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HOMOGENEOUS CATALYTIC HYDROCRACKING PROCESSES FOR CONVERSION OF COAL TO LIQUID FUELS: BASIC AND EXPLORATORY RESEARCH

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ABSTRACT

Our study in Task 1 of the effect of higher reaction temperature (300°C, 572°F) on treatment of coal with the $AlCl_3/HCl$ catalyst system has shown that with a 2/1 catalyst/coal weight ratio, the coal is almost entirely gasified, with 40% of the carbon converted to methane, and 50% to ethane. Our study of the importance of adding of HCl to the reaction system at this temperature showed that without added HCl, the gas yield was significantly reduced, and the H/C atomic ratio of the coal residue also decreased considerably. The added HCl, therefore, appears to be necessary for both coal hydrogenation and high yields of C_1 and C_2 gases.

The data are consistent with the scheme:

$$\text{coal} \xrightarrow[H_2/\text{Cat}]{1} \text{coal product} \xrightarrow[H_2/\text{Cat}]{2} C_1 + C_2$$

$$\text{coal} \xrightarrow{3} \text{char} + H_2$$

where $k_1 > k_2$ at 210°C (410°F), but $k_2 > k_1$ at 300°C (572°F). Step 3 becomes important, when HCl is not included in the system.

In Task 2A, we have studied the effects of several variables on coal conversion in i-PrOH and KOiPr at 335°C (635°F) for 90 min. Decreasing the reaction time to 30 min virtually eliminated the conversion. Using $CaCO_3$ in place of KOiPr gave results comparable with those obtained using i-PrOH alone, indicating that $CaCO_3$ has little effectiveness. KOH, on the other hand, was as effective as KOiPr. We have also found enough acetone after reaction to account for the hydrogen incorporated in the product coal. Finally, virtually no gas is produced during reaction.

Task 2B concerns the interactions of coal with Tetralin and with naphthalene. When treated with Tetralin at 430°C (806°F), Illinois No. 6 coal yields a product with pyridine solubility increasing from 80 to 97% when contact time is increased from 28 to 137 sec. Experiments were also performed at several reaction temperatures using coal and Tetralin for a fixed reaction time of about 2 min. Here the yield of pyridine-soluble material rose gradually from about 18% at 325°C (617°F) to 97% at 430°C (806°F). Pyridine solubility of coal treated with naphthalene was determined as a function of contact time at 400°C (752°F) and 430°C (806°F). For the former, the initial conversion (about 10 sec) is 20%, rising to approximately 40% in 2 min. At the higher temperature, about 40% pyridine-soluble material is formed in 28 sec with pyridine solubility of product remaining relatively constant for longer contact times (70 sec to 4 min). When the treatment with naphthalene was carried out at different reaction temperatures for a fixed reaction time (about 2 min), the product solubility in pyridine ranged from about 20 wt% at 325°C (617°F) to a maximum of about 40% in the 375°C to 400°C range (707 to 752°F), and then declined at higher temperatures. Preliminary results at 420°C (788°F) indicate that coal ash components have little effect on conversion to pyridine-soluble material in Tetralin media.

In Task 3A the extension of group additivity procedures to the estimation of thermochemical data for coal-related nitrogen-containing heterocycles has begun. We have modified the very low-pressure pyrolysis system to enable measurement of the stabilities of benzyl radical analogs that are likely intermediates in thermolytic reactions of coal. The system is now being calibrated.

Task 3B summarizes our new and older work on fractionation of coal extracts and SRCs. Number-average molecular weights of these fractions have been related to retention volumes of the same fractions in gel permeation chromatography in tetrahydrofuran. Our recent and older work on oxidations with aqueous sodium hypochlorite is reviewed. Improved procedures have given substantial yields of black, bicarbonate-soluble, water-insoluble acids, which provide a new and significant material for structure determinations.

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INTRODUCTION

This is the fifth quarterly report on our study of the fundamental aspects of coal liquefaction, under ERDA Contract EF-76-C-01-2202. Our goal is to increase our understanding of the conversion processes toward the development of an efficient system for the conversion of coal, lignite, and coal derivatives to distillate fuels.

Our work in the second year of the program proceeds on the same broad level as before, except that the soluble metals work (Task 1B) has been eliminated. Thus, the project now has five tasks:

Task 1:	Homogeneous Catalysis--Acid Catalysis
Task 2A:	Coal Dissolution--Supercritical Media
Task 2B:	Coal Dissolution--Reactive Solvents
Task 3A:	Thermochemistry and Kinetics of Coal Liquefaction
Task 3B:	Coal Structure Studies

All tasks except 3A use beneficiated Illinois No. 6 coal, -60 mesh, supplied by Pennsylvania State University, whose designation for this coal is PSOC-26. We are also using an unbeneficiated sample, which is from the same source and is designated PSOC-25. Task 3A is a theoretic study requiring no coal samples.

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Task 1: HOMOGENEOUS CATALYSIS--ACID CATALYSIS

(David S. Ross and James Y. Low)

Objective

Our objective in Task 1 is to study the use of selected acid materials as homogeneous catalysts for the hydrogenolysis of coal, coal liquids, and lignite. We are currently examining the usefulness of a number of Bronsted acids, some Lewis acids, and appropriate mixtures of the two acid types. The study is expected to result in the moderation of the conditions used currently for coal treatment, and in a selective and more efficient use of hydrogen in the process.

Experimental Procedures

Our earlier quarterly reports on this project described our experimental procedure for coal treatments in detail. Our recent experiments at 300°C (572°F) have yielded significant quantities of gases, and the following analytical procedure was used for gas determinations:

> After each reaction, the reaction mixture was cooled to room temperature and the pressure in the reactor recorded. A portion of the gas was expanded to 1 atm and a 0.2 ml sample withdrawn by syringe for analysis. The analyses were carried out on a dual column gas chromatograph. Hydrogen was determined at 25°C (77°F) on a 6 feet x 1/8 inch molecular sieve column, and analyses for methane, ethane, and propane were performed at 125°C (257°F) with a 10 feet x 1/8 inch Porapak Q column. The carrier gas used is 8% H_2 in helium. Response factors were

determined for each gas individually by using standard gases before each run. H_2S was determined only qualitatively; we could not obtain reproducible data even with the standard sample of H_2S. The absolute yields of gases were calculated based on the volume of reaction gas mixture and the response factors obtained from the standard gases. The procedure provides precision of 10%.*

Background

Our work to this point has been at 210°C (410°F). In this quarter, except for the double salt experiments discussed below, we are using 300°C (572°F). Kawa and co-workers[1]† have reported on the hydrogasification of coal with aluminum chloride and hydrogen, but without added HCl. They investigated the effect of temperature from 250° to 450°C (482°F to 842°F), and $AlCl_3$/coal ratios of 0.25 to 2, all at H_2 pressures of 4000 psi. At 300°C (572°F) and with $AlCl_3$/coal ratio of 2:1, 40% of the carbon in the coal was converted to hydrocarbon gases.

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* In our last report, we presented gas data for Run 69; these data were from our initial attempts at quantitative gas measurement, and the precision was poor. We subsequently discovered a defect in the gas syringe used. Our current results are with the use of a new syringe, and we now consider the data reliable.

† References for all tasks are listed at the end of the report.

At our earlier reaction conditions, 2600 psi, 210°C (410°F) with HCl, we found that about 50% of the coal was gasified.[2] This observation strengthens our belief that HCl is important in the catalyst system. Consistent with our findings are those by Ipatieff and Schmerling,[3] who noted that adding HCl to the $AlCl_3$ catalyst system promoted the hydrocracking of petane and heptane.

Larsen and co-workers[4] have performed experiments with coal and $AlCl_3$ in which NaCl and other alkali metal halides were added to the system to form double salts of the form $NaAlCl_4$. The double salts have melting points significantly below that of $AlCl_3$ (190°C, 374°F) suggesting that it might be possible to carry out $AlCl_3$-promoted reactions in molten media at relatively low temperatures.

Larsen reported no significant conversion of the coal to gases or liquids in runs at 150°C (302°F) and 380°C (716°F), with $AlCl_3/H_2$ systems including NaCl and KCl. No HCl was used in this work.

Prompted by these findings, we investigated the effects of higher temperatures with $AlCl_3$ as catalyst, focusing on the importance of added HCl, and the effect of double salt systems ($AlCl_3$/NaCl), again with HCl present.

Results and Discussion

Coal Gasification

Our current results are summarized in Table 1; for all runs, we used a catalyst/coal ratio of 2.0 (wt/wt) at 300°C (572°F). Both Run 83 and Run 85 are with HCl present; only small amounts of the coal were recovered as a residue. The major fraction of the coal was gasified, with about 90% of the carbon in the coal converted to methane (~ 40%) and ethane (~ 50%). No propane was found in these experiments.

Table 1

HYDROTREATMENT OF ILLINOIS NO. 6 COAL WITH HYDROGEN AND CATALYST AT 300°C (572°F), 90 MINUTES[a]

Run	Catalyst System	Loading Quantities (psi, cold)		Reaction Pressure (psi, hot)	Product Composition							Mass Balance[c] (%)
					Gases (% of Starting Carbon)[b]				Coal Residue			
		H_2	HCl		C_1	C_2	C_3	Total Gases	Yield[d] (%)	Pyr. Sol.[e] (%)	H/C	
83	$AlCl_3/HCl$	800	500	3250	40	56	none	96	18	78	0.72	114
85	$AlCl_3/HCl$	800	500	3250	45	45	none	90	18	83	0.74	108
86	$AlCl_3$	1400	-	2500	35	25	12	72	30	60	0.75	102
87	$AlCl_3$	1850	-	3400	36	16	4	56	49	31	0.68	115
88	$AlCl_3$	800	-	1500	13	11	12	36	68	28	0.64	104
84[f]	$AlCl_3/HCl$	800	500	3400	22	12	8	42	40	33	0.73	82

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[a] Unless otherwise specified, the stirred Hastelloy C reactor was charged with 4 g beneficiated Illinois No. 6 coal, 8 g $AlCl_3$ (0.06 mole).

[b] The gas yield is calculated by (No. of moles of carbon in the gas/No. of moles of carbon in 4 g coal) x 100.

[c] The mass balance is the sum of all absolute quantities of gases produced and residue recovered, and is not normalized. In all cases, there is no liquid fraction.

[d] Based on % of starting carbon.

[e] Fraction of residue soluble in pyridine.

[f] 4 g of lignite was used.

In light of Kawa's[2] result without HCl, we carried out Runs 86, 87, and 88 without HCl and at initial hydrogen pressures of 1400, 1850, and 800 psi, respectively. The overall yields of gases in these runs were considerably reduced, with significant yields of propane, indicating that hydrocracking is less extensive in the absence of HCl. The gas yields follow the run sequence (72%, 56%, 36%) rather than the hydrogen pressure values. Also, the gas yield decline parallels the increasing yields of coal residue (30%, 49%, 68%) with, in turn, declining pyridine solubilities (60%, 31%, 28%) and H/C ratios (0.75, 0.68, 0.64).

Thus, the absence of HCl had a substantial cumulative effect, and the importance of HCl to the process is clear. Moreover, with the lessening degrees of gasification, the coal residues are apparently increasingly crosslinked and depleted in hydrogen. We have no complete explanation for this result, although chemistry at the autoclave surface may be involved.

It is of interest to review some of our earlier data at 210°C (410°F)[2] shown in Table 2; at the time of that work, we had not attempted to quantify the gas yields in our experiments. The runs are placed in the table in order of declining residence time, and the last column in the table is the quantity of gas assumed produced, based on missing material. The gasification data from Table 2 are plotted in Figure 1.

The degrees of gasification are observed to increase rapidly with increasing residence time. At the same time, although the quantities of isolated residues decline, the H/C ratios for the residues from each of the six runs are essentially identical, clustering around 0.83. This value contrasts the declining ratios just discussed for runs at 300°C (572°F) without HCl.

Table 2

THE EFFECT OF RESIDENCE TIMES ON COAL GASIFICATION

(4 g Illinois No. 6 coal, 8 g $AlCl_3$, 500 psi HCl, 800 psi H_2, at 210°C (410°F), in a 300 ml stirred Hastelloy C autoclave)

Run	Residence Time	Coal Residue		% Coal Gasified[b]
		% Recovered[a]	H/C	
67	5 hr	39	0.83	61
46[c]		48	0.82	52
41	4 hr	49	0.84	51
66	90 min	47	0.85	53
69[d]	45 min	72	0.82	28[d]
71		66	0.84	34

[a] Based on 4 g of coal.

[b] Assumed, based on unaccounted for material.

[c] Run with 3 g coal and 6 g $AlCl_3$.

[d] An early attempt at gas analysis yielded a value of 5% gas formation and 23% unaccounted for material.

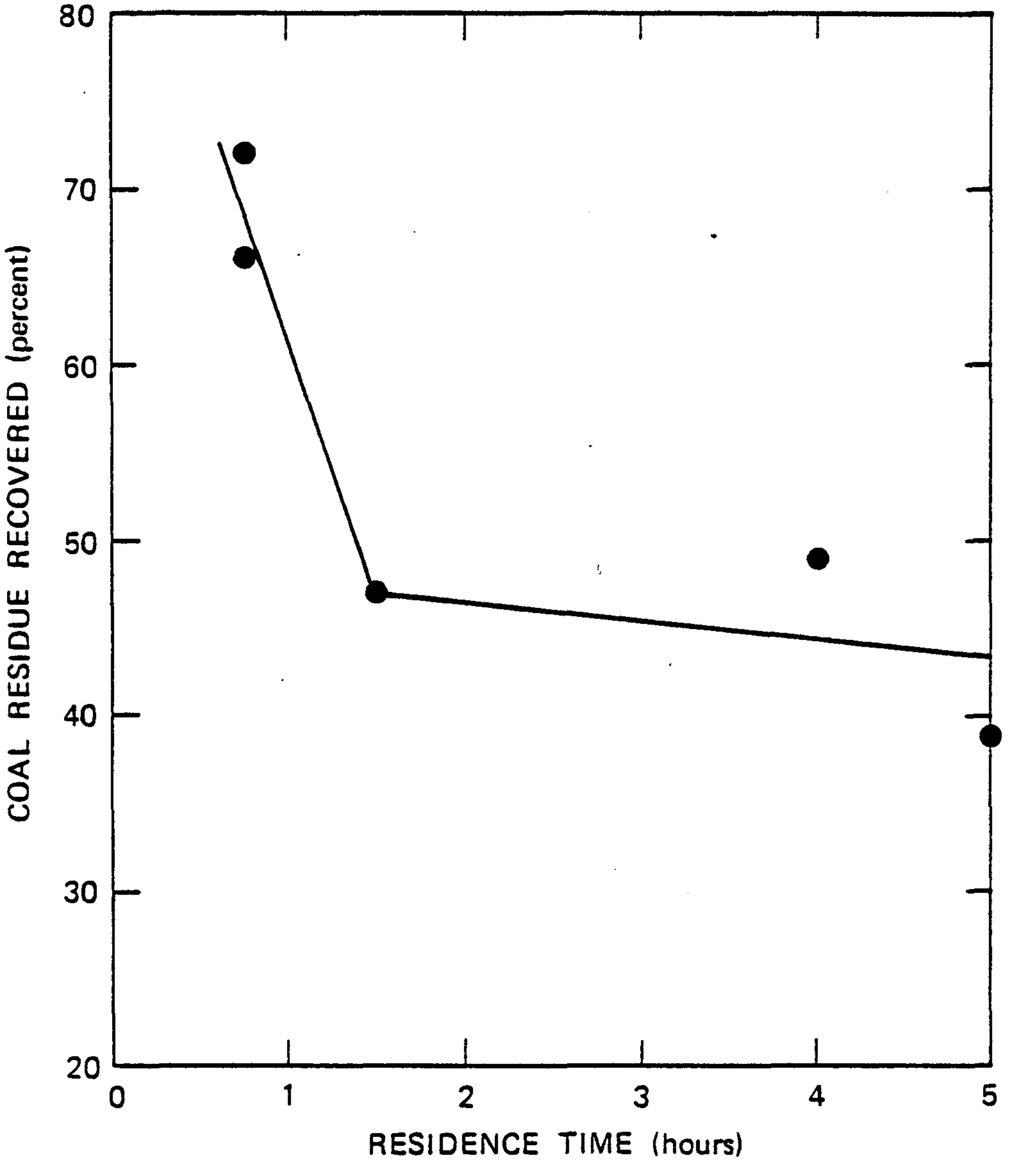

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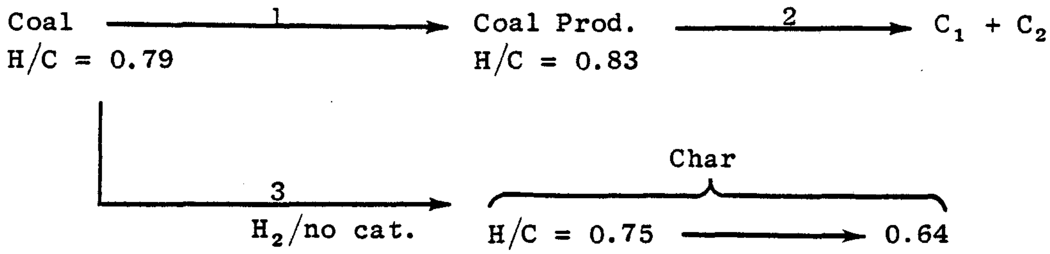
FIGURE 1 THE EFFECT OF RESIDENCE TIMES ON DEGREE OF GASIFICATION OF ILLINOIS NO. 6 COAL

(Conditions: 210°C (410°F), 8 g $AlCl_3$, 4 g coal, 500 psi HCl, 800 psi H_2, in a 300 ml Hastelloy C stirred Autoclave).

The following scheme can be suggested to explain these data



From Table 2, it is seen that in the presence of an effective catalyst, and at lower temperatures, $k_1 > k_2$. Thus the hydrogen-rich, pyridine-soluble coal product accumulates and can be isolated.

Next, from Table 1 it is seen that at high temperatures the relative rates of Steps 1 and 2 are reversed, $k_2 > k_1$, and gasification is the major finding. Then, when the catalyst is reduced in effectiveness with the elimination of HCl, Steps 1 and 2 are suppressed and 3 becomes dominant.

We plan to compare the properties and characteristics of the coal products of this task with those obtained in Task 2A from the isopropyl alcohol treatment.

In Run 84, we used lignite instead of Illinois No. 6 coal. The gas yield was less than half the yields obtained with coal, similar to results reported by Kawa et al.[1] Thus, the substantial quantities of water formed in the lignite experiment must deactivate the catalyst.

Other Systems

We carried out two experiments with the double salt $NaCl/AlC_3$ at 210°C (410°F). Runs 63 and 75 were performed with a molar excess and deficit of NaCl, respectively. The data presented in Table 3 show that the systems were totally ineffective. Thus, the utility of the double salts, even with HCl present, appears to be small.

Table 3

HYDROTREATMENT OF ILLINOIS NO. 6 COAL[a]

Run	Catalyst System	Temp. °C	Loading Quantities (psi, cold)		Reaction Pressure (psi, hot)	Product Yield[b] (%)	Pyridine Solubility (%)
			H_2	HCl			
63	$AlCl_3$/HCl/NaCl[c]	210	800	500	2750	99+	15
75	$AlCl_3$/HCl/NaCl[d]	210	800	500	2800	99+	16
78	$FeCl_3$/HCl	300	800	500	3400	95	18

[a] A stirred Hastelloy C autoclave was charged with 4 g beneficiated coal.

[b] Yield of solid product.

[c] 6 g of $AlCl_3$ and 6 g of NaCl used. (NaCl/$AlCl_3$ molar ratio of 2.22)

[d] 6 g $AlCl_3$ and 1.3 g NaCl used. (NaCl/$AlCl_3$ molar ratio of 0.50)

Run 78 was carried out with $FeCl_3$/HCl as the catalyst system at 300°C (572°F), the melting point of $FeCl_3$. The pyridine solubility for the product coal is only 17%, similar to that of the untreated coal. The solid product recovery is high, 95%. Thus, $FeCl_3$/HCl is not an effective coal conversion catalyst at this particular set of reaction conditions.

Task 2A: HYDRIDE-PROMOTED COAL CONVERSION

(David S. Ross and James E. Blessing)

Objective

The objective of this task is to establish an understanding of the reaction of coal and isopropoxide anion, and to exploit the process in terms of the production of useful fuels from coal. The isopropoxide/coal reaction at 335°C (635°F) produces a fully pyridine-soluble product. We are examining the effects of varying the reaction time and temperature, the base concentration, and the hydrogen pressure. We are also studying different bases and will study the fate of the sulfur and potassium. We plan to identify the bonds in coal that are likely to be cleaved by this treatment and will characterize the reaction products further.

Results and Discussion

To date we have partially investigated the effect of variation of isopropoxide anion concentration, reaction time, hydrogen pressure, and type of base added on conversion. The results are presented in Table 4. A comparison of the data for duplicate Runs 54 and 94 shows that the former was probably run with more than 1 g of potassium isopropoxide present.* Thus, for Run 54 the sulfur level and H/C ratio for the product, although favorable, are both out of line compared with those values for Run 94 and other similar runs. Our comparisons are thus more properly made with the results from Run 94. However, a system with larger potassium isopropoxide concentrations may be useful and will be investigated.

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*The laboratory balance used for Run 54 was subsequently shown to be unreliable and was replaced shortly after 54 was run.

Table 4

ILLINOIS NO. 6 COAL AND ISOPROPYL ALCOHOL SYSTEMS AT ρ = 0.32 AND 335°C(635°F)

Run	Solvent System	Reaction Time (min)	Reaction Pressure (psig)	Reaction Products						Mass Balance (%)
				% Filt[a]	% PS[b]	Molar H/C[c]	% S[c]	% N[c]	% Ash[c]	
-	Untreated Coal, Dried	-	-	-	13		2.1	1.7	2	-
38	i-PrOH	90	1800	11	40		2.1	2.1	-	97
62	i-PrOH + 0.5 g KOiPr	90	1900	19	89	0.85	1.5	1.5	0	92
54	i-PrOH + 1.0 g KOiPr	90	2000	40	97		0.4	1.7	6	96[d]
94	i-PrOH + 1.0 g KOiPr	90	1800	-	> 96	0.89	1.5	1.5	3	92
92	i-PrOH + 1.0 g KOiPr	30	1800	9	17	0.79	1.9	1.6	3	100
95	i-PrOH + 1.0 g KOiPr + H_2[e]	90	4000	14	92	0.90	1.5	1.4	3	94
97	i-PrOH + 1.0 $CaCO_3$	90	1800	10	30	0.84	1.9	1.6	4	96
98	i-PrOH + 0.6 g KOH	90	1900	11	96	0.87	1.6	1.6	3	103

[a] Filtrate ≡ material dissolved in i-PrOH after reaction, ash free basis.

[b] PS ≡ material soluble in pyridine, including "Filt", ash free basis.

[c] Composite of values for both filt and residue.

[d] Corrected from last report.

[e] 1000 psig of H_2 at room temperature.

Consistent with this discussion are the results for Run 62, performed with 0.5 g potassium isopropoxide. In this case, the H/C ratio of 0.85 is slightly less than that of the 1.0 g experiments. Significantly, however, the product coal is still almost fully pyridine soluble.

Reaction product yields decreased dramatically when we reduced the reaction time from 90 min to 30 min (Run 92). The product after reaction for 30 min is little different from the starting coal. Such a large reduction in upgrading for a two-thirds reduction in reaction time may be indicative of an autocatalytic process. We intend to study this observation further.

Hydrogen was added to the reaction in Run 95. Here the H/C value and the pyridine solubility are comparable with those for Run 94. It appears that the addition of H_2 has little effect on the process.

Adding elemental potassium to isopropanol for coal conversion is not likely to be economically feasible on an industrial scale. If an inexpensive, abundant base could be found to form the isopropoxide anion, however, such a process might be of value. We have tried $CaCO_3$ (lime) and KOH, in Runs 97 and 98, respectively. As shown in Table 4, the $CaCO_3$ system was not effective. The KOH run, on the other hand, appears to be as effective as the run with potassium isopropoxide (Run 94). Thus the equilibrium

$$OH^- + \text{i-PrOH} \rightleftharpoons H_2O + \text{i-PrO}^-$$

must lie significantly to the right under our conditions.

If isopropanol or isopropoxide anion is donating hydride to coal, then acetone should be formed during reaction. A chain process can be proposed

$$^-OCH(CH_3)_2 + \text{coal} \longrightarrow \text{coalH}^- + O{=}C(CH_3)_2$$

$$\text{coalH}^- + HOCH(CH_3)_2 \longrightarrow \text{coalH}_2 + {}^-OCH(CH_3)_2$$

where isopropoxide is regenerated with each cycle, and where the net reaction is the transfer of H_2 to the coal and the formation of acetone. Acetone was, in fact, found in our reaction solvents by gas chromatography after reaction.

To quantify our observations, we made one without coal present, but with a known quantity of acetone added (Run 93). The results of this run and others are shown in Table 5. For Run 93, the data show that not only does acetone survive the reaction conditions, but that it is formed in larger amounts in the absence of coal than when coal is present.

An earlier run, 38, is included in the table for comparison, and shows that with no added base there is little net hydrogen-transfer. The results for Runs 94, 95, and 98 indicate that more acetone is formed than can be accounted for by hydrogen transferred to the coal. The ratios of acetone formed to H_2 transferred are in the range 1.4 to 1.7, and thus about 30% of the hydrogen from the alcohol must be lost as H_2 by the reaction

$$^{-}OCH(CH_3)_2 + HOCH(CH_3)_2 \longrightarrow H_2 + O{=}C(CH_3)_2 + {}^{-}OCH(CH_3)_2$$

We have qualitative confirmation of this suggestion in the observation of H_2 in the autoclave head-space after the reactions. We are planning a quantitative assessment of the head gases for a hydrogen balance.

The last column in the table lists the ratios of hydrogen transferred to the coal to the quantities of base added. The values for Runs 94, 95, and 98 are consistent with the chain process referred to above, and thus the process appears to be catalytic in base, at least for about two cycles. It is clear that the 30-min and $CaCO_3$ experiments (Runs 92 and 97) were ineffective. CaO and $Ca(OH)_2$ will be considered as promoters in the next period.

Table 5

HYDROGEN TRANSFER TO COAL IN ISOPROPYL ALCOHOL SYSTEMS AT 335°C (635°F)

Run	Reaction System[a]	Reaction Time (min)	Base Added (mmoles)	Acetone Produced (mmoles)[b]	H_2 Transferred (mmoles)[c]	Acetone/H_2[d]	H_2/Base[e]
38	Coal[f]	90	0	-[g]	5	-	-
93	KOiPr/acetone[h]	90	5	149[i]	-	-	-
92	KOiPr/coal	30	10	6	5	1.2	0.5
94	KOiPr/coal	90	10	36	25	1.4	2.5
95	KOiPr/coal/H_2	90	10	36	25	1.4	2.5
97	$CaCO_3$/coal	90	10	24	9	2.7	0.9
98	KOH/coal	90	10	38	22	1.7	2.1

[a] All reactions done in 90 g isopropanol, with 5.00 g dried Illinois No. 6 coal where indicated. 1.0 g of base was used in all runs except Runs 93 and 98 in which 0.5 g and 0.6 g were used respectively.

[b] Acetone found after reaction by gas chromatography.

[c] H_2 added to coal in reaction. Calculated from the H/C ratios of the starting coal and those for the respective products.

[d] Acetone found per H_2 transferred to coal.

[e] H_2 transferred to coal per base added.

[f] Coal heated with 90 g isopropyl alcohol, no base added.

[g] Not determined.

[h] No coal. 18 mmoles of acetone added initially.

[i] Net acetone formed during reaction. Does not include acetone added initially.

Future Work

We have preliminary evidence that the pyridine-soluble coal products formed in isopropyl alcohol/base are similar, if not identical, to the preasphaltenes formed with coal and Tetralin. We refer here to the results both of Neavel[5,6] and Whitehurst, et al.[7] This result is significant, since it is likely that the initial coal products formed in the preheater in the SRC process are these same preasphaltenes. Thus, our apparent catalysis of the process in a medium with a relatively low boiling point and reaction temperature could be significant. We plan to continue our comparison of alcohol- and Tetralin-derived coal products.

Careful repeats of Runs 54 and 92 are planned. The repeated Run 54 will be a quantitative account of all products, especially the fate and form of sulfur and potassium. We are also planning a short model compound study to determine which bonds in coal are likely involved in the hydroaddition and hydrocracking that occur in the i-PrOH/KoiPr system.

Task 2B: ADVANCED COAL SOLVENT STUDIES

(David S. Ross and Manu Seth)

Objective

In this task, we are examining the interaction of reactive solvents with coal to gain information on reaction processes, as well as to improve dissolution techniques. We are using high temperature, and contact times ranging from several minutes to 20 seconds. The coal products formed are preasphaltenes, currently of significant interest, as observed in Task 2A.

Background

Neavel[5,6] found that vitrinite, when treated with Tetralin at 400°C (752°F), forms almost completely pyridine-soluble material within 5 min of reaction. Reaction in nondonor solvents such as naphthalene and dodecane resulted in similar initial dispersion, but further treatment lead to repolymerization and a decrease in pyridine solubility. Both bituminous and subbituminous coals have been reported to form more than 90% pyridine-soluble material when treated with hydrogen donor solvents at short contact times.[7]

The liquefaction of coal in Tetralin at longer reaction times was studied by Hill et al.[8] In the temperature range used (350 to 450°C, 662 to 842°F), the hydrogen transfer reaction was found to be a second order process. About 30 wt% was reported to be converted to asphaltenes within the first 10 min of reactions at 400°C (752°F). At 440°C (824°F), about 80% asphaltenes was formed in 5 min.

Weller and coworkers[9] tested several Co-Mo-Al_2O_3 catalysts with Tetralin for the liquefaction and hydrodesulfurization of coal. They obtained up to 90 wt% liquid product containing as much as 50% hexane soluble material in 2 hr reactions at 455°C (851°F). The extent of liquefaction was found to be unaffected by the catalysts. The presence of gas phase hydrogen and Co-Mo-Al_2O_3 catalyst, however, improved the extent of desulfurization and conversion of asphaltenes to oils.

In the first quarter of this contract year, we have established the effect of reaction time and reaction temperature on the interaction of Illinois No. 6 coal with Tetralin and naphthalene.

Experimental Procedure

We have established the following reaction procedure:

(1) Approximately 0.5 g coal (-60 mesh) and twice its weight of solvent are weighed into an reactor consisting of a 6-inch length of 1/4-inch stainless steel tubing capped on both ends with Swagelok fittings. A thermocouple is fitted into a well in one of the end caps to monitor the temperature of the reaction mixture. The reactor is sealed and fastened to a 60-cycle vibrator.

(2) A reaction is started by plunging the reactor into the molten salt bath and turning on the vibrator. Zero reaction time is considered to be the time when the reactor temperature is within 10°C of the desired reaction temperature, obtained within 10 to 15 sec.

(3) At the end of the reaction, the reactor is pulled out of the bath and quickly placed under cold running water. The reaction is considered terminated when the temperature drops 10°C below the reaction temperature.

(4) At the end of a run, the vessel is opened and the contents carefully washed out with approximately 50 ml pyridine.

(5) The pyridine slurry of reaction products is passed through a preweighed extraction thimble and refluxed in a Soxhlet extraction apparatus until extraction is complete (which takes between 4 and 24 hr).

(6) The residue is washed with 20 ml fresh pyridine, dried at 110°C (230°F) under vacuum for 12 hr, and weighed.

(7) Solvent is removed in a preweighed 100 ml flask on a rotary evaporator. The pyridine-free extract is then dried in a vacuum oven at 110°C (230°F) for 12 hr and weighed.

(8) The percent coal solubility in pyridine is calculated from the <u>ash-free</u> masses of residue m and starting coal m_o as

$$\% \text{ solubility} = [(m_o - m)/m_o] \times 100$$

A total mass balance is also calculated from the mass of extract m_e and ash-free residue m, as

$$\% \text{ mass measured} = [(m_e + m)/m_o] \times 100$$

For early Runs 18 to 31, a modified procedure was used. Steps (5) and (6) above were replaced by the following:

(5) The pyridine slurry of reaction products is transferred to a 100 ml flask and refluxed at 118°C (244°F) for 30 min.

(6) The product slurry is then centrifuged for 30 min at 1500 rpm, the mixture is filtered on a preweighed medium porosity sintered glass filter and washed with 20 ml of fresh pyridine, and the filter residue is dried at 110°C (230°F) under vacuum for 12 hr and weighed.

Lower temperature reactions tended to form products that were extremely difficult to filter. The Soxhlet extraction procedure discussed above was then developed. Two experiments were run to verify the consistency of the two procedures and to estimate experimental error. The results, shown in Table 6, indicate that experimental error is well within ± 5%.

Table 6

COMPARISON OF EXTRACTION AND
FILTRATION TECHNIQUES AT 375°C (707°F)

Procedure Condition and Results	Filtration	Extraction
Solvent	Tetralin	Tetralin
Time, sec	126	124
% Mass Recovered	102	98
% Pyridine Solubility	50	52
% Error in Pyridine Solubility	4	

Results

During this period, we studied the effect of reaction time and temperature on the interaction of coal with Tetralin and naphthalene.

Effect of Reaction Time/Tetralin

Runs 18 to 22 in Table 7 show the effect of reaction time on the formation of pyridine-soluble product when Illinois No. 6 coal is treated with Tetralin at 430°C (806°F). Reaction times as short as 23 sec yield about 80% pyridine-soluble material (compared with about 17% pyridine solubility of untreated coal). Approximately 2 min reaction time yields 97% pyridine-soluble material. These results are similar to those of Neavel.[6] The H/C ratios of the residue range from 0.70 to 0.75 compared with 0.83 for untreated coal. The H/C ratios of the extracts are being obtained.

Curve A in Figure 2 shows the variation of pyridine solubility of the product as a function of reaction time.

Effect of Reaction Temperature/Tetralin

Coal was treated with Tetralin for 2 min at 6 different temperature levels to determine the effect of reaction temperature on conversion (Runs 33 to 38). Within the range of temperatures studied, the yield of pyridine-soluble material rose gradually from about 18% at 325°C (617°F) (compared with about 17% for untreated coal) to 97% at 430°C (806°F); all for a fixed reaction time of approximately 2 min.

Curve D of Figure 3 is the plot of pyridine solubility of products as a function of reaction temperature.

Table 7

RESULTS OF FAST REACTION TIME EXPERIMENTS WITH TETRALIN[a]

Run	Temperature		Time (Sec)	Pyridine Solubility (%)	Mass Recovered (%)
	°C	°F			
18	430	806	28	80	-
19	↓	↓	42	87	94
20			63	91	-
21			84	94	98
38			127	94	87
22			137	97	98
33	325	617	127	19	100
33R	325	617	134	17	102
34	350	662	125	31	-
35	375	707	124	52	98
35R	375	707	126	50	102
36	400	753	123	63	99
37	420	788	125	87	92
38	430	806	127	94	96

[a] Coal Used: Illinois No. 6; Coal/solvent ratio = 1/2 (wt/wt)

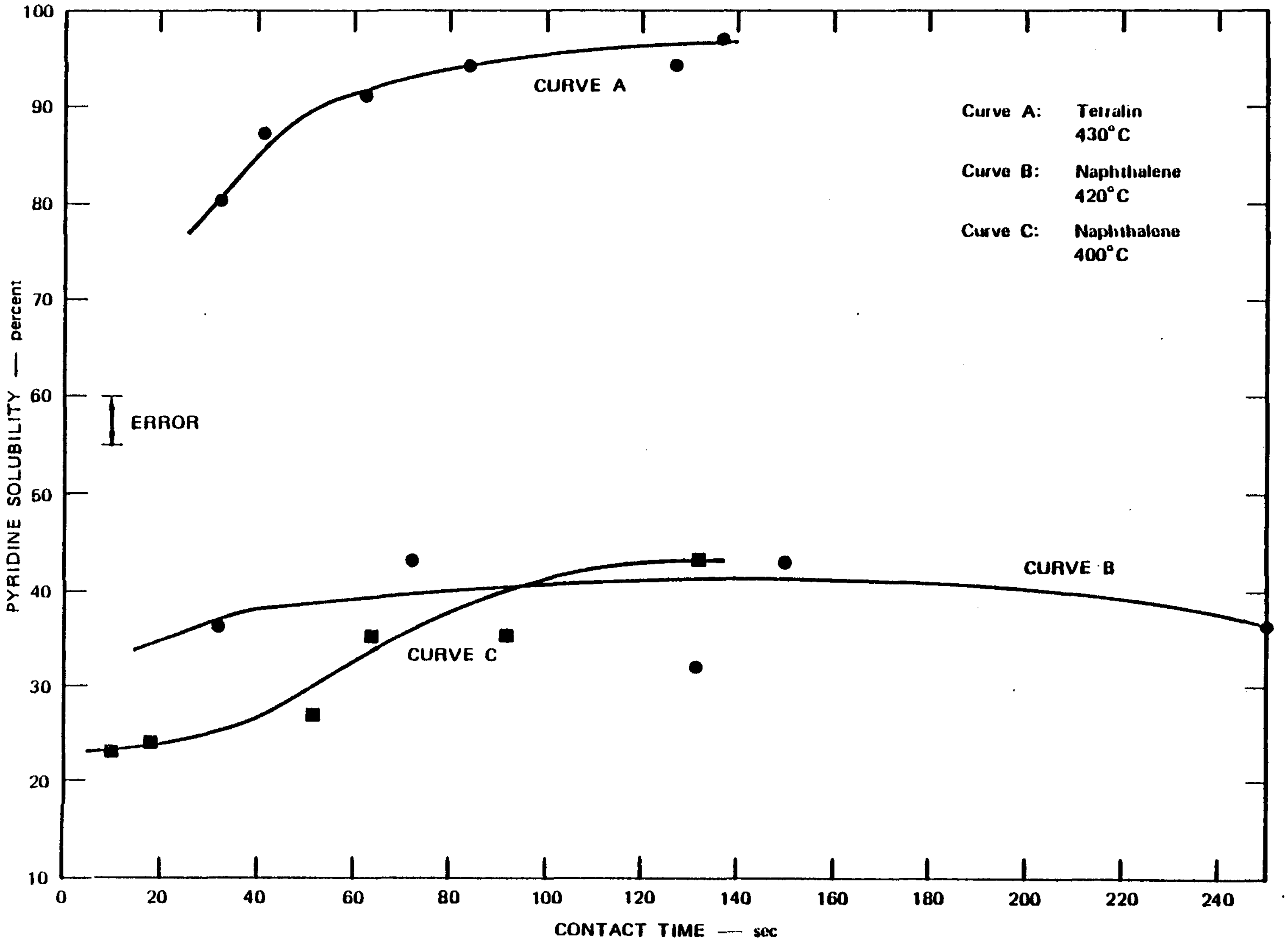

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FIGURE 2 PYRIDINE SOLUBILITY VERSUS CONTACT TIME FOR ILLINOIS NO. 6 COAL WITH TETRALIN AND NAPHTHALENE MEDIA. THE COAL/SOLVENT RATIO IS 1/2.

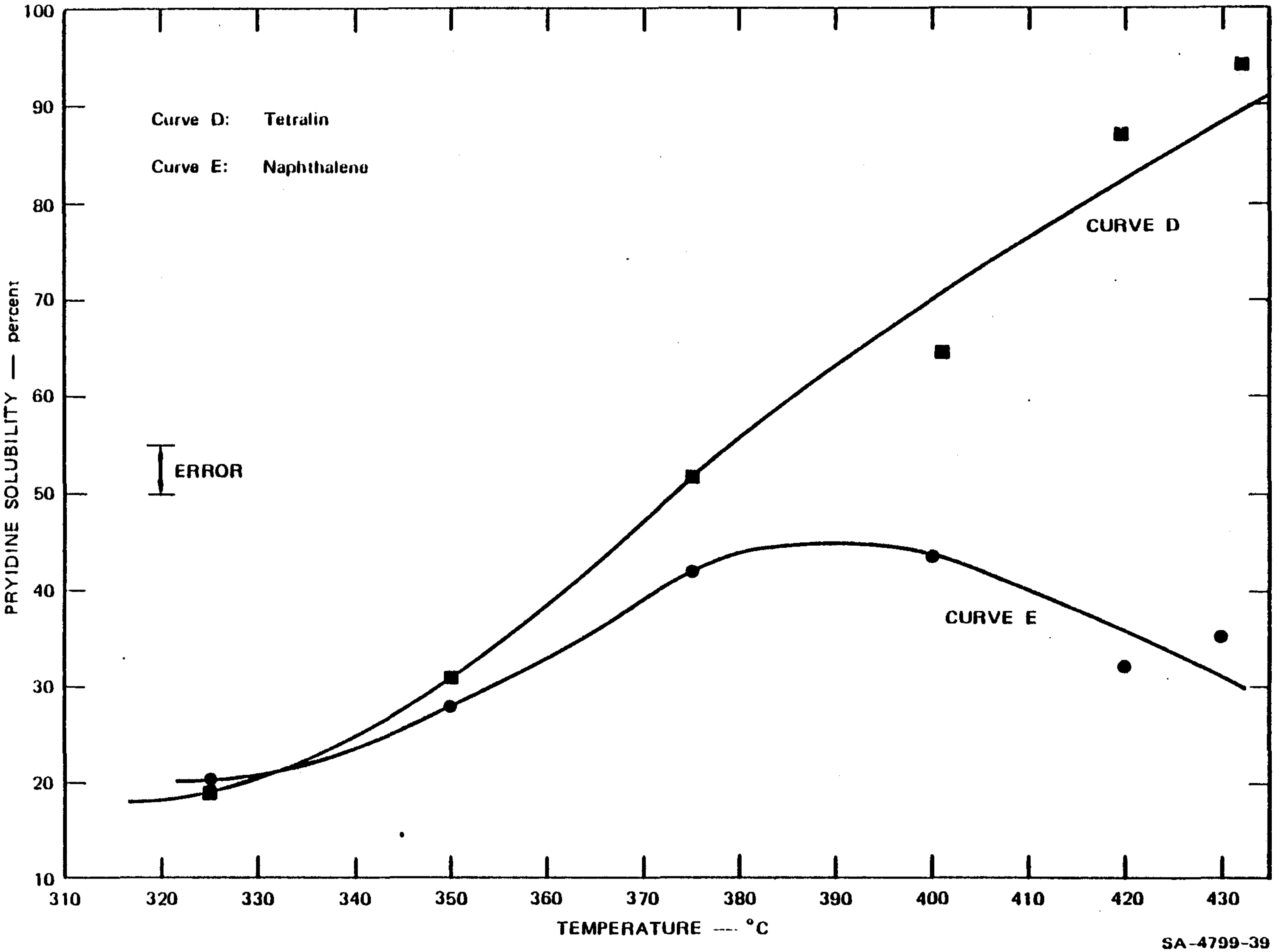


FIGURE 3 PYRIDINE SOLUBILITY VERSUS REACTION TEMPERATURE FOR ILLINOIS NO. 6 COAL WITH TETRALIN AND NAPHTHALENE MEDIA. THE COAL/SOLVENT RATIO IS 1/2 AND REACTION TIME IS APPROXIMATELY 2 MIN.

Effect of Reaction Time/Naphthalene

Pyridine-solubility of coal treated with naphthalene was determined as a function of reaction time at both 400°C (752°F) and 430°C (806°F). Results are shown in Table 8.

At 430°C, the resulting product is only about 30 to 40% soluble in pyridine. The solubility varies with reaction time to a maximum of 43%, then declines to about 37%. Within our error limits of ± 5%, these results indicate a relatively constant conversion with reaction time. When coal is reacted with naphthalene at 400°C, the initial conversion (at 10 sec) is about 20%, rising gradually to approximately 40% in 2 min. These results indicate that coal when treated with naphthalene for short contact times form about 40% pyridine-soluble material. The rate of conversion is rapid at 420°C (788°F) (with about 37% solubility in 28 sec) and relatively slow at 400°C (752°F) (43% solubility in 127 sec). Our results contrast with those of Neavel[5,6] who reported pyridine solubilities as high as 80% with naphthalene at 400°C.

Pyridine solubilities of products are plotted as a function of reaction time as Curve B (reaction temperature: 430°C, 806°F) and Curve C (400°C, 752°F) in Figure 2.

Effect of Reaction Temperature/Naphthalene

The interaction of coal and naphthalene was studied as a function of reaction temperature for a fixed reaction time of approximately 2 min. Reaction temperature ranged from 325° to 430°C (617 to 806°F). Results are shown in Table 8 and Figure 3 (Runs 39 to 44). Pyridine solubility increased from about 20% at 325°C (617°F) to a maximum of about 40% in the temperature range 375 to 400°C (707 to 752°F), similar to the result for Tetralin in this range. It then declined to about 30% at higher temperature. The naphthalene-based results in both Figures 2

Table 8

RESULTS OF FAST REACTION TIME EXPERIMENTS WITH NAPHTHALENE[a]

Run	Temperature		Time	Pyridine Solubility	Mass Recovered
	°C	°F	(sec)	(%)	(%)
24	420	788	32	36	99
25	↓	↓	67	43	95
43	↓	↓	126	32	94
26	↓	↓	145	43	88
27	↓	↓	250	37	93
45	400	752	11	23	135[b]
46	↓	↓	17	24	99
47	↓	↓	47	27	96
48	↓	↓	64	35	90
49	↓	↓	92	27	108
42	↓	↓	127	43	84
39	325	617	126	20	92
40	350	662	124	28	92
41	375	707	124	42	82
42	400	752	127	43	84
43	420	788	126	32	94
44	430	806	129	35	87

[a] Coal used: Illinois No. 6; coal/solvent ratio = 1/2 (wt/wt).

[b] Because of poor man balance, pyridine solubility is based on the recovered extract.

and 3 suggest that the maximum pyridine solubility obtainable in these systems is about 40%. It can be suggested that a series like that in Figure 3 run at shorter times would peak at higher temperatures, and conversely longer reaction periods would peak at lower temperatures. This time-temperature relationship has to be confirmed.

Influence of Mineral Matter

Preliminary experiments indicate that coal ash components have little effect on conversion of pyridine-soluble material. Runs at 420°C (788°F) both with beneficiated and unbeneficiated Illinois No. 6 coals yielded products with similar pyridine solubilties when treated with Tetralin for about 2 min.

Future Work

These results represent a satisfactory start of our short contact time work. Interpretation of the data will evolve with the gathering of more data.

During the next period, we will explore the interaction of coal with mixtures of phenanthrene and Tetralin. Experiments will also be done with pyridine extracted coals and Tetralin to determine the effect of the prior extraction of pyridine-soluble material on the solubilization process.

Task 3A: THERMODYNAMIC AND KINETIC ANALYSIS OF COAL LIQUEFACTION CHEMISTRY

(David M. Golden, Donald F. McMillen and Robert Shaw)

Objective

The objective of Task 3A is to carry out a thermodynamic and kinetic analysis of certain aspects of the chemical reactions involved in coal liquefaction.

Discussion

The objective of Task 3A is to be achieved by:

(1) Compiling published thermochemical data for coal-related structures

(2) Applying thermochemical estimation techniques to compounds for which no measured data are available

(3) Measuring in the laboratory the stability of certain key radical species

(4) Applying, based on these data, kinetic principles to the reactions of the chosen structures, thereby gaining additional insight into certain aspects of coal liquefaction chemistry.

Items (1) and (2) were largely completed, in the case of hydrocarbon species, in the first year. As part of that work, we developed a predictive scheme for the resonance stabilization energies of radicals most likely to be formed from coal-related molecules under thermolytic conditions.[10] We are now extending these analyses to include coal-related nitrogen and sulfur heterocycles. Full details will be given in subsequent reports.

Under Item (3), we have adapted our very low-pressure pyrolysis technique[11] for use with some coal analogs in order to test the parameters developed for estimation of radical stabilities.[10c] A new dual-aperture, fused-silica reactor has been constructed and the reactor inlet system modified for use with moderately low vapor-pressure substances. We are now debugging and calibrating the assembled reactor-mass spectrometer system and anticipate beginning the pyrolysis measurements shortly. Initially, we will measure the rate of the $ArCH_2$-CH_3 bond cleavage in 1-ethylnaphthalene, 9-ethylphenanthrene and 9-ethylanthracene, since the parent hydrocarbons (or their hydroaromatic derivatives) are judged to be common coal constituents, and since our estimation technique shows the benzyl type of radical produce from 9-ethylanthracene to be 12 kcal mol^{-1} more stable than the benzyl radical itself.[10c]

Future Work

Because we hope to eventually attempt to apply the desired kinetic analysis [Item (4)], to coal itself, we have surveyed the literature related to thermal cracking of petroleum fractions and thermal degradations of polymers. Researchers in these related fields have already undertaken the difficult task of applying gas-phase thermodynamic data to reactions in heavy liquids or polymer melts. This material will be discussed in subsequent reports.

Task 3B: COAL STRUCTURE STUDIES

(Frank R. Mayo and Norman A. Kirshen)

1. Objective

The immediate objective of this task is to compare the behaviors of fractions of Illinois No. 6 coal and solvent-refined coal (SRC) with several oxidizing agents, starting with aqueous sodium hypochlorite. Our ultimate goal is to aid in the development of coal liquefaction processes by increasing our knowledge of coal structure and by identifying selective oxidizing agents that may break the connecting links between condensed cyclic aggregates in coal.

2. Summary

Section 3 describes the fractionation of some SRCs with solvents and with hydrogen chloride. Section 4 develops a relation between retention volumes in gel permeation chromatography and number-average molecular weights ($\overline{M}_n$) for the fractions in Section 3 and other coal fractions. This relation is needed for following molecular weight changes in oxidation of coal and coal fractions. In Section 5, we summarize our older and more recent work on oxidations of extracted Illinois No. 6 coal with aqueous sodium hypochlorite and conclude that the effect of pH on rates and products of oxidation is probably small, but that improvements in techniques have given up to 70% recovery of the carbon reacting as bicarbonate-soluble, water-insoluble acids. These acids represent a new and important material for investigation.

3. Fractionations of SRCs

(a) Pyridine-Soluble, Toluene-Insoluble Fraction of Western Kentucky SRC

The main objective of this work was to separate the pyridine-soluble, toluene-insoluble fraction of our Kentucky SRC (because no Illinois SRC was yet available) into fractions that were soluble and insoluble in tetrahydrofuran (THF). As expected, this fractionation cut out the material of highest molecular weight and allowed us to examine the molecular weight distribution of most of the material by gpc in what has become the standard solvent for the project, THF.

Results are summarized in Table 9, but the only new data are the molecular weights. The fractions from the starting material show a consistent increase in H/C ratios and lightening of color with decreasing molecular weight. Although the material from which Fractions B to G were separated was wholly soluble in pyridine, the 29% Fraction B that was precipitated from pyridine by THF was not wholly soluble when the molecular weights were determined in pyridine. Although this partial insolubility could be due to some chemical change during fractionation, it seems more likely that the other fractions, especially the major fraction D, assist the solubility of B material in pyridine.

From the weights and molecular weights in Table 9, the number-average molecular weight of Fraction B is calculated to be 1674, but it probably contains appreciable material of molecular weight $>$ 2000, and the weight-average molecular weight may be in the same range.

The fractions in the table should also give a measure of the effect of polarity on retention time in gpc. Although Fractions B to G are insoluble in toluene, some have lower molecular weights than the toluene-insoluble Fraction III. These relations are discussed in Section 4.

Table 9

FRACTIONATION OF PYRIDINE-SOLUBLE, TOLUENE-INSOLUBLE FRACTION FROM WESTERN KENTUCKY SRC[a]

Fraction	Weight, g	H/C	$\bar{M}_n$[b]
Starting material, Fraction I[c]	15.0	0.68	1212
B, sol. in pyridine, insol. in THF	4.325	0.59	d
D, sol. in THF, pptd. by MeOH	8.633	0.66	1066
E } Increasing solubility in MeOH	0.315	0.72	423
F	0.406	0.82	393
G	0.368	0.94	332
Toluene-soluble, Fraction III[c]	--	0.82	562

[a] This fractionation was described in our Annual Report, Table 17, p. 69. Full analyses, but not the $\bar{M}_n$, were given in Table 18, p. 71, of the same report.

[b] Number-average molecular weight by vapor-pressure osmometry in pyridine.

[c] Fraction I is the title fraction. Fraction III is the toluene (and pyridine)-soluble, hexane-insoluble fraction of same SRC; (Quarterly Report 3, p. 56); data are given here for comparison with toluene-insoluble fractions E, F, and G. Fractionation of the whole SRC is described in Table 14, p. 56 of the same report,[12b]

[d] Not entirely soluble in pyridine although soluble originally in combination with the other fractions.

(b) SRC from Illinois No. 6 Coal

One hundred grams of SRC from Illinois No. 6 coal, kindly supplied by Mr. Everett Huffman of Southern Services, Birmingham, Alabama, was fractionated in essentially the same manner as the SRC from Western Kentucky Coal and the extract from Illinois coal, as described in the Appendix to Reference 12a. The results and analyses are given in Table 10. A fraction like 2 has not been separated previously; it contained material not precipitated when nine parts of toluene were added per part of pyridine in a SRC solution, but insoluble in pure toluene. The molecular weights, molecular distributions, and elemental analyses of fractions are close to those of the corresponding fractions of Western Kentucky SRC in Table 14 of Reference 13b. The new data permit direct comparison of corresponding fractions of Illinois SRC and of extracts of Illinois No. 6 coal. This comparison, with discussion almost unchanged from that published in the Preprints of the SRI Coal Chemistry Workshop,[13] will be submitted for publication in Fuel.

The nuclear magnetic resonance (nmr) peak areas and elemental analyses show that all fractions are predominantly aromatic. Fraction 4 has the highest H/C ratio (0.878) and also the least oxygen and the lowest molecular weight. The proportion of hydrogen in aromatic-H bonds (51%) is the highest of the fractions and is inconsistent with the decreasing trend in Fractions 1 to 3. If this proportion is indeed correct, it indicates more benzene and fewer condensed rings in Fraction 4.

(c) Illinois SRC with HCl

The toluene-soluble, hexane-insoluble fraction of our Illinois SRC ("Asphaltenes," Fraction 3 in Table 10) was separated into basic and acid plus neutral components by the procedure of Sternberg and coworkers.[14] Our objectives were to examine the behavior of the fractions in oxidation and in gpc. Details of the fractionation are given in Table 11;

Table 10

FRACTIONATION OF 99.55 GRAMS OF ILLINOIS NO. 6 SRC

Fraction	Solubility[a]	Weight g	M_n[b]	Chemical Shifts, Associated Structures, and Relative Peak Areas				
				0.6-1.3	1.1-2.0	1.5-3.5	2.60-4.8	5.8-9.2
				Me-	$-CH_2-$	$Ar-CH_2-$	$ArCh_2Ar$	Ar-H
1	Pyridine	35.05	1250	0.39		0.58	0.17	1
2	Toluene/pyridine, 90/10	23.09	720	0.16	0.18	0.72	0.15	1
3	Toluene	35.10	410	0.18	0.37	0.73	0.26	1
4	Hexane	4.81	185	0.09	0.27	0.54	0.07	1
Unaccounted for		1.50						

[a] Soluble in indicated solvent and solvents listed above it, but not in solvents listed below it.

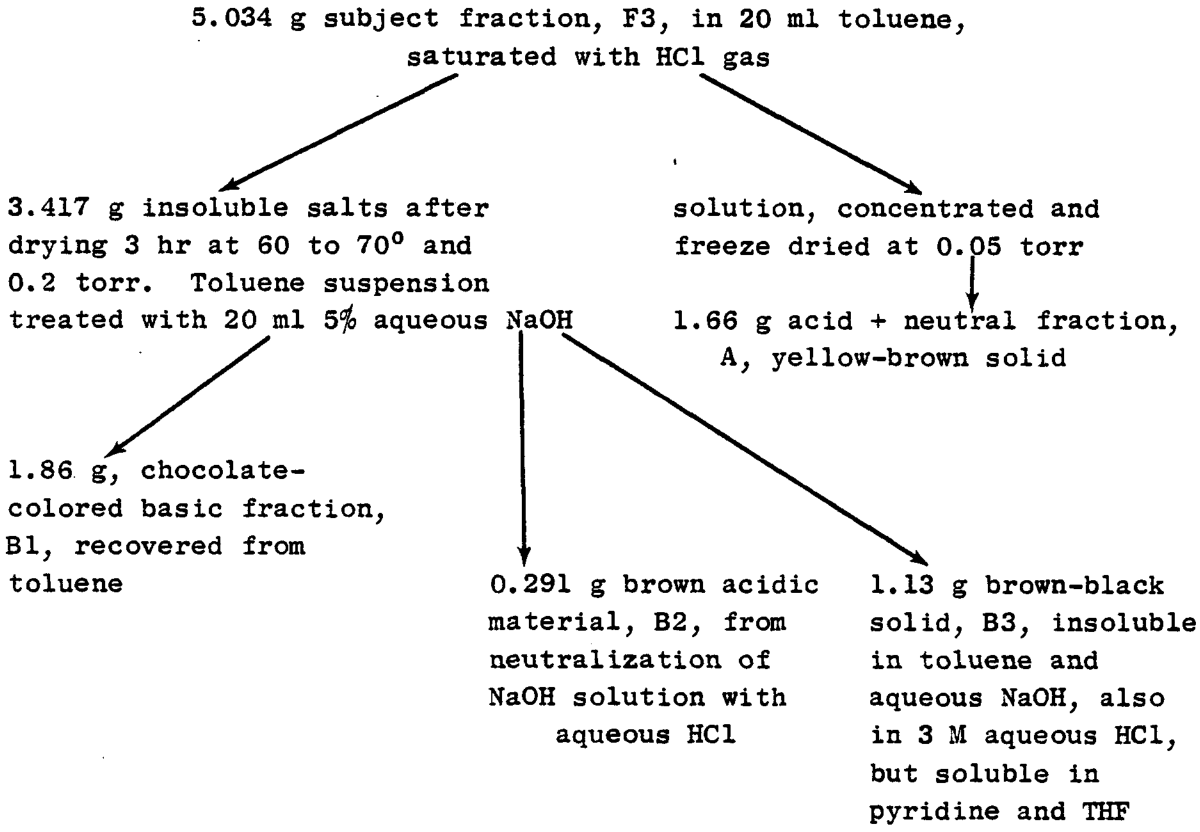
[b] Number average molecular weight by vapor-pressure osmometry in pyridine.

ELEMENTAL ANALYSES OF ILLINOIS NO. 6 SRC FRACTIONS

Fraction	Elemental Analyses (%)						
	C	H	N	S	O	H/C	Ash
1	86.11	4.87	2.58	0.76	5.68	0.674	0.33
2	85.78	5.27	2.23	0.89	5.83	0.732	0.32
3	87.39	6.12	1.59	0.89	4.01	0.834	0.20
4	89.87	6.62	0.66	0.82	2.03	0.878	0.00

Table 11

FRACTIONATION WITH HCl OF TOLUENE-SOLUBLE, HEXANE-INSOLUBLE FRACTION OF SRC FROM ILLINOIS NO. 6 COAL



5.034 g subject fraction, F3, in 20 ml toluene, saturated with HCl gas

3.417 g insoluble salts after drying 3 hr at 60 to 70° and 0.2 torr. Toluene suspension treated with 20 ml 5% aqueous NaOH

solution, concentrated and freeze dried at 0.05 torr

1.66 g acid + neutral fraction, A, yellow-brown solid

1.86 g, chocolate-colored basic fraction, B1, recovered from toluene

0.291 g brown acidic material, B2, from neutralization of NaOH solution with aqueous HCl

1.13 g brown-black solid, B3, insoluble in toluene and aqueous NaOH, also in 3 M aqueous HCl, but soluble in pyridine and THF

Total recoveries, 4.94 g

elemental analyses and molecular weights are presented in Table 12. The high oxygen contents of Fractions B2 and B3 indicate extensive absorption of oxygen on standing with aqueous NaOH, without loss of H or decrease in H/C ratio. This change suggests conversion of C-H to C-O-H, not to CO_2H.

4. Correlations of Gel Permeation Chromatography (gpc) and Vapor-Pressure Osmometry (vpo)

For some time we have been collecting data on gpc and number-average molecular weights ($\bar{M}_n$) on coal fractions in the hope of calibrating gpc with vpo. We have now collected enough data (Section 3) to summarize our results to date. The problems have been that narrow fractions are necessary for calibration and that previous relations for other polymers have been determined with linear polymers, which are not representative of coal. Our separations of coal extract and SRC into pyridine-, toluene-, and hexane-soluble fractions have yielded products of sufficiently narrow molecular weight distribution to be useful in calibration.

Figure 4 summarizes our results on $\bar{M}_n$s by vpo, mostly on fractions of coal extracts and fractions of SRC. The points for polystyrene and poly(ethylene glycol) are for standard samples supplied by Waters Associates. The point for phenanthrene is our own measurement on a commercial sample. All the other points, except one on a whole Illinois SRC, are for fractions of a pyridine extract of Illinois No. 6 coal or fractions of an Illinois No. 6 SRC or Western Kentucky SRC. All the $\bar{M}_n$s were determined in pyridine as solvent, and all the retention volumes correspond to peaks where the maximum signal was obtained with THF as solvent (mobile phase). Figure 5 shows some representative curves. The rather narrow, symmetrical peak, A, is representative of most of our gpc curves. Its shape, in comparison with B for pure phenanthrene or F for a

Table 12

ACID/BASE FRACTIONATION OF ILLINOIS NO. 6 SRC[a]

Fraction	Weight (g)	$\bar{M}_n$[b]	Elemental Analyses					
			C	H	N	Cl	O	H/C
Starting material[a]	5.034	410	85.78	5.27	2.23	< 0.1	5.83	0.732
A, acid + neutral	1.66	543	87.97	6.61	0.67	1.15	3.6	0.895
B, ·HCl salt	3.417	1230[c]	83.46	5.72	1.82	2.88	6.12	0.817
Regenerated bases								
B1, soluble in toluene	1.80	435	87.73	5.68	2.16	< 0.1	4.43	0.771
B2, soluble in aqueous NaOH	0.29	475	75.78	5.33	1.07	1.95	15.87	0.838
B3, insoluble in both	1.13	680	80.37	5.46	1.73	< 0.1	13.26	0.809

[a] Toluene-soluble, hexane-insoluble Fraction 3 in Table 10.

[b] Number average molecular weight by vapor-phase osmometry in pyridine.

[c] Calculated for one Cl per molecule

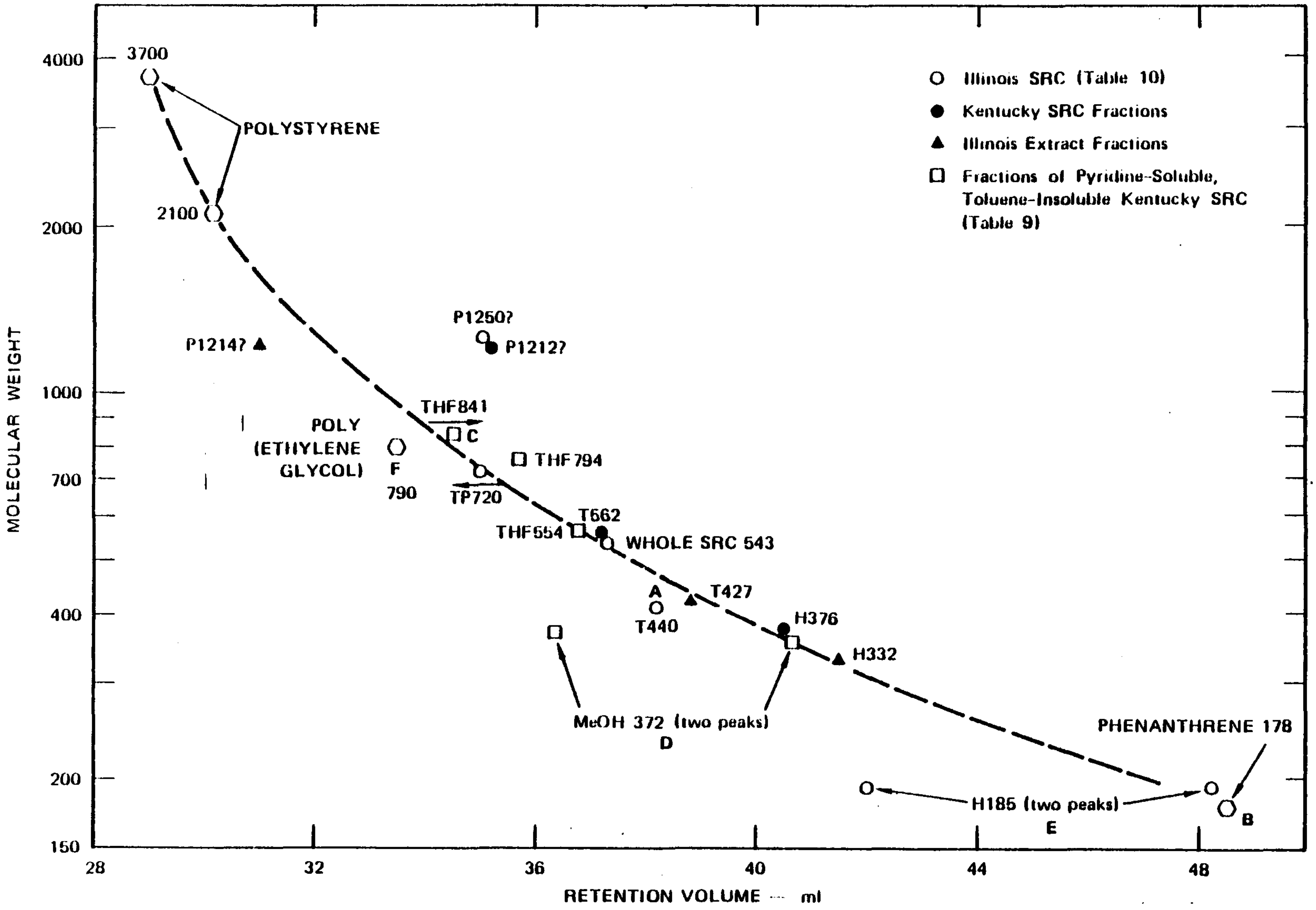


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FIGURE 4 MOLECULAR WEIGHTS AND GPC RETENTION VOLUMES FOR FRACTIONS OF EXTRACTS AND SRCs OF ILLINOIS AND KENTUCKY COALS

The letter associated with a point indicates whether the fraction was soluble in pyridine, toluene, or hexane. The number is the $\overline{M}_n$ measured by VPO. Designations A to E relate points in Figure 4 to curves in Figure 5.

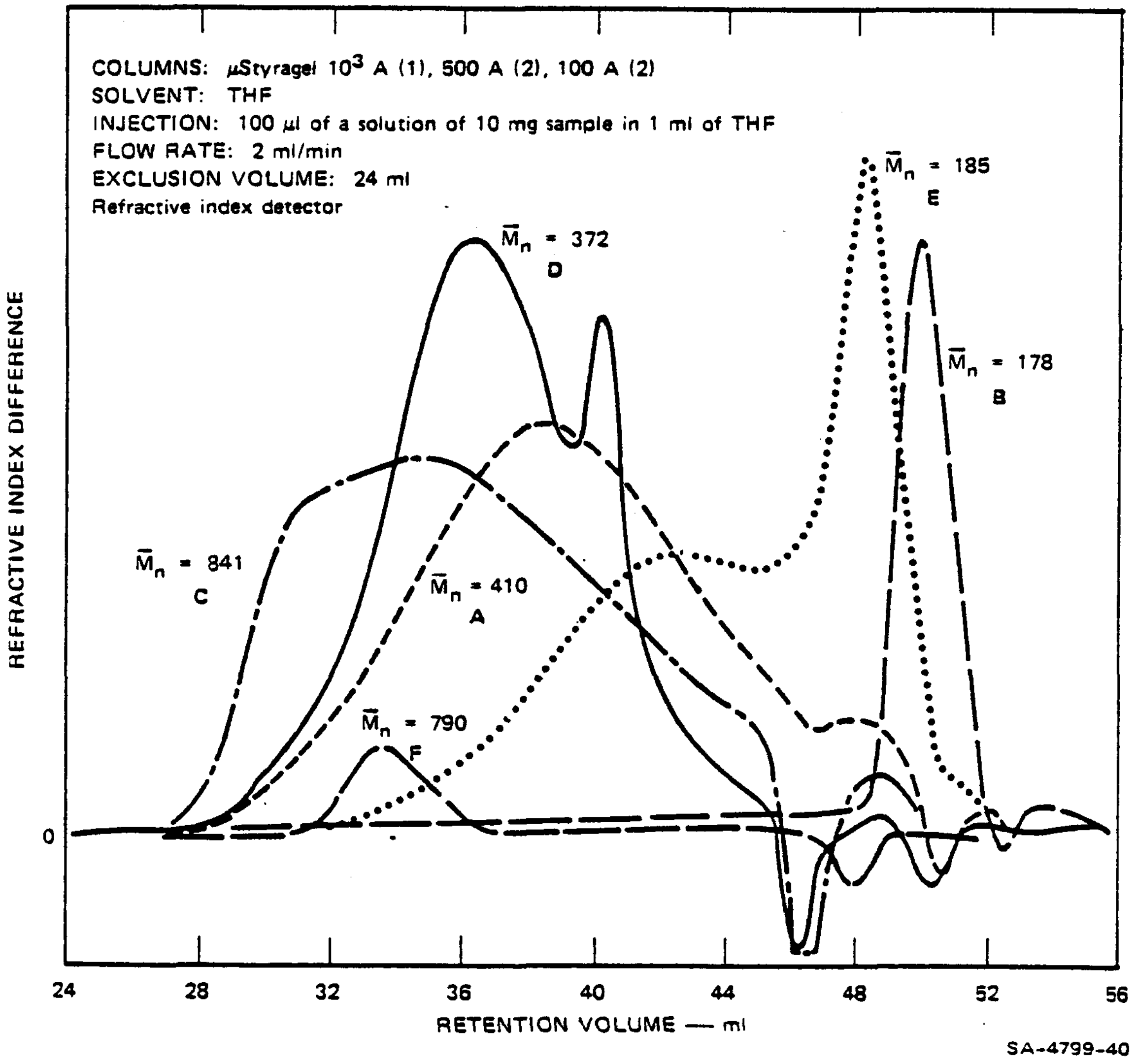

FIGURE 5 GPC CURVES FOR COAL EXTRACT FRACTIONS AND STANDARDS
Letters refer to fractions in Figure 4.

poly(ethylene glycol) fraction, indicates that our standard fractionation procedure, with pyridine, toluene, and hexane as solvents, results in molecular weight distributions that are narrow enough for our purpose, with a few exceptions: A few curves are slightly skewed, as shown in example C. Skewed curves are marked by arrows under the corresponding points in Figure 4, indicating whether the greater part of the fraction appears at smaller or larger retention volume than the peak. Samples D and E, represented by two pairs of points in Figure 4, show two peaks in Figure 5.

Points for fractions soluble only in pyridine are included in Figure 4, but with question marks, because these fractions were not entirely soluble in THF. This solvent has been used at SRI in several earlier projects, and we have continued to use it in the coal work because pyridine is incompatible with our styragel columns.

We now summarize the present status of our molecular weight studies. The broken line in Figure 4 correlates satisfactorily the retention volumes and $\overline{M}_n$s for nearly all of our fractions of coal extracts and SRCs up to molecular weights of 1000, even though the coal fractions contain 2 to 7% more oxygen than the SRC fractions. For molecular weights above 1000, the correlation for coal fractions may or may not be consistent with relations for linear polymers; to find out, we shall have to use a gpc solvent that will entirely dissolve the coal fractions. Fractions D and E, which show two peaks in Figure 5, are each represented by two points (correspondong to the two peaks) in Figure 4. It is not surprising that the points for larger retention volumes (lower molecular weights) lie closer to the curve in Figure 4; these materials should contribute most to the number-average (vpo) molecular weights.

For most of the pyridine, toluene, and hexane-soluble fractions, the gpc peaks are fairly sharp and vpo gives us a more precise and convenient measure of molecular weights than gpc. For fractions of these fractions, the gpc correlation is uncertain and vpo data are preferable. The pure phenanthrene fits our correlation.

The principal utility of gpc in our coal research should be to follow changes in molecular weight during oxidation; gpc will bring out broadened and double-peak relations that are undetectable by vpo.

Further work on this relation should follow three lines:

(1) The calibration should be extended to higher molecular weights by use of a better solvent for high molecular weight material. Pyridine is an obvious possibility if used with porous silica packings but piperidine, ethylene diamine, and N-dimethylformamide are also possibilities.

(2) $\bar{M}_n$s by vpo for some fractions should be checked in some solvents other than pyridine to see whether they are independent of solvent or whether they represent equilibria in dissociations of polyfunctional compounds.

(3) A few more pure aromatic compounds, with and without polar groups, should be examined.

5. Oxidations with Aqueous Sodium Hypochlorite

(a) Extracted Illinois No. 6 Coal

This section summarizes our four oxidations of extracted coal with 0.8 M aqueous sodium hypochlorite (Clorox) to determine the effects of pH and experimental procedure on the products obtained. Oxidations 1 to 3 were summarized in our Annual Report, Reference 2, starting on page 56. Oxidation 4, the most interesting to date, is new. All the analyses are now presented on a dry, ash-free basis (DAF). The ash contents are based on residues from analyses for C, H, and N, but we think that the differences from the mineral matter in the original are small. Our starting Illinois No. 6 coal had been beneficiated so that it contained only 2.22% ash. The 7.17% ash in the extracted coal is mostly porcelain accumulated in extensive ball-milling and would not affect the ash-mineral matter difference.

Table 13 summarizes results of four oxidations at nearly constant pH 9, 10, and 11. However, the steady increase in carbon recovery apparently results more from improvements in experimental procedures than from change in pH; the chlorine contents of the major, bicarbonate-soluble fraction are constant at about 8%, indicating little change in mechanism. As for technique changes, stepwise oxidation with smaller proportions of NaOCl improved recoveries of carbon. Recoveries were further improved by carrying out the oxidations in centrifuge tubes to facilitate separation of soluble and insoluble products, and washing the intermedicate precipitates with water to remove slightly soluble acids. Along with the recoveries in total carbon, the proportions of products in the black, acid fractions, soluble in bicarbonate solution but not in water, also increased. In the last and best experiment, 14% of the original carbon remained in the insoluble residue, 60% was in the water-insoluble acids, and the remaining 19% was presumably in CO_2.

On the assumption that chlorine replaces hydrogen in sodium hypochlorite oxidations, we now consider the C/(H + Cl) ratios in Table 14. All the oxidation products have lower ratios than the starting material. The decrease is less for the bicarbonate-soluble acids (1.37 to 1.20) and greater for the water-soluble acids. Because all the products also contain much more oxygen than the starting material, and because much of the oxygen replaces hydrogen, we conclude that the carbon-rich portions of the coal (condensed rings) are being oxidized preferentially. Our Annual Report[2] showed, from ^1H nmr, that the ether-soluble fraction C-1 of Oxidation 1 contained more aliphatic than aromatic protons, while the

Table 13

OXIDATIONS OF EXTRACTED COAL WITH NaOCl AT 30°C

Products	Analyses							
	Fraction	Weight g	$\bar{M}_n$	NE	Fraction	Weight g	$\bar{M}_n$	NE
	Oxidation 1 1 step at pH 9.0-9.2				**Oxidation 2** 4 steps at pH 9.0-9.2			
Original extracted coal		1.011				4.00		
Unreacted, insoluble residue		0.130			1[a]	0.31		
Soluble in aqueous $NaHCO_3$	B	0.128			D	1.49	776	274
Soluble in H_2O, Et_2O	C-1	0.307	238	104				
Soluble in H_2O, pyridine	C-2	0.513	287	179	A[c]	0.916	420	204
Insoluble in concentrated salt solution					E	0.423		
Not separated from salts					F	0.343[d]		
Carbon recovery	61% in soluble fractions				65%			
	Oxidation 3 6 steps at pH 10.0-10.2				**Oxidation 4** 4 steps at pH 11.0-11.5			
Original extracted coal		3.96				4.000		
Unreacted, insoluble residue	e	0.473			1	0.8065		
Soluble in aqueous $NaHCO_3$	f	2.665	991	394	2	3.033		352
Soluble in H_2O, Et_2O	h[b]	0.208	370	108	3	0.4223		146
Soluble in H_2O, pyridine	j[c]	0.503	227	279				
Insoluble in concentrated salt solution	g	0.197	303	291				
Not separated from salts	-	0.16[d]			5	0.0094[d]		
Carbon recovery	76%				79%			

[a] Left 48% ash on ignition.

[b] Ether extract of dry salts.

[c] Pyridine extract of dry salts

[d] Grams C in salts by combustion

Table 14

ANALYSES OF FRACTIONS OF NaOCl OXIDATIONS

Fraction	%, DAF basis						
	C	H	N[a]	Cl[a]	O + S (by difference)	$\frac{C}{H + Cl}$	Ash
Original extracted coal	78.07	4.78	2.26	0	12.61+2.35	1.37	7.2
Oxidation 1:							
C1	39.39	4.08	0.45				
C2	47.69	3.41	4.65[a]				
Oxidation 2:							
D	54.54	3.79	1.33	7.96	32.37	1.20	3.1
A	49.28	4.20	3.08[a]	8.17	35.27	0.99	1.1
E	36.97	3.09	1.11	8.08[a]	50.73[a]	1.01	12.7
D methylated	62.15	5.65	3.16[a]	4.28	24.76	0.90	
Oxidation 3:							
e	57.98	3.92	1.50	5.51	31.09	1.19	34
f	50.9	3.45	1.48	6.99[a]	37.18[a]	> 1.17	9
h	33.98	3.31	0.47	23.93	38.31	0.86	0
j	35.17	2.73	4.13[a]	43.45[a]	19.52[a]	--	31
g	36.98	2.23	1.15	22.03[a]	37.61[a]	> 1.09	8
f methylated	51.06	4.04	2.91[a]	9.00	32.99	1.00	0
Oxidation 4:							
1	66.95	4.38	1.92	4.72	22.02	1.23	27.1
2	58.08	3.77	1.78	8.96	27.1	1.21	2.2
3	49.00	3.60	8.20[a]	20.43	18.77	0.98	4.2
5	1.95	0.22	0.14				high

[a] High nitrogen contents indicate retained pyridine. Except in fractions 3 and 4-1, which could be washed thoroughly with water, high chlorine contents accompanied by high ash indicate presence of sodium chloride, duplication in Cl contents, and stated O+S contents (by difference) that are too low.

reverse is true of fraction C 2, and the bicarbonate-soluble fraction 3f of Oxidation 3 contained 1.45 times as many aliphatic as aromatic protons. Thus, the surviving material, even though it contains more carbon than hydrogen, contains more aliphatic than aromatic protons, at least until the aliphatic material is oxidized away, leaving benzene carboxylic acid. These results tend to support the conclusions of Chakrabartty and Berkowitz,[15] although their evidence is faulty,[16] that coal contains many bridged aliphatic ring systems. There is no reason why the coal-forming process should proceed so that the products are conveniently represented as planar.

The water-insoluble but bicarbonate-soluble acids now present a new and interesting material for investigation by nmr, ir, and several chemical methods.

(b) Pyridine-Soluble, Toluene-Insoluble Fraction of Illinois SRC

The object of this experiment was to compare the oxidation with aqueous NaOCl of the pyridine-soluble, toluene-insoluble fraction of Illinois No. 6 SRC (Fraction 1 in Table 10) with the oxidations of the extracted coal in the previous section. Four grams of starting material was dissolved in 13 g of pyridine and then added slowly to 150 ml water with vigorous stirring, producing a very fine suspension of swollen substrate in water. After centrifuging and several washings (by dispersion in water or very dilute HCl at pH 2 and centrifuging), 16.7 g (a fourfold expansion) of a rather firm black gel was obtained. This material was oxidized in four steps with 32 g of 0.8 M NaOCl at pH 10 to 10.5 at 30°C (as described in Section 5a). In general, the rate of oxidation was about the same as with the extracted coal, the NaOCl being exhausted in about 30 min, but the rate of solution of the substrate was slow. After the four oxidations, the residual centrifuged gel weighed 13.32 g. Washings with hot water reduced its weight to 6.0 g. Apparently, the acids from SRC are less soluble than those from extracted coal.

As of now, the 4.00 g of SRC has given 1.49 g of (dry) undissolved substrate, 2.25 g of bicarbonate soluble acids, and an undetermined quantity of water-soluble acids. On completion of the experiment, the bicarbonate-soluble acids will be compared with those from extracted coal (Section 5a).

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