64	3.57	8.69
82060	33.0	10.67	71.18	4.42	2.00	3.12	8.60
82056	34.9	10.34	70.60	4.80	2.41	3.13	8.72
82080	34.9	7.99	71.10	4.71	1.55	3.31	11.33
82071	30.8	9.41	74.64	4.64	2.12	1.52	7.68
82066	32.9	11.55	67.14	4.64	2.02	3.21	11.44
82051	35.7	7.86	69.04	4.89	2.06	2.94	13.21
82067	32.2	12.50	69.08	4.74	1.54	3.26	8.88
82076	33.7	10.69	68.91	4.64	1.75	3.60	10.41
82063	32.6	10.39	68.46	4.21	1.72	3.40	11.82
82061	33.3	13.82	65.50	4.47	1.95	3.68	10.59
82064	32.0	9.74	69.74	4.27	2.30	3.13	10.83
82073	31.6	12.36	70.90	4.49	1.37	4.24	6.83
82062	33.2	11.09	70.33	4.54	1.60	3.23	9.21
82057	30.1	26.64	56.12	3.87	1.65	3.56	8.16
82069	31.3	12.33	71.18	4.55	1.53	3.07	7.35
82058	31.0	23.46	56.53	4.16	1.61	3.55	10.70
82052	40.3	9.28	70.47	5.22	2.14	3.42	9.46
82059	33.4	11.96	69.01	4.39	1.98	3.91	8.75
82047	34.2	13.64	67.54	4.39	1.69	3.96	8.79
82054	35.9	10.39	69.40	4.73	1.83	3.55	10.09

^A Analytical values are reported as percentage by weight on a dry basis.

Table 3

Analytical Values^A for THF-Extracted Coals

<u>Coal No.</u>	<u>Vol. Matt.</u>	<u>Ash</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>Total Sulfur</u>	<u>O (by diff.)</u>
82074	28.4	7.95	72.09	4.79	1.39	1.42	12.36
82049	36.0	5.94	73.45	5.46	1.89	2.05	11.21
82048	36.6	10.47	68.62	5.07	1.51	3.41	10.92
82050	39.4	6.78	72.55	5.43	1.58	3.28	10.38
82077	34.5	8.89	71.94	4.71	1.33	3.60	9.53
82060	33.2	9.11	78.88	4.03	1.74	2.99	3.25
82056	35.2	9.56	70.27	5.17	2.10	3.22	9.68
82080	35.7	7.18	73.37	5.03	1.54	3.48	9.40
82071	32.4	7.70	77.11	5.20	1.90	1.47	6.62
82066	33.9	10.80	70.19	4.80	1.70	3.27	9.24
82051	39.7	7.14	71.66	5.52	1.78	3.13	10.77
82067	32.4	10.18	73.44	4.92	1.46	3.10	6.90
82076	34.5	9.84	71.23	5.00	1.66	3.82	8.45
82063	33.2	9.37	71.17	4.69	1.63	3.45	9.69
82061	33.7	12.25	69.93	4.68	1.72	3.69	7.73
82064	32.3	8.95	70.66	4.41	1.96	3.29	10.73
82073	32.7	9.85	73.86	4.91	1.47	3.89	6.02
82062	33.7	9.96	72.18	4.71	1.91	3.28	7.96
82057	31.2	23.53	60.67	4.16	1.44	3.48	6.72
82069	32.3	9.73	74.29	4.96	1.59	2.77	6.66
82058	33.1	19.59	60.76	4.45	5.78	3.34	6.08
82052	39.2	8.40	71.69	5.43	1.38	3.29	9.81
82059	30.6	9.68	66.89	3.13	1.71	3.37	15.25
82047	36.5	11.99	66.83	4.85	1.49	3.62	11.22
82054	36.0	9.50	70.27	5.18	1.95	3.56	9.54

^A Analytical values are reported as percentage by weight on a dry basis.

Table 4
Extraction Percentages and Organic Sulfur Values for Extracted Coals

Coal No.	% Coal ^A Extracted-DMF	% Coal ^A Extracted-THF	Raw Coal Org. S ^B	DMF-Ext. ^B Coal Org. S	THF-Ext. ^B Coal Org. S	Raw - DMF-Ext. Org. Sulfur	Raw - THF-Ext. Org. Sulfur
82074	18.7	10.7	0.76	0.54	0.78	0.22	-0.02
82049	18.7	13.4	0.84	0.62	0.83	0.22	0.01
82048	22.5	12.0	1.66	1.76	1.64	-0.10	0.02
82050	22.7	14.6	0.85	0.86	0.82	-0.01	0.03
82077	24.1	14.2	1.93	1.75	1.89	0.18	0.04
82060	32.3	17.2	1.82	1.63	1.74	0.19	0.08
82056	22.1	13.4	1.62	1.21	1.52	0.41	0.10
82080	23.0	15.4	2.03	1.98	1.92	0.05	0.11
82071	27.3	11.0	1.00	0.64	0.89	0.36	0.11
82066	23.1	15.6	1.80	1.86	1.68	-0.06	0.12
82051	21.1	12.6	0.95	0.88	0.83	0.07	0.12
82067	31.9	16.3	1.75	1.63	1.62	0.12	0.13
82076	23.0	14.5	1.98	2.07	1.83	-0.09	0.15
82063	23.5	13.9	1.70	1.60	1.55	0.10	0.15
82061	23.4	13.3	1.95	1.80	1.77	0.15	0.18
82064	21.0	13.3	1.74	1.63	1.56	0.11	0.18
82073	34.2	16.3	1.88	1.81	1.69	0.07	0.19
82062	26.4	14.9	1.89	1.79	1.67	0.10	0.22
82057	24.6	13.3	1.66	1.08	1.42	0.58	0.24
82069	33.0	14.2	1.54	1.36	1.30	0.18	0.24
82058	24.6	12.7	1.85	1.25	1.57	0.60	0.28
82052	22.6	17.4	1.91	1.59	1.63	0.32	0.28
82059	28.4	15.3	1.98	1.29	1.66	0.69	0.32
82047	24.2	12.8	1.83	1.85	1.66	-0.02	0.33
82054	22.9	12.4	1.90	1.65	1.50	0.24	0.40

^A Dry coal basis.

^B Dry, ash-free basis.

Figure 1. Organic Sulfur in Raw Coal vs. Organic Sulfur Extracted by THF

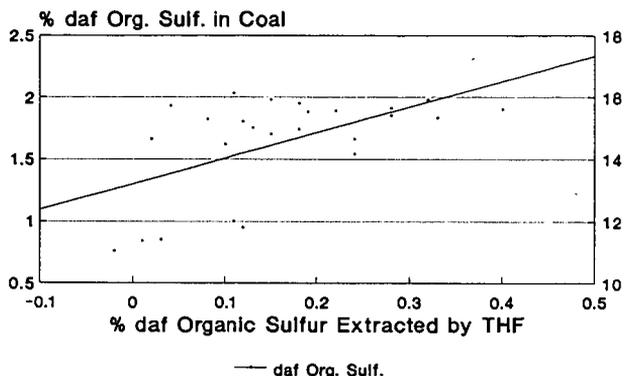
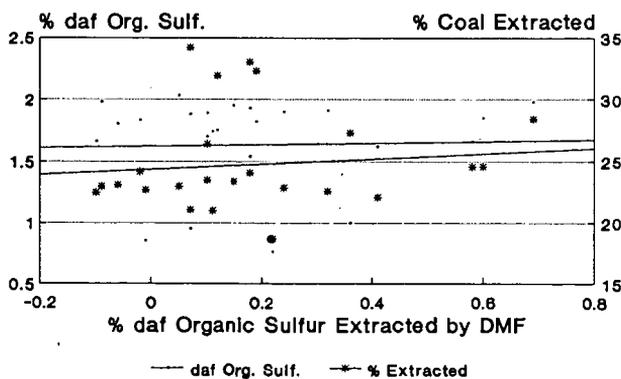


Figure 2. Organic Sulfur in Raw Coal vs. Organic Sulfur Extracted by DMF



EVALUATION OF COMBINATION FUELS FOR FLUIDIZED BED COMBUSTORS BY THERMAL ANALYTICAL TECHNIQUES

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Key words: thermogravimetry, coal, municipal solid wastes, fluid bed combustion

ABSTRACT

The objective of this study is to find suitable combinations of coal fines, municipal solid waste (MSW), and limestone to produce fuel pellets for fluidized bed combustion systems. The coal fines, MSW (paper), and sorbent limestone were mixed in different combinations and the volatile matter and char contents of all mixtures, as well as the original materials, were evaluated by thermogravimetric analysis (TGA). Using different rates of heating and variable atmospheres, information was obtained that can be useful in predicting the combustion behavior and efficiency of the combination fuels. Optimum limestone content can be determined by selectively introducing CO_2 during the final stages of the combustion process to check for excess CaO . The use of combined techniques such as TGA, differential thermal analysis (DTA), and TGA-FTIR can be utilized to determine detailed information on the combustion and thermal properties of the combination fuels.

INTRODUCTION

More than 150 million tons of municipal solid waste (MSW), are generated in the United States each year. This excessive amount of generated waste, combined with decreases in landfill sites, causes serious environmental problems and forces the establishment of programs for reducing the volume of waste deposited in landfills.

Mass burning of unprocessed MSW and preparation/firing of refuse-derived fuel (RDF), are the two main methods currently being evaluated for waste-to-energy technologies (1,2). There are several methods used for the firing of RDF. The chief method employed in this study is fluidized bed combustion. Fluidized bed combustion systems are particularly suited to waste fuels because of their ability to burn low grade and variable fuels as well as absorb sulfur oxides through the use of sorbents.

Fluidized bed combustion systems have been constructed in the U.S., Europe, and Japan, for the burning of RDF alone or combinations of RDF and wood waste (3). However, there is little or no information available regarding RDF firing in the presence of coal in fluidized bed combustion systems, or co-firing of wood wastes with coal. There have been several studies conducted on the preparation of fuel

pellets using coal fines and limestone, which serves as a sorbent for sulfur oxides (4-6). This information was valuable in the evaluation of the combustion performance of fuel pellets prepared from coal fines, MSW or wood waste, and limestone sorbent.

The burning profiles of coal and RDF are quite different, but there is a high probability that blends of these two fuels, when co-fired under the right conditions, perform suitably as a boiler fuel. This conjecture forms the basis of the study reported in this paper.

In general, normal production of coal yields millions of tons of coal fines each year (about 20% of total yield). These fines, however, can not be sold because of handling problems. The cost of recovery of these fines is small compared to the mining of coal. Coal fines are an excellent source of an energy-rich fuel that can be blended with RDF to produce pellets suitable for use in fluidized bed combustion systems.

When coal contains high amounts of organic sulfur it is impossible to remove the sulfur using conventional physical cleaning methods. Fluidized bed combustion systems utilizing coal-limestone-fuel mixtures have the potential for resolving this limitation since limestone, which is abundant in nature, can be used as a sorbent for emitted SO_2 .

SAMPLE PREPARATION AND RESULTS

Thermal Analysis of Raw Materials

The materials used for this study are coal fines (Illinois #6), Kentucky agricultural limestone, and newspaper. All samples were prepared and analyzed in Western Kentucky University's Coal and Fuel Characterization Lab. The three materials were studied by thermogravimetric analysis (TGA) to assess their thermal behavior. The TGA experimental conditions used were 10 mg sample size, air atmosphere with a flow of 50 mL/min, and a heating rate of 20°C/min. The instrument used was a Shimadzu HT 1500 TGA Thermogravimetric Analysis System.

Test results for the three materials are shown in Figure 1. The TG curve for coal depicts two weight loss stages, the first consisting of a 3.09% moisture loss followed by a second weight loss of 85.25% containing two overlapping DTG peaks. The first DTG peak is a result of the combustion of aliphatic materials in coal and the second is due to the combustion of the aromatic materials of coal. $T_{\text{Max}1}$ and $T_{\text{Max}2}$ occur at 417°C and 440°C, respectively.

Figure 1 also shows two decomposition stages for limestone. There is an initial moisture loss of 1.73% beginning at 397°C and a second weight loss of 40.95% beginning at 563°C. This is due to limestone being converted to CaO and CO_2 gas. R_{Max} (mg/min), was 0.76 at 817°C. Experimental conditions were identical to that used for coal.

Finally, Figure 1 represents three major weight loss stages for newspaper with the first being a moisture loss of 4.35%. The second weight loss of 88.57% represents the major decomposition of materials in newspaper and has an R_{Max} of 5.34 at 353°C. The overlapping peak is shown on the DTG curve and represents the decomposition of impure cellulosic materials with higher lignin content in the newspaper. The third and last weight loss phase of 5.91% is due to char gasification and has a small peak at 475°C. Experimental parameters were again identical to those used in the TG analysis of coal. It is evident from the TG curve that newspaper decomposes 150°C earlier than coal. Total weight losses of

coal, limestone, and newspaper (established on a moisture free basis), were 88%, 42.7%, and 98.8%, respectively.

Thermal Analysis of Coal-Limestone Mixtures

In order to decide upon an optimum amount of limestone for the combination fuels for the fluidized bed combustor, mixtures of coal and limestone were tested by TGA. Testing procedures preceding 800-850°C were identical to those previously examined. However, after 800°C or 850°C, temperatures were held constant for 5 minutes, the atmosphere was changed to CO₂ gas for 25 minutes, and a determination was then made as to the amount, if any, of weight gain that occurred (See Figure 2). If a weight gain did occur, this indicated that an excess of CaO was in the residue and was converted back to CaCO₃ when the CO₂ was added. If a weight gain did not occur, this indicated that all of the CaO reacted with the SO₂ to produce CaSO₄, leaving no excess CaO in the residue. This method was developed by R.F. Culmo and R. L. Fyans (7).

Next the optimum temperature at which the limestone completely decomposed needed to be determined. A 5% limestone, 95% coal mixture was used to obtain the suitable temperature values. The TG results show that there is no significant weight changes above 800°C. Therefore 800°C and 850°C were chosen for the isothermal temperature values for test runs.

Using the chosen optimum temperature values, the optimum limestone percentage needed to be determined. To accomplish this goal, different percentages of limestone (0,1,2,3,4,5, and 10%), were added to the coal. The results of these tests, as shown in Figure 3, indicate a suitable limestone percentage is between 1% and 3%. A plateau in the weight gain curve occurs between 1-3% and increases significantly with increased amounts of limestone (excess CaO). Thus, 2% limestone was chosen for the following study. It should be recognized that excess limestone will reduce the flame temperature in the fluidized bed combustion system and also increase the operational costs.

Considering that the heating rate is higher in fluidized bed combustors than that used in the experimental tests used thus far, higher heating rates for tests were chosen to observe the effect heating rates may have on the decomposition of the fuel mixtures. Heating rates of 20°C/min, 35°C/min, 40°C/min, and 50°C/min were chosen for additional experiments. These heating rates were used with 2%, 5%, and 10% limestone percentages. The TG results indicate the weight gain, due to absorbed SO₂, at different heating rates and limestone percentages was not significantly affected under these specific experimental conditions.

A determination of the change in weight loss during combustion as a function of varying coal-limestone mixtures was made. It was determined that the 2% limestone did not show any catalytic effect on the first thermodecomposition stage of coal. Similar results were obtained for the second thermodecomposition stage.

Finally, the effect of limestone on the thermal behavior of the mixture with respect to changes in the parameters T_{max} and R_{max} was determined. The TG results indicate that at heating rates of 20°C/min and increased limestone content, T_{max1} and T_{max2} shift to slightly higher temperatures. The TG curve also shows that R_{max1} and R_{max2} slightly decrease with increased limestone percentage. Both TG curves present the same results; higher limestone content may delay the decomposition and combustion slightly as T_{max} increases and R_{max} decreases.

Thermal Analysis of Combination Fuels

The combination fuels tested consist of coal, limestone, and newspaper (RDF), in varying percentages. According to the results of the preliminary

studies, it is believed that a 2% limestone content in the mixture is sufficient for absorbing the SO_2 emitted for the burning of the coal tested. The mixtures of coal, limestone, and newspaper are 90/2/8, 80/2/18, and 70/2/28, respectively.

The general TG curve of the combination fuel is shown in Figure 4. There were four thermodecomposition stages observed, excluding the moisture loss. The T_{Max} for each stage was 283, 384, 450, and 489°C. It is believed that the first and second stages are due to the decomposition of newspaper, with the first being mainly due to cellulosic materials and the second to lignin content. Previously, Figure 1 indicated that there was one overlapping DTG peak with $T_{\text{Max}} = 352^\circ\text{C}$. In the case of the combination fuel, however, the overlapping peak noted in Figure 1 became two separate peaks, and the first peak occurred 70°C earlier than noted for the newspaper alone. This may be due to reduced sample particle size that occurred during the grinding and preparation of the combination fuel. The third and fourth decomposition stages are due to the thermodecomposition of coal. However, the third stage was enhanced by two possible factors: (1) additional char gasification from the newspaper and/or (2) catalyzation of the char gasification by the limestone. The results for T_{Max} , R_{Max} versus newspaper content are shown in Table 1.

To better understand and further verify the proposed mechanisms involved in the TG curve analysis, 50% coal/50% newspaper, 50% newspaper/50% limestone, and 50% coal/50% limestone test mixtures were also studied.

The TG and DTG curves of the 50% limestone/50% newspaper indicate three thermodecomposition stages with the first two peaks being due to the thermodecomposition of newspaper. The third peak was due to the decomposition of limestone. T_{Max} for peak one did not significantly change compared to that for 100% newspaper. R_{Max} , however, decreases by 20%. T_{Max} of peak two did not show any significant change. However the value of R_{Max} was five times greater than 100% newspaper. This might be due to the catalytic effect on char gasification. It is presently unknown why the third peak shifted 10°C earlier than 100% limestone; however, R_{Max} values were similar.

One may assume that the experimental values such as those listed in Table 2 may be used to predict the effects of varying amounts of limestone by utilizing known decomposition values for pure limestone and pure newspaper. However, in this case, there were significant differences between calculated (predicted) values and those obtained through experimentation. The first peak was retarded by the calcium, yielding lower weight loss values, and the second peak is influenced by a catalytic effect from the calcium. The third weight loss phase, however, was not effected because it was only due to the decomposition of limestone.

The TG results for 50% coal/50% limestone showed two thermodecomposition stages. The first peak, a combination of two overlapping peaks, shifted 20°C higher than that for 100% coal. Again, the third peak, due to the thermodecomposition of limestone, occurred 20°C lower than that for 100% limestone. Likewise, R_{Max} for peak one was reduced by 50% compared to that for 100% coal. The TG results of 50% coal/50% newspaper showed three thermodecomposition stages with the first peak being due to newspaper, the second peak due to coal, and the third peak due to char gasification combined with less combustible materials from coal.

From reactivity studies, it can be concluded at this point in the analysis that the addition of limestone retarded the decomposition of coal and newspaper in the early stages, and then promoted the char gasification in the later stages due to the catalytic effect of calcium.

Ongoing research with combinations of TGA-FTIR and DTA techniques will provide a better understanding of the overall decomposition and combustion processes for coal-RDF-limestone fuels.

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REFERENCES

1. McGowin, C.R.; Petrill, E.M.; Peřna, M.A.; Rowley, D.R.; "Fluidized Bed Combustion Testing of Coal/Refuse-Derived Fuel Mixtures," Babcock and Wilcox, Report from EPRI Project RP718-2 (1989).
2. Hickman, C.E.; Center for Electric Power, Tennessee Technological University, personal communication.
3. "Summary of Recent Literature Pertaining to the Incineration of Municipal Solid Wastes," prepared by the Center for Environmental Information, Inc., NYSEG contract No. 87-372 (August, 1988).
4. Conkle, H.N.; Dawson, W.J.; Rising, B.W.; "Reconstitution of Coal and Limestone for Use in Industrial Stoker Boilers," paper presented at the 18th Biennial Conference of the Institute of Briquetting and Agglomeration, Colorado Springs, CO (August, 1983).
5. Giammar, R.D.; Hopper, D.R.; Radhakrishnan, E.; Webb, P.R.; "Evaluation of Emission from Industrial Stoker Boilers," presented at AIChE meeting, Boston, MA (August, 1979).
6. Rising, B.W.; Conkle, H.N.; Dawson, W.J.; Litt, R.D.; "Advanced Development of a Coal/Limestone Fuel Pellet for Industrial Boilers," Contract No. 68-02-3189, Final Report from Battelle's Columbus Laboratories for the U.S. EPA (October, 1983).
7. Culmo, Q.R.F.; Fyans, R.L.; "Thermogravimetry as a Tool for Determining Combustion Efficiency and Calcium Utilization of a Fluidized Bed Combustion Furnace" in Compositional Analysis by Thermogravimetry, C.M. Earnst, Ed., ASTM STP997, American Society for Testing and Materials, Philadelphia, PA, 1988, pp. 245-55.

Table 1
 T_{Max} and R_{Max} vs. Newspaper Content

	<u>8% Newspaper</u>	<u>18% Newspaper</u>	<u>28% Newspaper</u>
T_{Max1}	283	290	287
T_{Max2}	384	385	384
T_{Max3}	450	451	454
T_{Max4}	489	490	492
R_{Max1}	1.66	2.20	2.68
R_{Max2}	2.12	2.08	1.92
R_{Max3}	1.29	1.29	1.60
R_{Max4}	0.53	0.49	0.49

Table 2
 Calculated Values for Weight Loss of 50% Newspaper/50% Limestone

<u>Temp. °C</u>	<u>Tested Values %</u>	<u>Calculated Values</u>		<u>Difference %</u>
		<u>Newspaper</u>	<u>Limestone</u>	
150-381	37.05	42.12	0.015	-5.09
381-539	13.16	3.10	0.825	9.24
539-800	<u>20.77</u>	<u>0.10</u>	<u>20.5</u>	<u>0.17</u>
Total	71.04	49.4	22.1	-0.46

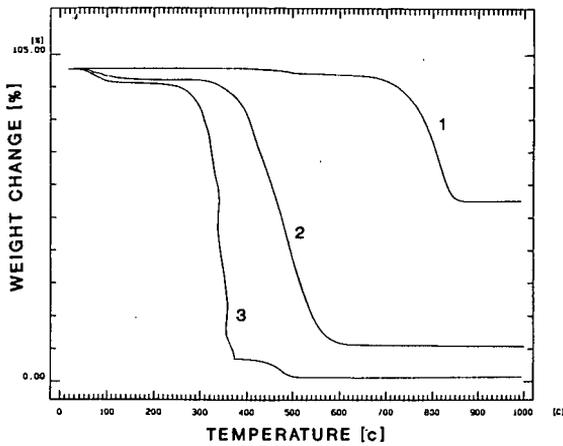


Figure 1. The TG Curves of three original samples
1-limestone; 2-coal; 3-newsprint;

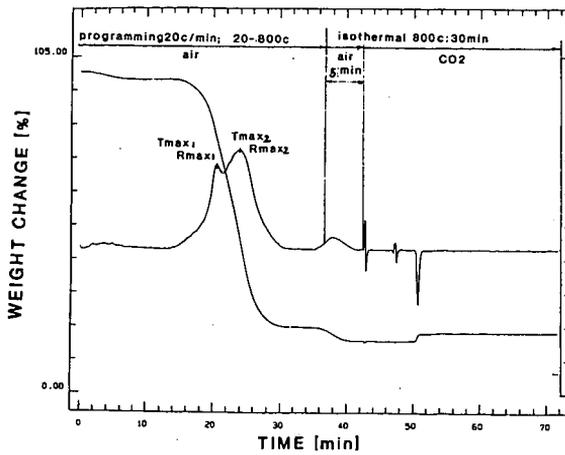


Figure 2. TGA analysis of coal/limestone mixtures

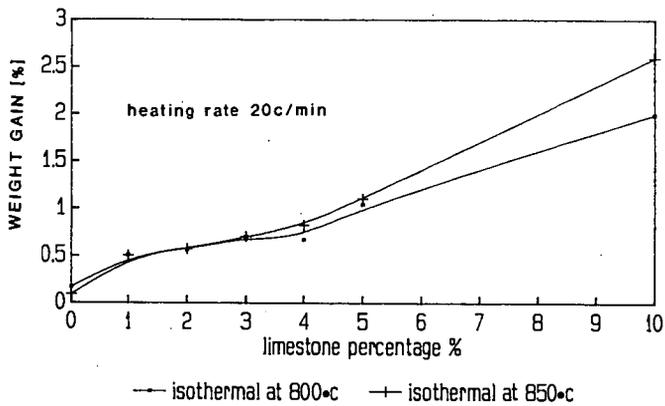


Figure 3. Weight gain vs. limestone percentage

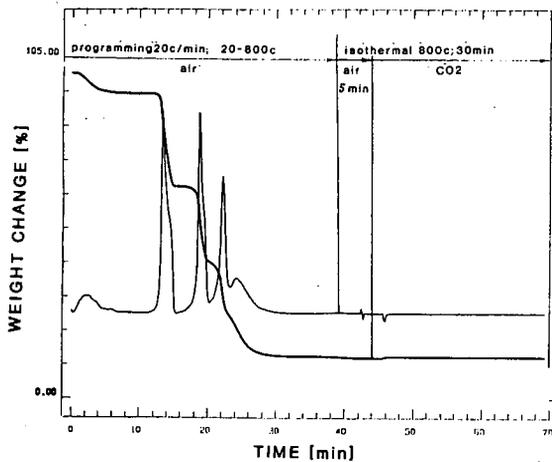


Figure 4. TGA analysis of combination fuels(C+L+N)

ARENECHROMIUM COMPLEXES IN COAL

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Keywords: Coal, Chromium, Hydrogenation.

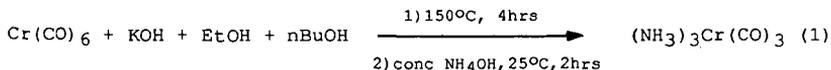
Introduction

When an arene is coordinated to $\text{Cr}(\text{CO})_3$, profound changes in its reactivity occur^{1,2}. Ring and benzylic hydrogen atoms exhibit enhanced acidity, and typical arene reactions such as electrophilic aromatic substitutions are quenched. In contrast, the ring carbon atoms are activated toward attack by nucleophiles¹. These changes in reactivity are manifestations of the forceful electron withdrawing nature of the $\text{Cr}(\text{CO})_3$ component, and of the ability of this group to stabilize charged intermediates. In addition, arenechromium tricarbonyl complexes have been proven to be good catalysts in the hydrogenation of dienes³. While most simple complexes such as toluenechromium tricarbonyl require the use of high temperatures and dihydrogen pressures, arenechromium tricarbonyl complexes with naphthalene, anthracene, and phenanthrene show remarkable activity under extremely mild conditions. Coal arenechromium tricarbonyl complexes may prove to be good internal hydrogenation catalysts for the hydrogenation of surrounding molecules.

Results and Discussion.

Experiments were carried out with a coal liquid in this exploratory investigation to avoid solubility problems inherent in the use of solid coals. The coal liquid used was distilled at approximately 850°C from run 250D at the Wilsonville pilot plant with Illinois No. 6 coal. In contrast to solid coals and heavy distillates, this material is soluble in all common organic solvents.

The first stage of research centered on the conversion of the aromatic hydrocarbons in the coal liquid into arenechromium tricarbonyl complexes. Reactions to form complexes with the coal liquid were carried out by a procedure for simple molecules in which the arene is refluxed in dioxane with chromium hexacarbonyl. However, this method required long reaction times and large excesses of chromium hexacarbonyl to achieve acceptable levels of complexation. To alleviate these problems, the use of an alternative reagent, triaminechromiumtricarbonyl, was investigated. This reagent is easy to synthesize⁵, equation 1, and has been used

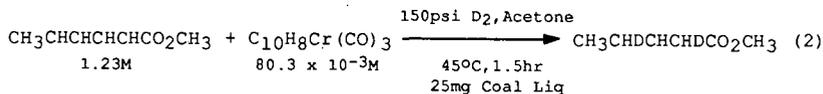


to obtain several organochromium complexes⁶. Reactions of the coal liquid with triaminechromiumtricarbonyl proved to be very successful. High yields of complexation with the coal liquid arene molecules were obtained. Indeed, the product was orange colored and crystalline in nature. The ¹³C NMR spectrum of one such product is shown in Figure 1. The carbonyl resonance appears at 234 ppm and

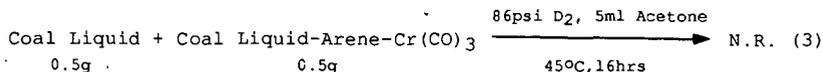
the aromatic carbon resonances shift to 80-100 ppm as anticipated.

The second stage of the investigation centers on hydrogenation transfer chemistry of the coal liquid arenechromium tricarbonyl complexes. Studies have been carried out with simple arenechromium tricarbonyl complexes^{1,7} as catalysts in the hydrogenation of methyl 2,4-hexadienoate in which the severity of reaction conditions varied from 150°C at 700 psi dihydrogen pressure for toluenechromium tricarbonyl to 27°C at 57 psi dihydrogen pressure for naphthalenechromium tricarbonyl. The dramatic increase in activity of the polycyclic arenechromium tricarbonyl complexes is that there are two long Cr-C bonds with the bridgehead carbon atoms that have bond orders less than one⁸. Thus, the longer and weaker bonds should be more easily displaced by the incoming diene ligand in the rate determining step. This advantage is not realized in the case of the monocyclic arenechromium tricarbonyl complexes such as benzenechromium tricarbonyl where all of the Cr-C bonds have equal length with bond orders close to unity. The effect of solvent was also examined. Coordinating solvents such as tetrahydrofuran or acetone increased the rate of the hydrogenation reaction presumably by facilitating the initial ligand substitution step.

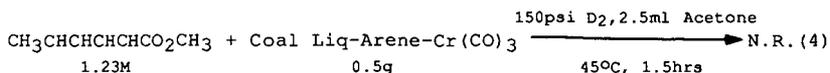
Hydrogenation reactions were carried out under mild conditions in a glass microhydrogenation apparatus at pressures lower than 200 psi and temperatures less than 50°C using dideuterium gas. The use of dideuterium allows the reduction step to be detected by means of deuterium NMR. A hydrogenation reaction was carried out with naphthalenechromium tricarbonyl to catalyze the hydrogenation of methyl 2,4-hexadienoate in the presence of small amount of coal liquid to test whether or not the coal liquid would poison the catalyst. This reaction, equation 2, proved to be successful with a



63% conversion of methyl 2,4-hexadienoate to methyl hex-3-enoate-2,5-d₂. It was evident that the presence of the coal liquid does nothing significant to inhibit the catalyst. The next set of experiments were carried out with the coal liquid arenechromium tricarbonyl complexed material. The coal liquid arenechromium tricarbonyl complexed material proved to be unsuccessful in catalyzing the hydrogenation of the surrounding molecules. In part, this could be due to the fact that all of the possible active sites for hydrogenation may of have been rendered unreactive by complexation with Cr(CO)₃. To test this line of reasoning, experiments were carried out on a mixture of the coal liquid arenechromium tricarbonyl complex and unreacted coal liquid as shown in equation 3. Analysis of the ²H NMR spectrum of the coal liquid arenechromium tricarbonyl reaction product showed that no significant deuteration had taken place.

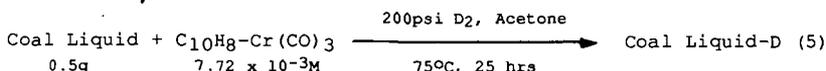


In order to clearly test the catalytic activity of the coal liquid arenechromium tricarbonyl complex, experiments were carried out with methyl 2,4-hexadienoate as the substrate and the coal liquid arenechromium tricarbonyl complex as the catalyst as shown in equation 4. The ^2H NMR of the reaction product showed the coal liquid and unreacted methyl 2,4-hexadienoate indicating no reaction.



Although the activity of the coal liquid arenechromium tricarbonyl complex as a hydrogenation catalyst appears to be small for methyl 2,4-hexadienoate as well as for unreacted coal liquids under the mild conditions employed, it may well prove to be viable under moderately more severe conditions. In addition, the nature of the aromatic rings in this particular coal liquid may actually lead to very inactive coal liquid arenechromium tricarbonyl complexes. A slightly heavier distillate may contain more polycyclic aromatic hydrocarbons and yield more active complexes while still affording the conveniences provided by the use of a coal liquid.

In order to test the hypothesis that hydrogenation substrates do not exist in the coal liquid, a reaction was carried out with naphthalenechromium tricarbonyl, an active catalyst, and unreacted coal liquid as the substrate, equation 5. A comparison of the ^2H



NMR spectra of the unreacted coal liquid before and after the reaction, Figure 2, shows that dideuterium addition has taken place. First, the relative aromatic deuterium content has decreased and the aliphatic deuterium content has increased. Second, the two major resonances of the unreacted coal liquid at approximately 1.54 ppm and 1.16 ppm are no longer the dominant resonances. Rather, the new dominant resonances in the reacted coal liquid are at approximately 2.27 ppm and 1.45 ppm. In addition, two other new signals have appeared at 3.57 ppm and 2.71 ppm. Thus, it can be concluded that hydrogenation of the coal liquid had occurred.

Conclusions

A synthetic method for the preparation of coal arene chromium tricarbonyl complexes has been established. The series of hydrogenation reactions with coal liquid arene chromium tricarbonyl complexes shows that there is nothing inherent in coal materials that poison the arenechromium tricarbonyl catalyst and that there are active sites in the coal liquid for hydrogenation. However, the actual arenechromium tricarbonyl complexes formed in the coal liquid are not active enough for extensive hydrogenation under the mild experimental conditions that we used. As mentioned before, monocyclic complexes require higher temperatures and pressures for hydrogenation than polycyclic complexes do. Research in this area is continuing to test the capacity of coal liquid arenechromium tricarbonyl complexes to catalyze dihydrogen addition.

Experimental.

The coal liquid was obtained through Amoco Research Center from the Wilsonville Pilot Plant, Run 250D. The ^{13}C NMR spectra were recorded on a General Electric GN 300 operating at 300MHz. The ^2H NMR spectra were recorded on a Varian XL 1000 operating at 400MHz. The ^1H NMR spectra were recorded on the University of Chicago 500MHz spectrometer. Tetrahydrofuran, dibutyl ether, and dioxane were freshly distilled from sodium benzophenone ketyl immediately before use. Hexane was shaken with sulfuric acid prior to use. All solvents were deoxygenated by means of standard freeze-pump-thaw methods. Potassium hydroxide, acetone, and chromium hexacarbonyl were used as received.

Triaminechromium tricarbonyl

Chromium hexacarbonyl (17.6g, 0.08mol), potassium hydroxide (32.0g), ethanol (80ml), n-butanol (80ml) and water (25ml) were placed in a flame dried three neck flask fitted with a stirrer and a reflux condenser. The reaction flask was placed in an oil bath which was warmed gradually to 150°C. Chromium hexacarbonyl, which sublimed initially, was washed out later by the solvent and no more sublimation took place. The reaction solution gradually turned red. After 4h at reflux, the mixture was collected, 150mL of concentrated aqueous ammonia solution was added and the mixture was slowly stirred for two hours. A yellow precipitate was collected on a glass filter, washed with aqueous ammonia and ether.

Coal liquid arenechromium tricarbonyl

Triaminechromium tricarbonyl (4.68g, 0.025mol), coal liquid (5g), and dioxane (25mLs) were loaded into a 100 mL flask provided with a magnetic stirrer, and a reflux condenser. The solution was refluxed on an oil bath for 48 hrs. The reaction mixture was filtered through Celite in a glass filter and the flask and Celite were washed with ether. The product was purified over a column of silica gel with a 1:1:4 chloroform : dichloromethane : hexane.

Napthalenechromium tricarbonyl

Napthalenechromium tricarbonyl was prepared by a slightly modified procedure¹⁰ to that described by Pauson⁴. A mixture of napthalene (5.3g, 0.042mol) and chromium hexacarbonyl (4.4g, 0.020mol) were refluxed in dibutyl ether (100 mL), hexane (10mL), and tetrahydrofuran (1mL) for 70 hrs. The heating bath was maintained at 160°C for 15 hrs and at 145°C for the remaining time. Solvent and excess napthalene were removed under vacuum and the product purified on a column of silica gel with a 1:1:4 chloroform : dichloromethane : hexane.

Hydrogenation reactions

Hydrogenation reactions were carried out on a 10mL micro hydrogenation apparatus. Typically, the reactants and dried, deoxygenated acetone were placed in the reactor and it was evacuated and flushed with dinitrogen three times, dideuterium three times and then brought up to the final dideuterium pressure at the desired temperature. After the reaction time, the mixture was filtered through Celite in a glass filter and concentrated under vacuum.

Acknowledgement. We are indebted to the Office of Fossil Energy of the U. S. Department of Energy for their support of this investigation.

References

1. Semmelheck, M. F. J. *Organom. Chem. Library* 1976, 1, 371.
2. Jaouen, G. in 'Transition Metal Organometallics in Organometallics in Organic Synthesis', Vol. 2, H. Alper (ed), Academic Press 1978.
3. Cais, M., Fraenkal, D., Weidenbaum, K. *Coord. Chem. Rev.* 1975, 16, 27.
4. Mahaffy, C. A., Pauson, P. L. *Inorg. Synth.* 1979, 19, 154.
5. Razuvaev, G. A., Artemov, A. N., Aladjin, A. A., Sirotkin, N. I. *J. Organometal. Chem.*, 1976, 111, 131.
6. Moser, G. A., Rausch, M. D. *Synth. React. Inorg. Met. -Org. Chem.*, 1955, 280, 255.
7. Cais, M., Rejoan, A. *Inorg. Chim. Acta*, 1970, 4, 509.
8. Muir, K. W., Ferguson, G., Sim, G. A. *Inorg. Chem.* 1966, 5, 1851.

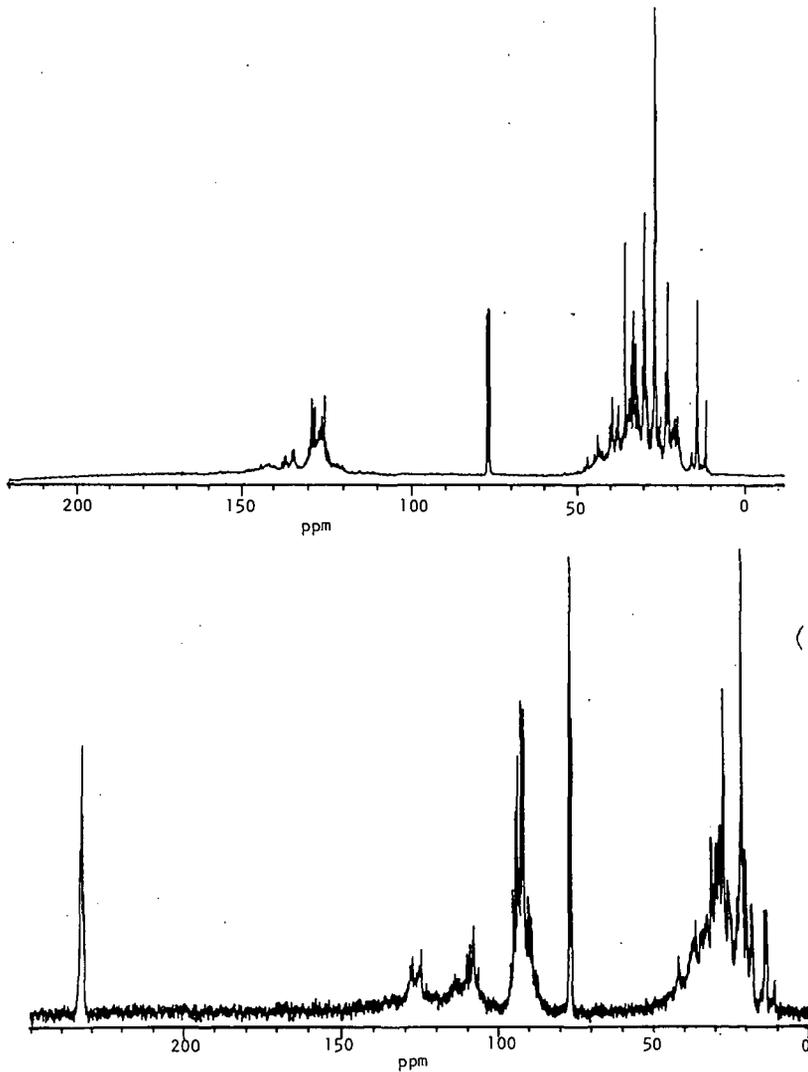


Figure 1. (a) ^{13}C NMR Spectrum Of Wilsonville Coal Liquids in CHCl_3 .
(b) ^{13}C NMR Spectrum Of Coal Liquid Arene- $\text{Cr}(\text{CO})_3$ in CHCl_3

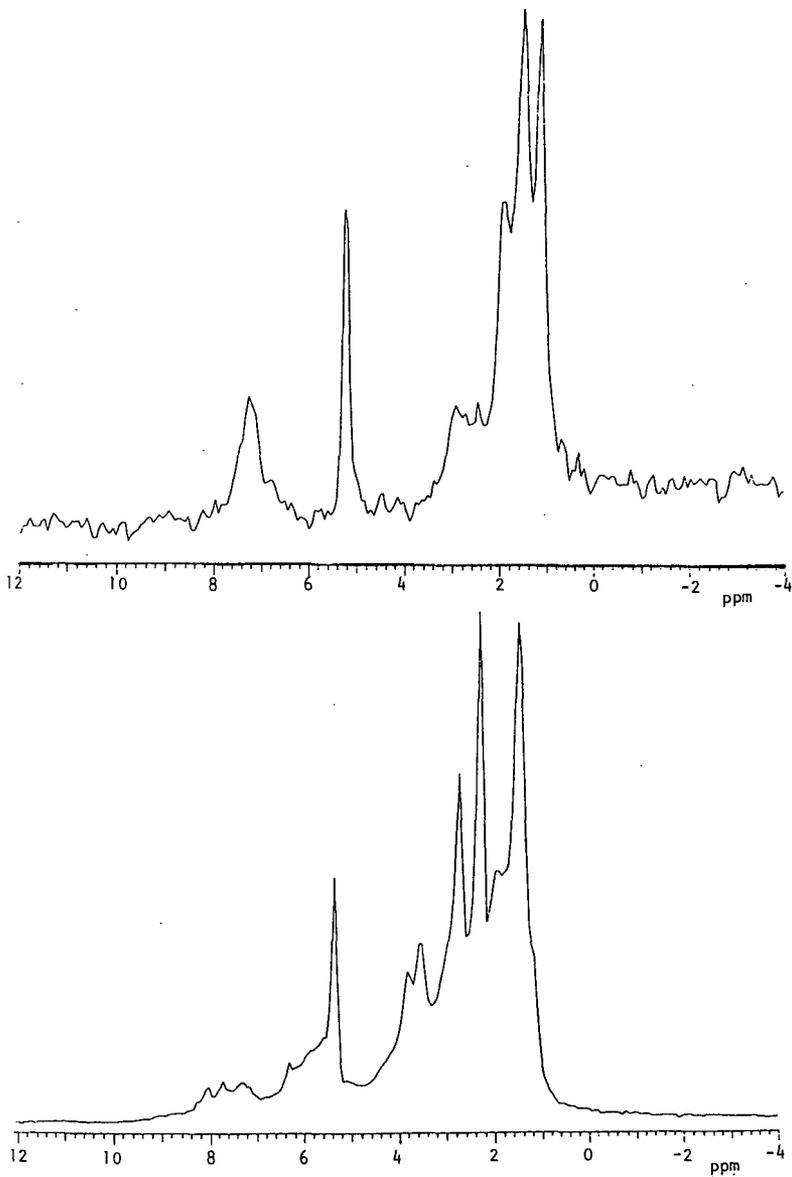


Figure 2. (a) ^2H NMR Spectrum of Unreacted Coal Liquid in CH_2Cl_2
(b) ^2H NMR Spectrum of Equation 6 Product in CH_2Cl_2 .

SYNTHESIS AND CHARACTERIZATION
OF PYRIDINE AND 2,6-DIPHENYL-PYRIDINE ETHERS

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Key words: Ethers; Pyridine Ethers; Synthesis of Ethers;

INTRODUCTION

Three novel pyridine ethers have been synthesized for extension of studies on coal systems¹. Past studies have revealed that hydrogen bonding activates alkyl-aryl ethers toward cleavage by iodide ion in pyridine involving hydrogen bonding to coal². Pyridine ethers have been synthesized *de novo* from 2,6-diphenyl-1,3,5-pentanetrione which had also been synthesized *de novo* from 1-phenyl-1,3-butanedione after formation of its mono-then di-anion and combination with methyl benzoate^{3,4}. These reactions seem to provide good yields because of the driving force of the charged molecular species. Coal is now thought to be as elastomer in which strong internal hydrogen bonding gives it high glass transition temperatures. The same acidic hydrogen donors and basic hydrogen receptors that provide strong hydrogen bonds in the bulk structure populate the surface of coal powders⁵. As in experiments using 1,3-dimethylnaphthalene and decalin⁶, solvation properties of the pyridine ethers will be tested on coal fractions in contemplated experiments.

RESULTS

1,5-Diphenyl-1,3,5-pentanetrione The enolate carbanion of 1-phenyl-1,3-butanedione was obtained by proton extraction with sodium hydride in the aprotic solvent, 1,2-dimethoxy ethane (monoglyme). Condensation of this carbanion with methyl benzoate yielded the triketone, 1,5-diphenyl-1,3,5-pentanetrione. This arylation apparently involves the di-anion of the β -diketone which is formed in a step-wise extraction of its α -hydrogens. The terminal α -hydrogen is not the first extracted from the β -diketone, but is only extracted after mono-anion formation and in the presence of methyl benzoate. The terminal α -hydrogen is, however, the site of reaction of the β -diketone with the carbonyl carbon of the ester. The methoxide group of the ester neutralized by the Na⁺ counter ions, then leaves the condensation product. Exposure to air with its incipient moisture and neutralization of the reaction mixture with 6N HCl provide the protons for neutralization of the carbanions present and formation of the triketone.

This reaction occurs with a high degree of efficiency since 86.9% yields could be obtained (See Table 1).

Apparently once formed, the di-anion is quite reactive and the

reaction is evidently specific for the terminal carbon of the dianion. As expected, the symmetric triketone formed was soluble in diethyl ether, but its solubility varied considerably depending on the pH of the reaction mixture (Table 2)

These differences could be a reflection of minor changes in the structure of the triketone. Variation of the color, crystalline form and melting points of triketone which substantiate similar earlier observations are also suggestive of small variations in the structure of the triketone. Because of the H-bonding, various keto-enol tautomeric forms can be envisioned and as pH changes occur in the solvent all of these forms are undoubtedly present in the solution. At low pH values the triketone is probably found as a doubly H-bonded enolic structure (Formula 1), at intermediate pH values as a mono-H-bonded structure (Formula 2) and at high pH values as a keto form (Formula 3) with little H-bonding (Fig. 2).

2,6-Diphenyl-4(1H)-pyridinone This pyridinone was produced by the cyclization of the 1,5-diphenyl-1,3,5-pentanetrione with liquid ammonia. Because of the high pH of the reaction milieu, which causes the enolization of the ketone groups, the addition product is the primary amine-enol or dienol intermediate.

Cyclization by addition of the primary amine to the other terminal carbon of the pentanetrione chain then readily occurs. This di- or trienolic structure is then dehydrated to form the highly conjugated diphenylpyridine derivative with its quinoid-like pyridine ring.

The synthesized pyridinone possessed the literature values of the physical properties. In addition, the physical properties of the triketone and pyran were considerably different. These results suggest because of their interdependence that the structural parameters attributed to these isolates are consistent and reputable.

DISCUSSION

As expected the product, 1,5-diphenyl-1,3,5-pentanetrione, is formed with a high degree of efficiency (86.9% yields). Although the symmetric triketone was soluble in diethyl ether, variations of the pH of the reaction mixture produced slight variations in the structure of the triketone and therefore variation of the color, crystalline form and melting points of triketone products. Because of the H-bonding, various keto-enol tautomeric forms can be envisioned and as pH changes occur in the solvent all of these forms are undoubtedly present in the reaction milieu.

The ultrastructure of coals is susceptible to study using small molecular weight organic molecules which are not susceptible to alteration by the interior of the coal pores. We have chosen to use the commonly accepted organic molecules which are very resistant to alteration in such an organic milieu- ethers. Theoretically these molecules can be used as molecular sieves to approximate the size of coal pores⁷. Unfortunately, the ethers which we have used have

proven to be unreasonable solvents since they react with the coal ultrastructure.

Another problem in interpretation occurs because of the interaction of the pyridine ethers with the coal structure⁸. For example, the results of the study involving the use of 4-methylpyridine reported above.

SUMMARY

1-Hydrogen bonding is a significant interference in the synthesis of 2,6-diphenyl-1,3,5-pentanetrione, yet yields of 90+% prove this specific synthesis effective.

2-Because of the very prominent unsaturation of the products of this synthesis-the product compounds are very colorful.

3-These ethers cannot be considered inert and make interpretation of these results difficult.

EXPERIMENTAL

Melting points (uncorrected) were determined on a Thomas Hoover Capillary Melting Point Apparatus (Uni-melt) and observed at a rate of 2°C/min. 1H-NMR Spectra were measured on a Varian T-60 Nuclear Magnetic Resonance Spectrometer using tetramethylsilane (TMS) as an internal standard. The solvents used were either chloroform-d or acetone-d₆. Infrared spectra were recorded on a Perkin-Elmer 337 grating Spectrophotometer with calibration peaks at 1601 and 907 cm⁻¹. Mass spectral analysis was conducted on a Dupont 21-490 Mass Spectrometer. TLC was performed on precoated Silica Gel 60F-254 plates (Merck, Darmstadt, 0.25 mm thickness). HPLC analysis was carried out on a Model 342 Gradient Liquid Chromatograph system, retention times and area measurements were recorded by a Shimadzu Chromatopac C-R1B. The column used for the HPLC was 4.6 mm x 25 cm CB reverse phase. Pre-injection clean up of HPLC samples included centrifugation in a Beckman Microfuge TM 11 at 11,000 rpm. Organic solids were dried under vacuum for at least 2 h over CaSO₄ before analysis.

Preparation Of 1,5-diphenyl-1,3,5-pentanetrione^{3,4} Sodium hydride (36.99 g/1.54 moles in a 60% mineral oil dispersion) was added to 100 mls of dried 1,2-dimethoxyethane under a blanket of anhydrous nitrogen. After stirring for 15 m at room temperature the glyme which contained mineral oil and suspended fines was removed, discarded and replaced at least three times to insure removal of the mineral oil after addition of 200-300 ml of glyme. The slurry was then heated to reflux and the 1-phenyl-1,3-butanedione (50.00 g/0.31 moles) in 150 mls of solvent was added dropwise (over 30-60 m) from an addition funnel. After 45 m from completion of the addition, a solution of methyl benzoate (50.32 g/0.37 moles) in 100 ml of glyme was added dropwise. The reaction mixture was then heated at reflux for 4-8 h. After equilibration with the atmosphere and cooling, the reaction mixture which was usually

thick and crusty, was resuspended with additional glyme, if necessary, stirred and adjusted to pH=6 with concentrated HCl. The glyme was then removed in a rotary evaporator. The tar-like residue was extracted with diethyl ether, and the yellow-brown ethereal solution was dried over anhydrous Na_2SO_4 . After removal of most of the ether, the crude 1,5-diphenyl-1,3,5-pentanetrione was recrystallized from the residue with 95% ethanol as yellow-brown crystals to give 47.33 g (57.7% Yd.): mp 107.0-109.0°C, (lit., 106-109°C)¹; NMR (CDCl_3): δ = 11.8-12.0 (d, 1), 7.8-8.0 (m, 6), 7.4-7.6 (m, 7), 6.0 (s, 1); IR (KBr): 3450, 3150, 2950, 2880, 1630, 1590, 1500, 1400, 1300, 1290, 1170, 900, 780, 690 cm^{-1} ; Mass Spectrum, m/e : 266, 105.

*Preparation of 2,6-diphenyl-4(1H)-pyridinone*³ 1,5-diphenyl-1,3,5-pentanetrione (43.95 g/0.17 moles) was dissolved in 200 ml of anhydrous ethanol. Commercial anhydrous liquid ammonia was then bubbled through the mechanically stirred slurry until the solution became dark brown and the reaction mixture cooled to room temperature. The solution was then taken to dryness by heating in an open round bottom flask at 90-100°C until a brownish tar remained. This procedure was then repeated and slightly modified by the addition of 50 g of anhydrous Na_2SO_4 before the final evaporation. Recrystallization is accomplished directly from the residue with benzene. After drying 27.21 g (66.6% yield) of a white powder was isolated and identified as 2,6-diphenyl-4(1H)-pyridinone: mp 176-179°C (lit., 176-179°C²); NMR (CD_3COCD_3): δ = 8.0-8.3 (m, 7), 7.3-7.4 (m, 7), 7.2 (s, 1); IR (KBr): 3450, 3150, 3080, 2950, 2825, 1640, 1600, 1550, 1260, 975, 950, 780, 705, 555; Mass Spectrum (m/e): 247, 247.

*Preparation of 4-methoxy pyridine*⁷. To 10 ml of dried methanol were added 1.7 g/0.074 moles of metallic sodium. After disappearance of the sodium and cessation of H_2 evolution, 5.00 g/0.033 moles of dried 4-chloropyridine hydrochloride (Aldrich) dissolved in 30 ml of dried methanol were added dropwise over 2 h. The reaction mixture was then heated at reflux for 7 days. TLC revealed only trace amounts of 4-chloropyridine and the 4-methoxy pyridine (Yd. = 2.80 g/0.026 moles, 76.9%) was isolated by vacuum distillation: bp 152-154°C (=400 torr) or 41-45°C (0.7-0.8 mm) [lit., 95-96°C at 31 mm⁵ or 190.5-191.0°C (738.3 mm)⁴]; NMR (CD_3COCD_3): δ : 8.4-8.6 (d, 4), 6.7-6.9 (d, 4), 3.8 (s, 1); IR (KBr): 3450, 3050, 2990, 2960, 2860, 1600, 1460, 1440, 1295, 1220, 1035, 828, 820, 540, cm^{-1} ; Mass Spect (m/e): 109.

*Preparation of 4-phenoxy pyridine*⁸. Phenol (12.44 g/0.073 moles) was dissolved in dried toluene under a blanket of anhydrous nitrogen (Fig. 5). Metallic sodium (3.04 g/0.132 moles) was then slowly added to the stirred reaction mixture. After 1 h 4-chloropyridine-hydrochloride (6.61 g/0.044 moles) was slowly added through one side neck of the three neck flask. This caused formation of H_2 and care was taken to control the reaction. After addition of the hydrochloric acid salt, the reaction was heated at reflux for 10 days. At this time, TLC revealed only trace amounts

of remaining reactant. Work up involved¹⁴ neutralization of the reaction mixture to pH=7 followed by steam distillation of the reaction mixture. The distillate was extracted with liberal quantities of diethyl ether, the ethereal extracts were dried with Na₂SO₄ and the diethyl ether partially removed in a rotary evaporator. Vacuum distillation of the remaining extract gave 3.2 g of 4-phenoxy-pyridine (35.1 % Yd.): bp 78-79 (50 u1) [lit., 134-136 (10 mu)¹²; NMR (CD₃Cl) δ: 8.2-8.4 (d, 2), 7.0-7.4 (m, 10), 6.8-7.0 (m, 6); IR(neat): 3007, 3005, 2950, 2850, 2730, 2620, 2500, 1595, 1500, 1270, 1220, 886, 760, 700, 532 cm⁻¹; Mass Spect (m/e): 208.

*Preparation of 2,6-diphenyl-4-chloropyridine*¹² 2,6-diphenyl-4(1H)-pyridinone (12.17 g/0.049 moles) and phosphorus pentachloride (30.75 g/0.993 moles) were mixed under nitrogen and moistened with dry phosphorus oxychloride (8 ml)(Fig. 5). While heating to 150°C for 2 h the liquid milieu progressed from a cloudy white to clear red appearance. The phosphorus oxychloride was then removed by distillation and the melt poured into cold water. After stirring the cooled suspension until the viscous reaction mixture became a flocculent precipitate, the precipitate was collected on a Buchler funnel. 10.50 g (86.3% Yd.) of 2,6-diphenyl-4-chloropyridine was recrystallized from the precipitate with 95% ethanol: mp 83-84°C (lit., 72)¹⁰; NMR (CDCl₃) δ: 7.9-8.2 (m, 8), 7.6 (s, 1), 7.3-7.5 (m, 9) or NMR (CD₃COCD₃) δ: 8.0-8.4 (m, 8), 7.8 (s, 1), 7.4-7.6 (m, 9); IR (KBr): 3450, 3150, 1570, 1420, 1240, 865, 770, 735, 690 cm⁻¹; Mass Spect (m/e) 265.

*Preparation of 2,6-diphenyl-4-methoxypyridine*¹⁸ Metallic sodium (0.65 g/0.028 moles) was added slowly and carefully to 10 ml of dried methanol in a three neck reaction vessel(Fig. 5). After disappearance of the sodium and abatement of H₂ evolution, the solution was refluxed for 1 hr. After cooling, 2.15 g/0.094 moles of 2,6-diphenyl-4-chloropyridine dissolved in 15 mL of dried methanol was added to the reaction vessel. The temperature was again raised to reflux of the reaction mixture. After 6 days HPLC revealed that 50% of the 2,6-diphenylpyridine was 2,6-diphenyl-4-chloropyridine and 50% was 2,6-diphenyl-4-methoxypyridine. Therefore, 0.65 g/0.028 moles in 10 mL of dried methanol was again added to the reaction mixture. After refluxing for four more days, the reaction mixture was then poured into ice water and the aqueous solution extracted several times with diethyl ether. The ether extracts were then combined and concentrated to give 1.83 g/0.007 moles of impure 2,6-diphenyl-4-methylpyridine. Recrystallization was accomplished with absolute methanol giving 1.14 g/0.004 moles of 2,6-diphenyl-4-methoxypyridine (46.3 %Yd.): mp 79-80°C (lit., 79-80°C)⁵; NMR (CDCl₃) δ: 8.0-8.2 (m, 4), 7.3-7.6 (m, 8), 7.1 (s, 1), 3.8 (s, 1); IR (KBr): 3050, 2850, 2000, 1550, 1400, 1350, 1210, 1070, 1020, 895, 860, 835, 770, 690, 630 cm⁻¹; Mass Spect (m/e) 261.

REFERENCES

1. Mayo, F. R.; Buchanan, D. H.; Pavelka, L. A. *Prepr. Pap., Am. Chem. Soc., Div. Fuel Chem.* 1980, 25(2), 182. (b) Mayo, F. R.; Buchanan, D. H.; Pavelka, L. A.; Hirschon, A. S., manuscript submitted to *Fuel*.
2. Buchanan, D. H.; Takemura, N.; Sy, J. N. O. "Intramolecular Hydrogen Bonding Enhances the Rate of Nucleophilic Cleavage in Alkyl-Aryl Ethers" *J. Org. Chem.* 1986, 51, 4291-4294.
3. Light, R. J.; Hauser, C. R. "Aroylations of β -Diketones at the Terminal Methyl Groups to Form 1,3,5-Triketones. Cyclizations to 4-Pyrones and 4-Pyridones" *J. Org. Chem.* 1960, 25, 538-546.
4. Miles, M. L.; Haris, T. M.; Hauser, C. R. "Aroylations at the Methyl Group of Benzoylacetone and Related β -Diketones with Esters to Form 1,3,5-Triketones by Sodium Hydride. Other Terminal Condensations." *J. Org. Chem.* 1965, 30, 1007-1011.
5. Fowkes, F. M., Jones, K. L., Li, G., & Lloyd, T. B. Surface Chemistry of Coal by Flow Microcalorimetry. *Energy & Fuels* 1989, 3, 97-105.
6. Bockrath, B. C., Schroeder, K. T. & Smith, M. R. Investigation of Liquefaction Mechanisms with Molecular Probes. *Energy & Fuels* 1989, 3, 268-272.
7. Black, S. H. & Gerhardt, P. The Void Volume of Bacterial Spores. *J. Bacteriol.* 1960, 59, xx.
8. Sy, J. & Buchanan, D. H. *J. Org. Chem.* 198X, xxx, xxx.
9. Renshaw, R. R.; Conn, R. C. "Quaternary Derivation of Pyridyl Ethers. Onium Compounds. XVI" *J. Am. Chem. Soc.* 1937, 59, 297-303.
10. Haake, P.; Miller, W. B.; Tysee, D. A. *J. Amer. Chem. Soc.* 1964, 86, 3577-xxxx.
11. Koenig, E.; Greiner, H. "Über 4-Pyridyl-pyridinium-dichloride und das Synthese von γ -Derivaten des Pyridins." *Ber.* 1931, 64, 1056-.
12. Patrenko-Kritschenko, P.; Shottly, S. "Über die Kondensation der Aceton-dicarbonsaureester mit Aldehyden vermittele Ammoniak und Aminen." *Chem. Ber.* 1909. 42, 2020-2025.

TABLE

Table 1. Physical Properties of Synthetically Prepared Precursors and Ethers

Table 2. Physical Properties of 1,5-Diphenyl-1,3,5-pentanetrione

- a-Moles 1-diphenyl-1,3-butanedione:mole NaH:mole methyl formate
 b-Solvent not dried immediately before synthesis
 c-Only one crystallization, second was usually not fruitful

Figures

Name	Recrystallization Solvent	Color	Mp (Bp)	% Yd
1,5-Diphenyl-1,3,5-pentanetrione	95% Ethanol	Yellow	107-109	57.7
2,6-Diphenyl-4(1H)-pyridinone	Benzene	Cream	176-179	66.6
2,6-Diphenyl-4H-pyran-4-one	Ethanol-Water	White	137-139	79.8
2,6-Diphenyl-4-chloropyridine	95% Ethanol	White	83-84	86.3
2,6-Diphenyl-4-methoxypyridine	Methanol	White	79-80	46.3
4-Methoxypyridine	Distilled Water	Clear	41-45	
4-Phenoxypyridine	Distilled Water	Clear	78-79	

Preparations	Mole Ratio ^a	Solvent (Recrys.)	Color	%Yd.	mp
F-1A	1-3.3-1	95% EtOH	brown	58.6	106-108
P-2A	1-4.2-1.2	95% EtOH	lime-yellow	86.9	108-110
P-2B	1-4.2-1.2	95% EtOH	lime-yellow	86.9	108-110
P-21A	1-4-1.2	95% EtOH	lime-yellow	— ^b	107.5-110
P-21B	1-4-1.2	95% EtOH Hexane Cyclohexane	browns	—	113-122
P-29A	1-5-1.2	95% EtOH	brown	57.7	107-109
P-29A-A	1-5-1.2	95% EtOH Hexane Cyclohexane	brown	57.7	106-108
P-29B	1-5-1.2	95% EtOH	brown	57.7	107-109
P-III-A	1-4-1	95% EtOH	brown	38.0 ^c	105-108

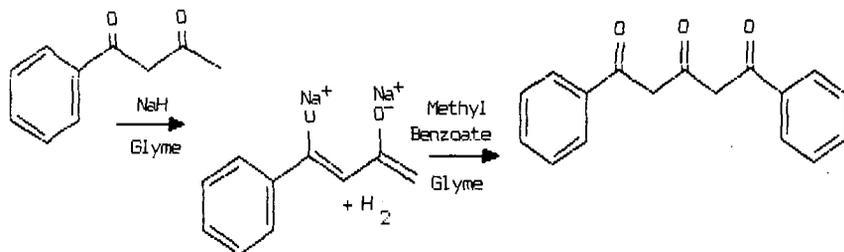


Fig. 1. Synthesis of 1,5-Diphenyl-1,3,5-pentanetrione

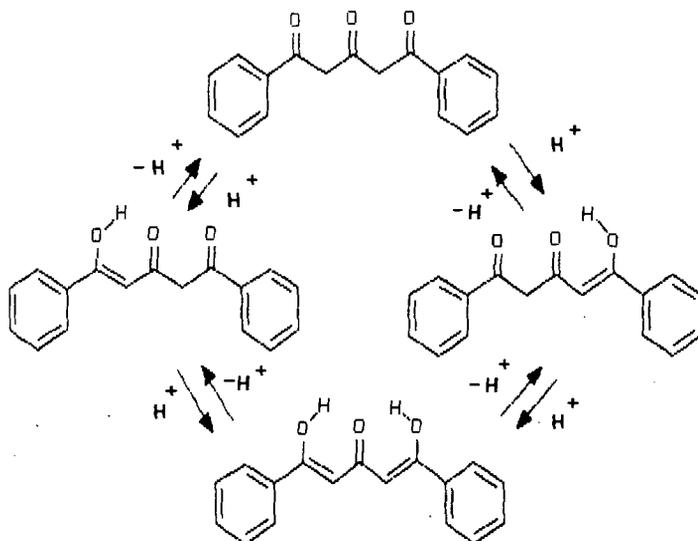


Fig. 2. Hydrogen Bonding of 2,6-Diphenyl-1,3,5-pentanetrione

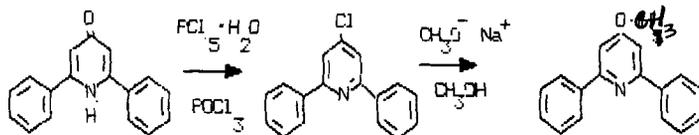


Fig. 3. Synthesis of 2,6-Diphenyl-4-methoxypyridine