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

Quarterly Report

Covering the Period March 16, 1978 — June 15, 1978

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ABSTRACT

Work has begun on the investigation of the CO/H_2O/base system for upgrading Illinois No. 6 coal. Reactions of coal in $CO/H_2O/KOH$ at 400°C for 20 minutes provide products that appear favorable compared with SRC. The results of a blank $CO/H_2O/KOH$ run demonstrate the presence of formate in our system, and the production of hydrogen, which is catalytic with respect to base. Model compound results from i-PrOH/KOH, MEOH/KOH, and $CO/H_2O/KOH$ systems indicate that anthracene-like structures in coal would be hydrogenated in these systems, but phenanthrene-like structures would not. Furthermore, phenyl ether-like bridges would be cleaved, while bibenzyl- and biphenyl-like bridges would not. The fact that coal is converted in these basic systems, while bibenzyl and benzyl-phenyl ether are not, raises some important questions about the mechanism of coal conversion.

On tasks to study the role of intermediate and acid-base complexes in hydrogen donor liquefaction processes, we have begun the attempt to reconcile differences between findings in the present work and those of Whitehurst and coworkers. The results support our observation that removal of initially pyridine-soluble materials from an Illinois No. 6 coal significantly decreases, by approximately a factor of two, the subsequent donor solvent conversion of the pyridine-insoluble portion. Further experiments indicate that this decrease results from a combination of two factors: the initially pyridine-soluble materials have an important role in the donor solvent dissolution, and pyridine residues in the extracted coal can act as a poison for dissolution in Tetralin. Experiments run in quartz ampoules indicate that the reactor surface is not a significant factor. Possible causes of the difference between Whitehurst's results and the present finding are traced to differences between his experimental procedures and those used in the present work. Future experiments will be directed toward further elucidation of the detrimental effect of pyridine and toward a corollary understanding of conditions that will improve donor solvent conversion.

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INTRODUCTION

Work has resumed on DOE Contract No. EF-76-C-01-2202, and this quarterly report covers the period March 16, 1978 to June 15, 1978 of our study of the fundamental aspects of coal liquefaction. The overall goals of the project are to increase our understanding of the conversion processes for developing an efficient system for the conversion of coal to distillate fuels. Important considerations include moderation of reaction conditions and minimum hydrogen consumption

The project is being carried out in three tasks:

Task 1: Study of the Use of Inorganic Bases in Coal Liquefaction,

Task 2: Hydrogen Transfer Intermediates in Coal Liquefaction,

Task 3: Acid-Base Complexes in Coal Liquefaction.

In Task 1 we use a beneficiated Illinois No. 6 coal, -60 mesh, supplied by Pennsylvania State University, whose designation for the coal is PSOC-26. A sample of the same coal which has not been beneficiated is being used in Tasks 2 and 3.

TASK I: STUDY OF THE USE OF INORGANIC BASES IN COAL LIQUEFACTION

David S. Ross and James E. Blessing

Objective

The objective of this task is to explore the potential of inorganic-base/CO/H_2O systems for converting Illinois No. 6 coal to a low sulfur, low nitrogen, distillate syncrude. The primary system of interest is $CO/H_2O/KOH$, but bases other than KOH may be tried as time and funds permit. The addition of an organic solvent comparable to a process recycle solvent may also be tried. Also, model compounds may be used in place of coal to further our understanding of the system and thereby aid in directing our experiments on coal.

Background

This task is the direct outgrowth of our previous work with isopropanol/base and methanol/base systems in the conversion of Illinois No. 6 coal.[1,2] That work showed that both alcohols can donate hydrogen to coal, apparently by base-catalyzed hydride donation and subsequent proton transfer from another molecule of alcohol. The products were reduced in both nitrogen and sulfur and, in some cases, were room temperature liquids. Our observation of CO and H_2 generation in MeOH/KOH/coal experiments at 400°C led to initial experiments with $CO/H_2O/KOH$ and coal.

Experimental Procedure

Ten grams of coal or model compound is added to a 300-cc, stirred, Hastelloy C or 316 stainless steel autoclave. The coal, -60 mesh, is dried overnight at 120°C and < 1 torr. Typically 10 g of KOH pellets is dissolved in 40 ml of H_2O and added to the autoclave, which is then flushed with N_2. The reactor is sealed and pressurized with 700 psig of CO (0.5 mole).

The reactor is heated to temperature and held there for the duration of the reaction. Heat-up time is 40-45 minutes, cool-down time is $\sim$ 60 minutes. Any product gases are sampled and analyzed for H_2, CO, CH_4, and CO_2 by gas chromatography. The aqueous suspension is then acidified (∿ pH 3) with concentrated HCl. In model compound studies, products from $CO/H_2O/KOH$ runs are extracted with a solvent such as Et_2O before analysis. Coal products of $CO/H_2O/KOH$ reactions are worked-up as described in Appendix A.

Results and Discussion

Our work with coal in the $CO/H_2O/KOH$ system has been published in Fuel as a note. The full manuscript is presented in Appendix A, and a summary of the work is presented below. (Manuscripts to be submitted to Fuel on our isopropyl alcohol and methanol work are included as Appendices B and C, respectively.) Work with model compounds and a blank run with $CO/H_2O/KOH$ in which no coal was present are also discussed.

Results of $CO/H_2O/KOH$ Runs with Coal

These experiments at 400°C for 20 minutes yielded a product that was fully pyridine-soluble, 50% benzene-soluble, and 18% hexane-soluble. We stress that, in contrast to the earlier work by Appell et al. with CO/H_2O and bituminous coal in the presence of phenanthrene as a vehicle solvent,[3] our results were obtained with only water as the reaction medium. Since the temperature here is above the critical temperature of water, the exact nature of the reaction medium is not clear at this time.

As shown in Appendix A, there is an increase in H/C ratio over that of the starting coal and reductions in nitrogen and sulfur contents. The products of these runs differ significantly from SRC derived from Illinois No. 6 coal. Table 1 compares some important characteristics of the non-gaseous products of Run A (see Appendix A) with those of an Illinois No.6 derived SRC. The $CO/H_2O/KOH$/coal product has a significantly higher H/C ratio. This product contains more sulfur than SRC, but substantially less nitrogen. This significant reduction in nitrogen seems to be characteristic of the basic conversion systems we have studied.[2]

Table 1

COMPARISON OF $CO/H_2O/KOH$/COAL PRODUCT AND SRC

Product	Hexane Solubility	Benzene Solubles[a]					Whole Product		
		%	H/C	%S	%N	H_{ali}/H_{arom}[b]	H/C	%S	%N
Run A	18	51	1.08	1.0	1.2	3.5	0.87	1.3	1.2
SRC[c]	5	40	0.84	0.9	1.5	1.2	0.74	0.8	2.0

[a] Benzene solubles of Run A, toluene solubles of SRC. Includes hexane solubles.

[b] Ratio of aliphatic ($\delta < 5$) to aromatic ($\delta > 5$) protons as determined by proton NMR.

[c] SRC supplied by Southern Services from the Wilsonville plant, sample No. 16573.

Benzene solubles from $CO/H_2O/KOH$/coal, while somewhat greater in yield and having higher H content, are also much more aliphatic than the SRC fraction. These factors may make such a $CO/H_2O/KOH$ product more desirable than SRC with respect to further upgrading.

Results of a Blank $CO/H_2O/KOH$ Run

We have noted that substantial quantities of H_2 and CO_2 were formed during our $CO/H_2O/KOH$ runs with coal, and we suggested that formates were involved in the conversion process. A blank $CO/H_2O/KOH$ experiment, one without coal, was run to determine gas yields, production of any hydrocarbons, and the fate of KOH in the system. Because of the rapid development of high pressures, we were forced to stop the reaction after less than 1 minute at 400°C. Substantial reaction occurred, nonetheless, as shown by the material balances for this run in Table 2.

Table 2

MATERIAL BALANCES OF $CO/H_2O/KOH$ RUN AT 400°C FOR 1 MIN[a]

Initial Loading	Recovered Products	Total Recovery
535 mmoles CO	57 mmoles CO ∿78 mmoles $KHCO_2$ 297 mmoles CO_2 ∿44 mmoles $KHCO_3$	∿476 mmoles carbon
	317 mmoles H_2	317 mmoles H_2
150 mmoles KOH	∿78 mmoles $KHCO_2$ ∿44 mmoles $KHCO_3$	∿122 mmoles potassium
2.85 moles H_2O	no balance attempted	

[a] The $KHCO_2$ and $KHCO_3$ were identified by IR spectroscopy.

We are clearly observing the water-gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{1}$$

This conclusion can be drawn since (1) we see equal quantities of H_2 and CO_2 as product gases and (2) substantially more H_2/CO_2 is formed than starting base added. (The reaction may be promoted by the walls of the Hastelloy C autoclave, and an experiment without added base will be run to assess that possibility.)

The observation of potassium formate as an intermediate is not surprising since it is readily formed from CO and base. The reaction sequence for H_2 formation is thus

$$CO + OH^{-} \rightleftharpoons HCO_2^{-} \tag{2}$$

$$HCO_2^{-} + H_2O \rightleftharpoons H_2 + CO_2 + OH^{-} \tag{3}$$

Note that OH^{-} is regenerated in the sequence, and reaction (1) is the net process. This supports our suggestion (Appendix A) that formate is an intermediate in the coal upgrading process and is intercepted as a hydride donor.

An alternative process stoichiometric in base would be one in which the product CO_2 reacted with base, forming carbonate. (At our reaction temperatures bicarbonate is unstable, going to carbonate and CO_2.) In this case the net reaction would be

$$OH^{-} + CO + \tfrac{1}{2}H_2O \longrightarrow H_2 + \tfrac{1}{2}CO_3^{=} + \tfrac{1}{2}CO_2 \tag{4}$$

where OH^{-} is consumed with the stoichiometric formation of 1 H_2 and $\frac{1}{2}CO_2$. Our results clearly indicate that reaction (4) is not operative in our system; the process appears to be catalytic in base.

Results of Model Compound Runs

The results of several model compound experiments are presented in Table 3. Anthracene shows substantial conversion to 9,10-dihydroanthracene in both i-PrOH/KOH at 335°C and in $CO/H_2O/KOH$ at 400°C (runs 126 and 131).

Bibenzyl on the other hand is unreactive at 400°C in either MeOH/KOH or $CO/KOH/H_2O$, being recovered unchanged. Similarly, benzylphenyl ether was not converted to the expected reduction products, toluene and phenol. In fact, no product possibly derived from it was observed, and the ether was apparently consumed in polymerization reactions.

Table 3

EXPERIMENTS WITH MODEL COMPOUNDS IN SYSTEMS CONTAINING KOH[a]

Run No.	System	Model Compound	Temp (°C)	Time (min)	Products Recovered	
					Unreacted Starting Material, %	Other
126	iPrOH[b]	Anthracene	335	90	11%	64% 9,10-dihydroanthracene 10% other
127	iPrOH[b]	Benzylphenyl ether	335	90	∿20	No identifiable products[c]
132	MeOH[d]	Bibenzyl	400	20	95	∿5% toluene
130	CO/H_2O[e]	Bibenzyl	400	20	95	∿1% toluene
131	CO/H_2O[e]	Anthracene	400	20	65	35% 9,10-dihydroanthracene

[a] 10 g of model compound was used in all cases except Run 127 were only 4.2 g were used.

[b] 90 g i-PrOH and 5 g KOH were used

[c] Only i-PrOH condensation products were found. No $PhCH_2OPh$-related products were seen.

[d] 48 g MeOH and 10 g KOH were used.

[e] 36 g H_2O and 10 g KOH were used.

The results for this model compound work and the work done earlier (Appendix C), are diagrammed in Figure 1, along with results for coal in the same systems. Coal, anthracene, and diphenyl ether were converted to products that are reduced relative to the starting material;* biphenyl, phenanthrene, bibenzyl, and benzylphenyl ether were not. Bibenzyl and benzylphenyl ether are commonly studied as model compounds in coal conversion studies, and yet we show here that coal can be converted under conditions where these model compounds are not.

This result raises the question of whether there is more than one mechanism by which coal can be converted to upgraded products. The conventional reaction scheme is considered to be

$$\text{coal-coal} \longrightarrow 2\ \text{coal}\bullet \xrightarrow[\text{H-donor}]{} 2\ \text{coalH} \qquad (5)$$

in which a bond in the coal is thermally cleaved, yielding two free radicals. The radicals are then "capped" via H-donation by an H-donor solvent present in the system. Presumably this type of chemistry proceeds in current systems where Tetralin is used as the H-donor.

In our work there is no H-donor present, at least in the conventional sense. The process of reduction seems to be one of initial hydride transfer, followed by proton transfer, a sequence consistent with the known chemistry of these ionic reduction systems with simple substrates.

$$\text{coal} \xrightarrow[\text{H-donor}]{} \text{coalH}^{-} \xrightarrow[\text{H}^{+}\text{-donor}]{} \text{coalH}_2 \qquad (6)$$

The fact that the ionic system works for coal but not for compounds considered adequate models for coal conversion sutdies suggests that there may be two conversion mechanisms: the free radical scheme for "conventional" H-donors and an ionic scheme for systems such as ours. On the

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*It is likely that the conversion of PhOPh (to polymethylated phenols) is due to the nucleophilicity of the system, rather than to its reducing potential. Thus we suggest an initial displacement such as

$$\text{Ph-O-Ph} + \text{CH}_3\text{O}^{-} \longrightarrow \text{PhO}^{-} + \text{CH}_3\text{OPh}\bullet$$

IPA/KOH (335°C)

coal $\longrightarrow$

anthracene $\longrightarrow$

$PhCH_2OPh \not\longrightarrow$

MeOH/KOH (400°C)

coal $\longrightarrow$

anthracene $\longrightarrow$

$Ph_2O \longrightarrow$

Phenanthrene $\not\longrightarrow$

$PhCH_2CH_2Ph \not\longrightarrow$

$CO/H_2O/KOH$ (400°C)

coal $\longrightarrow$

anthracene $\longrightarrow$

$PhCH_2CH_2Ph \not\longrightarrow$

FIGURE 1 SUMMARY OF RESULTS FOR COAL AND SELECTED MODEL COMPOUNDS IN SOME STRONGLY BASIC CONVERSION SYSTEMS.

The arrows indicate that conversion to reduced products was observed. The "x'ed" arrows indicate that no reduction was observed.

other hand, a case can be made for a single mechanism that operates overall. It is not unreasonable to suggest that the ionic process is operative even in Tetralin-based systems, since it has been observed that Tetralin acts as a hydride donor in its reduction of quinones.[5] In this case we would expect coal products from both systems to be very similar in composition.

We intend to clarify this issue by submitting for careful analysis freshly obtained coal products from treatment with Tetralin and $CO/KOH/H_2O$ in separate experiments at 400°C for 20 minutes to establish any similarities in content and overall makeup. Dr. Duayne Whitehurst of Mobil Research and Development Corporation has kindly offered to carry out the analyses using Mobil's SESC liquid chromatography procedure. We expect to discuss this work in a future report.

Future Work

Blank runs of CO/H_2O without base are planned for coal, anthracene, and a blank containing only CO/H_2O. Additional runs with coal will follow to investigate the potential of this system for upgrading coal using other bases, an added solvent, and longer times. Comparable runs will be made with coal in both Tetralin and $CO/KOH/H_2O$, and the products subjected to careful analysis.

TASK 2: HYDROGEN TRANSFER INTERMEDIATES IN COAL LIQUEFACTION

Donald F. McMillen and Georgina P. Hum

Objective

The objective of Task 2 is to determine the part played by two classes of materials in the transfer of hydrogen from donor solvent (or hydroaromatic coal structures) to the coal substrate. These two classes are:

(1) Materials initially present in the coals that are hydrogen carriers or otherwise aid in hydrogen transfer.

(2) Coal-derived materials that are generated during solvent treatment.

Results obtained in last year's work indicated that removal of initially pyridine-soluble materials has a detrimental effect on subsequent donor solvent conversion.[6] These results are in striking contrast to those of Whitehurst and coworkers at Mobil[4] which indicated that removal of pyridine-soluble material had no effect on subsequent conversion. Differences in the procedures of Whitehurst and those followed in this work could be responsible for the difference in results. Those we consider most likely to be responsible are discussed later in this report.

Experimental Procedure

Our reactor system was similar to those used by Curran et al.[7] and by Neavel.[8] It consisted of a 16-cm-long stainless steel tube, 4.6-mm., 0.9-mm wall thickness, sealed on both ends by Swagelok caps. Normally, 0.5 g of coal and 1 g of solvent were weighed into the reactor. Air was not removed from the reactor before sealing except for the pyrolysis experiments (no solvent present) when the reactor was flushed with dry nitrogen. The reaction tube was attached to a vibrator and plunged horizontally into a molten salt bath maintained at reaction temperature. The reactor was then vertically agitated at about 60 cps. At the end of a run, the reactor was pulled out of the bath and quickly placed under cold running water. For the first 50 experiments, a thermocouple was mounted into a well in one of the end caps of the reactor to monitor the temperature of the reaction mixture. The temperature rose to within 10 degrees of the equilibrium within 32 seconds. Cool-down time was about 8 seconds. Reaction times reported here refer to the residence time in the salt bath, less heat up time, plus cool-down time.

At the end of a run, the vessel was opened and the contents carefully worked out with approximately 50 ml of pyridine. The pyridine slurry of the reaction mixture was passed through an extraction thimble and refluxed with pyridine in a soxhlet extraction apparatus until extraction was complete. Pyridine was removed from the extract on a rotary evaporator. Both the extract and the residue were dried in a vacuum oven at 140°C and 0.1 torr and weighed. Mass balances generally ranged from 95% to 108%. Pyridine solubility is reported on a moisture- and ash-free basis.

In addition to the stainless steel reactor tubes, sealed quartz ampoules were used in a number of experiments. These experiments were carried out without agitation since:

(1) experiments in which a thermocouple was included inside the quartz tube indicated that heat up time was no longer than with the agitated steel tubes;

(2) visual observation suggested that 60 cycle agitation was of questionable large scale effectiveness; and

(3) the results of Whitehurst and coworkers revealed, under their experimental conditions, no particle size dependence in the donor solvent conversion of coal.

Ultimate analysis of the Sahara Mine coal used in the experiments is given below

Sahara Mine Illinois No. 6

%C	%H	%N	%S	%O(diff.)	%Ash
63.5	5.0	1.2	3.6	10.5	16.2

The coal samples were ground to -60 mesh (Tyler) and stored under nitrogen until used.

Results and Discussion

Figure 2 plots the pyridine solubility of Tetralin-treated coal as a function of reaction time at 400°C for three different substrates: an untreated Illinois No. 6. (Sahara Mine, PSOC-25), the same coal from which the initially pyridine-soluble material has been removed by Soxhlet extraction, and coal which has been "reconstituted" by combining the pyridine extract with the pyridine unsoluble residue. The curve for the whole coal has been approximately corrected for the amount initially soluble in pyridine (17%), by substraction of 17 from the total percent conversion. Both curves thus represent the fraction of the original coal that is not initially pyridine-soluble but becomes so on conversion in Tetralin at 400°C.

Inasmuch as the conversion of the whole coal is three times greater than conversion of the extracted coal at short reaction time and twice as great at "long" time (4 minutes), the initially pyridine-soluble material seems to play a very substantial role in the initial dissolution process. To verify this, we conducted a series of experiments with coal that had been "reconstituted" by adding the pyridine-soluble extract back to the pyridine-insoluble residue. Curve C in Figure 2 shows that this reconstitution restores some but not all ofthe lost convertibility. This appears to be partially analogous to the well documented[9,10] characteristic of coking coals: the removal of chloroform-soluble materials destroys the coking characteristics of these coals, but re-addition of this material to the insoluble residue regenerates the coking characteristics.

The failure of reconstitution to restore all the original convertibility of the coal has three possible explanations:

(1) Reconstitution does not return the pyridine soluble material to its original location.

(2) Removal of pyridine from the extracted coal (residue) was not complete and this "incorporated" pyridine poisons the subsequent conversion in Tetralin (the extraction mass balance was ~103%.

(3) The process by which the pyridine was removed from the extracted coal (110°C, 0.1 torr, 16 hours) itself altered this coal so as to decrease the subsequent donor solvent conversion.

The third explanation was eliminated by subjecting a sample of the whole coal to the pyridine removal conditions. Figure 3 shows that conversion of the "redried" coal is unchanged from that of the original coal.

Figure 3 also shows, in addition to the three curves shown in Figure 2, data for an "enriched" coal. This was a whole coal to which an amount of pyridine-soluble extract equal to that in the whole coal was added, using the same technique as for the reconstitution. The conversion of the "enriched" coal was no greater than the reconstituted coal. Unfortunately, no definite conclusions can be drawn from this result alone as to whether enrichment resulted in no further improvement because incorporated pyridine was carried into the coal when the extract was added and could have acted as a poison. It is also possible that, before the pyridine could be evaporated, some of the pyridine-soluble material in the whole coal was "extracted" from within the coal particles and deposited preferentially on the outside of the particles. The result does indicate, however, that the presence of the pyridine-soluble material is not, by itself, of overwhelming importance.

To determine the effect of pyridine as a possible poison for donor solvent conversion, we conducted several experiments in which the whole coal was subjected to reaction with Tetralin diluted with various amounts of pyridine or a solvent (Decalin) judged from previous experience to be more nearly inert. The results are shown in Tables 4 and 5 which contain this year's data and in Figures 4 and 5, which contain data from the previous year[6] and from this year, determined in both stainless steel tubes and in quartz ampoules. The extract-based conversions obtained in quartz ampoules are generally slightly higher than those obtained in stainless steel tubes, but show the same effect of pyridine. As in the previous year's work, the mass balances were generally between 98% and 108% due to pyridine incorporation. The extent of pyridine incorporation could not be readily correlated with other factors. Results for mass balances that fall outside the range 95-108% have not been included.

The above difficulties notwithstanding, the data do indicate that the presence of 5% pyridine in the donor solvent medium reduces the conversion at 2 minutes reaction time by 7 to 10 percentage points with both metal and silica surfaces. The reduction is significant, but less than that observed with the pyridine-extracted coal. The data are thus consistent with (though by no means do they prove) the suggestion that the

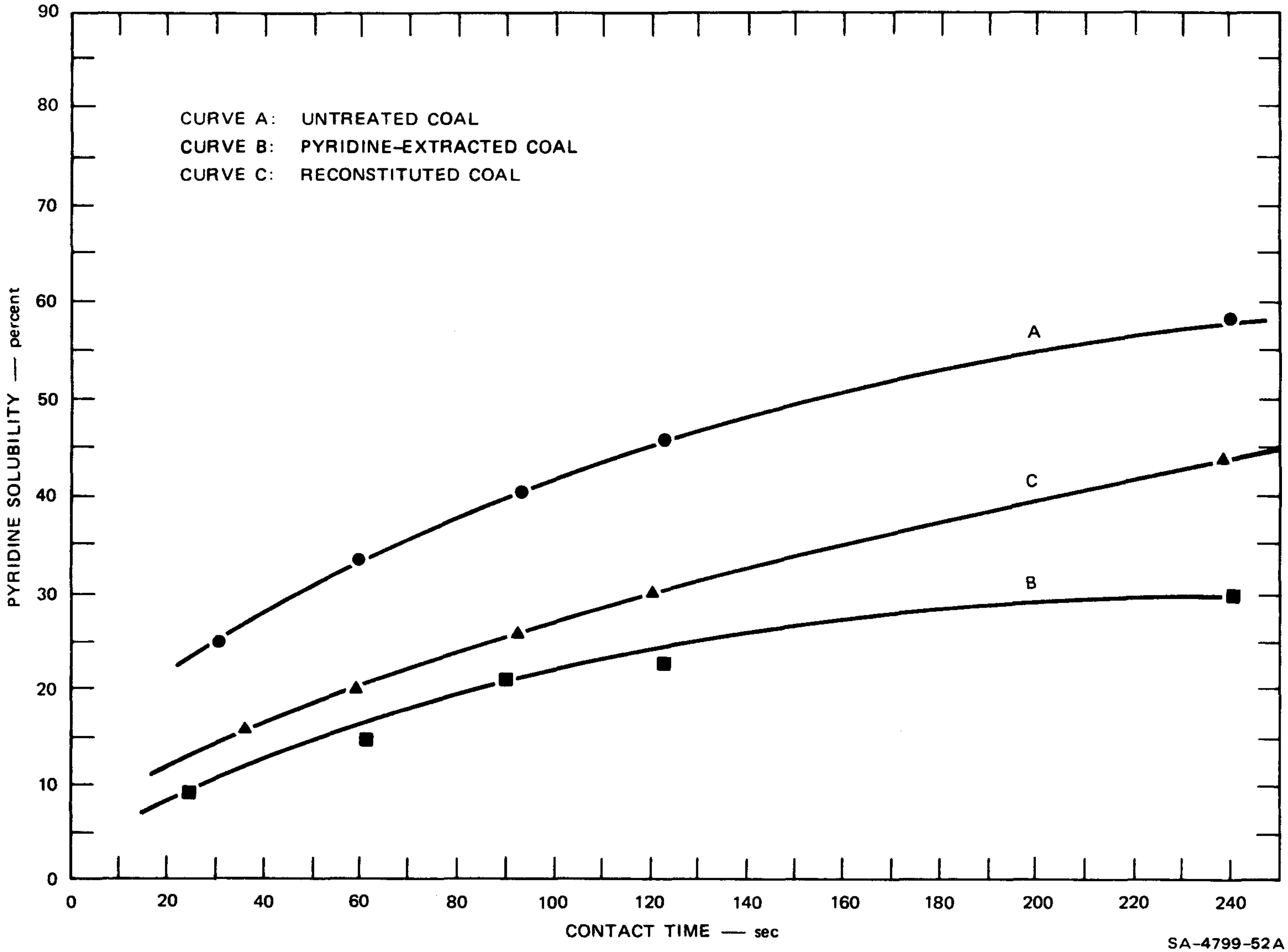

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FIGURE 2 CONVERSION OF INITIALLY PYRIDINE-INSOLUBLE MATERIALS IN VARIOUS COAL FRACTIONS TO PYRIDINE SOLUBLE MATERIALS

Total pyridine solubles as a percent of maf coal, less the 17% initially soluble. Coal/solvent ration: 1/2.

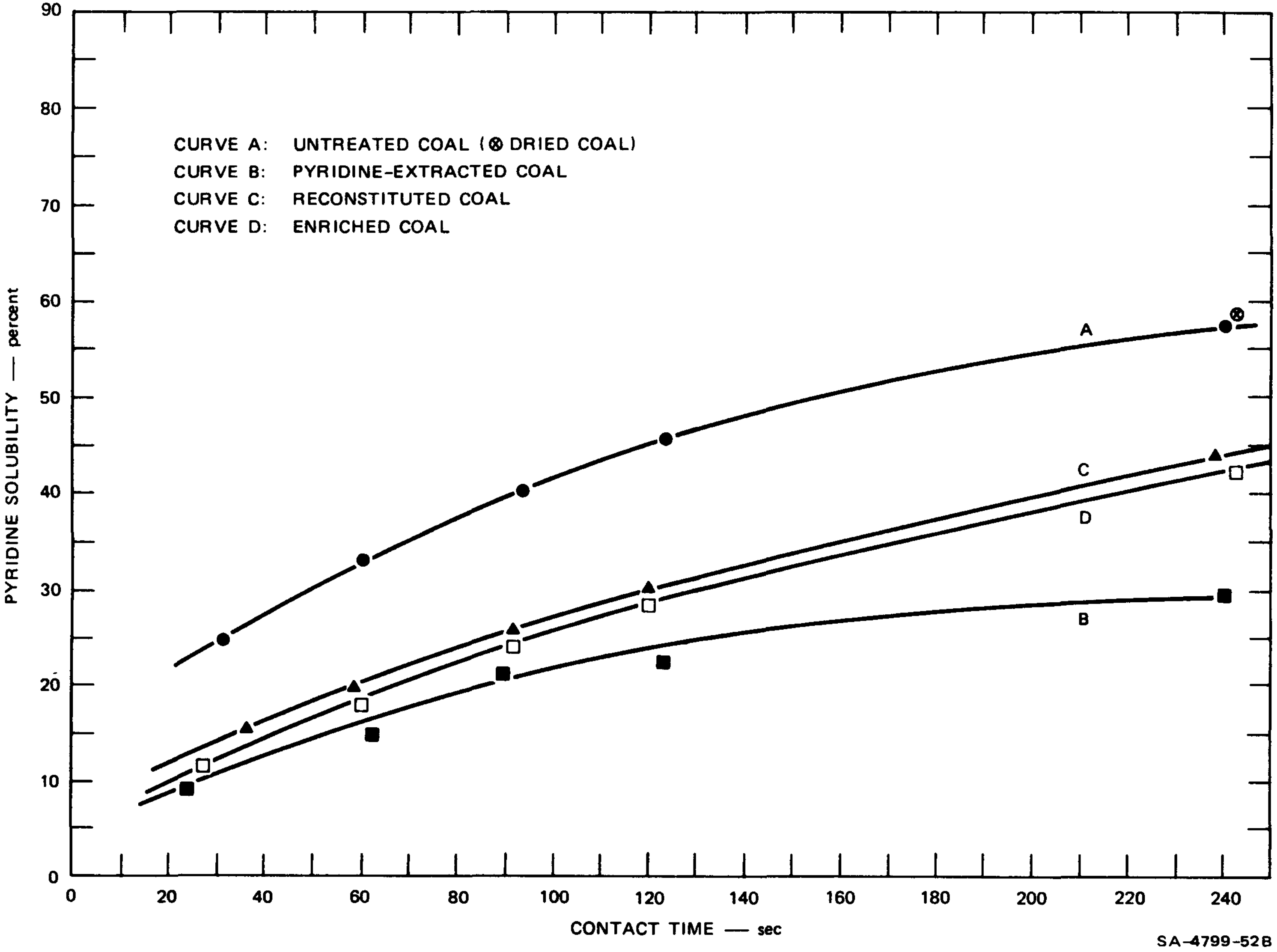

FIGURE 3 CONVERSION OF INITIALLY PYRIDINE INSOLUBLE MATERIALS IN VARIOUS COAL FRACTIONS TO PYRIDINE SOLUBLE MATERIALS

Total pyridine solubles as a percent of maf, less the 17% initially soluble. Coal/solvent ratio: 1/2.

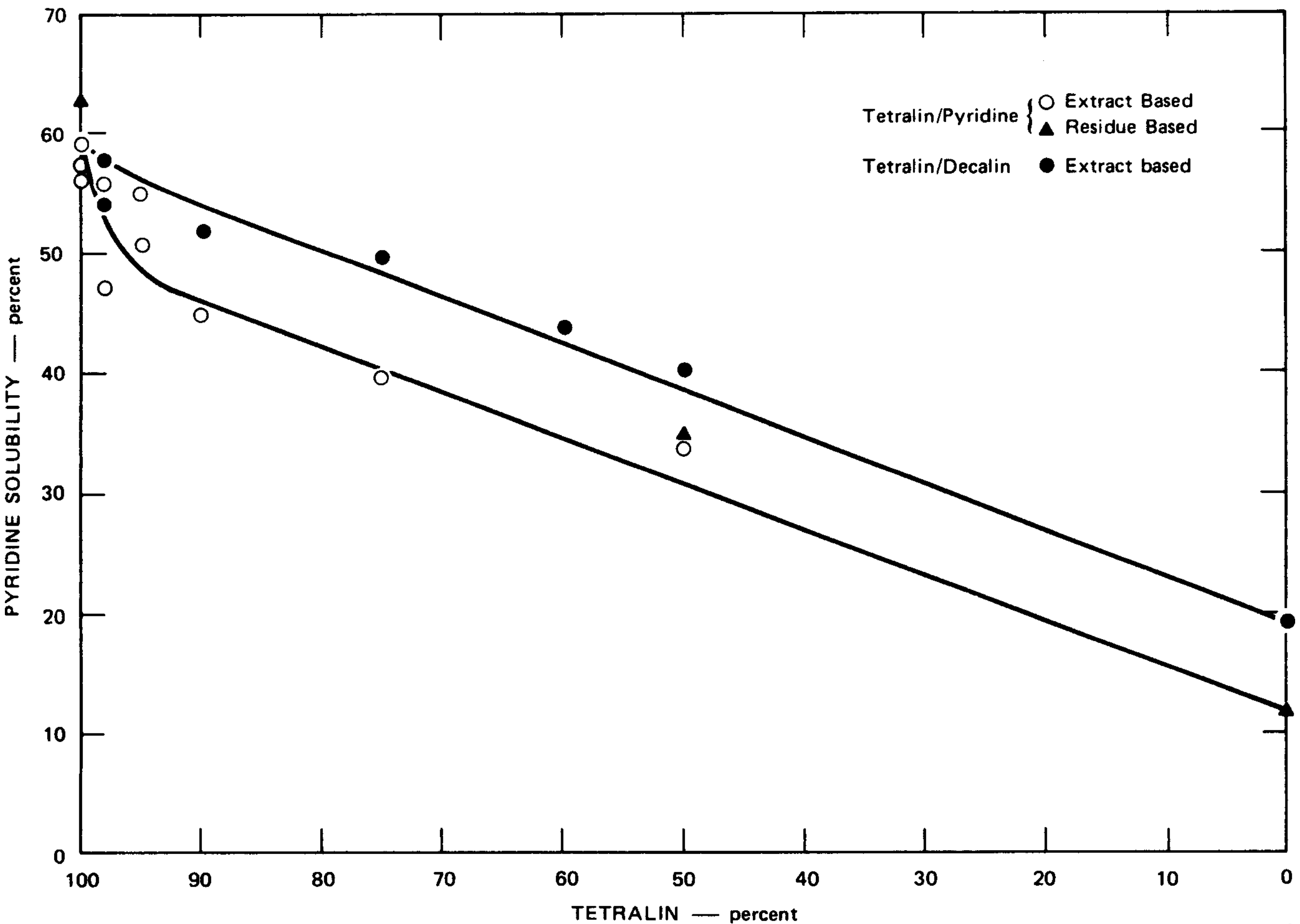

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FIGURE 4 COAL CONVERSION AS A FUNCTION OF TETRALIN DILUTION (Reaction in Stainless Steel Tubes)

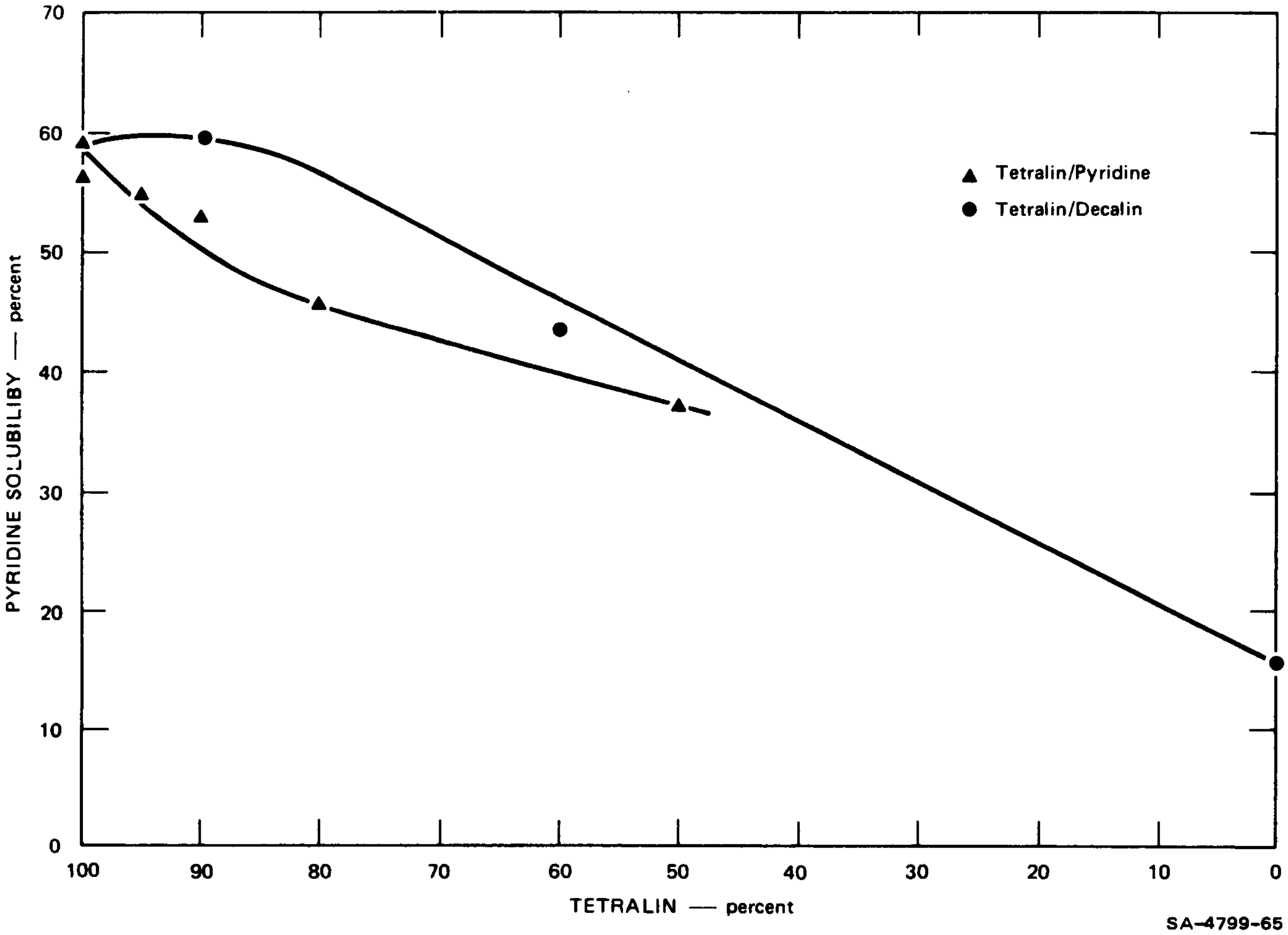

FIGURE 5 COAL CONVERSION AS A FUNCTION OF TETRALIN DILUTION (Reaction in Quartz Ampoules, Conversion Based on Extract Yield).

Table 4

RESULTS OF REACTIONS WITH DECALIN/TETRALIN MIXTURES
(400°C for 2 minutes)

Run No.	Decalin in Solvent (wt %)	% Pyridine-Soluble (Extract Based)	% Pyridine-Soluble (Residue Based)	% Mass Balance
50	2	54.44	54.09	100.31
56	2	63.55	55.54	107.41
59	2	56.98	52.89	103.65
37	5	64.78	55.25	108.49
51	5	69.44	59.95	108.47
57	5	58.56	55.84	102.43
60	5	65.75	59.24	105.80
19[a]	10	59.76	54.99	104.25
36	10	51.76	56.83	95.47
55	25	49.43	43.12	105.63
38	40	43.52	40.72	102.50
47	50	39.90	36.27	103.24
26[a]	100	15.94	23.55	93.22
35	100	19.77	31.51	89.53
43	100	19.12	16.15	102.65

[a] Quartz tube.

Table 5

RESULTS OF REACTIONS WITH PYRIDINE/TETRALIN MIXTURES (400°C for 2 minutes)

Run No.	Pyridine in Solvent (wt %)	% Pyridine-Soluble (Extract Based)	% Pyridine-Soluble (Residue Based)	% Mass Balance
23[a]	0	56.73	51.02	105.09
53[a]	0	59.71	51.16	107.62
27	0	58.74	49.36	108.36
28	0	58.52	47.69	109.66
29	0	55.95	51.88	103.63
32	0	64.17	54.14	108.94
39	0	59.20	55.05	103.69
42	0	57.51	51.54	105.23
16[a]	2	56.73	49.81	106.17
40	2	55.38	45.79	108.55
41	2	47.08	41.54	104.94
49	2	55.60	50.83	105.96
22[a]	5	55.05	48.07	106.22
34	5	50.98	53.46	97.78
52	5	55.12	49.15	105.32
17[a]	10	53.20	50.93	102.02
31	10	44.90	42.01	102.58
18[a]	20	45.45	39.76	105.08
48	25	39.27	38.63	102.19
21[a]	50	37.06	34.80	102.01
33	50	34.97	39.65	95.82
44	50	33.83	24.35	108.45
20[a]	5[b]	53.30	43.71	108.55
58	5[b]	54.60	46.19	107.49

[a] Quartz tube.

[b] 5% pyridine, 20% *p*-cresol.

decreased conversion observed with the pyridine-extracted coal is due to a combination of two effects: the removal of pyridine-soluble material, which aids the donor solvent process, and the incorporation of pyridine in the extract, which partially poisons the dissolution. A series of conversions, run at a single pyridine percentage, confirms the reproducibility of the effect of pyridine, as shown in Figure 6.

Thus it seems clear that, under our reaction conditions, initially pyridine-soluble materials aid in the hydrogen transfer process, and that pyridine itself partially poisons the donor solvent conversion. What is not yet clear is why Whitehurst and coworkers at Mobil did not observe this effect.[4] We hope that the answer to this question will lead us to an answer to the broader question of why pyridine is detrimental.

The difference in results may be due to differences between our procedures and those used by Whitehurst and coworkers.[4] Table 6 lists the differences that we consider most likely to be responsible. For example, the presence of 2% γ -picoline in the standard "synthetic solvent" used by Whitehurst may have provided a constant depressing effect on the conversion, masking the effect of any further addition of pyridine-like materials. More probable is that the 17% p-cresol complexes with pyridine or its derivatives or otherwise counteracts any poisoning effects they may have.

To test this latter possibility, we conducted several experiments in which our Tetralin solvent was diluted with 5% pyridine and 20% p-cresol. Difficulties with mass balances require that the results be considered preliminary, but they indicate that the convertibility lost when Tetralin is diluted with 5% pyridine is not restored when the donor solvent contains, in addition, 20% p-cresol. (This preliminary result is consistent with our earlier finding[11] that, for this coal and our reactions conditions, a mixture of phenol and Tetralin does not provide a better donor solvent than either component alone; however, Orchin and coworkers[12] did observe an apparent synergism with these two solvents.

If further experiments confirm that p-cresol does not counteract the effect of pyridine, then the cause of the difference between Whitehurst's

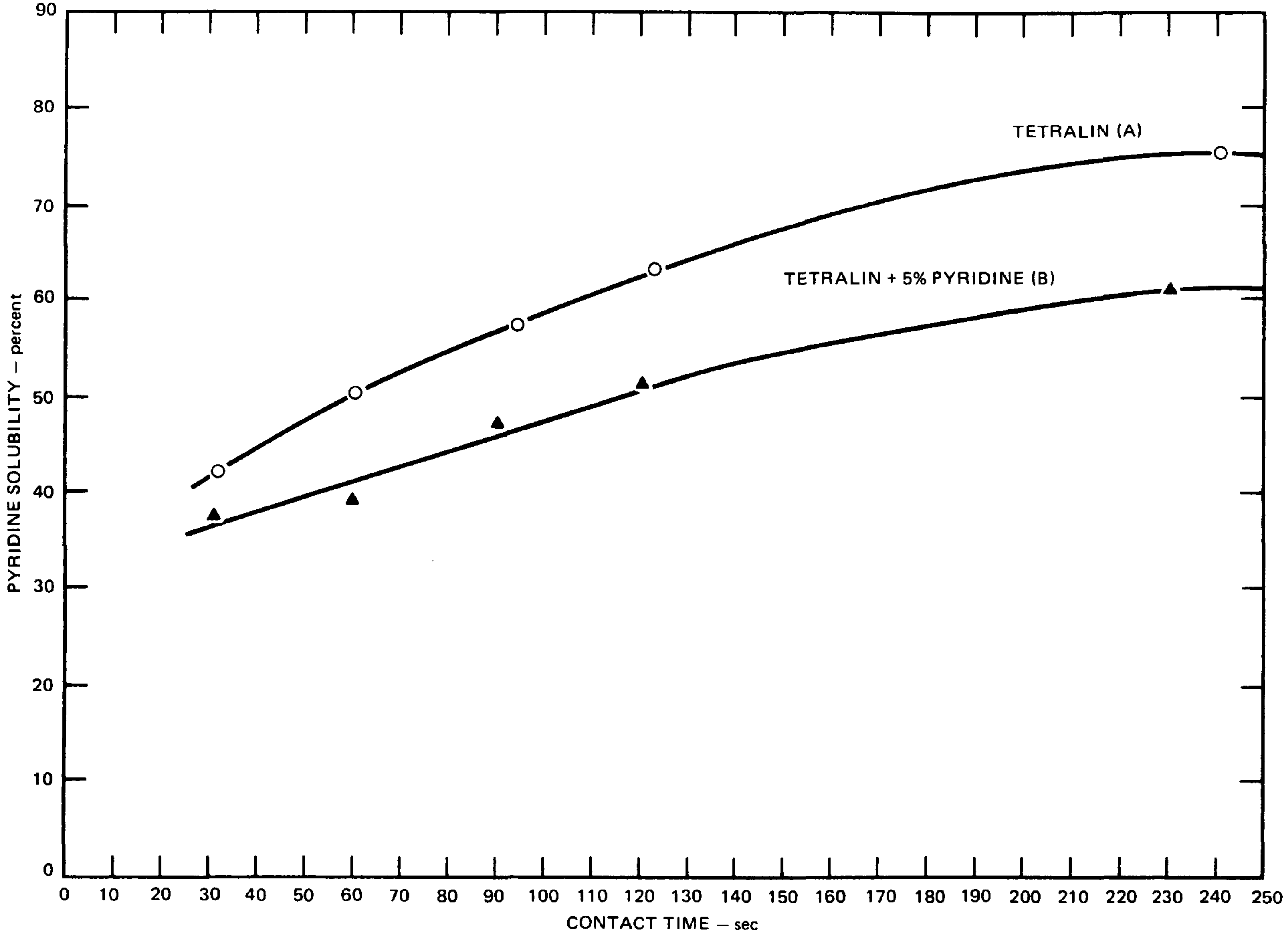

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FIGURE 6 PYRIDINE SOLUBILITY VERSUS CONTACT TIME FOR ILLINOIS NO. 6 COAL WITH TETRALIN AND A PYRIDINE-TETRALIN MIXTURE AT 400°C

Table 6

PROCEDURE DIFFERENCES IN CONVERSION OF PYRIDINE-EXTRACTED COALS

	Conditions	
Factor	SRI	Mobil
Reactor atmosphere	Tube sealed under N_2 or air	~1500 psi H_2
Solvent/coal ratio	2.0	~6
Temperature	400°C (752°F)	427°C (800°F)
Coal	Illinois No. 6, Sahara (PSOC 25)	West Kentucky 14
Donor solvent medium	Tetralin	Synthetic solvent containing 2% γ-picoline, 17% *p*-cresol
Coal particle size	0-250 μm	0.600 μm
Agitation	Micro-reactor vibrated at 50 cps	Stirred autoclave

results[4] and ours will probably lie with one of the other factors listed in Table 3. Foremost among these may simply be the difference in coals, and we are in the process of obtaining a sample of the West Kentucky (No. 4) used by Whitehurst.

Other experiments conducted by the workers at Mobil are consistent with pyridine having a deleterious effect.[13] When attempts were first made to submit an SRC to further donor solvent conversion, the SRC, being gummy, was slurried in the injector with the solvent that provided maximum solubility, which was pyridine. The resulting conversions were evidently less than had been anticipated, so the secondary conversion was repeated, using Decalin instead of pyridine as the injector "solvent." Decalin, of course, precipitated much of the SRC, which was then injected into the reactor as suspended solid. Nevertheless, the conversion was substantially increased over that obtained when pyridine was used as the injector solvent. These experiments used SRCs, not from the West Kentucky coal, but from an Illinois No. 6 coal.

Other factors to be considered are that:

(1) Whitehurst et al. found no significant correlation between conversions and coal particle size.[4]

(2) The studies of Summerfield and coworkers, in which unstirred, short contact time, donor solvent-treated coals were examined by electron microscopy, reveal that as much as 86% of the coal weight can be converted to material that will dissolve in pyridine (on subsequent pyridine extraction) but remains in place in the intact coal particle after the donor solvent treatment.[14]

(3) Conversion is very definitely improved by the presence of the donor solvent.

If the donor solvent action takes place within the coal particle, without transfer of donor solvent into the particle being rate limiting, the transport mechanism must be one that is faster than a diffusional process. One possibility is that when the coal becomes plastic, movement of the coal micelles (e.g., "rotation" of the micelles) may become fast enough[10] to quickly transport donor solvent absorbed on the outer surface of the coal particles to locations deep within the particles. If this rapid transport depended on the presence of initially chloroform-soluble or pyridine-soluble materials to produce the semifluid state, then the removal of pyridine soluble materials could markedly slow down this transport.

It is possible that the resulting increased importance of mass transport limitations was not so readily observable in Whitehurst's experiments[4] because of mechanical degradation by vigorous stirring or because of smaller initial particle size. Our experiments were conducted with -60 mesh (≤ 250 μm), which was nominally (but not necessarily) finer than the 0-600 μm (-28 mesh) used by Whitehurst,[4] so the explanation for this larger conversion apparently does not lie there. The importance of mechanical agitation in breaking up the less plastic, pyridine-extracted particles will be ascertained by determining the conversion of larger particle size, pyridine-extracted coal.

Another comment to be made about the deleterious effect of pyridine on solvent conversion concerns the finding of Orchin and coworkers[12] that extraction of a bituminous coal with phenanthrene at its atmosphere boiling point (340°C) resulted in dispersion of 95% (maf) of the coal. In addition, the nitrogen-containing analogs phenanthridine (b.p. 360°C) and 5,6-benzoquinoline (b.p. 351°C) were just as effective, dispersing 89% and 95% of the coal, respectively.[12] We now know that this process involves substantial hydrogen shuttling[15] and presumably substantial internal dehydrogenation-hydrogenation of the coal. If the pyridinic nitrogen, by its nature, somehow interferes with donor solvent dissolution, one would have expected phenanthridine and its isomer to be much poorer dispersing agents for the coal than phenanthrene.

Finally, if pyridine does "poison" donor solvent dissolution process (or some part of it), then the traditional donor solvent mechanism--rate-determining homolytic bond scission followed by abstraction by the coal fragment radicals of hydrogen from the donor molecule--cannot account for all the dissolution. If pyridine "poisons" the process, it must be in some way a catalyzed process. Homolytic bond scission cannot be catalyzed, since the reverse process, radical recombination, is known to proceed with essentially no activation energy[16] ($\leq \sim 1$ kcal/mole).

$$\mathrm{R{-}R} \rightleftarrows 2\mathrm{R}\bullet$$

In other words, the intrinsic activation energy for homolytic bond scission (the activation energy observed over and above any reaction endothermicity) is essentially zero, and the rate in the endothermic direction (bond scission) cannot be increased without changing the reaction thermodynamics. Similarly, the second step in the traditional donor solvent mechanism, radical abstraction of a hydrogen atom, has a low intrinsic activation energy (∿ 6 kcal/mole) and is not likely to be susceptible to catalysis.[17] On the other hand, to the extent that donor solvent conversion consists of heterolytic processes, they would be expected to be much more readily susceptible to catalysis and the catalysis, hence, to poisoning.

In any case, it seems clear that pyridine, though a very good solvent, can substantially interfere with the donor solvent dissolution process(es). A better understanding of why pyridine hurts the dissolution should lead to conditions that improve the dissolution of coal.

Future Work

We hope to further establish the mode by which pyridine degrades the donor solvent conversion of coals by conducting the experiments indicated above as well as by other experiments suggested by the differences in procedures listed in Table 6.

We also plan to examine the nature of the interaction between coal and Tetralin to determine how radical ions or other pathways involving charge separation contribute to the donor solvent dissolution of coal. This work will include reaction of coal with Tetralin modified by substitution of electron donating and withdrawing substituents.

Finally, we plan to determine the relative reactivity to further reaction of coal-derived intermediates produced in the course of donor-solvent conversion. The work will be complementary to that of Whitehurst and other workers and will begin by focusing on the question: To what extent does the ease with which preasphaltenes are upgraded depend on the severity (temperature, time) and other conditions of their formation? Other conditions include the type of hydrogenation medium, e.g., low polarity donor solvent vs. hydride donor medium. The question is prompted by the well documented fact that coals can be rapidly converted at ~400°C in a variety of solvents to materials that are largely pyridine soluble,[4,6b,8] but the conversion of the preasphaltene portion of this product to asphaltenes, and eventually oils, is much more difficult. The obvious question is: Does the conversion of coals to the types of preasphaltenes produced under the normal range of SRC conditions already represent a retrograde reaction, and can such reaction be avoided in favor of producing, under other conditions, preasphaltenes that are more easily upgraded?

TASK 3: ACID-BASE COMPLEXES IN COAL LIQUEFACTION

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Objective

The objective of Task 3 is to determine what effect the formation of (or the prevention of the formation of) acid-base complexes during the conversion process has on the liquefaction yield and what the origin of this effect is.

Future Work

We anticipate starting work on this task in the third quarter.

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APPENDIX A

THE HYDROCONVERSION OF A BITUMINOUS COAL WITH CO-H_2O

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Hydroconversion of a bituminous coal with $CO-H_2O$

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Hydrogen-donor solvents such as tetralin[1] are commonly used to convert coal to upgraded coal products. It has also been reported that hydrogen donation to bituminous coals by simple alcohols such as isopropanol[2] and methanol[3] can be promoted by the presence of bases such as KOH. Low-rank coals have been readily converted to benzene-soluble products by $CO-H_2O$ systems, in which the source of hydrogen was the water[4–8]. Appell and Wender found that bituminous coals are less successfully treated, requiring a vehicle solvent such as phenanthrene[4]. In this case the process probably involves formation of dihydrophenanthrene, which then acts as a hydrogen-donor solvent in the system.

In a more recent study with slurries of bituminous coal in creosote oil and $CO-H_2O$, Handwerk *et al.* found that although about 70% of the product was soluble in benzene, no hydrogen was incorporated into the benzene extracts[9]. The benzene solubility was probably due, at least in part, to thermal degradation of the coal[10], and not necessarily to the CO and water. The authors reported a 30% reduction in sulphur content at 400°C.

We report here on the conversion of Illinois No. 6 coal, with significant production of a hydrogen-rich, benzene-soluble fraction, in a $CO-H_2O-KOH$ system requiring no organic vehicle solvent. The work developed as a logical extension of our alcohol–base work[2,3].

For our experiments we used a 300 cm^3, 316 stainless steel, stirred batch reactor. The experimental procedure was to place 10 g each of dried coal and 85% aqueous KOH in the reactor and then to charge the system to the desired pressures of CO (and H_2 in some cases). The reactor temperature was held at 400°C for 20 min, and the reactor was then allowed to cool. The product gases were analysed by gas chromatography, and the reaction slurry was neutralized with aqueous HCl. Much of the CO_2 produced was dissolved in the solution as $KHCO_3$ and was accounted for in assessing the conversion of CO to CO_2*.

The product was then filtered and freed from water using benzene in a Dean-Stark trap, filtered again, and both fractions dried. This step also determined the degree of extraction by benzene of the product. Hexane and pyridine extractabilities were determined by recombination of these fractions, followed by room-temperature dissolution of a 0.5 g sample in 50 ml solvent.

The results of two experiments are presented in *Tables 1* and *2*. The conditions for the two runs are given in *Table 1*, along with the initial gas loadings and post-reaction gas recoveries. We used more CO in run A than in run B. Also, run B included initial H_2 and more water than run A.

Table 2 shows that the runs yielded products essentially fully pyridine-soluble. The benzene extractabilities are similar to those found by Appell and Wender[4], and somewhat lower than those of Handwerk *et al.*[9]. However, in contrast to the data of Handwerk *et al.*, hydrogen incorporation into the benzene-soluble fractions was significant. Thus 40 to 50% of the starting coal was converted to a benzene-soluble product with an H/C value of approximately 1.0. Additionally, 18% of the run A product was soluble in hexane.

Our data also show about 50% reduction of organic sulphur content, 25% reduction in nitrogen content, and about 50% reduction in oxygen content. The $CO-H_2O$ system with added base thus appears to be effective for conversion of bituminous coal.

The H/C ratios for the whole products are only slightly higher than that for the starting coal, indicating considerable

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* At the elevated reaction temperature, $KHCO_3$ is thermally unstable relative to KOH and CO_2. Thus the base strength is maintained throughout the reaction period

Table 1 Reaction conditions and product gases[a] for experiments at 400°C and 20 min

Run	Reaction temperature (°C)	Reaction pressure[b] (MPa)	H_2O loading (mmol)	KOH (mmol)	CO (mmol)		H_2 (mmol)		CO_2 found (mmol)
					Initial	Final	Load.	Found	
A	400	29.4	1833	152	500	90	0	250	400
B	394	31.4	3944	152	295	28	300	350	228

[a] 10 g of dried, beneficiated Illinois No. 6 coal and 10 g of 85% KOH are used. The coal is designated PSOC-26 by Pennsylvania State University and is further characterized in *Table 2*
[b] The observed pressure at the reaction temperature

Table 2 Coal product characterization

Run	Extraction (%)[a]			H/C (molar)		N (%)[b]	S (%)[c]	O (%)[b] (by diff.)	Mass bal.[b,d]
	Hexane	Benzene	Pyridine	Benzene extract	Whole product				
PSOC-026[e]	<1	<1	13	–	0.78	1.7	2.2	12	–
A	18	51	97	1.08	0.87	1.2	1.3	7	95
B	–	40	99+	0.98	0.81	1.3	1.1	5	95

[a] Room temperature extractability, as described in the text. [b] Whole product. [c] Organic sulphur. [d] Based on % carbon recovered. [e] Dry untreated coal

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Table 3 Stoichiometric factors for runs A and B

Run	Δ CO (mmol)	ΔH_2 (mmol) ullage	ΔH_2 (mmol) coal	ΔCO_2 (mmol)	Δ S (mmol)	Δ N (mmol)	Δ O (mmol)	$\Delta\Delta H_2$[a] (mmol)
A	410	250	11	400	3	4	31	69
B	267	50	−7	228	3	3	44	121

[a] $\Delta\Delta H_2 = CO - (\Delta H_{2\,ullage} + \Delta H_{2\,coal} + 2\Delta S + 3\Delta N + 2\Delta O)$

internal shuttling of hydrogen within the coal.*

The CO–H_2O system can yield hydrogen through the water-gas shift reaction

$$H_2O + CO \rightarrow CO_2 + H_2$$

and since the addition of H_2 to the system makes little difference, we suggest a hydride-transfer scheme as the reaction route, similar to that proposed earlier[2,7],

$$CO + OH^- \rightleftharpoons HCO_2^-$$

$$HCO_2^- + \text{coal} \rightarrow CO_2 + \text{coal}H^-$$

$$\text{coal}H^- + H_2O \rightarrow \text{coal}H_2 + OH^-$$

where coalH^- and coalH_2 are an intermediate and a final reduced product, respectively, of unstated structure. The overall process is a chain reaction with no net consumption of OH^-, the net process being

$$CO + H_2O + \text{coal} \rightarrow CO_2 + \text{coal}H_2$$

Table 3 gives some stoichiometric values for runs A and B and shows that most of the hydrogen ultimately produced is found in the head space of the autoclave at the end of the reaction. The coal overall has received virtually no net hydrogen, as mentioned above. Although the Δ CO and ΔCO_2 values agree rather well, as shown in the $\Delta\Delta H_2$ column, agreement is poor between the quantity of hydrogen available (on the basis of consumed CO) and that accounted for, even if we assume that all the oxygen, nitrogen, and sulphur losses occur through water, ammonia, and hydrogen sulphide formation, respectively. We expect this work to continue.

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* Alternatively, if the hydrogen in coal is not homogeneously distributed, the treatment liberates the hydrogen-rich, benzene-soluble portions

APPENDIX B

ALCOHOLS AS H-DONOR MEDIA IN COAL CONVERSION

I. BASE-PROMOTED H-DONATION TO COAL BY ISOPROPYL ALCOHOL

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ALCOHOLS AS H-DONOR MEDIA IN COAL CONVERSION

I. BASE-PROMOTED H-DONATION TO COAL BY ISOPROPYL ALCOHOL[*]

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ABSTRACT

Isopropyl alcohol can act as a hydrogen donor to coal, similarly to the action of Tetralin. In contrast to the Tetralin case, however, the transfer of hydrogen by the alcohol can be promoted by the presence of either potassium isopropoxide or KOH. Acetone is formed from the alcohol in quantities in accord with the amounts of hydrogen transferred to the coal. In runs at 335°C for 90 min, coal was converted with isopropyl alcohol in the presence of either the alkoxide or KOH to a fully pyridine-soluble product with H/C ratios from 0.88 to 1.13, in contrast to coal of 0.79. The organic sulfur content of the coal was reduced from 2.1% to 1%. Model compound studies with anthracene and diphenyl ether showed that the anthracene was reduced in the system to 9,10-dihydroanthracene, but the ether was recovered unchanged. The coal products from the alcohol/base treatment are very high in aliphatic hydrogen and have number-average molecular weights in the 450-500 range. The scheme suggested to explain the conversion at these temperatures includes initial hydrogenation of anthracene-like structures in the coal, followed by thermolysis of the dihydro- intermediate.

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[*] The material discussed here was presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, LA, March 20-25, 1977.

The use of Tetralin and similar-H-donor solvents in the hydroconversion of coal to liquid fuels is well known[1] and is important in large-scale coal conversion processes.[2] Isopropyl alcohol (*i*-PrOH) has been studied as a reaction medium, and there is evidence that it can act as an H-donor solvent, yielding products similar to those generated in Tetralin-based systems.[3] We have found that, contrary to Tetralin, the action of the isopropyl alcohol can be promoted by the presence of bases. We report here the results of our studies with *i*-PrOH/base mixtures in the conversion of Illinois No. 6 coal to upgraded products. A subsequent study with methanol is reported in an accompanying paper.

EXPERIMENTAL PROCEDURES

The experiments described here were conducted in a 300 ml Magne-Drive, 316 stainless steel autoclave from Autoclave Engineers. The substrate was beneficiated Illinois No. 6 coal supplied by Pennsylvania State University (PSOC-26) and was ground under nitrogen in a ball mill to -60 mesh. In each run, we used 5-g samples of the coal and 75 to 150 g of isopropyl alcohol solvent. Experimental conditions were 335°C for 90 min, with typically 45 min heat-up and 60 min cool-down periods. In most of the experiments described, no hydrogen was used and the pressures were those generated by the solvents themselves. The reaction temperature of 335°C was above the critical temperature of isopropyl alcohol (235°C).

In these experiments, the product mixture was filtered, the residue washed with more solvent until the washings were colorless, and the filtrate recovered by evaporation of the solvent under vacuum. In experiments where alkoxide salts and KOH were used, all fractions were appropriately neutralized with concentrated HCl and the salts were removed by filtration and extraction with water. Both the filtrate and residue were then dried overnight at 110°C under < 1 torr pressure. Mass balances were generally greater than 95%. In all cases the isolated filtrate was found to be fully pyridine-soluble.

Pyridine solubilities of the residues were determined at room temperature, with 0.5 g of a residue stirred for 1 hr in 50 ml of pyridine. The pyridine solubilities of the residues were established for all cases and recorded as the fraction of the residue soluble in pyridine. It was convenient to refer to the composite pyridine solubilities and elemental composition values, that is, these values for the entire coal product. Accordingly, the individual values for both the filtrates and residues were appropriately summed and recorded. The oxygen contents of the products were established by difference.

Nuclear magnetic resonance (nmr) spectra were run on a Varian EM 360 spectrometer using nearly saturated solutions of sample in pyridine-d_5 or CS_2/pyridine-d_5 mixtures. Amounts of H_2 and acetone formed in the reactions were quantitatively determined by gas chromatography (gc). The model compound work included analysis on an HP Model 5711A gas chromatograph with an OV-1 column.

RESULTS AND DISCUSSION

Autoclave Experiments

The results of a series of experiments at 335°C (see Table 1) show that the untreated coal has a pyridine solubility of 13%. In Run 21, in which the coal was treated with isopropyl alcohol, the resulting product coal was 50% pyridine-soluble. In a similar experiment with Tetralin (Run 48), the resultant coal product was 48% pyridine-soluble. The surprising similarity of the elemental analyses for these two runs suggests that, like Tetralin, isopropyl alcohol acts as an H-donor under these conditions. This suggestion is confirmed by the result of Run 36 with t-butyl alcohol in place of isopropyl alcohol. Here, the produce is less soluble in pyridine than the starting coal. Isopropyl alcohol must thus be donating hydrogen to the coal, yielding acetone, as we shall see below.

Alkylation and/or alkoxylation might be suggested to explain the increased solubility of the coal product. However, these routes are not consistent with the following: (1) the O/C ratio for the product of the

Table 1 Treatment of beneficiated Illinois No. 6 coal in alcohol systems at 335°C for 90 minutes[a]

Run No.	Solvent	Density[b]	Base		Products				
			Type	mmoles	% Pyridine solubility[c]	Elemental analysis[d]			
						molar H/C	molar O/C	%N	%S
50	Untreated Coal				13	0.78	0.12	1.7	2.1[e]
21	*i*-PrOH	0.5	-	-	50	0.81	0.09	1.6	1.8
48	Tetralin	liq.[f]	-	-	48	0.81	0.08	1.6	1.8
53	*i*-PrOH	0.3	(*i*-PrO)$_3$Al	6	61	0.87	0.07	1.6	1.8
54	*i*-PrOH	0.3	*i*-PrOK	10	91	0.91	-	1.6	1.4
62	*i*-PrOH	0.3	*i*-PrOK	5	89	0.84	-	1.6	1.5
98	*i*-PrOH	0.3	KOH	10	96	0.88	-	1.6	1.6
95[g]	*i*-PrOH	0.3	*i*-PrOK	10	92	0.88	-	1.4	1.4
92[h]	*i*-PrOH	0.3	*i*-PrOK	10	17	0.79	-	1.6	1.9
101[i]	*i*-PrOH	0.3	*i*-PrOK	10	96	1.13	-	1.0	0.5
36	*t*-BuOH	0.3	-	-	13	-	-	-	-
61	*t*-BuOH	0.5	*t*-BuOK	9	12	-	-	-	-

[a] For most runs no hydrogen is added to the system; the pressure during a run is in the range of 2000 psi, and due only to the pressure of the medium. The starting coal has been beneficiated to about 2% ash. In all cases 5 g of coal is used.

[b] Since 335°C is above the T_c of both alcohols, the amount of solvent present is expressed as the density of the reaction medium at temperature.

[c] Solubility of recovered material in pyridine, based on ash-free weight of the starting coal. Composite values, as discussed in the text.

[d] Ash-free basis. Composite values, as discussed in the text.

[e] This value represents the organic sulfur content of the starting coal.

[f] The critical temperature of Tetralin is 484 ± 32°C, thus the medium here was subcritical; 83 g of Tetralin was used.

[g] 1000 psig H_2 added at room temperature.

[h] Reaction time of only 30 minutes.

[i] Substrate was residue from Run 98, not untreated coal.

isopropyl alcohol run is lower than that of the starting coal, (2) the mass balances are generally in the 95^+% range, and (3) isopropyl alcohol was successful at coal conversion, but t-butyl alcohol was not.

These results suggest a mechanism similar to the known Meerwein-Pondorff reduction of carbonyl groups, most commonly with aluminum isopropoxide [(i-PrO)$_3$Al] in isopropyl alcohol.[4] In this reaction, hydride from the oxygen-bearing carbon in the alcohol is transferred to a carbonyl group, thereby reducing it. To test this possible mode of reaction, we added aluminium isopropoxide to the reaction mixture in Run 53 and potassium isopropoxide [i-PrOK] in Run 54.

The product coal from Run 53 was 61% soluble in pyridine, somewhat more than when isopropyl alcohol was used alone. For the potassium isopropoxide case, the result was striking. The product coal was almost fully soluble in pyridine. In addition, the organic sulfur content of the coal was significantly reduced. Moreover, while the solubility of the starting coal in isopropyl alcohol is < 1%, the solubility of the coal products was 12%, 19%, and 11% in Runs 54, 62, and 98, respectively. Data for a number of runs are shown in Table 1, including Run 98 with KOH, which was as effective as i-PrOK.

Although these data strongly support a hydride transfer process, it might be proposed that the results were due to some kind of base-promoted dissolution. This possibility was eliminated, however, by the data from Run 61, in which potassium t-butoxide in t-butyl alcohol was used. Here the result is little different from that for t-butyl alcohol alone (Run 36). Furthermore, the process does not involve the simple incorporation of molecular hydrogen, since the addition of 1000 psig of H_2(25°C) to the i-PrOH/i-PrOK system provides only very moderately increased pyridine solubility (Run 95).

The product yields were highly dependent on reaction time, the pyridine solubility being only slightly greater than that of untreated coal after reaction with i-PrOH/i-PrOK at 335°C for only 30 min (Run 92).

The favorable reducing ability of the system at longer reaction times was demonstrated in Run 101, where the alcohol-insoluble residue from Run 98 was run for an additional 90 min in i-PrOH/i-PrOK. Further conversion took place as shown by the fact that the product from this run was itself about 50% soluble in i-PrOH, and after isolation had a melting point of 65°C. The composite product had an H/C ratio of 1.13 and was significantly reduced in both N and S, relative to the starting coal.

Higher reaction temperatures proved to be too severe, and the alcohol itself broke down at a significant rate. On the other hand, methanol was a satisfactory medium at 400°C. That work is discussed in the accompanying paper.

Thus, isopropyl alcohol can act as an H-donor solvent for coal conversion in a process involving hydride transfer from the alcohol, or alkoxide salt, to the coal. The net transfer of H_2 to the coal could involve a chain process, such as

$$^{-}OCH(CH_3)_2 + \text{coal} \rightarrow O{=}C(CH_3)_2 + \text{coalH}^{-} \qquad (1)$$

$$\text{coalH}^{-} + HOCH(CH_3)_2 \rightarrow \text{coalH}_2 + {}^{-}OCH(CH_3)_2 \qquad (2)$$

in which coalH^{-} and coalH_2 are, respectively, an anionic intermediate and reduced coal. In this scheme, alkoxide ion is regenerated with each cycle, H_2 has been transferred to the coal, and acetone is formed.

The formation of acetone has in fact been confirmed quantitatively, and the results for several runs are shown in Table 2. The quantity of hydrogen added to the coal is consistently about 70% of the acetone formed. The additional hydrogen is found in the head space of the autoclave, and there is generally a good H-balance.

Product Characterization

The notation coalH_2 in reaction (2) does not necessarily imply simple hydroaddition to multiple bonds. The question of the specific site of hydrogen reaction remains open, and it is of interest to establish the degrees to which hydroaddition and hydrocracking have taken place.

Table 2 Hydrogen transfer to coal in isopropyl alcohol systems at 335°C (635°F) for 90 min

Run	Reaction system[a]	Base added (mmoles)	Acetone[b] produced (mmoles)	H_2[c] transferred (mmoles)	H_2/acetone[d]	H_2/base[e]
38	Coal[f]	0	-	5	-	-
94	*i*-PrOK/coal	10	36	25	0.7	2.5
95	*i*-PrOK/coal/H_2	10	36	25	0.7	2.5
98	KOH/coal	10	38	22	0.6	2.1

[a] All reactions run in 90 g isopropanol with 5.00 g dried Illinois No. 6 coal.

[b] Acetone found after reaction by gas chromatography.

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

[d] Hydrogen transferred to coal per acetone found.

[e] Hydrogen transferred to coal per base added.

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

Figure 1 shows spectra for a series of products from the experiments discussed above as well as from runs with heptane and benzene under the same conditions (335°C, 90 min). Each spectrum represents the fraction of the starting coal (noted as the percent values) soluble in the respective reaction medium after reaction, and at ambient conditions. (The solubilities of the starting coal in these media were less than or equal to 1%.) The extracts were dried in a vacuum oven at 110°C/< 1 torr overnight. The number-average molecular weights for all the fractions were in the range 450 to 500.

Spectrum (c) clearly shows that all the Tetralin cannot be removed under these conditions. However, if the Tetralin contribution is ignored, the qualitative similarity of all the spectra is apparent.

For the heptane system, spectrum (a), 3.2% of the starting coal is heptane soluble, and the spectrum for the system shows about three times more aliphatic hydrogen than aromatic hydrogen. The high aliphatic content is not unexpected, however, since heptane should extract the aliphatic-rich portions of the coal.

Moving to the other systems, a larger fraction of the starting coal is extracted, and one would expect that the ratio of aliphatic to aromatic hydrogen would decrease. This trend is in fact observed for the progression from heptane through i-PrOH (again ignoring the Tetralin contribution).

For the i-PrOH/i-PrOK system, however, where 40% of the starting coal has been solubilized, the H_{al}/H_{ar} ratio is 3.4, significantly greater than that for the other systems. As stated above, the number-average molecular weight for the fraction is below 500. Thus at 335°C, a significant fraction of the starting coal is converted to a highly aliphatic product with low molecular weight. It therefore becomes necessary to explain how this system brings about the apparent ready hydrogenolysis of critical cross-links in the coal structure at temperatures below 350°C, where cracking begins.

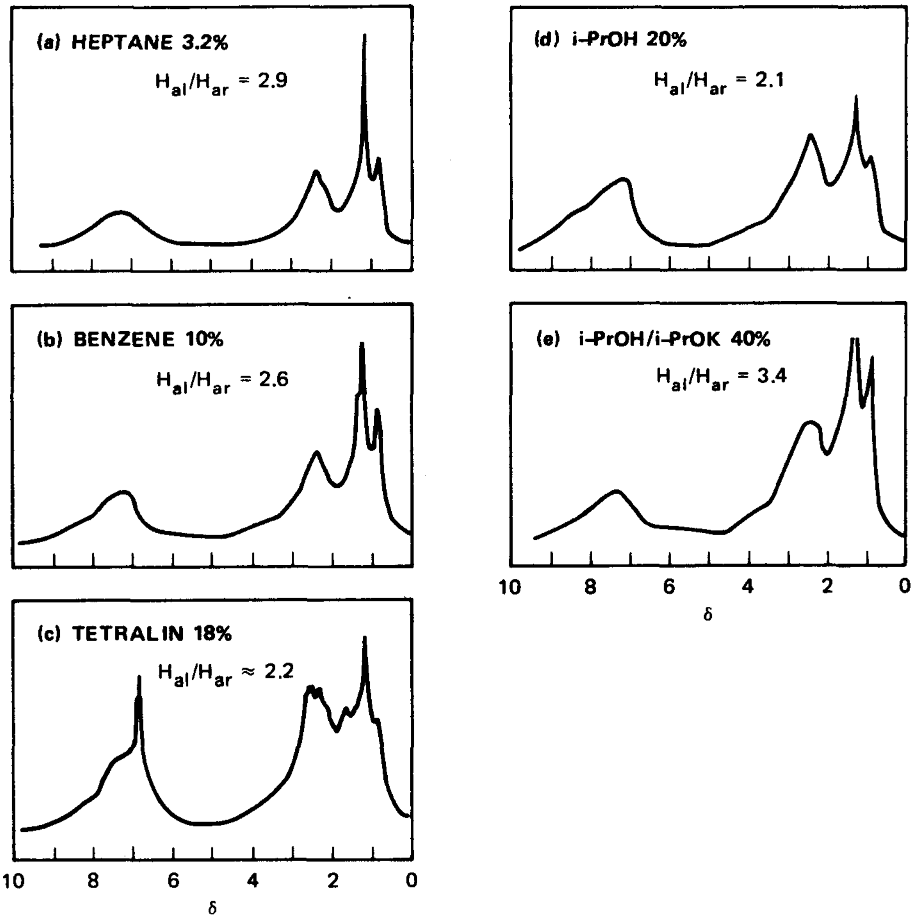

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FIGURE 1 ^{1}H NMR SPECTRA OF COAL EXTRACTS WITH VARIOUS SOLVENT SYSTEMS AT 335°C FOR 90 MINUTES

The %-values represent the fraction of the starting coal extracted.

Anthracene and Diphenyl Ether in the i-PrOH/KOH System

To determine what types of bonds or sites in the coal are being affected in this system at these comparatively low temperatures, we performed experiments using anthracene and diphenyl ether as models for potential hydrogenation sites and cross-links, respectively, in coal. The experiments were done with *i*-PrOH/KOH, since this system would provide virtually the same results as *i*-PrOH/*i*-PrOK and also would be easier to use.

The results, presented in Table 3, show that the anthracene was largely converted to 9,10-dihydro-anthracene. These results are similar to those of Orchin, who found that Tetralin, in the presence of a catalyst, converted anthracene to its 9,10-dihydro- and 1,2,3,4,-tetrahydro-derivatives.[5]

It might be expected that diphenyl ether under the strongly basic conditions would be cleaved by nucleophilic displacement. However, it is seen that, unlike anthracene, most of the ether was recovered unchanged, even with a reaction temperature of 360°C. The shorter time at the higher temperature was necessary because of the rapid decomposition of isopropanol to acetone and H_2, causing the pressure to increase rapidly to the limit of our reactor (∿5000 psig). Nonetheless, we conclude that the alcohol/base medium serves as a hydrogenation system, but does not readily cleave diphenyl ethers.

Considerations of Thermochemistry and Mechanism

The central bond in bibenzyl

$$PhCH_2\text{-}CH_2PH$$

is commonly considered a reasonable model for the bonds in coal that might undergo thermolysis in the H-donor process.[6] A simple thermochemical calculation can show that, while such an assumption may be reasonable at 400°C, it cannot apply at 335°C. Thus the central bibenzyl bond has a strength of 56.8 kcal/mole, and the unimolecular rate constant for

Table 3 Anthracene and diphenyl ether in isopropyl alcohol and KOH[a]

Model compound	Time-temp (min-°C)	Products recovered[b]		Mass balance (%)
		Starting compound (%)	Reaction products	
Anthracene	90-335	11	64% 9,10-dihydro anthracene 10% unknown[c]	85
Diphenyl ether	20-360	81	No identifiable Ph-O-Ph related products[d]	81

[a] 5.0 g KOH, 90 g isopropanol, and 10.0 g model compound used in each experiment.

[b] Expressed in mole-percent of starting quantities.

[c] Eluted cleanly just before anthracene. Its response factor was assumed to be that of anthracene.

[d] Large quantities of acetone/isopropanol condensates were isolated.

the thermal decomposition of bibenzyl in the gas phase is estimated to be[7]

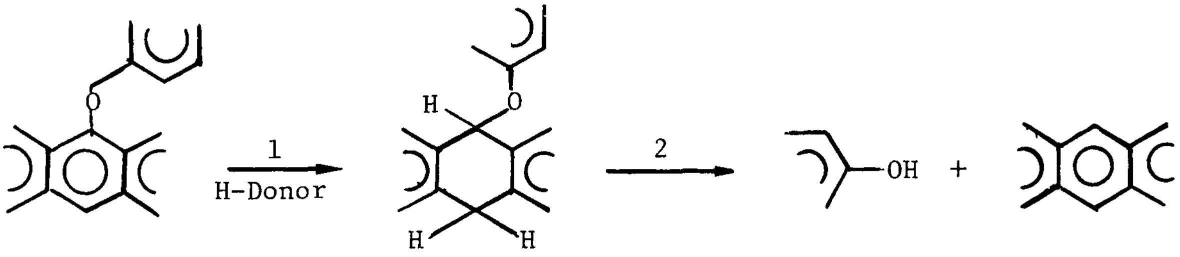
$$\log_{10} k(\sec^{-1}) = 14.4-56.8/2.303RT$$

At 400°C the half-life for the reaction is about 2 hr, and thus the assumption may be appropriate. In contrast, the half-life is about 160 hr at 335°C; therefore, such a reaction is not likely to play a significant role in the processes operative in our system.

Since the NMR data in Fig. 1 show that hydrogen addition clearly takes place, it is thus of interest to consider the kinds of systems that might be made amenable to thermolysis at relatively low temperatures by adding hydrogen.

The addition of hydrogen to several aromatic substrates is considered in Table 4. The equilibrium constants are tabulated, as are the equilibrium positions, under 2000 psi H_2. Table 4 shows that anthracene systems are far more easily hydrogenated than the others listed, and our model compound work, like that of Orchin,[5] is consistent with this observation.

We suggest therefore that the ready hydrogenation of anthracene-like structures may be the key to conversion at these low temperatures, according to the following scheme



(3)

Table 4 Thermochemistry of the addition of H_2 to various aromatic systems at 335°C[a]

Equilibrium system[b]	K_p (atm^{-1})	$(ArH_2/Ar)_{eq}$ at 2000 psi H_2
H_2 +  [c]	1.6×10^{-9}	2.1×10^{-7}
H_2 + 	1.6×10^{-6}	2.1×10^{-4}
H_2 + 	0.59	80.3
H_2 + 	1.4×10^{-7}	0.02

[a] The data in this table were derived from values given in Shaw, R., Golden, D., and Benson, S. J. Phys. Chem. 1977, 81, 1716.

[b] Chosen for the aromatic substrate going to its most stable dihydro derivative.

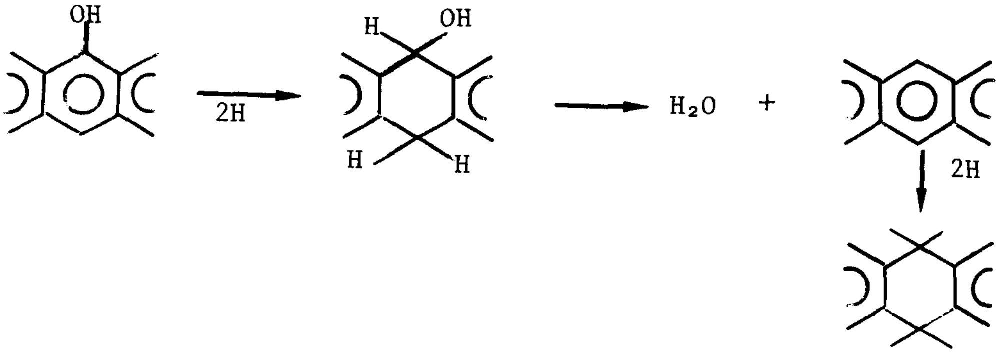
[c] The 1,4-derivative is only slightly less stable than the 1,2-isomer.

Here in step 1, an H-donor system adds hydrogen across an anthracene-like portion of coal, linked in turn through an ether oxygen to the remainder of the structure.

The dihydroether intermediate then is rapidly thermalized in step 2, yielding a rearomatized fragment and an oxygen-containing fragment. The thermolysis of this intermediate is expected to be rapid at these temperatures, in accord with Brower's observation that, in Tetralin, anthraquinone is converted all the way to anthracene.[8]

The net result is the hydrogenolysis of an Ar-O bond at temperatures far lower than would be required to break the bond thermally.* However, it is seen that the system is easily fragmented at lower temperatures by the initial addition of hydrogen. The reformed anthracene nucleus is of course rapidly hydrogenated subsequently, yielding hydroaromatic products.

Finally, if the ether linkage in equation (3) is replaced with an OH- group, then the net process is the loss of water.[10]



This type of sequence may be operative generally in coal conversion processes with H-donors, where conversion includes both ether cleavage and dehydroxylation.

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*The Ar-O bond has a strength of 100-110 kcal/mole,[9] and therefore would require temperatures above 880°C to break reasonably rapidly in 90 min.

ACKNOWLEDGMENT

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APPENDIX C

ALCOHOLS AS H-DONOR MEDIA IN COAL CONVERSION

II. BASE-PROMOTED H-DONATION TO COAL BY METHYL ALCOHOL

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ABSTRACT

At 400°C in 20 min runs, coal was converted by methanol/KOH systems to a product which was fully pyridine soluble, and 15-25% soluble in methanol. The methanol-soluble product is significantly enriched in hydrogen relative to the starting coal, reduced in both N and organic S, and was fluid at room temperature. It was established that this liquid product was derived from the coal, and not the methanol. The liquid was distillable at 300°C/1 torr and an analysis of the liquid by gas chromatography/mass spectrometry techniques shows it to consist of significant quantities of butyrolactone, polymethyl phenols, and some unidentified compounds having major C_4H_7O and $C_4H_7O_2$ ms fragments. The methanol-insoluble products were hydrogen-enriched also, but to a lesser degree. The suggested conversion scheme is similar to that proposed for isopropyl alcohol, where alkoxide ion donates hydride to the coal, followed by proton abstraction by the anionic intermediate from the alcohol medium. In model compounds studies at 400°C with the system, it was found that phenyl ether was converted in 33% yield to a collection of polymethyl phenols, similar to those found in the coal distillate. Anthracene was converted in about 80% yield to 9,10-dihydroanthracene. Biphenyl, phenanthrene and bibenzyl were found to be unreactive in our system.

It is well-known that hydrogen donor solvents such as Tetralin readily convert coal to upgraded products.[1] In recent work we found that isopropanol was virtually identical to Tetralin in its ability to convert coal to pyridine-soluble material at 335°C, though the mechanisms may be different.[2] Isopropanol apparently acts by initial hydride donation of its α-hydrogen, followed by proton transfer. In contrast to the process with Tetralin, this transfer can be catalyzed by the addition of base, providing significantly greater upgrading of coal.

We found, however, that isopropanol rapidly becomes unstable above 335°C in the presence of base, and decomposes to acetone and H_2. Methanol, on the other hand, was found to be less reactive than isopropanol at 335°C. However, the MeOH/KOH system is sufficiently stable to be used at 400°C, where the coal itself is more reactive, and substantial upgrading occurs. This paper describes our work with the MeOH/base system and Illinois No. 6 coal, including the characterization of the coal products and the results of reactions with some model compounds.

EXPERIMENTAL

Reaction procedure

Experiments were carried out in a 300-ml, 316 SS MagneDrive-stirred autoclave from Autoclave Engineers. KOH or other appropriate base was dissolved in MeOH (1.5 mol, 60 ml) and added to the reactor, followed by 10 g of coal or model compound. Reagent-grade KOH pellets were used. The weights of KOH specified here are of the KOH pellets, which are only 87% KOH by weight.

The coal used was a beneficiated Illinois No. 6 obtained from Pennsylvania State University (PSOC-26), ground and sieved to -60 mesh under nitrogen, and dried overnight at 120°C and < 1 torr. The coal is characterized in Table 1.

The reactor was purged with two 1000-psig charges of N_2, while stirring took place. The reactor was then heated to reaction temperature, held there for the duration of the run, and allowed to cool down with 1500 rpm stirring. Heat-up and cool-down were typically 45 and 60 min, respectively.

Table 1 Characterization of Beneficiated Illinois No. 6 Coal PSOC-26[a]

%C	%H	Molar H/C	%N	%S_o[b]	%S_i[c]	%O[d]	% Ash	% Pyr sol.[e]	% MeOH sol.[e]	% i-PrOH sol.[e]
77.2	5.1	0.79	1.7	2.1	$\sim$0	11.9	2.0	13	< 1	< 1

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[a] PSOC-26 is a Pennsylvania State designation. Coal was dried overnight at 120°C and < 1 torr.

[b] Organic sulfur.

[c] Inorganic sulfur removed in beneficiating.

[d] Determined by difference.

[e] Solubility of 0.50 g in 50 ml of solvent at room temperature.

Coal product work-up

After reaction, any product gases were sampled and quantified by gas chromatography; generally, H_2, CO, CH_4, and CO_2 were present. The reactor contents were filtered on a medium-porosity fritted-glass filter (10-15 μ). When a base had been used, the solids were neutralized by stirring in diluted aqueous HCl for 1 hr; then they were filtered as above and washed with water. The solid fractions were finally dried overnight at 120°C and < 1 torr and then weighed.

When base had been used, the filtrates were neutralized by the addition of concentrated aqueous HCl. The resulting KCl largely precipitated and was separated from the solvent by filtration. The solvent was then removed on a rotary evaporator, leaving a solid or thick liquid coal product and some residual salt. This mixture was separated into water and an appropriate organic solvent, such as diethyl ether. The solvent was again removed from the organic fraction by evaporation, and the remaining coal product was weighed and designated the "filtrate". Solids and filtrate mass recoveries, based upon the ash-free weight of the initial coal, were typically 95% or better.

The pyridine solubility of the solid-product fraction was determined by stirring 0.50 g of dry sample in 50 ml of pyridine for 1 hr at room temperature and filtering. The filtrate fractions, that is, those soluble in alcohol, were always fully pyridine-soluble. Thus, the composite pyridine solubility for the entire product is:

$$\mathrm{PS} \equiv \left(\%\ \mathrm{Filt}\right) + \left[\left(\frac{100\% - \mathrm{Filt}}{100}\right)\left(\begin{matrix}\%\ \text{pyridine solubility}\\ \text{of solids}\end{matrix}\right)\right]$$

These composite "PS" values are used in Tables 2-4.

Model compound work-up

Product gas analyses were performed as described above. The reaction mixture was collected, doped with a known quantity of naphthalene to provide an internal standard, and then analyzed by gas chromatography using an 8' (2.4 m) by 1/8" (0.3 cm) OV-1 column. The instrument was programmed over a temperature range of 35-250°C. When a product was insoluble in the product mixture, additional solvents such as acetone or toluene were used to bring all products into one or two liquid phases. Gas-chromatography/mass-spectrometry was also used for some identifications.

RESULTS AND DISCUSSION

Experiments with coal, alcohol, and base at 335°C

Data for experiments with methanol, both with and without KOH, are presented in Table 2. Results with isopropanol[2] are presented for comparison.

The data show that the use of isopropanol alone substantially increases the pyridine solubility of the coal, whereas methanol at slightly lower density actually brings about a decrease. (See reference 2.) In contrast, the addition of KOH to both systems resulted in similar upgraded coal products. Thus, the products from Runs 98 and 107 have substantial pyridine solubilities and increased H/C ratios with respect to the starting coal. The base-promoted hydride transfer discussed for isopropanol[2] is probably operative for methanol as well.

Table 2 Experiments with coal in alcohol at 335°C for 90 min[a]

Run no.	Medium	Filtrate[b] (%)	%PS[c]	H/C[d]	%S[e]	%N[e]	Mass bal[f] (%)
38	i-PrOH	11	40	0.82	1.8	---	97
98	iPrOH + 0.6 g KOH	11	96	0.88	1.6	1.6	103
51	MeOH[g]	2	7	--	---	---	96
104	MeOH + 0.6 g KOH	7	90	0.90	1.3	1.6	98

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[a] All experiments use 5 g of dried, Ill. No. 6 coal and 1.5 moles of alcohol. MeOH and i-PrOH are both supercritical at 335°C.

[b] Fraction of starting coal soluble in the reaction medium at the end of the run. The solubility of the untreated coal in these alcohols is < 1%.

[c] Composite pyridine solubility of products, as defined in text.

[d] Atomic ratio of composite product.

[e] Weight percent sulfur or nitrogen of the composite product.

[f] (Recovered coal ÷ initial coal), ash-free basis.

[g] Only 1.25 moles of alcohol was used.

The filtrates, or alcohol-soluble products, of these four reactions are all low melting solids. Their number-average molecular weights are ∿ 450, and H/C values are 1.0 or greater.

Experiments with coal at higher temperatures

We expected greater product upgrading to occur at higher reaction temperature, and the results of experiments at 400°C (Table 3) show greater product yields and upgrading with both methanol and isopropanol in the absence of KOH.

In Run 120 with KOH, however, isopropanol decomposed so rapidly as the temperature was raised above 350°C that the pressure limit of the autoclave was exceeded; hence, the run was discontinued. Conversely, methanol proved stable enough to allow 30 min of reaction at 400°C with coal and KOH, before our limit of 4800-psig was reached.* A fraction of the starting coal (23%) was converted to a methanol-soluble product with an H/C ratio of 1.37. This product was a viscous liquid at room temperature.

The solids from this reaction were substantially upgraded as well, being fully pyridine-soluble and having an H/C value of 0.87. The products of this run as well as the products of subsequent experiments with MeOH/base and coal at 400°C are further characterized in Table 4.

Table 3 Initial experiments with alcohol and coal at 400°C[a]

Run no.	Reac. time (min)	Medium	Filtrate[b] % Yield	Filtrate[b] Molar H/C	Solids molar H/C	PS[c]	Mass balance (%)
64[d]	90	i-PrOH	28	--	--	68	86
123	60	MeOH	7	1.21	0.66	9	97
120	--	i-PrOH/KOH	---- system unstable at 400°C[e] ----				
107	30	MeOH/KOH[f]	23[g]	1.37	0.84	100	101

[a] 1.5 moles of alcohol and 10.0 g of dried coal were used in each case.

[b] Alcohol-soluble fraction (see text).

[c] Composite pyridine solubility of entire product (see text).

[d] Only 5 g of coal was used in this experiment.

[e] Before the system reached 400°C, the pressure exceeded the limit of the autoclave (see text). 5 g of KOH was used.

[f] 10 g of KOH used.

[g] Liquid at room temperature.

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* At 400°C under our conditions of volume and solvent loading the equilibrium

$$CH_3OH \rightleftharpoons CO + 2H_2$$

is about 33% to the right which corresponds to about 5800 psig. However, the kinetics are slow enough that after 20 to 30 min we have only about 22% of the MeOH converted.[3]

Table 4 Experiments with Methanol/Base and Coal at 400°C[a]

Run no.	Reac. time (min)	Base		Filtrate				Solids Molar H/C	PS[b] (%)	Product Gases[c] (psig)	CH_4 Produced (g)	Mass Balance[d] (%)
		Type	Grams	Yield[e] (%)	Molar H/C	N (%)	S (%)					
107	30	KOH	10.0	23	1.37	0.4	0.5	0.86	99$^+$	1020	0.8	108
123	30	none	none	7	1.21	1.0	1.5	0.66	9	170	1.0	107
110	30	KOH	2.7	--[f]	1.44	0.4	0.3	--	--	1000	0.05	---
125	10	KOH	10.0	14	1.30	1.2	0.6	0.89	94	1310	0.6	104
109	15	KOH	5.0	17	1.30	0.6	0.7	0.79	81	1290	1.3	105
124	30	KOH	3.3	18	1.33	0.8	0.7	0.73	53	1330	1.2	110
115	20	CaO	5.0	15[g]	1.24	2.4	1.3	0.75	92	150	0.3	110
119	20	NH_3	14.3	13[g]	1.18	5.1	1.2	0.70	24	0	0	99
112	30	Pyridine	80.0	35	0.99	10.6	0.6	0.63	35	240	1.4	155

---

[a] 48 g of MeOH and 10.0 g of coal were used in each case, except in Run 112 where 24 g MeOH was used.

[b] Composite pyridine solubility of filtrate and solids (see text).

[c] Psig at room temperature. Free volume in reactor is ∿205 ml, except in Run 112 where volume is ∿155 ml. Gases usually were $H_2 > CO > CO_2 > CH_4$.

[d] Mass recovered, including CH_4, divided by weight of initial coal sample, ash-free basis.

[e] Based on ash-free mass of initial coal sample. All filtrates were fluid at room temperature.

[f] No coal used in this reaction; 300 mg of material was recovered (see text).

[g] Not fluid at 25°C. Low melting (< 50°C) solids.

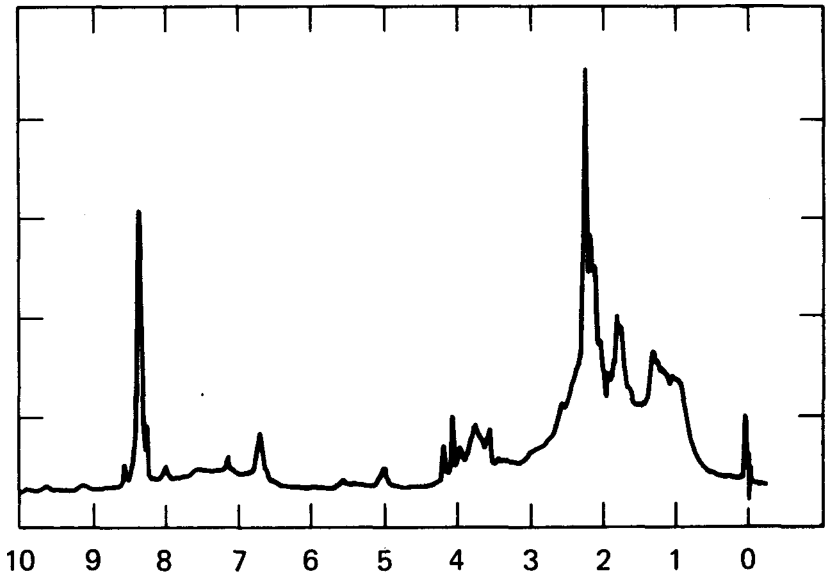


FIGURE 1 ^{1}H-NMR OF RUN 107 FILTRATE

Spectrum taken on a Varian EM-360 60 MHz ^{1}H-NMR spectrometer. The solvent is CS_2/Pyridine-d_5.

A MeOH/KOH run generally yielded 15-25% of a methanol-soluble product; relative to the starting coal, the product was significantly enriched in hydrogen, significantly reduced in S and N, and remained fluid at room temperature. The solids were similarly hydrogen-enriched although to a lower degree; they had no nitrogen reduction, had a sulfur content of $\sim$ 0.7%, and were generally almost fully pyridine-soluble. Figure 1 shows the ^{1}H-NMR of this material, which has an $H_{aliphatic}/H_{aromatic}$ value of 5.1.

To assess the possibility that these filtrates were derived primarily from the methanol rather than the coal, we performed Run 110 with MeOH/KOH but no coal present. Very little product material was isolated and the quantity, 300 mg would represent a 3% filtrate yield had 10 g of coal been used as in Run 107. Furthermore, the nitrogen and sulfur contents of this material indicate that it may be substantially of coal origin anyway, probably residue from earlier runs washing out of the deep, narrow ports in the autoclave during the reaction.

The mass balances for the MeOH/KOH runs were in the range of 104-110%, suggesting some incorporation of the medium in the products. However, we are confident that the filtrates of methanol/KOH/coal runs are products of the coal.

The gases formed in runs with MeOH/KOH produced pressures of about 1100 psig (see Table 4). In Run 110 without coal the quantities of product gases were in the order $H_2 > CO > CO_2$. On the other hand, in runs with coal, quantities of H_2 and CO were similar. Significant quantities of CH_4 were found only when coal was present, and these represented up to 12% of the starting coal. Therefore, CH_4 is included in the material balance column for runs with coal. Small increases in CO_2 were also noted.

The effect of varying the amount of KOH in these reactions can be seen by comparing Runs 123, 124, and 107 in Table 4, where 0 g, 3.3 g, and 10 g of KOH were used, respectively. The filtrate yield increases with KOH concentration (7, 18, 23%) as does product pyridine solubility (9, 53, 100%) and solids H/C (0.66, 0.73, 0.86) for these 30-min reactions.

Thus, at least for a KOH/coal weight-ratio of up to 1/1, increasing KOH concentration provides increasing product yield and quality.

The effect of varied reaction time at a 1:1 ratio of KOH/coal is shown in Runs 107 and 125, which lasted 30 min and 10 min, respectively. As would be expected, the product of the 30-min run has a significantly higher yield of filtrate than the 10-min run. The filtrate of the 30-min run also has a much lower nitrogen content than that of the 10-min run.

It is of interest to compare the products of Run 124, where 3.3 g of KOH was used for 30 min, with the products of Run 125, where the reaction time was only one-third as long but three times the amount of KOH was used. The product of Run 124 has a slightly higher filtrate yield and quality, and twice the CH_4 production of the Run 125 product. The solid residue from Run 124, however, has a much lower H/C and pyridine solubility than that of Run 125.

From the above discussion, it appears that increased reaction period favorably affects the yield of liquid product, whereas increased base concentration brings about an increased overall H/C ratio and pyridine solubility. The reduction of nitrogen in the liquid product is substantially increased by both longer reaction time and higher base concentrations.

MeOH and bases other than KOH

Also shown in Table 4 are the results of three reactions in which bases other than KOH were used. It may be desirable to find effective bases that are less expensive and/or easier to separate from coal products than KOH. Run 115 with CaO was moderately effective in all aspects of upgrading except nitrogen removal, but the CaO was very difficult to separate from the solid product due to its low solubility in water. Another such base with higher solubility should be easier to wash out and recover, and may prove more effective.

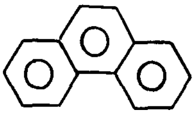
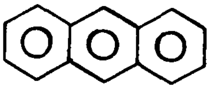
The two nitrogen bases--ammonia and pyridine--were tried for different reasons. Ammonia, like CaO, is inexpensive, but it may be simply separated from coal products by volatilization. The results in Table 4 show, however, that NH_3 was only slightly effective, and it resulted in large incorporation of nitrogen into the products (Run 119). Pyridine was thought potentially desirable for its availability from coal. Moreover, its good solvent properties might be expected to bring about greater contact of the coal, base, and MeOH. However, the effectiveness of pyridine was low and pyridine incorporation was very high, as shown by the high N content and mass balance in Run 112 of Table 4.

Model compounds in MeOH/KOH at 400°C

Studies of the MeOH/KOH system have been performed with several model compounds to determine what types of bonds are affected by reaction with MeOH/KOH at 400°C. The compounds used were phenyl ether, biphenyl, phenanthrene, anthracene, and bibenzyl. The results of these experiments are presented in Table 5. The results show that links directly bridging two aromatic groups (e.g., biphenyl) are essentially inert under our conditions. Similarly most of the phenanthrene and bibenzyl were recovered unchanged. We must conclude that any such portions of coal are not directly affected under our conditions.

Anthracene, however, was very reactive, being almost entirely converted to 9,10-dihydro anthracene and any similar positions in coal would be easily reduced. Phenyl ether was also significantly converted, probably due to the high nucleophic activity of methoxide. Benzene, phenol, and perhaps anisole or other methoxylated products were expected and though 10% anisole was found, the primary products were multiply methylated phenols and, to a lesser extent, anisoles. It has been suggested that this observation may be due to CO and formaldehyde attack, with subsequent reduction of the benzyl alcohol.[4] In fact, preliminary experiments with coal in $CO/H_2O/KOH$ for 20 min at 400°C yielded products comparable to those of Run 107 in Table 4.[5]

Table 5 Experiments with model compounds in MeOH/KOH at 400°C for 20 min[a]

Run no.	Model Compound	Products recovered (%)			
		Reactant	Products		Mass balance[b]
113	Phenyl ether; Ph-O-Ph	53	∿33	∿15-20% trimethyl phenol ∿10% anisole ∿ 5% other polymethyl phenols and anisoles	∿85
116	Biphenyl; Ph-Ph	96	∿ ½	∿ ½% benzene, nothing else	97
117	Phenanthrene; 	88	< 1	no significant products	89
118	Anthracene; 	10	∿80	∿77% dihydroanthracenes[c] ∿ 3% methylanthracene trace of anthraquinone	90
132	Bibenzyl; Ph-CH$_2$-CH$_2$-Ph	95	∿ 3	∿ ½% toluene ∿ 2% other	98

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[a] All reactions were done with 5 g of KOH, in 48 g of MeOH, using 10 g of starting compound. Reactions produce ∿1000 psig product gases -- mostly H$_2$ and CO.

[b] Fraction of starting material accounted for.

[c] Virtually all 9,10-dihydro anthracene.

GC/MS analysis and comparison of coal and model compound products

In an effort to correlate the above findings with our coal products of similar reactions, we vacuum-distilled some of our No. 107 filtrate; at < 1 torr and ∿ 300°C (572°F), about 85% was volatile and distilled off. This distillate was analyzed by the same GC-MS procedures used for the model compound products and was found to consist of butyrolactone, alkylated (mostly polymethyl) phenols, and some unidentifiable compounds having major C_4H_7O and $C_4H_7O_2$ fragments. All products had molecular weights less than 200. The similarity of these products and those of phenyl ether suggests that a significant portion of the upgrading observed in MeOH/KOH at 400°C is due to ether cleavages and subsequent methylation and not only to hydride donation, as was thought to be the case in i-PrOH/KOH at 335°C. The abundance of C_4 products and fragments is currently unexplained.

As previously mentioned, our run with methanol/KOH but without coal present (No. 110) yielded a small quantity of a dark oil, equivalent to only a small fraction of the oil recovered when coal is present. This product was found by GC/MS to have no distinguishable compounds in common with the coal product of Run 107. This finding further supports the earlier conclusion that the products obtained from coal after reaction in MeOH/KOH for 10 to 30 min at 400°C are derived from the coal itself.

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