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DISSOLVING COAL AT MODERATE TEMPERATURES AND PRESSURES

Final Report for the Period August 20, 1982—September 30, 1984

By
Frank R. Mayo
Albert S. Hirschon
Karen A. Sundback

September 21, 1984

Work Performed Under Contract No. FG22-82PC50788

For
U. S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania

By
SRI International
Menlo Park, California

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Final Report
Covering the Period August 20, 1982, to September 30, 1984

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By: Frank R. Mayo, Albert S. Hirschon, and Karen A. Sundback

Prepared for:

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ABSTRACT

The main objectives of this research were to make Illinois No. 6 coal liquid or soluble with inexpensive reagents (e. g., solvolysis with methanol and acids), without high pressure equipment, and to see if our soluble products would be more reactive than whole coal in liquefaction processes. These efforts are unpromising. However, efforts to make coal soluble by oxidation with nitric acid gave encouraging results. When Illinois No. 6 and Wyodak coals were allowed to stand in sunlight for 282 days, 27% of the original weight and 32% of the original carbon were lost. Concurrent experiments in the dark at 24°C indicate that these coals are fairly stable in air in the dark; light causes most of the oxidation. The solubility properties of these aged coals will not be available before the end of this grant period.

Several other minor lines of work, some very interesting, are summarized in order of decreasing significance.

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1. SUMMARY OF RESEARCH ON DOE GRANT NO. DE-FG22-82PC60788

1.1 Introduction

Section 1 of this report summarizes the work reported in detail in the four Quarterly Progress Reports and more recent work described in detail in Section 2 of this Report. References in parentheses refer to Reports 1 through 4, and to this Report (F); the first number refers to the report and the second number refers to the page number (e. g., 3-5 is report 3, page 5). Section 3 is an Index to all reports submitted under this project.

The main objectives of this research were to make Illinois No. 6 coal liquid or soluble with inexpensive reagents (e.g., solvolysis with methanol and acids), without high pressure equipment, and to see if our soluble products would be more reactive than whole coal in liquefaction processes. These efforts, described on pages 1-4, are unpromising. However, efforts to make various coal fractions soluble by oxidation with nitric acid gave encouraging results (F-4). When Illinois No. 6 and Wyodak coals were allowed to stand in sunlight for 282 days, a 27% loss in weight and 32% loss of carbon resulted (F-5). Concurrent experiments in the dark at 24°C indicate that these coals are fairly stable in air in the dark; light causes most of the oxidation. The solubility properties of these aged coals will not be available before the end of this grant.

Several other minor lines of work done or completed since Report 4, some very interesting, are detailed on pages 9-23 this report, in order of decreasing significance, and summarized on pages 5-8.

1.2 Coal Beneficiation

The Illinois No. 6 coals used in this work, PSOC 26 and PSOC 1098, have high and variable ash contents. We therefore tried to convert them to more uniform, low-ash coals. We tried several comminutions of 1098 by methanol and ammonia and then separation by density with chloroform ($D = 1.48$). The comminutions were successful, but the best product still contained 5.2% mineral matter (F-5).

In our last demineralization (4-2), 271 g of PSOC 26 coal was ball-milled with 0.5 M aqueous HCl under nitrogen. After washing, drying, and sieving, we obtained 175 g of powdered coal, of which 155 g passed through a 200-mesh sieve. The latter portion was separated with 10/90 v/v $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ ($D = 1.32$) into 113 g containing 2.8% ash and 29 g containing 39% ash. In the future, this solvent mixture should be used on comminuted coal.

The PSOC 26 coal was also demineralized by the conventional HCl/HF procedure (2-4). The ash content was reduced from 12.2 to 2.7%, but the coal lost much of its solubility in pyridine; hence, it was not used.

1.3 Solvolysis of C-O Bonds

Work on our previous contract (22-81ET11423.001) showed that benzylamine (BnNH_2) and ethylenediamine would dissolve 45% of the carbon in PSOC 25 coal, whereas only 16% would dissolve in pyridine. The additional solubility in strong bases was attributed to cleavage of ether groups. A major objective of the work on this grant was to accomplish this cleavage faster and with cheaper reagents. Several reactions were tested on TIPS fractions (toluene-insoluble, pyridine-

soluble) and PI fractions (pyridine-insoluble portion of pyridine-extracted coal), but all were unpromising; some were even counterproductive. Reagents included MeOH/PhMe and toluenesulfonic or methanesulfonic acid at 100 to 200°C (2-6), ammonia in MeOH/toluene (2-9) and LiI, phenol, thiophenol, ethylamine, Na₂S, NaOH, ZnCl₂, and Bu₄NOH (3-4). In the most promising experiment, 9% of pyridine-soluble material was obtained by refluxing one g of PI 25 coal with 1 mL of MeSO₃H and 1 g of phenol with a Dean-Stark trap for 48 h. However, this product incorporated considerable phenol (3-5). We conclude that methanol is a poor nucleophile for cleaving ethers. Sulfur compounds are better nucleophiles, but they incorporate sulfur in the coal.

Solvolyses of lignite and semibutiminous coals, which contain much more oxygen, are more promising for investigations.

1.4 Liquefactions with Tetralin or CO

When whole 1098 coal was heated with tetralin for 2 h at 400°C, 87% became soluble in THF; however, this is no advance over present practice. Less coal dissolved when the tetralin was mixed with an equal volume of pyridine or when the starting coal was porous PI coal (2-10). In similar experiments with 1098 TIPS and tetralin, THF solubility was no better than with whole 1098 coal (3-6).

Black acids from a NaOCl oxidation, already soluble in aqueous base, were also heated with tetralin at 400°C but 28% remained insoluble in THF. When the same black acids were treated with CO and dilute aqueous KOH for 1 h at 400°C, all but 3% became soluble in THF, comparable to results with whole coal. However, in the same time at

300°C, 95% of the product was insoluble in THF (4-14). Thus, starting with water-soluble black acids instead of whole coal appears to offer no advantage.

1.5 Pyrolyses of Black Acids

A 150-mg sample of black acids from oxidation of Wyodak coal with 20% nitric acid was heated gradually over 30 min at 0.025 torr from room temperature to 850°C. Yields on carbon were: solid sublimate, 0.13%; distillate (probably mostly water), 5.6%; residue, 84.2%; and loss, 10.1% (4-13). A similar experiment with 20 torr of hydrogen present gave 0.06% sublimate, 3.5% distillate, and 99.2% residue. These results indicate no advantage in using soluble black acids for pyrolyses instead of whole coal.

1.6 Oxidations

Oxidations of coals gave better results, and now have more promise for making coal soluble, than any of the work described above.

TIPS 26, PI 26, PI 1098, and Wyodak coals were oxidized at 50°C with 15-30% nitric acid (4-7). The best yield of black acids was 78% from TIPS 26. The next best yield was 71% from PI 1098 and 30% acid. The best yield of black acids from Wyodak was 61% with 30% nitric acid at 25°C, but 18% of soluble acids was also obtained. These data suggest that yields can be optimized by balancing acid strength, reaction temperature, and number of oxidation steps, but that we are unlikely to reduce carbon losses below 15%. There may be considerable potential in using a combination of nitric acid and oxygen in coal oxidation.

Some oxidations of TIPS 26, PI 26, and PI Wyodak with NaOCl and of TIPS and PI 26 with oxygen (4-10) gave poorer yields of black acids than earlier experiments with TIPS and PI 25. Recent oxidations of PI 26 coal by oxygen in acidic and basic suspension in water (page 16) were discouragingly slow. However, oxidations of PI coals at the same state of subdivision are needed to compare reactivities of various coals.

Several oxidations of coal from the standpoint of the material lost as carbon oxides and other volatile and water-soluble products are discussed starting on page 15. In all the oxidations from which reasonable balances could be obtained, the H/C ratio for the missing material is between 0.5 and 0.6, presumably higher aromatic material.

Experiments on exposure of Illinois No. 6 and Wyodak coals to sunlight and air under Pyrex showed 27% weight loss in 282 days (F-19). However, exposure of similar samples to air in the dark at 24°C showed weight gains of only 0.14% for Illinois No. 6 and 1.51% for Wyodak coal in 311 days. It appears that coals are fairly stable in air in the dark, and that light greatly accelerates their oxidation.

1.7 Chromatography of Black Acids and Related Products

Pages 2-5 summarize work closely related to the main objective of our grant. This and the next section describe work done mostly under our previous contract, but completed under this grant. Pages 7-8 describe some miscellaneous efforts related to coal liquefaction.

Of all the work summarized in this report, work on gel permeation chromatography and high performance liquid chromatography probably has the most potential for an understanding of the oxidation and structure

of coal. A TIPS fraction and several black acid fractions were subjected to these chromatographic techniques (2-11). Different patterns were found with acids made in various ways, but the remarkable finding was that there is a common product (by gpc) in many of these black acids and the proportion of this product is sometimes 75-95% of the material chromatographed. It appears that many of the black acids are closely related, formed in good yields, and available for further purification and structure determination, as by IR and NMR. These black acids have not been heated above 100°C since the coal was mined and they incorporate as much as 75% of the carbon in the initial coal. These techniques also appear well adapted for comparing experimental procedures in oxidations of coal.

1.8 Solubilities of Ten Coals in Pyridine and Benzylamine

The solubilities of ten coals in pyridine and benzylamine were determined under the previous contract. The ash contents of some of these coals were high and variable; hence, the carbon contents of the dry mineral matter-free coals were uncertain. To a first approximation, the ratio of the solubilities in BnNH_2 /pyridine increased from 0.23 for a coal containing 92% carbon to about 3 for coal with 77% carbon (2-16). However, we are now primarily interested in determining what proportion, P, of the pyridine-insoluble coal will dissolve in BnNH_2 . The following equation applies:

$$P = (\% \text{ soluble in } \text{BnNH}_2 - \% \text{ soluble in pyridine}) / \% \text{ insoluble in pyridine}$$

P was recently found to be in the range 0.14 to 0.19 for five coals with 77 to 86% C, but P is 0.35 for our PSOC 25 coal and less than 0.09 for three coals with more than 83% carbon. Differences in P appear to reflect differences in the proportion of oxygen in cleavable ether groups, a number that should be significant in coal liquefaction. We propose to obtain solubility data on Wyodak coal and then to submit a Note to Fuel.

1.9 High Temperature Reaction of Benzylamine

Having conducted many reactions of BnNH_2 with coal at 100°C , we decided to find out what happens at higher temperatures. Details for PI 25 coal are given beginning on page 12. At higher temperatures, especially in stainless steel, much of the coal dissolves and a polymer, $(\text{C}_7\text{H}_6)_n$ is incorporated in the soluble product. At 300°C in stainless steel, this polymer becomes the principal product.

1.10 Field Ionization Mass Spectra of a TIPS Fraction and Its Benzylamine Reaction Product

Analyses of some FIMS spectra of a TIPS fraction and its BnNH_2 cleavage product start on page 18. The most plentiful products in the TIPS fraction are phenols, starting with cresol; however, above mass number 160, all mass numbers up to the volatility cutoff at about 700 are represented. The BnNH_2 cleavage product is similar, but it contains relatively high proportions of BnNH_2 fragments; 53% of this product was volatilized during measurement, whereas only 22% of the TIPS fraction was volatilized. These results are consistent with cleavage of TIPS by BnNH_2 with incorporation of nitrogen.

1.11 Attempted Reductions of PI 26 Coal With Isopropanol or Formic Acid

Pages 21-23 of this report describe attempted reductions of PI 26 coal with isopropanol + KOH at 100°C or with potassium formate plus formic acid at 200°C. The first experiment is encouraging enough to be worth running at 150°C, but the second experiment offers little prospect of reducing coal with formates or CO at 200°C.

2. RESULTS OBTAINED SINCE REPORT 4

2.1 Analyses of Coal Products

Table 1 lists the elemental analyses of the substrates and products mentioned in this section of the report. Except as noted, yields are based on carbon analyses.

2.2 Aging of Illinois No. 6 and Wyodak Coals

A paper by Liotta et al.* on weathering of Illinois No. 6 coal led to some similar experiments at SRI. Their coal was crushed to a maximum size of 6.4 mm, spread on the ground, allowed to weather, and mixed daily. Over 56 days the portion soluble in THF decreased from 21.3% to 14.5%; the carbon content decreased by 2.4% and the organic oxygen content increased by 2.3%. No carbonyl was found by FTIR and the oxygen gain and hydrogen loss are explained by formation of ethers:

(There is no precedent for this reaction, which is possible only at low oxygen concentrations.) The oxidation stopped after 56 days, supposedly because the potential ether sites were exhausted. (Cessation of oxidation seems more likely to be due to coating of the fairly large coal particles.)

*R. Liotta, G. Brons, and J. Isaacs, Fuel, 62, 781 (1983).

Table 1

ANALYSES OF COAL PRODUCTS

Code No.	Description	Derived From	Yield (%)	% C	% H	% N	% Other	H/C
4678-23A	68A + BnNH_2	68A		75.6	5.81	3.31	15.3	0.916
68A	TIPS	PSOC25	12.9	82.1	5.03	2.21	10.7	0.738
5536-31B	Demineralized Ill. 26	—	—	77.5	4.8	1.4	16.3	0.738
11608-23A	Whole PSOC 1098			67.0	4.59	1.22	7.92 ^a	0.817
24B	Whole Wyodak Coal			6.51	4.70	0.92	20.5 ^b	0.860
28A	PI Ill. 26	31B	—	75.7	4.89	2.69	16.7	0.769
28B	100°C insoluble	28A	65.4	77.7	5.18	2.91	14.3	0.795
29C	100°C soluble		26.8	80.6	5.59	3.39	10.4	0.827
29D	200°C glass insol.	28A	42.9	74.6	5.10	2.74	17.6	0.815
29E	200°C glass soluble		62.5	80.2	5.55	3.42	10.8	0.825
33A	300°C insoluble	28A	11-26	66.0	4.34	3.38	26.3	0.784
33B	300°C soluble		955-2100	84.9	5.71	4.93	4.4	0.801
47-1	Aged in sun	23A	72.6	62.2	4.08	0.94	32.8	0.782
47-2	Aged in dark	23A	99.9	66.5	4.54	1.18	27.8	0.814
47-3	Aged in sun	24A	73.7	68.7	4.07	0.89	34.4	0.799
47-4	Aged in dark	24B	98.5	62.6	4.53	0.83	32.0	0.862
12042-2A	200°C steel insoluble	28A	28.3	76.1	5.15	2.71	16.0	0.806
2B	200°C steel soluble		92.0	82.4	5.68	4.18	7.7	0.821
4A	Undissolved by i-PrOH	28A	78.9	74.82	4.80	2.12	18.3	0.764
4B	"Salts" from i-PrOH		0.61	3.96	1.37	0.18	94.5	4.12
4C	Base-sol. from i-PrOH	28A	1.3	15.8	1.74	0.39	82.0	1.31

^a Also 19.32% mineral matter.^b Also 8.76% mineral matter.

In the experiments at SRI, samples of Illinois No. 6 coal and Wyodak coal were exposed to sun and air on the laboratory roof in Menlo Park in Petrie dishes protected from wind and rain, or in a dark cabinet at 24°C. The temperature of the outside samples ranged from 0° to 60° (solar heating).

Results are summarized in Table 2. After 282 days in the light, both coals lost about 27% of their original weight, 32% of their original carbon, and 20-40% of their original oxygen. In 311 days in the dark, there were small losses of carbon and net gains in oxygen. In three out of four instances there was no significant change in H/C ratio during the exposures. The results show that these coals are fairly stable to oxidation in the dark but quite susceptible in the light. Much of the available oxygen is lost in the light but retained in the dark.

We plan to measure the solubilities of the initial coals and their products in pyridine and benzylamine to see how these solubilities were affected. Some other properties may also be measured but none of this work can be done under the present grant.

2.3 Reaction of PI 26 Coal with Benzylamine

The objective of this work was to extend the reaction of coal with BnNH_2 from 100° to 300°C. The coal was pyridine-extracted (pyridine-insoluble) PSOC 26, formerly 5556-49B, now 11608-28A. For the runs in glass, 1 g of coal and 25 mL of BnNH_2 were heated with occasional shaking, in sealed evacuated glass tubes. For the runs in stainless steel, 0.6 g of coal and 15 mL BnNH_2 were heated in a 30-mL reactor, flushed with nitrogen before closing. The 300°C run was made in a

Table 2

AGING OF ILLINOIS NO. 6 AND WYODAK COALS

	<u>No. 6, Sun^a</u>	<u>No. 6, Dark^b</u>	<u>Wyodak, Sun^a</u>	<u>Wyodak, Dark^b</u>
Initial weight (g) ^{c,d}	3.5925 (23A)	4.9901 (23A)	3.4164 (24B)	3.9342 (24B)
Wt. change (g), (%)	-0.9863 (27.4)	+0.0071 (0.14)	-0.8986 (26.3)	+0.0596 (1.51)
Gain or loss (% of orig.) ^d	(47-1)	(47-2)	(47-3)	(47-4)
C	-32.6	-0.90	-31.3	-5.31
H	-35.5	-1.22	-36.2	-5.08
N	-44.1	-3.45	-28.7	-11.0
Other (assuming no change in mineral matter)	-43.4	+7.1	19.3	+11.0
H/C, starting material	0.817	0.817	0.860	0.860
Final product	0.782	0.814	0.860	0.862
Lost material	0.89	1.11	0.995	0.824

^a November to August outdoors under Pyrex in Menlo Park, 282 days.

^b 311 days in dark cabinet at ~ 24°C.

^c Corrected for sample withdrawal and losses.

^d Sample numbers in parentheses, all NB11608; analyses in Table 1.

stainless steel bomb to withstand the expected pressure. The results of the glass and steel runs were so different that another run in steel was made at 200°C.

In each run, the products were centrifuged and the insoluble fractions were quickly extracted twice more with BnNH_2 . The extracts were concentrated at reduced pressure, treated with excess HCl , and washed twice more with 3M HCl and twice with 3M NH_3 , then dried with concentrated sulfuric acid in an Abderhalden drier at 76°C and 2 torr. The insoluble fractions were treated similarly. Analyses are given in Table 1; these results are corrected for excess nitrogen in Table 3 as follows. The demineralized PSOC 26 (5536-31B) from which 28A was made contained 1.4% N. The excess N in 28A is assumed to be associated with pyridine. The excess N in the BnNH_2 products is assumed to be associated with BnNH_2 , which displaced the pyridine in 28A. When the 300°C products were worked up, gas was lost and then some heavy black foam blew out. Much of this was recovered, but only 6.9 g of coal product and BnNH_2 were recovered from 15.32 g of starting material. Strong odors of NH_3 and benzaldehyde were noted. Recoveries for the 300° run in Table 2 are calculated both on all the original coal (corrected for its pyridine content) and for 55% loss of the original coal.

After concentration, the BnNH_2 -soluble product from the 300°C run was treated with excess aqueous HCl . It turned into a black material with the consistency of tough chewing gum, weighing much more than the starting coal. It was pressed out in both aqueous HCl and NH_3 . On drying at 76°C, it flowed slowly and bubbled. Its analysis (33B in

Table 3) corresponds to $C_7H_{5.6}N_{35}O_{27}$, close to polybenzal $(C_7H_6)_n$ or the polymer from benzyl chloride, with a little oxygen and nitrogen substituting for the missing hydrogen. The insoluble 33A must contain most of the original ash, but its swelling ratio in $BnNH_2$, 7.9, shows, that it still contained coal network.

Table 3 establishes that stainless steel catalyzes the conversion of benzylamine and yields a product corresponding, to polybenzal and NH_3 at 300°C. Therefore, the high recoveries of coal products at 200°C, greater in stainless steel, are due to incorporation of a similar product. At 100°C in glass, $BnNH_2$ is incorporated, but mechanical losses

Table 3

EXTRACTIONS OF PI 26 COAL WITH $BnNH_2$

Temp. (°C)	Reaction Time (h)	Initial Coal (g) ^a	Soluble ^a	Insoluble ^a	Recovery (%) ^a	H/C ^{a,b}
Reactions in glass						
100	168	0.9228	29C, 0.2663 g 26.8%	28B, 0.6495 g 65.4%	92.2	0.734 0.724
200	24	0.9273	29E, 0.5793 g 62.5%	29D, 0.3983 g 42.9%	105.4%	0.730 0.751
Reactions in stainless steel						
200	24	0.9199	2B, 0.8465 g 92.0%	2A, 0.2606 g 28.3%	120.4%	0.678 / 0.758
300	35	0.558 to 0.2501 ^c	33B, 5.3060 g ^a 955 to 2121%	33A, 0.0636 g ^a 11.4 to 25.4%	966 to 2150%	0.801 0.784

^a Corrected for excess of N above 1.4% except in 300°C experiment.

^b First number for each run is for soluble product; second is, for insoluble product. Uncorrected H/C values are in Table 1.

^c Starting coal and coal recovered after losses, respectively.

exceed any incorporation of polybenzal. Although incorporation of pyridine and BnNH_2 increases the H/C ratio in the products (Table 1), there is no convincing evidence (Table 3) that BnNH_2 reduces coal.

2.4 Oxidations

2.4.1 Losses in Oxidations. Table 4 summarizes an effort to determine the nature of the part of the coal that is lost in oxidations in terms of H/C ratios. The hydrogen and carbon contents of the starting coal (PI or TIPS) and all the products are determined, and then the H/C ratio of the volatile missing material is calculated. Some values for the H/C ratios of the water-soluble acids had to be assumed. Table 4 shows clearly that the lost material is aromatic, probably phenols or condensed rings.

Table 4

LOSSES IN OXIDATION

Oxidation No.	Reference ^a	Starting Material	H/C	Black H/C Acids	H/C, Lost Material
NaOCl 13	4-19	PI	0.712	0.708	0.53
36	15-16	PI	0.72	0.683	0.57 ^b
Oxygen 2	4-22	PI	0.703	0.777	0.5
8AB	4-22	TIPS	0.75	0.77	0.51 ^c
HNO_3 2	10-9	PI	0.733	0.725	~ 0.55

^a Report number and page for DOE Contract No. 22-81ET11423.001.

^{b,c} For H/C = 1.10^b, 1.20^c in H_2O -soluble acids.

2.4.2 Oxidations of Pyridine-Insoluble PSOC 26 Coal by Oxygen.

The objectives of this work were to compare oxidations of demineralized PSOC 26 (with 0.5 M HCl and flotation, page 2) with oxidations of beneficiated PSOC 25 (with which most of our previous work was done) to compare oxidations in acid and basic solutions, and to determine the effect of soluble iron on the oxidations.

A 4.0 g sample of PI PSOC 26 (11608-28A) was swollen and partly dissolved in 15 mL of pyridine and then poured into 200 mL of H₂O. This mixture was centrifuged and the swollen coal was washed twice more with water. Half of this product was then transferred with water to a 100-mL, round-bottom flask; 0.1963 g of potassium ferricyanide (to make 0.01 M) was added as a water solution. The pH was adjusted to 10.5, and water was added to make 60 g of reaction mixture. The mixture was then shaken with oxygen in a 60°C oil bath. Oxygen absorption was measured from a buret at 24°C and 760 torr.

Results for three consecutive intervals at 60°C and one at 80°C are summarized in Table 5. They show that the rate of oxygen absorption decreases in each interval, but is partly restored by interruptions. Restoration of 0.01 M ferricyanide increased the rate by about 50%, but this increase was soon lost. Increase in reaction temperature to 80°C then increased the rate fourfold, but this rate subsequently decreased to the lowest shown in Table 4. Repeated extractions with dilute base showed that some soluble black acids had formed, but the reaction flask broke soon after oxidation was resumed. In oxygen Oxidation No. 2 (Report 4, p. 22 of previous contract), 4.44 mmols of oxygen were

consumed by 1.00 g of coal in 75 h in six steps at 50°C, a rate of 0.059 mmols O₂/g coal·h. Thus, the first average rate in Table 5 is consistent with the previous result (considering the difference in temperature), but the final rate, even at 80°C, is much slower.

Table 5
OXIDATIONS OF PI PSOC 26 BY OXYGEN

Reaction Temp. (°C)	Time (h)	O ₂ Absorbed (mmols)	R _O (mmols O ₂ /g·h) Range	Average	pH
Alkaline Suspension					
60	31.4	7.39	0.35 to 0.016	0.117 13.8	10.5 to
extract with water, light extract					
	2.7	0.111	0.0205	13	
add 0.1983 g K ₃ Fe(CN ₆)					
	18.7	0.813	0.032 to 0.015	0.0217	~ 13
80	11.8	0.529	0.062 to 0.007	0.0224	12.6
extract with water, dark extract, end					
Acid Suspension					
60	22.3	0.193	0.0023 to 0.0044	0.00426	3-4
80	25.0	0.821	0.033 to 0.0025	0.0164	3-4

The other half of the swollen PI 26 coal was used for the oxidation

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FIGURE 1 FIELD IONIZATION MASS SPECTRA OF TIPS FRACTIONS

at pH 3-4 with 0.3063 g (0.013 M) ferrous ammonium sulfate. The initial rate of oxidation was about 1% of that in alkaline suspension, but it was increased more in reaction at 80°C.

These oxidations were so slow that other oxidations, including use of NaOCl to supplement oxygen, are more promising.

2.5 Field Ionization Mass Spectra of TIPS Fractions

Field ionization mass spectra obtained in May 1983 by S. E. Buttrill, Jr., and G. A. St. John on a TIPS fraction, before and after treatment with excess BnNH_2 for 9 days at 100°C (see Figure 1), have recently been analyzed further. In Figure 1, the mass numbers of the parent peaks are plotted as the percent of the summed intensities for all peaks from each sample. Table 6 shows the distributions of mass numbers according to their molecular formulas. The U numbers indicate the numbers of double bonds and rings in the average formulas. Thus alkanes and naphthalenes, which have the same series of molecular weights to a few tenths of a unit, are designated U0, whereas alkenes and cycloalkanes are designated as U1, etc. Each oxygen atom decreases the U number by one, and compounds with one N atom have odd molecular weights (underlined in the table). The formulas in each column differ by multiples of 14, as would homologs.

Table 6 lists components by formula weight in order of their intensities for those formula weights of relative intensities of 0.32% or above. In the TIPS fraction, the four most plentiful compounds appear to be phenols—cresols at 108 and xylenols at 122—but the higher the formula weight, the more nearly all possible combinations of C, H, O, and N appear to be represented.

Table 6

MASS NUMBER DISTRIBUTIONS FOR TIPS FRACTION

Relative Intensity (% x 100)	U0 Alkanes Naphtha- lenes	U1 Alkenes, cyclo- alkanes	U2 Bicyclo- alkanes	U3 Tricyclo- alkanes, Phenols	U4 Alkyl- benzenes	U5 Indanes, Tetralins	U6 Indenes, Alcohols, Naphthols
48				108			
44				262			
42				122			
				276			
40		364					
39	352	300					
	366						
37		378	376	248	260	314	326
			362		274		
36	380		264				312
35	338	365	336	290	288	328	340
34	226		390	388		300	
33	324	351	363		316		298
			349		386		354
32	394	379	224	404	374	414	398
							382

In the BnNH_2 reaction product, many of the outstanding new peaks are nitrogen compounds. The strongest peak is at 175, which could be dibenzylamine, then 107 (BnNH_2), 106 (benzaldehyde), 195 (possibly N-benzyl-benzalimine), and 105 (benzalimine). Although the average

molecular weights of the volatile materials are higher for the BnNH_2 -treated than for the untreated TIPS, this result is probably due to less volatilization from the untreated TIPS and retention by the highest molecular weight material of intermediate molecular weight material. Thus, these results are consistent with cleavage of TIPS by BnNH_2 , but they do not establish it.

2.6 Reaction of PI 26 Coal With Isopropanol and KOH

An effort was made to reduce and solubilize PI 26 coal with isopropanol and KOH at 100°C . A mixture of 1.1036 g of coal, 11608-28A + 1.0751 g KOH flakes + 10 mL each of isopropanol and toluene was heated for 24 h at 100°C in a sealed, evacuated glass tube, with occasional shaking. The products were then washed out with isopropanol, pyridine, and water and evaporated nearly to dryness. The remaining solid was acidified, washed three times with 1 M HCl, and twice with 3 M NH_3 . After drying, rewashing and grinding to remove salts (apparently ammonium chloride) and redrying, the following products were obtained:

<u>Product</u>				
<u>No.</u>	<u>Product (g)</u>		<u>% of original C</u>	<u>H/C</u>
12042-4A	0.8814,	g undissolved coal	78.9%	0.764
4B	.1286,	g salts	0.61%	4.12
4C	.0709,	g base-soluble	1.3%	1.31
Loss			19.1%	

The main product, 4A, showed little change in H/C and very little dissolved in pyridine. However, if the lost material resembles 4C, then

considerable reduction occurred. This experiment should be repeated at 150°C or with powdered stainless steel or nickel.

2.7 Reaction of Potassium Formate and Formic Acid with PI 26

The author has long thought that reduction of coal by formate ions should be possible at 200°C or below. To investigate this theory, experiments were conducted using nearly equimolar mixtures of potassium formate and formic acid to relieve build-up of CO₂ pressure and to provide plenty of formate ion, considered to be the reducing agent. The experiments were run in sealed glass tubes heated for 24 h at 200°C in a rocker bomb containing toluene, to compensate for the pressure inside the glass. The first three glass tubes exploded, apparently because there was insufficient free space to contain the expanded charge and the gas formed. In the last experiment, 0.5953 g of 87% KOH (24.8 mmols) was dissolved in a few mL of water, and then formic acid to give pH 5.5 was added. When this solution was evaporated at 12 torr and 100°C, it crystallized on cooling. Then 1.284 g of 89% formic acid (24.8 mmols), 5 mL each of absolute alcohol and toluene, and 2.007n g of PI 26 coal (28A) were added. The Pyrex tube (51 mL capacity) was then cooled, evacuated to 12 torr, and sealed off. After heating for 24 h at 200°C in a rocker bomb, the tube was cooled in liquid nitrogen and opened. There was considerable pressure in the cold tube, which must therefore have contained hydrogen.

A 0.1278-g portion of the products was soluble in toluene or refluxing THF and another 0.0299 g was obtained in Soxhlet extraction by pyridine, a total of 7.86% of the starting material. After correction for bound pyridine, 1.8305 g of insoluble coal was obtained, for a total

recovery of 99.06%. From this experiment, dissolution of coal by formates at 200°C is unpromising.

3. CONCLUSIONS

- A practical method for beneficiation of Illinois No. 6 coal has been developed.
- Solvolysis experiments with Illinois No. 6 coal and methanol are unpromising but solvolysis of Wyodak coal, which contains much more oxygen, should be more successful.
- Conventional coal liquefaction and pyrolysis starting with soluble products is no easier than when whole coal is used.
- Although some promising results were obtained from oxidations of coal fractions with nitric acid, future comparison of oxidizing agents and coals should start with coals of the same particle size. Oxygen may be a useful supplementary oxidizing agent with either sodium hypochlorite or nitric acid.
- Gel permeation chromatography has been applied to analysis of a soluble coal fraction and of several coal oxidation products. Different patterns were found with soluble oxidation products made in various ways, but the remarkable finding was that there is a common product (by gpc) in many of the high molecular weight acids made by oxidation and that as much as 75 to 95% of this fraction can be isolated by gpc. These techniques appear to be well adapted for comparing experimental procedures in oxidations of coal and for determining average structures of large but soluble coal fragments.
- Previous work showed that the action of benzylamine on coal in glass at 100°C results in cleavage of coal molecules and incorporation of benzylamine. An experiment in stainless steel at 300°C shows that most of the benzylamine is condensed to $(C_7H_6)_n$, now being further investigated.

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