

EFFECTS OF MINERAL MATTER ON THE HYDROLIQUEFACTION OF COAL

by

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INTRODUCTION

Several previously published studies have shown that the naturally occurring minerals in coal may play a significant role in hydroliquefaction (1-6). The extent of conversion was shown to correlate with total mineral content (1,2,4). Iron - in the form of pyrite, pyrrhotite and liquefaction residue - has been shown to affect conversion and hydrogenation (2-4). Coal ash, pyrrhotite and liquefaction residues have all exhibited some activity for the desulfurization of coal (2,5), and pyrrhotite has been shown to be more active than pyrite for the desulfurization of thiophene (5). Pyrite and several clays were shown to catalyze the isomerization of tetralin to methyl indane and the transfer of hydrogen from hydroaromatic to aromatic structures (6).

We have shown, for a series of high-volatile bituminous coals having similar maceral contents, that the extent of conversion, product viscosity and hydrogen consumption could be correlated with the mineral content (4). The combined role of pyrite, clays and organic sulfur was shown, but the independent effect of each of these components was not investigated in our previous work. To better understand the role of minerals in the hydroliquefaction of coal, we decided to carry out a number of experiments, in a stirred autoclave, in which pure minerals, liquefaction residues and a commercial catalyst were added to the feed coal. The experimental conditions (temperature, heating rate, pressure, residence time and solvent-to-coal ratio) were held constant for each run. Illinois No. 6 coal was selected for this work because of its moderate liquefaction reactivity (4). It was assumed that greater differences in conversion and product composition would be observed by augmenting the mineral content of a moderately reactive coal than by utilizing a very reactive (e.g., western Kentucky) coal.

EXPERIMENTAL PROCEDURES

The coal used in all of the experiments was Illinois No. 6 (Orient 4 Mine), which was pulverized to minus 100 mesh. Proximate, ultimate and sulfur forms analyses are given in Table 1. The mineral matter composition, also shown in Table 1, was obtained from the x-ray diffraction analysis of low temperature ash (7,8). The percentages of pyrite and mixed layer clays were approximately

one-half the corresponding values that were reported for the more reactive Kentucky No. 11 (Fies Mine) coal (4).

The solvent used was creosote oil, No. 4 cut, which was obtained from the Reilly Tar & Chemical Co. This oil had a specific gravity of 1.12 and a boiling range of 270-400°C. The solvent-to-coal (daf) ratio used in all runs was 2.50.

The minerals, catalyst and residue used for the spiking experiments are described in Table 2. Pyrite, pyrrhotite (FeS), clay and the liquefaction residue were included in this study because of their potential catalytic importance (1-6). Zinc sulfide was included because several Illinois coals have been found to have extremely high zinc contents (8). The zinc presumably occurred in the form of the mineral sphalerite (zinc sulfide). The commercial Co/Mo hydrodesulfurization catalyst was included as a reference "standard" with which to compare the activity of the other added species. The minerals were blended with the dry coal by milling in a mortar and pestle for a minimum of 15 min. In each of the spiking experiments, 2.50 g of the mineral, residue or catalyst was used; this was equivalent to 5% of the daf coal charge.

All of the liquefaction runs were carried out in a one-liter, stirred autoclave. The reactants were placed in a stainless-steel liner that had a volume of 0.7 liter. Nominal reaction conditions were:

Initial (cold) pressure	:	1000 psig hydrogen
Heatup time	:	1.0 hr
Temperature	:	405°C
Residence time at temperature:	:	0.5 hr
Cooldown time	:	overnight (18 hr)

At the end of each run, following cooldown, the overhead gases were vented through caustic scrubbers, and the liquid product was removed. Material accountability was routinely 95% or better. Solids separation was effected by centrifugation at 2200 rpm for 45 min. Product analysis included viscosity (Brookfield), elemental composition and Soxhlet solvent extraction. Conversion was calculated on the basis of both pyridine and benzene insolubles. The former was calculated from a forced ash balance (9), the latter was obtained from the expression:

$$\text{Percent conversion} = 100 \left[1 - \left(\text{OBI}_f / \text{OBI}_i \right) \right]$$

where OBI_f and OBI_i are the weight fractions of organic benzene insolubles in the final liquid product and initial reactants, respectively.

A crude estimate of hydrogen consumption was made by calculating the difference between the initial pressure (1000 psig in all cases) and the final pressure after cooldown. The pressure difference, ΔP , was normalized to that of the experiment in which no mineral or catalytic agent was added. A pressure ratio was then defined as:

$$\text{Pressure ratio} = \Delta P / \Delta P_0$$

where ΔP_0 was the pressure difference for the control (no added minerals) run. As defined above, the greater the pressure ratio, the greater was the hydrogen consumption. The formation of hydrocarbon gases could have had an effect on the ratio, but it was assumed that this would not alter the observed trends.

RESULTS AND DISCUSSION

Data from the autoclave experiments are given in Table 3. It has been shown in the literature that coal can be converted to greater than 90% pyridine solubles in less than three minutes under the proper reaction conditions (9,10). In the present case of relatively long heatup and residence times, reaction temperatures in excess of 400°C and use of a good liquefaction solvent, it is clear that transformation to pyridine solubles reached a plateau (92 to 94% conversion) that was independent of any added species.

The conversion of the initially solubilized coal to molecular constituents that are soluble in benzene is a slower process (9). This, in part, may be seen by the lower conversions to benzene solubles as shown in Table 3. Whereas the addition of mineral matter did not affect the conversion to pyridine solubles, certain species such as FeS, liquefaction residue and Co/Mo did have an effect upon the conversion to benzene solubles. It is of some interest to note that pyrite did not affect conversion, but pyrrhotite - both as FeS and as the predominant form of iron in the liquefaction residue (3,6,11) - did result in an increase in conversion. The Co/Mo catalyst had the greatest positive effect on conversion, and ZnS seemed to have a slightly negative effect as seen by the decrease in conversion.

Significant decreases in the viscosity of the liquid products were observed for the runs in which pyrite, pyrrhotite (FeS) and Co/Mo had been added. A smaller decrease in viscosity, which is probably not statistically significant, was noted when the liquefaction residue had been used. In the experiment with kaolinite, the viscosity of the product increased. This increase could have been caused by suspended particulate matter that was not removed by centrifugation. Zinc sulfide did not have any effect on product viscosity.

We have previously shown, for West Virginia coal, that the viscosity of a coal-derived liquid was dependent upon the organic benzene insolubles and asphaltene content, but the benzene insolubles had a significantly greater effect on viscosity than did asphaltene (4,12). The largest decrease in viscosity in the spiking experiments (Table 3) was observed when Co/Mo had been added to the feed. In this case, the asphaltene content of the resulting liquid product was essentially the same as that obtained in the control experiment, in

which no mineral or catalyst had been added. The addition of Co/Mo, however, resulted in a significant reduction in organic benzene insolubles, and the large decrease in viscosity was probably a direct consequence of this. The addition of pyrite resulted in the largest decrease in asphaltene content in the entire test series, but did not affect the benzene insolubles. The addition of pyrrhotite (FeS and residue) resulted in decreases in both the asphaltenes and organic benzene insolubles. The observed decreases in viscosity in these cases were attributed to corresponding shifts in the relative quantities of the asphaltenes and benzene insolubles. An interesting selectivity has been observed in which pyrite significantly affected only the asphaltene content, whereas pyrrhotite affected both the organic benzene insolubles and asphaltenes.

The hydrogen-to-carbon ratios of the centrifuged liquid products were quite similar (Table 3). The present data show that hydrogen consumption, as indicated by changes in the pressure ratio, increased in all of the spiking experiments. This increase was particularly significant in the run with Co/Mo, in which the pressure ratio increased almost three-fold. Since the H/C ratios of the liquid products were similar, it is proposed that hydrogen was primarily consumed for heteroatom removal, conversion of (initially solubilized) coal to benzene solubles and production of hydrocarbon gases. In the case of Co/Mo, the high hydrogen consumption, without a concomitant increase in the hydrogen content of the liquid product, would appear to be undesirable with respect to process economics.

Significant decreases in the sulfur content of the liquid products were found in the runs with FeS, ZnS and Co/Mo. In the experiment with pyrite, the sulfur content of the product was higher than the corresponding product from the control run where no minerals or catalysts had been added. This may have been due to the presence of extremely fine particles of inorganic sulfur that could not be removed by centrifugation. On the other hand, this could have been a consequence of the fact that pyrite is not an effective desulfurization catalyst. Work at Auburn University has shown that pyrite was less effective than no catalyst at all for the desulfurization of creosote oil (2). We have shown that pyrrhotite, FeS, was considerably more active for sulfur removal than either pyrite or the liquefaction residue (Table 3). This is in good agreement with the Auburn work (2), and with the data from a recent pulse microreactor study, where it was demonstrated that pyrrhotite was approximately four times more active than pyrite for the hydrodesulfurization of thiophene (5). It is conceivable, therefore, that the non-stoichiometric iron sulfides, which are formed from the pyrite during coal hydroliquefaction (6,11), are the active species for desulfurization.

SUMMARY

Batch autoclave experiments have been carried out with Illinois No. 6 coal (Orient 4 Mine) in creosote oil. Various minerals, a dry liquefaction residue and a Co/Mo catalyst were added to the feed coal, while all process parameters (pressure, temperature, residence time, heating rate and solvent-to-coal ratio) were held constant. Significant increases in conversion to benzene solubles were observed when pyrrhotite (FeS), residue and Co/Mo had been used. Decreases in the viscosity of the liquid products were found in the spiking runs with pyrite, pyrrhotite and Co/Mo. The largest decrease in viscosity occurred in the experiment with Co/Mo and, in this case, a concomitant decrease in the organic

benzene insolubles was found. A selectivity was observed in which pyrite affected only the asphaltene content of the liquid product, but pyrrhotite affected both the asphaltenes and the organic benzene insolubles. The data have shown that pyrrhotite and Co/Mo were active for desulfurization, but pyrite and most of the other minerals were not. Hydrogen consumption, as estimated from differences in the venting pressure, increased in all spiking experiments - especially when Co/Mo had been added to the feed. The H/C ratios of the liquid products, however, were similar. This would imply that hydrogen had been utilized primarily for heteroatom removal, conversion to benzene solubles and hydrocarbon gas formation.

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Table 1. Analysis of Illinois No. 6 Coal^a

<u>Proximate Analysis</u>		<u>Sulfur Forms</u>	
Volatile Matter	36.69	Pyritic	1.27
Fixed Carbon	52.60	Sulfate	0.09
Ash	10.71	Organic	1.64
<u>Ultimate Analysis</u>		<u>Mineral Matter</u>	
Carbon	71.48	Pyrite	2.80
Hydrogen	4.89	Quartz	2.20
Nitrogen	1.45	Calcite	0.78
Sulfur	3.00	Kaolinite	0.82
Oxygen (difference)	8.47	Mixed Clays	6.35
Ash	10.71		

^aAll data given as a percent of the coal on a dry basis.

Table 2. Minerals and Catalysts Used for the Spiking Experiments

<u>Mineral</u>	<u>Description</u>
FeS ₂	Single crystal pyrite from Sinaloa, Mexico. Pulverized to minus 200 mesh.
FeS	Obtained from Cerac/Pure, Inc. as minus 100 mesh powder. Identified as pyrrhotite, Fe _{1-x} S, by x-ray diffraction (x = 0.14).
ZnS	Obtained from Cerac/Pure, Inc. as minus 325 mesh powder.
Kaolinite	Obtained from a clay deposit in Lewiston, Montana. Pulverized to minus 100 mesh.
Co/Mo	Commercial hydrodesulfurization catalyst (Harshaw O402T). Crushed and screened to 45 x 100 mesh.
Residue	Acetone-washed filter cake obtained from previous run with Illinois No. 6 coal in creosote oil. Used in the form of a dry, minus 100 mesh powder. (Ash = 48.4%; sulfur = 4.9%).

Table 3. Data from the Autoclave Experiments

	Added Minerals or Catalyst						
	None	Pyrite	FeS	ZnS	Kaolinite	Residue	Co/Mo
Conversion (% , daf)							
Pyridine Solubles	93	94	93	93	92	92	93
Benzene Solubles	38	38	46	34	38	44	63
Viscosity ^a (cps @ 60°C)	355	271	290	351	418	338	112
Solvent Analysis (% , daf)							
Organic Benzene Insol.	17.7	17.6	15.4	18.9	17.8	16.1	10.4
Asphaltenes	19.6	15.3	16.8	16.2	19.6	18.9	19.8
Pentane-soluble Oils	62.7	67.1	67.8	64.9	62.6	65.0	69.8
Elemental Analysis ^a (% , daf)							
Carbon	87.93	88.04	88.02	88.09	87.40	87.99	87.95
Hydrogen	5.84	6.00	5.92	5.92	5.83	5.89	6.02
Nitrogen	1.34	1.32	1.38	1.30	1.37	1.25	1.23
Sulfur	0.75	0.86	0.57	0.67	0.73	0.72	0.49
Oxygen (difference)	4.14	3.78	4.11	4.03	4.67	4.15	4.31
H/C	0.80	0.82	0.81	0.81	0.80	0.80	0.82
Pressure Ratio ^b	1.0	1.3	1.2	1.1	1.1	1.3	2.9

^aCentrifuged liquid product.

^b $\Delta P/\Delta P_0$ as defined in text.