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IN SITU MINING OF BITUMINOUS COAL WITH FLUORINATED SOLVENTS

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5 Summary:

This project was designed to explore the suitability of using fluorinated inorganic materials as solvents for the in situ mining of thin seamed, heavily overburdened coal: to build a data base for the selection of an inorganic solvent for use for coal cleaning; to determine if fluorinated solvents will reduce the organic and inorganic sulfur contents of the coal, as well as to lower the ash content.

The coal samples have been combined with pure solvent, as well as with aqueous solutions at atmospheric pressure and at increased pressure. The increased pressure experiments are important since they duplicate the conditions anticipated for an in situ cleaning and mining operation.

Trifluoroacetic, difluorophosphoric (phosphorodifluoridic), and trifluoromethanesulfonic acids have been found to be effective for the cleaning of high sulfur, high ash coal at 300°C and at atmospheric pressure. At pressures up to 20,000 psi the effectiveness of these reagents is not decreased.

I. Introduction and Summary

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II. Reactions of Small Covalent Molecules with Coal: Trifluoracetic Acid

A. Introduction

Samples of Morris coal, a high-volatile bituminous coal found in Oklahoma, do not comminute readily with aqueous or anhydrous ammonia, water or glacial acetic acid at temperatures up to 100°C in sealed tubes at autogenous pressure. The present study was undertaken to find a more active communition reagent for Morris coal.

Trifluoroacetic acid (TFA), a strong nonoxidizing acid ($K_a = 5 \times 10^{-1}$), is an excellent solvent for aliphatic and aromatic organic compounds. TFA is completely miscible with water, ether, acetone, ethanol, benzene, carbon tetrachloride, straight-chain hexane and perfluoro-n-hexane.[1] It has an excellent liquid range (mp., -15.4°C, bp., 72.4°C) and a high density (1.489 g cm^{-3} at 20°C) which means that it will generate a hydrostatic pressure 50% greater than that due to pure water at the same depth. This material, therefore, has physical characteristics which merit consideration as a recyclable coal solvent.

Trifluoroacetic acid has been used to uncoil protein polymers; e.g., the polymer poly-L-methionine, which exists as an α-helix in chloroform, is converted to a random coil by TFA.[2] TFA is used to provide temporary blocking of -OH or $-NH_2$ groups in carbohydrates and peptides while synthetic operations are carried out at other sites in the molecule, the acyl group being afterwards removed by hydrolysis.[3]

$$ROH + CF_3CO_2H \rightarrow CF_3CO_2R + H_2O$$

$$RNH_2 + CF_3CO_2H \rightarrow CF_3CONHR$$

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[1] Woolf, C., "The Chemistry and Chemical Technology of Fluorine," H.F. Mark, Ed., John Wiley, New York, pp. 771, 1966.

[2] Chambers, R.D., "Fluorine in Organic Chemistry," John Wiley, New York, pp. 213, 1973.

[3] Shappard, W.A. and Charts, C.M., "Organic Fluorine Chemistry," W.A. Benjamin, Ed., New York, pp. 370, 1969.

B. Experimental

The Morris coal was obtained from the Oklahoma Geological Survey. The subbituminous (PSOC-636) and low-volatile bituminous (PSOC-688) coals were supplied by the Coal Research Section of the Pennsylvania State University.

Samples of bulk coal for analysis were prepared according to ASTM standards. Coal pieces employed for treatment by TFA were at least 2 cm long with a "diameter" just large enough to fit through a 24/40 ground joint (20 mm). The coal (50 g) was refluxed with solvent for 24 hours, vacuum-filtered, and the residue was washed with water and dried at 110°C. Hydrolysis experiments using boiling water or 15% aqueous sodium hydroxide were carried out on the treated coal.

Model compound reactions were carried out at reflux conditions or in sealed tubes. The products were identified and confirmed using two or more of the following measurements: IR, NMR, or mass spectroscopy, melting or boiling point, and elemental analysis.

SEM micrographs were obtained using ETEC Autoscan scanning electron microscope with gold sputtered samples. IR spectra were measured in the 4000-300 cm^{-1} region using a Beckman Model IR-10 double-beam grating spectrophotometer. Volatile materials were confined to reduced pressure in a 100-mm gas cell fitted with KBr windows sealed with rubber O-rings. Mass spectra were determined with a Hewlett-Packard Model 5985B GC/MS spectrometer and a Varian T-60 spectrometer was employed for NMR spectra. Analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN), Williams Brothers Laboratories (Tulsa, OK), and by the Oklahoma Geological Survey. Sulfur analyses were performed according to ASTM D2492.

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[4]Hagen, A.P. and Morrison, D.L., Inorg. Synth., 13, 65, 1972.

Covalent fluorine (1-2%) may reduce the accuracy of this analysis; selected coals were therefore doped with a 3-4 wt% of anhydrous $Mg(O_2CCF_3)_2$ and the samples were handled in a N_2-filled glove bag. There was no significant difference between the sulfur analyses of the doped and undoped coals.

C. Results and Discussion

Trifluoroacetic acid readily comminutes the coals used in this study. At room temperature low-volatile bituminous coal, 2 cm diameter, was reduced to a fine powder within an hour. The other coals comminute more slowly at room temperature, but under reflux (72°C) they were communited rapidly. The main function of the trifluoroacetic acid appears to be the physical alteration of the coal as only 1-2% of it is consumed during the process. The fragmentation and cleaning appears to occur along the mineral matter boundaries forming fractures parallel to and at right angles to the bedding plane. It is reasonable, therefore, to speculate that an important function of the trifluoroacetic acid is to interact with the inorganic minerals. Swelling takes place due to the internal pressure of the liquid which builds internal stresses exceeding the fracture strength of the solid. The larger pieces of coal which remain are friable.[5]

The surface area of the Morris coal was measured by the Brunauer-Emmett-Teller (BET) method using nitrogen absorption at -196°C. There was little change in the surface area of the treated coal, ($0.471\ m^2g^{-1}$) as compared to that of an untreated sample ($0.548\ m^2g^{-1}$). These values are in the same range as those reported for a Japanese bituminous coal

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[5] Sleevi, P., Glas, T.E., and Dorn, H.C., Anal. Chem. 51, 1931, 1979.

which had been treated with liquid ammonia.[6]

Tables 1 and 2 summarize the analytical data. The Morris coal has a high sulfur content and ash yield, both of which were reduced by interaction with TFA and its aqueous solutions. The elemental analysis data supports the addition of 1-2 acetate groups per 100 carbon atoms of coal.[7] This is the same order of magnitude as noted by Hodek and Kölling for acylation using acid chlorides with aluminum chloride catalyst.[8] However, in the present study no evidence was obtained for acylation at a carbon atom by trifluoracetic acid. The fluorine content of the treated coal can be reduced to almost zero by washing the treated coal with dilute aqueous sodium hydroxide. This corresponds to the hydrolysis of the esters which form during the communition process.

$$\text{Coal} - O_2CCF_3 + NaOH(aq) \rightarrow [\text{Coal} - O^-][Na^+] + CF_3CO_2H$$

It is interesting to note that water appears to be removed from the coal via a dehydration reaction because when anhydrous TFA which has contacted the dried coal is distilled, two to three times the amount of water anticipated from the analysis is removed as the azeotrope. A similar reaction takes place when glucose or certain alcohols are refluxed with anhydrous TFA. Water and aqueous solutions containing <50% TFA were not effective reagents for the communition of the Morris coal. Pure TFA and aqueous solutions containing 50 and 79 wt% were very reactive. The 79 wt% solution, as a reactant, is important as this is the concentration of the water-TFA azeotrope which is easily recovered by distillation from the reaction mixtures. As there is little loss of

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[6] Matida, M., Nishiyama, Y., and Tamai, T., Fuel, 56, 177, 1977.

[7] Given, P.H., Cronauer, D.C., Spackman, W., Lovell, H.L., Davis, A., and Biswas, B., Fuel, 54, 40, 1975.

[8] Hodek, G. and Kölling, G., Fuel, 52, 220, 1973.

TABLE 1

Analytical data: Oklahoma bituminous (moisture free basis)

	Untreated	100 wt%	70 wt%	50 wt%
Proximate analysis (wt%)				
Moisture	[1.6]	[0.0]	[0.0]	[1.6]
Volatile	38.9	38.1	40.9	37.9
Ash	17.0	8.1	2.7	3.2
Fixed Carbon	44.1	53.8	56.4	58.9
Ultimate analysis (wt%)				
H	3.8	3.4	3.9	3.5
C	57.3	66.3	70.4	68.8
N	1.5	1.6	1.8	2.0
O (by difference)	10.7	12.0	14.8	17.5
F	0.1	5.5	3.9	3.2
S	9.5	3.1	2.4	1.8
Cl	0.1	0.0	0.1	0.0
Ash	17.0	8.1	2.7	3.2
Calorific value ($MJ\ kg^{-1}$)	28.37	26.51	28.37	28.14

Note: All samples were dried at 110°C prior to submission for analysis. The treated samples were washed with boiling water prior to drying.

The data was calculated according to ASTM 388.

TABLE 2

Analytical data for sulfur contents

Sulfur forms (wt%)	Morris Coal	100 wt% TFA	79 wt% TFA	50 wt% TFA
Sulfate	0.1	0.0	0.1	0.1
Pyritic	3.5	2.8	2.1	1.5
Organic	5.9	0.3	0.2	0.2
Total	9.6	3.1	2.4	1.8
	PSOC-688	100 wt% TFA	PSOC-636	100 wt% TFA
Sulfate	0.1	0.0	0.2	0.0
Pyritic	0.9	0.1	1.7	0.1
Organic	1.6	1.3	0.9	0.5
Total	2.6	1.4	2.8	0.6

Note: All samples were dried at 110°C prior to submission for analysis.

TFA, it is possible to reuse the acid for a large number of experiments.

The comparison coals were also rapidly broken into small pieces by pure TFA. At room temperature the low-volatile bituminous coal is converted into a fine powder within an hour. The sulfur contents for the treated coals are presented in Table 5. The ash yields also decrease: from 16.0 to 4.4 wt% for PSOC-688 and from 18.3 to 9.6 wt% for PSOC-636.

The analytical data indicates that the acid extract should be very rich in organic sulfur compounds as well as in minerals. Indeed, metal (Na^{+}, Mg^{+2}, and Al^{+3}) trifluoroacetates are readily isolated as transparent colorless crystals when the trifluoracetic acid is slowly removed in vacuo.[9] A mass spectrometric examination of the extract is consistent with organic sulfur compounds being in the mixture.

1. Model compounds

The possibility of chemical interaction of TFA with coal must be examined. The coal model proposed by Heredy and Wender,[10-12] in which hydroxyl is the only active functional group, fits well reversible esterification as the major chemical interaction of coal with TFA. The reaction of trifluoroacetic anhydride or trifluoroacetylchloride with phenols or alcohols is a common route for the formation of esters of TFA.[13] In the present study TFA has been shown to react with aromatic

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[9] Garner, C.D. and Hughes, B., Adv. Inorg. Radiochem., 17, 1, 1975.

[10] Heredy, L.A. and Wender, I., Symposium on Structure and Reactivity of Coal and Char., Am. Chem. Soc. Div. Fuel Chem., 25(4), 38, 1980.

[11] Wiser, W.H., "Chemistry of Coal Liquefaction: Status and Requirements, Scientific Problems of Coal Utilization," DOE Symposium Series, 46, 219, 1978.

[12] Given, P.H., Fuel, 39, 147, 1960.

[13] See: Sleevi, et al., page 4.

and aliphatic hydroxyl groups to form esters. Methanol, ethanol, straight-chain butanol, benzyl alcohol and 2-napthyl-ether, and dibenzyl ether are cleaved.

$$[C_6H_5CH(CH_3)]_2O + CF_3CO_2H \rightarrow C_6H_5CH(CH_3)OC(O)CF_3 + C_6H_5CH(CH_3)OH$$

The alcohol then eliminates water to form styrene which polymerizes as follows:

$$XC_6H_5CH(CH_3)OH \rightarrow (C_6H_5CHCH_2)_x + XHOH$$

Benzyl ether forms an ester and benzyl alcohol which polymerized to poly(phenylenemethylene) analogous to the reaction of benzyl alcohol with concentrated sulfuric acid.[14,15]

$$(C_6H_5CH_2)_2O + CF_3CO_2H \rightarrow C_6H_5CH_2O_2CCF_3 + C_6H_5CH_2OH$$

The alkyl-aryl ether 2-naphthylethyl ether did not cleave at 72°C but readily at 180°C. Diphenyl ether does not react at temperatures up to 180°C.

Model coal structures also contain -SH, -S-, and -S-S- groupings. Trifluoroacetic acid reacts with benzenethiol to form the S-phenylester of trifluoroacetic acid.

$$C_6H_5SH + CF_3CO_2H \rightarrow C_6H_5SC(O)CF_3 + H_2O$$

Diphenylsulfide does not react with trifluoroacetic acid at temperatures up to 140°C. The interaction with diphenyldisulfide is interesting; no reaction takes place with pure TFA up to 180°C, but when a mixture of TFA and $Mg(CF_3CO_2)_2$, or TFA or Mg metal, is employed at 100°C the S-S linkage is cleaved and polymers are formed:

$$C_6H_5S\text{-}SC_6H_5 + CF_3CO_2H \rightarrow C_6H_5S(C_6H_5S)_xC_6H_5$$

where x = 1-5.

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[14] Marsh, J.P. and Goodman, L., J. Org. Chem., 30, 2491, 1965.

[15] Hagen, A.P., Miller, T.S., Bynum, R.L., and Kapila, V.P., J. Org. Chem., 47, 1345, 1982.

III. Reactions of Trifluoroacetic Acid with Alcohols, Phenols, Ethers, and their Sulfur Analogues

A. Introduction

When bituminous coal is treated with trifluoroacetic acid (TFA) at 72°C it forms a powder having greatly reduced sulfur and ash contents. This report describes the reaction chemistry of TFA with pure substances having functional groupings that would be anticipated for bituminous coal.[16,17]

B. Results and Discussion

The importance of trifluoroacetate derivatives of biochemical and organic substances has been well established.[18,19] The derivatives are normally formed by the addition of trifluoroacetic anhydride or trifluoroacetyl chloride to the substrate or by the in situ generation of the acid anhydride from trifluoroacetic acid (TFA) and a dehydrating agent, e.g., tetraphosphorus decaoxide.[20] The formation of trifluoroacetic acid esters would be anticipated from the reaction of the acid with an alcohol or phenol. The practical need for a nonreversible reaction dictates for many acids the use of the acid chloride or the acid anhydride; however, a number of esters have been isolated in this study without the use of these reagents. Quantitative yields of the ethyl, n-butyl, benzyl, methyl, and 2-naphthyl esters are obtained by refluxing the hydroxyl compound with commercial TFA. A notable exception is that phenol requires

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[16] Miller, T.S., M.Sc. Thesis, The University of Oklahoma, 1980.

[17] Hagen, A.P., Bynum, R.L., Kapila, V.P., and Miller, T.S., Fuel, 61, 840, 1982.

[18] Heuser, E., "Cellulose Chemistry," John Wiley, New York, pp. 230, 1944.

[19] Haschemeyer, R. and Haschemeyer, A., "Proteins: A guide to a Study by Physical and Chemical Methods," John Wiley, New York, pp. 362, 1973.

[20] See: Sleevi, et al., page 4.

the addition of tetraphosphorus decaoxide to the reaction mixture. The phenol ester is the most rapidly hydrolyzed of the esters isolated in this study.

The cleavage of benzyl and of tert-butyl ethers by TFA has been noted;[21,22] however, the general use of this reagent for cleaving ether linkages has not been demonstrated.[23] Several ethers have been found to cleave in this study. The most probable reaction route would have an oxonium ion intermediate since TFA is a very strong acid; K_a = 0.5 in acetic acid.[24] The complex then decomposes with

$$CF_3CO_2H + n\text{-}C_4H_{10}OC_2H_5 \rightarrow [n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3]$$

cleavage of the ether linkage. The decomposition products can form by a substitution process or by elimination. The initially formed substances then undergo

$$[n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3] \rightarrow n\text{-}C_4H_{10}OH + C_2H_5O_2CCF_3$$

$$[n\text{-}C_4H_{10}O(H)C_2H_5][O_2CCF_3] \rightarrow n\text{-}C_4H_{10}OH + C_2H_4 + CF_3CO_2H$$

their characteristic reactions including polymerization, addition, and esterfication. In this specific reaction the major products are the ethyl and n-butyl esters of TFA.

Ethyl and diphenyl ethers do not cleave in a sealed tube at temperatures up to 180°C; however, n-butyl ethyl ether cleaves at 72°C to form the ethyl and n-butyl esters of TFA.

Bis(1-phenylethyl) ether cleaves to initially form an alcohol and an

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[21] Beyerman, H.C. and Heiszwolf, G.J., Recl. Trav. Chim. Pays-Bas, 84, 203, 1965.

[22] Beyerman, H.C. and Bontekoe, J.S., Recl. Trav. Chim. Pays-Bas, 81, 691, 1962.

[23] See: Marsh, et al., page 9.

[24] Howells, R.D. and McCown, J.D., Chem. Rev., 77, 69, 1977.

ester. The alcohol then splits out

$$[C_6H_5CH(CH_3)]_2O + CF_3CO_2H \rightarrow C_6H_5CH(CH_3)OH + C_6H_5CH(CH_3)OC(O)CF_3$$

a molecule of water to form styrene which polymerizes. The water hydrolyzes the ester to give TFA and additional alcohol which loses water. Therefore, the overall reaction becomes:

$$[C_6H_5CH(CH_3)]_2O \xrightarrow{TFA} (C_6H_5CHCH_2)_x + H_2O$$

Benzyl ether reacts to form poly(phenylene methylene) analogous to the reaction of benzyl alcohol with concentrated sulfuric acid.[25] The TFA reaction can take place via an oxonium complex which decomposes to form benzyl alcohol and an ester which then undergoes further reactions.

Benzylphenyl ether is also cleaved by TFA. The products include the benzyl and phenyl and phenyl esters in addition to poly(phenylene methylene). The benzyl oxygen linkage is believed to be present in subbituminous and bituminous coals; therefore, the low-temperature cleavage of this linkage is important in coal chemistry.[26,27]

The interaction of 2-naphthylethyl ether with TFA leads to 2-naphthol and ethyl trifluoroacetate being isolated.

$$C_{10}H_7OC_2H_5 + CF_3CO_2H \rightarrow C_{10}H_7OH + C_2H_5O_2CCF_3$$

The strongly electron-attracting $CF_3CO_2^-$ grouping should facilitate alkyl oxygen scission, making the esters excellent alkylating agents. Except when the benzyl ester is refluxed with benzyl alcohol, no alkylation reaction

$$C_6H_5CH_2O_2CCF_3 + C_6H_5CH_2OH \rightarrow (C_6H_5CH_2)_2O + CF_3CO_2H$$

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[25] Shriner, R.L. and Berger, A., J. Org. Chem., 6, 305, 1941.

[26] Schlosberg, R.H., Davis, W.H., Jr., and Ashe, T.R., Fuel, 60, 201, 1981.

[27] Schlosberg, R.H., Ashe, T.R., Pancirov, R.J., and Donaldson, M., Fuel, 60, 155, 1981.

was noted for any alcohol ester combination noted in this study. The transesterification reaction products are isolated as a function of the relative concentration of the reagents.

At temperatures up to 200°C and pressures up to 1 x 10^6 Pa, diphenyl sulfide, diphenyl disulfide, and thioanisole did not react with TFA. Thiophenol did react to form the thioester under these conditions.

$$C_6H_5SH + CF_3CO_2H \rightarrow C_6H_5SC(O)CF_3 + H_2O$$

The cleavage of sulfur linkages is important for rationalizing the sulfur removal properties of TFA. In the coal samples metal trifluoroacetates are isolated. When diphenyl disulfide is heated at 150°C with TFA in the presence of magnesium trifluoroacetate, the S-S linkage is cleaved. The major sulfur product of this reaction is

$$C_6H_5S(C_6H_4S)_xSC_6H_5, \text{ where } x = 1\text{-}5.$$

The TFA reactions noted in this effort are important since they may help explain the dramatic effect of this acid on the coals examined in this study. Typical analyses show the ash contents are reduced by 50-75% and sulfur is reduced by 50-80%. Inorganic sulfur is reduced, e.g., from 3.5% to 2.8%; however, organic sulfur in the same sample drops from 6% to 0.3%. The coal samples comminute to a fine powder within 1 h at 70°C which is low in sulfur and ash, while maintaining a high heating value. Petrographic analyses suggest that secondary liptinite and attrital liptinite macerals are removed but that large primary liptinite macerals (sporinite, cutinite, resinite) are not attacked by TFA. It is, therefore reasonable that oxygen linkages are cleaved.

C. Experimental

A borosilicate glass vacuum system with a Teflon stopcock (Fischer & Porter Co.) was employed to purify and to analyze volatile materials.

Volatile products were identified by infrared spectroscopy and confirmed by gas-phase molecular weight measurement. Infrared spectra were obtained in the 4000-300 cm^{-1} region by using a Beckman Model IR-10 double-beam grating spectrophotometer. Volatile materials were confirmed in a 100-mm gas cell fitted with KBr windows sealed with rubber o-rings at reduced pressure. Solid spectra were obtained by using KBr pellets, and liquid spectra were obtained between AgCl disks. Mass spectra were measured by a Hewlett-Packard 5985B GC/MS system. Experiments above the normal boiling point of one component were carried out in borosilicate tubes closed with Teflon stopcock.[28,29] The chemicals and solvents used in this work were obtained from commercial sources.

General Procedure for Model Compound Reactions. Trifluoroacetic acid (25 mL) and the reactant (0.05 mol) were refluxed for 24 h in a 50 mL single-necked flask with a spiral reflux condenser and a magnetic stirring bar. After the reaction period the reflux condenser was replaced by a short path distillation head and the mixture distilled to recover water, trifluoroacetic acid, and low-boiling product(s). When substances boiled between 200 and 300°C, a vacuum pump was added for reduced pressure (10 Pa) distillation. Sublimable products were recovered by using a vacuum (10 Pa) sublimination device.

Ethanol reaction: 100% yield of the ethyl ester based on ethanol; bp 55-57°C (Lit.[30] b.p. 59.5 - 60.5°C); confirmed by IR.[31]

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[28] All melting and boiling points are uncorrected. The 2-naphthol ester gave analyses within ±0.3% of the theoretical values (Galbraith Laboratories, Inc.)

[29] Morrison, D.L. and Hagen, A.P., Inorg. Synth., 13, 65, 1972.

[30] Zarubinskii, G.M., Kol'tsov, A.1, Orestova, V.A., and Danilov, S.N., Zh. Obshch. Khim., 35, 1620, 1965; J. Gen. Chem. USSR (Engl. Transl.) 35, 1624, 1965.

[31] Crowder, G.A., J. Fluorine Chem., 1, 219, 1971/72.

Benzyl Alcohol Reaction: 100% yield of the benzyl ester based on benzyl alcohol; bp 172-174°C [lit.[32] bp 177-178°C (755 mm)]; confirmed by IR.[33] About 1 mL of yellow liquid remained in the distillation flask which was identified by infrared spectroscopy as benzyl ether. This material formed during the high-temperature distillation.

Phenol Reaction: The phenyl ester was isolated only when P_4O_{10} was employed: 100% yield based on phenol; bp 153-155°C [lit.[32] bp 144°C (750 mm)]; confirmed by IR.[31]

Methanol Reaction: 100% yield of the methyl ester based on methanol; bp 49-51°C [lit.[33] bp 43-44°C); confirmed by IR.

2-Naphthol ester: 100% yield of the 2-naphthol ester based on 2-naphthol; mp 66-68°C; IR 2910, 2850, 1800, 1455, 1375, 1350, 1225, 1152, 895, 805, 752, 735, 470 cm^{-1}; mass spectrum, m/e (relative intensity) 240, (84.1), 241 (10.7), 242 (1.0), 115 (100); confirmed by elemental analysis.

Cleavage of Bis(1-phenylethyl) Ether: 100% cleavage; polystyrene, identified by IR taken as the chloroform evaporate and confirmed by elemental analysis.

Cleavage of 2-Napthyl Ethyl Ether: No reaction was observed at 72°C. In a sealed tube at 180°C, 100% cleavage occurred: 2-naphthol, mp 122°C; confirmed by IR; ethyl trifluoroacetate, bp 55°C; confirmed by IR.

Cleavage of Benzyl Ether: 100% cleavage; polybenzyl polymer; identified by IR taken of the acetone evaporate; confirmed by NMR and elemental analysis.[34] Authentic polymer was synthesized by adding

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[32]Bourne, E.J., Stacey, M., Tatlow, J.C., and Worrall, R.J., J. Chem. Soc. pp. 3268, 1958.

[33]Peirce, A.G. and Joullie, M.M., J. Org. Chem. 28, 658, 1963.

[34]Arata, K, Fukui, A, and Toyoshima, I., J. Chem. Soc. Chem. Commun., pp. 121, 1978.

concentrated H_2SO_4 to ice-cold benzyl alcohol.[35] The product was poured onto crushed ice and washed with water and dioxane.

Cleavage of Benzyl Phenyl Ether: There was 100% cleavage. The products include TFA esters of benzyl alcohol and phenol, as well as some polybenzyl polymer. The materials were identified by IR and mass spectral analysis.

Cleavage of Benzyl Ethyl Ether: There was 90% cleavage. The major products include trifluoroacetic acid benzyl and ethyl esters along with a small amount of polymeric material (confirmed by IR and mass spectroscopy).

Cleavage of Ethyl n-Butyl Ether: There was 90% cleavage. The major products include n-butyl and ethyl trifluoroacetates along with a small amount of polymeric material (confirmed by IR and mass spectroscopy).

Cleavage of Diphenyl Ether: No reaction was observed up to 180°C in a sealed tube.

Synthesis of $C_6H_5SC(O)CF_3$: Trifluoroacetic acid (4.0 g, 35 mmol) and C_6H_5SH (2.0 g, 18 mmol) were heated in a sealed reactor for 12 h at 190°C. The mixture was vacuum distilled to give a 65% yield of pure material.[36,37,38]

Reaction of $(C_6H_5S)_2$: Trifluoroacetic acid (8.0 g, 70 mmol), $(C_6H_5S)_2$ (1.0 g, 4 mmol), and Mg (0.025 g, 1 mmol) were heated in a sealed reactor for 12 h at 150°C. The TFA was removed in vacuo to leave an oil and a white solid. This mixture was then sublimed/molecular

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[35] See: Shriner, et al., page 12.

[36] Nyquist, R.A. and Potts, W.J., Spectrochim. Acta, 15, 514, 1959.

[37] Sakakibara, S and Inukia, N., Bull. Chem. Soc. Jpn., 38, 1979, 1965.

[38] Bock, E., Queen, A., and Nour, T., Can. J. Chem., 52, 3113, 1974.

stilled at 60°C (10 Pa). The sublimate, as well as the residue contained phenylene sulfide polymers with n = 1-5 (mass spectroscopy).[39-43]

Hydrolysis Experiments: Distilled water (5 mL) and an equal volume of the ester were heated at reflux for 2 h. The products were identified by IR and confirmed by boiling or melting points. Except for the butyl ester, complete hydrolysis took place. The butyl ester did not hydrolyze. Equal volumes (2 mL) of the benzyl ester and water were heated at 190°C in a sealed tuve for 2 h. The major additional material isolated was polybenzyl polymer.

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[39] Montaudo, G. and Przybyiski, M., Makromol. Chem., 176, 1753, 1975.

[40] Cameron, G., Hogg, R.D., and Stachowiak, S.A., Makromol. Chem. 176, 9, 1975.

[41] Montaudo, G., Bruno, G., and Marauigna, P., J. Polym. Sci., 11, 65, 1973.

[42] Hawkins, R.T., Macromolecules, 9, 189, 1976.

[43] Neale, A.J., Bain, J.S., and Rawlings, T.J., Tetrahedron, 25, 4583, 1969.

IV. Reactions of Small Covalent Molecules with Coal: Trifluoromethane-, Methane-, Fluoro-, and Chloro- Sulfonic Acids

A. Introduction

In continuation of our studies, this section of the report concerns the reaction of coal with several sulfonic acids, CF_3SO_3H, CH_3SO_3F, HSO_3F, and HSO_3Cl.

B. Experimental

Samples of subbituminous PSOC 636 and low volatile bituminous PSOC 688 were provided by the Coal Research Section of Pennsylvania State University. The pure acids, as well as the indicated aqueous solutions are available from commercial sources.

Samples of bulk coal were prepared according to ASTM standards for analysis. Coal pieces employed for treatment by the acids, were normally at least 2 cm long with a diameter just large enough to fit through a 24/40 ground joint (about 20 mm). These pieces (50 g) of chunked coal were refluxed with the methanesulfonic acid for about 12 hours. The mixture was allowed to cool and then it was filtered. The reaction with trifluoromethane-, chloro-, and fluorosulfonic acid is very rapid, therefore, the pure acids were diluted with an equal mass of dichloromethane to moderate the reaction. The reactions were quenched by pouring the mixture into an ice-water mixture. The mixture was vacuum filtered and the residual coal washed with hot water and then dried at 110°C. Hydrolysis experiments using boiling water of 15% aqueous sodium hydroxide were carried out on the treated coal.

Analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN), by William Brothers Laboratories (Tulsa, OK), and by the Oklahoma Geological Survey. Calorific values were obtained using an ETEC Autoscan scanning electron microscope with gold sputtered samples.

C. Results and Discussion

The acids used in this study have the general formula $(HO)SO_2X$, where X is $-CH_3$, $-CF_3$, -Cl, -F. Measurements of the conductivity of strong acids in acetic acid have shown that trifluoromethanesulfonic acid is one of the strongest simple protonic acids. It is difficult to distinguish the acid strengths of the halogenated acids since they are very strong and they vary with the choice of base; however, CF_3SO_3H is 427 times stronger than trifluoroacetic acid and CH_3SO_3H is 17 times stronger than trifluoroacetic acid when acetic acid is the reference base.[44]

Trifluoromethanesulfonic acid is a clear colorless liquid which fumes in air, with a bp of 162°C. It is miscible with water in all proportions and is soluble in many polar organic solvents such as dimethylformamide, acetonitrile, sulfolane, dimethylsulfoxide and sulfene.[45] It is a high density (1.698 gm/cc) liquid; therefore, it will generate a hydrostatic pressure about 65% greater than water at the same depth. It reacts with alcohols to give esters. It has been successfully employed as a catalyst in various Friedel-Crafts type, alkylation, acylation, and polymerization reactions.[46] It, therefore, has a reaction chemistry which should make it suitable for the chemical communition of coal.

Trifluoromethanesulfonic acid readily comminutes the coal in this study. At room temperature the low volatile bituminous coal becomes a fine powder, whereas the subbituminous coal breaks into very small pieces. The ash and sulfur yields of the cleaned coal are reduced by

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[44] See: Howells, et al., page 11.

[45] Ibid.

[46] Hagen, A.P., Miller, T.S., Bynum, R.L., and Kapila, V.P., J. Org. Chem. 47, 1345, 1982.

treatment with this acid. It is also important to note that the 60% aqueous solution is an effective comminution and cleaning reagent since it is commerically available.

The main function of the trifluoromethanesulfonic acid appears to be the physical alteration of the coal since only a small amount of the acid is consumed by the reactions with the coal (1-2%). It appears that much of the fracturing that takes place is due to the secondary build up of internal pressures. Such fracturing would allow further penetration of the acid, leading to further reaction with the coal, additional pressure build up, more fracturing, and so forth. Scanning electron microscopy shows that the fragmentation takes place along the mineral matter boundaries forming fractures parallel to and at right angles to the bedding plane.

The fluorine content of the residue can be reduced by washing the treated coal with a 15% aqueous solution of sodium hydroxide to remove esters. The organic sulfur yield of the treated coal consists of coal sulfur, as well as sulfur present in trifluoromethanesulfonic acid esters of the coal. Upon NaOH hydrolysis of the coal to remove the ester the organic sulfur of the residue becomes less than the amount given in Tables 3 and 4.

Methanesulfonic acid is the weakest acid investigated in this study. The commercial 70% aqueous solution is representative of ground water diluted acid. When refluxed it extensively comminutes the subbituminous coal, but it has only a small effect on the low volatile bituminous coal.

Fluoro- and chlorosulfonic acids are strong oxidizing acids that react violently with water. The pure acids react with coal rapidly to form a fine powder with a very low calorific value. When diluted with an

TABLE 3

Analytical Data: Subbituminous Coal PSOC-636

	Original Coal	Methanesulfonic Acid (70%)	Trifluoromethane-sulfonic Acid	Trifluoromethane-sulfonic Acid (60%)	Fluorosulfonic Acid*	Chlorosulfonic Acid*
Proximate Analysis (wt%)						
Moisture	7.6	0.5	1.5	1.2	3.0	1.6
Volatile Matter	53.4	42.6	45.7	46.0	46.5	39.5
Ash	18.3	5.2	4.5	6.1	7.7	14.6
Fixed Carbon	20.7	51.7	48.3	46.7	42.8	44.3
Ultimate Analysis						
H	4.9	4.4	4.8	5.0	3.1	3.3
C	60.9	60.6	65.9	66.8	56.5	58.3
N	1.1	1.1	1.1	1.1	1.0	0.9
O (by difference)	12.0	26.2	21.1	18.6	21.7	14.7
S	2.8	2.5	1.8	1.6	8.9	6.1
Cl	0.0	0.0	0.0	0.4	0.1	2.1
F	0.0	0.0	0.8	0.4	1.0	0.0
Sulfur Forms						
Sulfur	0.2	0.0	0.1	0.1	0.7	1.2
Pyritic	1.7	1.6	0.9	0.7	0.2	0.2
Organic	0.9	0.9	0.8	0.9	8.0	4.7
Calorific Value (MJ/kg)	29.1	23.3	25.7	26.6	19.2	20.3

*50% Solution in CH_2Cl_2

TABLE 4

Analytical Data: Low Volatile Bituminous Coal PSOC-688

	Original Coal	Methanesulfonic Acid (70%)	Trifluoromethane-sulfonic Acid	Trifluoromethane-sulfonic Acid (60%)	Fluorosulfonic Acid*	Chlorosulfonic Acid*
Proximate Analysis (wt%)						
Moisture	1.3	0.4	0.9	0.8	4.0	2.3
Volatile Matter	16.2	13.9	26.6	25.3	42.5	40.2
Ash	16.0	20.1	6.1	15.0	5.7	10.5
Fixed Carbon	66.5	65.6	66.4	58.9	47.8	47.0
Ultimate Analysis						
H	3.9	3.8	3.8	4.0	2.7	3.0
C	71.0	65.0	66.6	67.1	55.6	57.9
N	1.2	1.0	1.2	1.1	0.9	1.0
O (by difference)	5.3	7.6	18.5	10.7	26.5	20.3
S	2.6	2.5	2.1	1.5	7.8	5.3
Cl	0.0	0.0	0.0	0.0	0.1	2.0
F	0.0	0.0	1.7	0.6	0.7	0.0
Sulfur Forms						
Sulfur	0.1	0.0	0.0	0.0	1.0	1.2
Pyritic	0.9	1.1	0.7	0.5	0.2	0.2
Organic	1.6	1.4	1.4	1.0	6.6	3.9
Calorific Value (MJ/kg)	26.1	21.5	24.8	25.1	18.3	19.2

*50% Solution in CH_2Cl_2

equal amount of dichloromethane the reaction occurs at a reasonable rate; however, as would be anticipated, the oxidizing acids leave a powdered coal which is not suitable for use as a premium fuel.

D. Model Compound Reactions

Exentsive model compound studies were not carried out since these acids have a well known reaction chemistry.[47] However, since the ability of a nonoxidizing acid to cleave ether linkages appears to correlate with the acids ability to comminute the coals examined in this research, selected experiments were performed. Trifluoromethanesulfonic acid cleaves dibenzylether, benzylethylether, benzylphenylether and 2-napthylethylether at 25°C.

$$C_{10}H_7OC_2H_5 + CF_3SO_3H \rightarrow C_{10}H_7OH + CF_3SO_3C_2H_5$$

In each case the hydroxyl moieties are recovered as the acid ester. This

$$C_{10}H_7OH + CF_3SO_3H \rightarrow CF_3SO_3C_{10}H_7$$

is reasonable since the anhydrous trifluoromethanesulfonic acid reacts readily with hydroxyl groupings to form esters.

The ether cleavage reaction would be anticipated for the anhydrous strong acid; however, the 60% aqueous solution cleaves these same ethers at 100°C with the recovery of the hydroxyl compounds rather than the esters. This is an important observation since any commercial use of trifluoromethane-sulfonic acid will most likely employ the commercially available 60% aqueous solution.

Anhydrous methanesulfonic acid cleaves benzyl ethers at 120°C, but the 2-naphylethylether does not react at 120°C. Commercial 70% aqueous methanesulfonic acid cleaves the same ethers at 100°C.

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[47] Cady, G.H., "Fluorine Containing Compounds of Sulfur," Adv. Inorg. Chem. Radiochem., 20, 105, 1960.

The methanesulfonic acids were combined with model compounds containing sulfur linkages thought to be present in coal. Diphenyldisulfide, diphenylsulfide, phenylmethylsulfide, and phenylethylsulfide do not react with aqueous or anhydrous methanesulfonic acid below 100°C; however, they do react with thiophenol at 100°C to form a complex mixture of products which includes $(C_6H_5S)_2$. The same results are obtained with aqueous trifluoromethanesulfonic acid.

V. Reactions of Small Covalent Molecules with Coal: Difluorophosphoric and Phosphoric Acids

A. Introduction

Difluorophosphoric acid (DFPA) has been found to be effective for the comminution of low volatile bituminous, high volative bituminous and subbituminous coals. Approximately 5% of the original coal dissolves during the acid treatment leaving a material which has a high heating value. The sulfur yield of the coal is greatly reduced by commercial difluorophosphoric acid or when a 75% solution in water is employed. The ash content is also reduced. Samples of Morris coal, a high volatile bituminous coal found in Oklahoma were found not to readily comminute with aqueous or anhydrous ammonia, water, or glacial acetic acid at temperatures up to 100°C in sealed tubes at autogenous pressure. This study was undertaken to find a more active comminution reagents for Morris coal.

Difluorophosphoric acid has been used by the oil industry to open sand formations in oil-bearing strata. In water it slowly hydrolyzes to monofluorophosphoric, phosphoric, and hydrofluoric acids. It has an excellent liquid range (mp -96.5°C, bp 116°C) and a high density (1.583 g/cm^3 at 20°C), therefore, it will generate a hydrostatic pressure about 60% greater than water at the same depth. This acid undergoes slow decomposition upon distillation at atmospheric pressure and it is an alkylation and polymerization catalyst.[48,49]

B. Experimental

The Morris coal was obtained from the Oklahoma Geological Survey.

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[48] White, W.E. and Pupp, C., "The Chemistry and Chemical Technology of Fluorine," H.F. Mark, Ed., John Wiley, New York, pp. 635, 1966.

[49] Ember, L.R., Chem. Engr. News, 58, 22, 1980.

The subbituminous (PSOC-636) and low volatile bituminous (PSOC-688) coals were generously supplied by the Coal Research Section of the Pennsylvania State University.

Samples of bulk coal for analysis were prepared according to ASTM standards. Coal pieces employed for treatment by DFPA were normally at least 2 cm long with a diameter just large enough to fit through a 24/40 ground joint (about 20 mm). These pieces (50 g) of chunked coal were refluxed with 500 g of the solvent for 24 h using Teflon vessels. The mixture was vacuum filtered and the residual coal washed with water and then dried at 110°C. Hydrolysis experiments using boiling water or 15% aqueous sodium hydroxide were carried out on the treated coal.

Analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN) by Williams Brothers Laboratories (Tulsa, OK), and by the Oklahoma Geological Survey. SEM micrographs were obtained using an ETEC Autoscan scanning electron microscope with gold sputtered samples.

C. Results and Discussion

Difluorophosphoric acid readily comminutes the coals used in this study. At room temperature the low volatile bituminous coal chunks 2 cm on edge were reduced to a fine powder within an hour. The other coals comminute more slowly at room temperature; however, at reflux (116°C) they comminute rapidly to a powder. The main function of the difluorophosphoric acid appears to be the physical alteration of the coal since only 1-2% of it is consumed during the process. Swelling can take place due to the internal pressure of the liquid which builds internal stresses exceeding the fracture strength of the solid. Larger chunks become quite friable after treatment. The SEM data clearly shows that fragmentation takes place along the mineral matter boundaries forming

fractures parallel to, and at right angles to, the bedding plane.

Tables 5 and 6 summarize the anlaytical data. The Morris coal has high sulfur and ash yields which were reduced by interaction with DFPA and its aqueous solutions. The fluorine content of the residue can be reduced by washing the treated coal with 15% aqueous sodium hydroxide to less than the original amount.

It is possible that the reactive agent in the DFPA is a contaminate or a hydrolysis product.

$$F_2P(O)OH + 2H_2O \rightarrow P(O)(OH)_3 + 3HF$$

Phosphoric acid has been investigated as a catalyst for the hydrogenation of high-sulfur bituminous coal and as a solvent for the removal of sulfur.[50-52] In experiments analogous to the DFPA work phosphoric acid was combined with the coals used in this study. The coals readily comminuted; however, the sulfur and ash yields were not reduced as much as when DFPA was employed.

Anhydrous hydrogen fluoride has been shown to be effective for the comminution of coal.[53] The coals examined in this study were combined with 50% aqueous HF and they readily comminuted; however, the sulfur content did not change even though the ash content was greatly decreased (50-75%).

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[50] McLean, J.B. and Vermeulen, T., "Coal Liquefaction Studies Using Phosphoric Acid at Moderate Temperatures and Pressures," M.Sc. Thesis, University of California at Berkeley, 1977.

[51] Santangelo, J.G. and Dorchak, T.P., "Desulfurized Char with Phosphoric Acid," U.S. Patent 3,812,017 (21 May 74); Chem. Abst., 81, 108435g, 1974.

[52] Meyers, R.A., "Solvent Extraction of Sulfur and Nitrogen Compounds from Coal," Ger. Offen. 2,108,786 (24 Feb 70); Chem. Abst., 75, 131553d, 1971.

[53] Jensen, H.P., "Comminuting and Reducing the Sulfur and Ash Content of Coal," U.S. Patent 4,169,710 (2 Oct 79); Chem. Abst., 92, 25391r, 1980.

TABLE 5. Analytical Data: Oklahoma Bituminous (Moisture Free)*

	Untreated	100% DFPA	75% DFPA
Proximate Analysis, wt%			
Moisture	[1.6]	[2.3]	[0.0]
Volatile	38.9	32.3	35.9
Ash	17.0	9.3	14.6
Carbon, Fixed	44.1	58.4	49.5
Ultimate Analysis, wt%			
H	3.8	4.1	4.7
C	57.3	66.1	68.5
N	1.5	1.9	2.0
O (by difference)	10.8	13.4	6.8
F	0.1	1.6	0.8
S	9.5	3.6	2.6
Sulfate	0.1	0.0	0.1
Pyritic	3.5	1.5	0.9
Organic	5.9	2.1	1.7
Ash	17.0	9.3	14.6
Calorific Value+			
(MJ/kg)	27.6	25.1	24.9

* All samples were dried at 110°C prior to submission for analysis. The treated samples were washed with boiling water prior to drying.

+ Calculated according to ASTM 388.

TABLE 6. Analytical Data for Comparison Coals (Moisture Free) *

PSOC-688	Untreated	100% DFPA	85% PA
Ash Yield	16.2	8.2	20.8
Sulfur Yield	2.6	0.9	2.5
Sulfate	0.1	0.0	0.0
Pyritic	0.9	0.4	0.9
Organic	1.6	0.5	1.6
Calorific Value (MJ/kg)[2]	26.0	25.1	22.6
PSOC-636			
Ash Yield	19.8	7.6	11.0
Sulfur Yield	3.0	0.3	1.7
Sulfate	0.2	0.0	0.0
Pyritic	1.8	0.2	0.9
Organic	1.0	0.1	0.8
Calorific Value (MJ/kg) +	29.1	27.2	23.5

* All samples were dried at 110°C prior to submission for analysis. The treated samples were washed with boiling water prior to drying.

\+ Calculated according to ASTM 388.

Commercial DFPA can contain small amounts of hexafluorophosphoric acid which arises from the manufacturing process. Samples of each coal were refluxed with commercial aqueous 65% HPF_6. This reagent was effective neither for comminution nor for cleaning of the coal.

Difluorophosphoric acid and its 75% aqueous solution are excellent reagents for reducing the sulfur and ash contents of the coals examined in this study. The functional groupings present in coal (e.g., -OH and $-[S]_x-$) react with the DFPA to form esters and thioesters. This reagent would appear to be ideal for coal cleaning; however, it should be noted that some esters and thioesters of phosphorus (V) oxyfluorides have been used as nerve gases.[54,55] Extensive model compound work should be carried out before the DFPA is used for the commercial cleaning of coal.

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[54] See: White, et al., page 25.

[55] See: Embers, et al., page 25.

VI. High-Pressure Reactions

The influence of increased pressure upon chemical reactions has been well established.[56] It would be reasonable to assume that reaction parameters of 300°C at pressures up to 20,000 psi would be representative of conditions suitable for hydrostatic mining of coal using the reagents noted in sections II-IV. In this investigation, no significant influence of pressure on the reactions of trifluoroacetic, methanesulfonic, or trifluoromethanesulfonic acid was noted. This observation is very important since it implies that the effectiveness of these reagents will not be reduced at increased pressure. Tables 7 to 20 summarize the experimental results.

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[56] Hagen, A.P., J. Chem. Educ., 55, 615, 1978.

TABLE 7

Increased Pressure at 300°C: Morris Coal

70% Trifluoroacetic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	[1.6]	[0]	[0]	[0]
Volatile	38.9	39.0	41.0	38.2
Ash	17.0	3.8	2.2	1.3
Fixed Carbon	44.1	57.2	56.8	60.5
Sulfur Forms				
Sulfate	0.3	0.0	0.0	0.0
Pyritic	3.5	1.9	1.4	0.5
Organic	5.9	0.7	0.5	0.3
Total	9.6	2.6	1.9	0.8
Calorific Value				
(MJ kg^{-1})	28.37	28.60	27.21	27.60

TABLE 8

Increased Pressure at 300: PSOC-688

70% Trifluoroacetic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	1.3	1.1	1.0	1.1
Volatile	16.2	16.8	25.2	27.3
Ash	16.0	2.3	2.6	1.8
Fixed Carbon	66.5	79.8	71.2	69.8
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	0.1	0.0	0.0
Organic	1.6	1.1	0.6	0.3
Total	2.6	1.2	0.6	0.3
Calorific Value				
(MJ kg^{-1})	26.1	25.8	26.8	26.8

TABLE 9

Increased Pressure at 300°C: PSOC-636

70% Trifluoroacetic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	7.6	1.1	1.0	1.1
Volatile	53.4	50.0	58.6	60.1
Ash	18.3	5.8	1.2	1.2
Fixed Carbon	20.7	43.1	39.2	37.6
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.7	0.1	0.0	0.0
Organic	0.9	0.4	0.4	0.4
Total	2.8	0.5	0.4	0.4
Calorific Value				
($MJ\ kg^{-1}$)	29.1	29.1	29.3	28.8

TABLE 10

Increased Pressure at 300°C: PSOC-636

70% Methanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	7.6	0.5	0.8	0.7
Volatile	53.4	40.2	47.8	49.2
Ash	18.3	5.2	6.3	4.8
Fixed Carbon	20.7	59.1	45.1	45.3
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.7	1.3	1.0	0.8
Organic	0.9	0.9	0.8	0.6
Total	2.8	2.2	1.8	1.4
Calorific Value				
(MJ kg^{-1})	29.1	24.6	25.0	22.2

TABLE 11

Increased Pressure at 300°C: PSOC 688

70% Methanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	1.3	0.5	0.6	0.2
Volatile	16.2	13.5	18.1	16.2
Ash	16.0	20.1	22.3	19.1
Fixed Carbon	66.5	65.9	59.0	64.5
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	1.1	1.2	1.2
Organic	1.6	1.5	1.3	1.6
Total	2.6	2.6	2.5	2.8
Calorific Value				
($MJ\ kg^{-1}$)	26.1	21.0	19.0	20.2

TABLE 12

Increased Pressure at 300°C: PSOC-636

Trifluoromethanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	7.6	1.0	1.2	0.5
Volatile	53.4	44.9	47.1	48.2
Ash	18.3	4.0	3.5	3.9
Fixed Carbon	20.7	50.1	48.2	47.4
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.7	0.8	0.5	0.5
Organic	0.9	0.7	0.7	0.8
Total	2.8	1.5	1.2	1.3
Calorific Value				
($MJ\ kg^{-1}$)	29.1	26.2	27.1	26.9

TABLE 13

Increased Pressure at 300°C: PSOC-688

Trifluoromethanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	1.3	1.0	0.8	1.6
Volatile	16.2	25.2	24.3	19.0
Ash	6.0	5.8	5.0	4.8
Fixed Carbon	66.5	67.0	69.9	74.6
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	0.6	0.6	0.4
Organic	1.6	1.2	1.0	1.1
Total	2.6	1.8	1.6	1.5
Calorific Value				
(MJ kg^{-1})	26.1	25.8	26.2	24.9

TABLE 14

Increased Pressure at 300°C: PSOC-636

60% Trifluoromethanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	7.6	1.2	0.8	1.5
Volatile	53.4	48.6	45.7	44.6
Ash	18.3	6.0	5.4	3.8
Fixed Carbon	20.7	44.2	48.1	50.1
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.7	0.6	0.6	0.4
Organic	0.9	0.9	0.8	0.8
Total	2.8	1.5	1.4	1.2
Calorific Value				
(MJ kg^{-1})	29.1	27.2	28.4	29.0

TABLE 15

Increased Pressure at 300°C: PSOC-688

60% Trifluoromethanesulfonic Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	1.3	0.8	0.7	0.9
Volatile	16.2	26.2	24.3	22.1
Ash	16.0	15.0	12.9	12.5
Fixed Carbon	66.5			
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	0.4	0.4	0.3
Organic	1.6	0.9	0.8	0.8
Total	2.6	1.3	1.2	1.1
Calorific Value				
(MJ kg^{-1})	26.1	24.8	24.8	27.1

TABLE 16

Increased Pressure at 300°C: Morris Coal

100% Difluorophosphoric Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture	[1.6]	[0.0]	[0.1]	[0.1]
Volatile	38.9	33.5	34.5	31.0
Ash	17.0	8.6	9.0	7.2
Fixed Carbon	44.1	57.9	56.5	61.8
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	3.5	1.4	1.2	1.0
Organic	5.9	2.1	1.8	1.7
Total	9.5	3.5	3.0	2.7
Calorific Value				
(MJ kg^{-1})	27.6	26.2	25.2	27.1

TABLE 17

Increased Pressure at 300°C: PSOC-636

100% Difluorophosphoric Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture				
Volatile				
Ash Yield	19.8	6.2	6.2	5.8
Fixed Carbon				
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.8	0.2	0.1	0.0
Organic	1.0	0.1	0.1	0.1
Total	3.0	0.3	0.2	0.1
Calorific Value				
(MJ kg^{-1})	29.1	27.6	26.5	29.0

TABLE 18

Increased Pressure at 300°C: PSOC-688

100% Difluorophosphoric Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture				
Volatile				
Ash Yield	16.2	14.2	14.3	10.2
Fixed Carbon				
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	0.8	0.7	0.8
Organic	1.6	1.3	1.2	1.1
Total	2.6	2.1	1.9	1.9
Calorific Value				
($MJ\ kg^{-1}$)	26.0	24.3	25.0	22.1

TABLE 19

Increased Pressure at 300°C: PSOC-636

85% Phosphoric Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture				
Volatile				
Ash Yield	19.8	10.2	12.3	8.5
Fixed Carbon				
Sulfur Forms				
Sulfate	0.2	0.0	0.0	0.0
Pyritic	1.8	0.8	1.0	0.6
Organic	1.0	0.9	0.8	0.9
Total	3.0	1.7	1.8	1.5
Calorific Value				
($MJ\ kg^{-1}$)	29.1	24.5	24.5	25.2

TABLE 20

Increased Pressure at 300°C: PSOC-636

85% Phosphoric Acid

Proximate Analysis (wt. %)	Untreated	5,000 psi	10,000 psi	20,000 psi
Moisture				
Volatile				
Ash Yield	16.2	21.0	18.2	20.0
Fixed Carbon				
Sulfur Forms				
Sulfate	0.1	0.0	0.0	0.0
Pyritic	0.9	0.9	0.9	0.9
Organic	1.6	1.5	1.7	1.4
Total	2.6	2.4	2.6	2.3
Calorific Value				
(MJ kg^{-1})	26.0	25.2	23.0	24.1

VII. Reactions of Small Covalent Molecules with Coal: Acetic Anhydride, Acetic-, Mono, Di-, and Trichloroacetic Acid

This section describes the interaction of acetic acid and its chloro derivatives, as well as acetic anhydride with selected coals.

A. Experimental

The subbituminous (PSOC 636) and low volatile bituminous (PSOC 688) coals were generously supplied by the Research Section of the Pennsylvania State University. The acids are commercial reagents which were used as supplied or as aqueous solutions.

Coal samples for analysis were prepared according to ASTM standards. Coal pieces employed for treatment with acetic anhydride were normally at least 2 cm long with a diameter just large enough to fit through a 24/40 ground joint. Acetic anhydride (250 ml) was placed in a one liter round bottom flask equipped with a reflux condenser containing 50 g of the chunked coal. The solution was allowed to reflux for 24 hours, after which it was cooled to room temperature and then suction filtered. The residual coal was washed with hot water until there was a complete removal of acetic acid, and finally the residue was dried in an oven at 110°C. Similar experiments were performed with the other acids. Hydrolysis experiments with the treated coal were performed using a 15% aqueous solution of sodium hydroxide.

Oil, asphaltene, and preasphaltene contents were determined in each case for the untreated coal, as well as for the materials which were soluble in the acid anhydride/acid and the cleaned coal residue. Coal was refluxed with hexane 4-5 hours. The residue was filtered and washed with hexane. The filtrate and washing were mixed together and the hexane was removed by distillation at atmospheric pressure to yield the oil. The residue was dried and then, following the same procedure, it was

refluxed and washed with toluene. The residue was measured as asphaltenes. The remaining residue left after treatment with toluene was treated with pyridine in a similar fashion. The pyridine soluble material was defined as being preasphaltene and the remaining material was designated residue.

Model compound reactions were carried at the reflux conditions or in sealed tubes. The products were identified and confirmed using two or more of the following measurements: melting point, boiling point, elemental analysis, infrared, NMR, or mass spectroscopy.

Infrared spectra were measured in the 4000-300 cm^{-1} region using a Beckman IR-10, double beam grating spectrophotometer. Mass spectra were determined with a Hewlett-Packard Model 5985B GC/MS and a Varian T-60 spectrometer was employed for NMR spectra. Analysis were performed by Galbraith Laboratories, Inc. (Knoxville, TN), Williams Brothers' Laboratories (Tulas, OK), and the the Oklahoma Geological Survey. Sulfur analysis were performed according to the ASTM D2492. It should be noted that the "original coal" analysis are not for the same exact piece of coal which was treated with the acid. The reported analytical data is for the sample on an "as received" basis, except that the calorific value was calculated according to ASTM 388.

B. Results and Discussion

Acetic anhydride is a colorless liquid with a mp of -73°C and a bp of 140°C. It is soluble in chloroform and ether and in water with which it forms acetic acid. It is widely used in organic synthesis; e.g., as a dehydrating agent in nitrations and sulfonations. In industry it is used for the esterification of polyhydroxy compounds, especially cellulose. Acetic anhydride comminutes the low volatile (PSOC 688) and subbituminous (PSOC 636) coals at its reflux temperature but not at 25°C.

For both coals the pyritic and organic sulfur yields are reduced with a similar reduction in ash yield value.

Acetic acid has a K_a of 1.8×10^{-5}. It is a clear, colorless, highly associated liquid with a pungent odor at room temperature. It is a nonoxidizing acid with a convenient liquid range and relatively low viscosity. It is soluble in benzene, carbon tetrachloride, cyclohexane, 1,1-dichloroethane, ether, alcohol, and water. It forms additional compounds with a large number of inorganic and organic compounds. It reacts with alcohols to give esters.[57]

Glacial acetic acid does not comminute the coal in this study as rapidly as the chlorinated acids. At the reflux temperature of acetic acid (116-118°C) the subbituminous coal comminutes and becomes friable to a much greater extent than the low volatile bituminous coal. In PSOC 636 and PSOC 688 coal, the sulfur yields are reduced. In the case of PSOC 636, the ash yield is reduced while in the case of PSOC 688, ash yield is increased.

The chlorinated acids are stronger than acetic acid (monochloro-, $K_a = 136 \times 10^{-5}$; dichloro-, $K_a = 5530 \times 10^{-5}$; trichloro-, $K_a = 23200 \times 10^{-5}$). Monochloracetic acid is a crystalline solid with mp 61-62°C, bp 189°C, and d = 1.53 g/cm^3. It is a miscible with water and organic solvents. It has been used in organic synthesis[58] and also used in substitution reactions.[59]

Monochloroacetic acid comminutes the low volative bituminous and subbituminous coal examined in this study more rapidly than acetic acid.

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[57] Alexander, Popous, "Anhydrous Acetic Acid as Non-Aqueous Solvent," T.C. Waddington, Ed., Academic Press, London, 1966.

[58] Gupta, R.P., Ind. J. Chem., Section B, 17, 572, 1979.

[59] Detty, M.R. and Wood, G.P., J. Org. Chem., 45, 80, 1980.

The pure acid above the melting point, as well as its aqueous solutions is effective for reducing the ash and sulfur yields of the low volatile bituminous coal.

Dichloroacetic acid is soluble in water, alcohol, and ether. Its physical properties are as follows: mp 9-11°C; bp, 191-194°C; and dipole moment = 2.59. It forms esters with alcohols and it forms complexes with many metals. Dichloroacetic acid and its aqueous solutions comminute the low volatile bituminous and subbituminous coal more rapidly at its reflux temperature (191-194°C). The ash and sulfur yields of both coals are reduced.

Trichloroacetic acid is a white crystalline solid, with mp of 57-58°C and bp of 196-197°C. It is miscible with water, alcohol and ether. It has a characteristic smell and is very corrosive. Trichloroacetic acid comminutes the subbituminous coal and reduced its sulfur and ash yields. Based on the overall trends noted in this effort the trichloroacetic acid should have been the best comminution agent since it is the strongest acid; however, it did not comminute the low volatile bituminous coal.

The main function of the reagents investigated in this study appears to be the physical alteration of the coal, since very small amounts of it are consumed during the reaction. The chlorine content (in the case of mono-, di-, and trichloroacetic acid) of the treated coal can easily be reduced to zero by washing the treated coal with dilute aqueous solution of 15% sodium hydroxide. This corresponds to the hydrolysis of an ester that would form during the comminution process.

Tables 23 and 24 present the hexane/toluene/pyridine solubilities of the coals before and after treatment with the reagents. The anhydrous

chlorinated acids dissolve about 5% of the coal; this solution contains the oils and asphaltenes from the original coal. Acetic anhydride and acetic acid remove these substances from the subbituminous but not the low volatile bituminous coal. The presaphaltene content of the coals is unchanged or increased by all of the anhydrous reagents.

C. Model Compounds

The high calorific values, as well as the minimal physical alteration of the treated coal, implies only limited chemical interactions of these non-oxidizing reagents with the original coal.

Acetic anhydride forms esters with phenols and alcohols. The acids should interact to form esters and reasonable yields of esters are historically obtained when a reagent is present to remove water which forms during the reaction since esters are often unstable with respect to hydolysis.

Acetic, mono-, di-, and trichloroacetic acids react at reflux conditions to form esters with benzyl alcohol, but not with phenol or 2-naphthol unless a dehydrating agent is present. Thiophenol forms the appropriate ester when heated at 190°C in a sealed tube without the addition of a dehydrating agent.

The chlorinated acids readily cleave the ether linkage in benzyl ethyl ether, benzyl phenyl ehter, and dibenzyl ether at reflux conditions.

With benzyl phenyl ether the isolated products include the benzyl ester and phenol.

$$C_6H_5CH_2OC_6H_5 + CH_2ClCOOH \rightarrow C_6H_5CH_2O_2CCH_2Cl + C_6H_5OH$$

$$C_6H_5CH_2OC_6H_5 + CHCl_2COOH \rightarrow C_6H_5CH_2O_2COCHCl_2 + C_6H_5OH$$

$$C_6H_5CH_2OC_6H_5 + CCl_3COOH \rightarrow C_6H_5CH_2O_2CCCl_3 + C_6H_5OH$$

TABLE 21

Analytical Data: Subbituminous Coal PSOC-636

	Original Coal	Acetic Anhydride	Acetic Acid	Acetic Acid (50%)	MCAA Acid	MCAA Acid (50%)	DCAA Acid	DCAA Acid (50%)
Proximate Analysis (wt%)								
Moisture	7.6	0.8	5.1	6.6	1.1	0.4	0.5	0.3
Volatile Matter	53.4	57.1	52.0	51.2	58.7	60.4	26.9	19.0
Ash	18.3	9.3	5.6	4.5	20.2	21.8	12.2	18.4
Fixed Carbon	20.7	32.8	37.3	37.7	20.0	17.4	60.4	62.3
Ultimate Analysis								
H	4.9	5.3	5.1	5.5	3.3	4.0	3.3	3.5
C	60.9	66.5	65.1	62.9	63.7	66.8	66.7	67.9
N	1.1	1.0	1.1	1.1	1.1	1.3	0.8	1.0
O (by difference)	12.0	16.3	21.7	24.7	9.2	3.4	11.9	5.1
S	2.8	1.6	1.3	1.3	1.6	2.0	0.5	1.0
Cl	0.0	0.0	0.1	0.0	0.9	0.9	4.7	3.1
Sulfur Forms								
Sulfate	0.2	0.1	0.0	0.0	0.0	0.0	0.1	0.0
Pyritic	1.7	0.9	0.6	0.5	0.8	0.8	0.0	0.3
Organic	0.9	0.7	0.7	0.8	0.8	1.2	0.4	0.7
Calorific Value (MJ/kg)	29.1	27.2	26.9	27.0	24.8	24.7	24.1	28.3

*MCAA Monochloroacetic Acid
DCAA Dichloroacetic Acid

TABLE 22

Analytical Data: Low Volatile Bituminous Coal PSOC-688*

	Original Coal	Acetic Anhydride	Acetic Acid	Acetic Acid (50%)	MCAA	MCAA (50%)	MCAA Acid (75%)	DCAA Acid	DCAA Acid (50%)	TCAA Acid	TCAA (50%)
Proximate Analysis (wt%)											
Moisture	1.3	0.7	1.2	1.0	2.4	1.8	3.8	1.7	11.0	3.1	5.8
Volatile Matter	16.2	17.4	14.9	14.1	51.8	42.4	54.1	76.8	64.5	44.9	55.1
Ash	16.0	12.9	23.4	29.0	7.4	4.1	3.9	1.5	6.2	9.5	6.9
Fixed Carbon	66.5	69.0	60.5	55.9	38.4	51.7	38.2	20.0	18.3	42.4	32.3
Ultimate Analysis											
H	3.9	3.6	3.6	3.2	5.0	5.0	5.0	4.3	4.6	4.9	4.9
C	71.0	65.9	64.2	60.1	62.5	66.5	63.3	58.8	56.8	62.2	58.4
N	1.2	1.2	1.2	1.1	0.9	1.1	1.1	0.6	0.8	0.9	0.8
O (by difference)	5.3	15.1	5.9	5.5	20.4	20.3	21.5	23.0	19.0	13.3	14.3
S	2.6	1.3	1.5	1.2	1.3	1.3	1.5	0.6	1.2	1.1	1.4
Cl	0.0	0.1	0.1	0.1	2.5	1.7	3.7	11.2	11.4	8.1	13.3
F	0.0										
Sulfur Forms											
Sulfate	0.1	0.0	0.1	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.1
Pyritic	0.9	0.5	0.7	0.6	0.3	0.7	0.8	0.1	0.6	0.5	0.6
Organic	1.6	0.8	0.8	0.6	0.4	0.6	0.6	0.5	0.6	0.6	0.7
Calorific Value (MJ/kg)	26.1	30.0	26.3	24.1	25.5	26.2	25.6	23.4	24.3	25.3	25.7

*MCAA Monochloroacetic Acid
DCAA Dichloroacetic Acid
TCAA Trichloroacetic Acid

TABLE 23

Solubility of PSOC 688 in Hexane, Toluene, Pyridine (Per 100 g of Coal)

Acid	Hexane (Oils)	Toluene (Asphaltenes)	Pyridine (Preasphaltenes)
Original Coal	0.17	0.33	0.63
Acetic Anhydride	2.01	2.16	0.58
Acetic Acid	2.31	2.38	0.59
Acetic Acid (50%)	1.47	1.87	0.18
MCAA	0.04	0.97	1.61
MCAA (75%)	0.00	0.16	1.38
MCAA (50%)	0.00	0.17	1.99
DCAA	0.00	0.00	3.56
DCAA (50%)	0.00	0.05	3.01

TABLE 24

Solubility of PSOC 636 in Hexane, Toluene, Pyridine (Per 100 g of Coal)

Acid	Hexane (Oils)	Toluene (Asphaltenes)	Pyridine (Preasphaltenes)
Original Coal	0.88	1.60	3.05
Acetic Anhydride	0.09	0.52	3.11
Acetic Acid	0.07	0.56	3.41
Acetic Acid (50%)	0.24	1.08	4.62
MCAA	0.06	1.18	3.80
MCAA (75%)	0.57	1.24	4.70
MCAA (50%)	0.26	1.60	2.64
DCAA	0.00	0.00	7.99
DCAA (50%)	1.06	1.25	2.99
TCAA	0.00	0.25	3.01
TCAA (50%)	0.22	0.63	3.99

Similarly, mono-, di-, and trichloroacetic acid cleave benzyl ethyl ether to form the benzyl and ethyl esters. 1-1'-diphenyldiethyl ether cleaves at 300°C in a sealed tube with acetic, as well as monochloro acetic acid and the major product isolated in both cases was polystyrene.

At 180°C in a sealed tube acetic acid cleaves dibenzyl ether, but not the other ethers. None of the acids cleave diphenyl ether at temperatures up to 180°C. These acids also do not cleave diphenyl disulfide, diphenyl sulfide, phenyl methyl sulfide or phenyl ethyl sulfide.

VIII. Fragmentation Experiments

Large pieces of Oklahoma bituminous coal (Table 1, page 5) were treated with selected acids to model a mining operation. A typical chunk of coal about 20 cm on an edge was bored with a 0.25 inch star drill to make a cavity inside of the chunk having a volume of about 50 mL. The coal was placed in a water bath and a thermometer inserted to determine when the internal temperature reached equilibrium with the bath. The cavity was checked for water leaks and then pre-warmed acid was added. As the acid was utilized more acid was added until the coal fragmented. Table 25 summarizes the results.

TABLE 25

Fragmentation Experiments

Acid	Temperature (°C)	Time to Fragment (hr.)
Difluorophosphoric	50	2.5
Phosphoric (85%)	50	3.8
Trifluoromethanesulfonic	50	2.0
Methanesulfonic	50	4.2
Trifluoroacetic	50	3.5
Acetic	90	very slow
Monochloracetic	90	10.5
Dichloroacetic	90	8.5
Trichloroacetic	90	8.5

IX. Conclusions

1. Trifluoroacetic, difluorophosphoric, fluorosulfonic, hydrofluoric, trifluoromethanesulfonic, phosphoric, acetic, and chlorinated acetic acids are effective for the comminution of bituminous and subbituminous coal.

2. Methanesulfonic acid is effective for the comminution of bituminous coal.

3. Oxidizing acids comminute the coal to a fine powder having a greatly reduced calorific value.

4. Trifluoroacetic, trifluoromethanesulfonic, chlorosulfonic, and difluorophosphoric acids reduce the ash and sulfur yields of the coals used in this study.

5. Trifluoroacetic, difluorophosphoric, chloroacetic, and acetic acids, as well as acetic anhydride, extract organic, as well as pyritic sulfur, from the coals used in this study.

6. Hexafluorophosphoric acid does not interact with the coals.

7. Pressures up to 20,000 psi do not reduce the effectiveness of the comminution reagents.

8. The acids react with -OH, -SH, and ether groupings in the coal.