

MINERAL MATTER EFFECTS IN COAL LIQUEFACTION

1. AUTOCLAVE SCREENING STUDY*

by

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INTRODUCTION

Several processes have been developed for converting coals to liquid fuels. In order to produce a pumpable, environmentally acceptable fuel, it is necessary to understand how the properties of the feed coals affect the composition of the resulting liquid products -- especially the viscosity and sulfur content. It has been shown, for example, that the petrographic (maceral) composition of the feedstock plays a significant role in coal conversion processes.¹⁻² The role of mineral matter, however, has not been as clearly defined or as extensively studied.

Mukherjee and Chowdhury showed that the extent of conversion to liquid products increased with both ash content and with the concentration of iron and titanium.³ Iron, as contained in the residues from coal liquefaction experiments, has been shown to increase the hydrogen transfer capacity of anthracene oil.⁴ It was found that pyrite, and solids from the SRC (Solvent Refined Coal) process had a significant effect on the hydrogenation of creosote oil, and that coal ash, reduced iron and SRC solids exhibited a considerable activity for desulfurization.⁵ In that same study, it was shown that the conversion of a Kentucky No. 9/14 coal to cresol-solubles was dependent upon mineral content.

It is clear from the published data that coal minerals may play a significant role in liquefaction processes. It is, therefore, important to establish predictive correlations between mineral content and liquid product composition. Our studies on matter effects in coal hydroliquefaction have been directed toward this objective. We utilized batch autoclave experiments, under closely controlled conditions of temperature, heating rate, pressure and residence time, to evaluate the reactivities of several coals having similar petrographic composition but widely varying mineral content. This paper will present the autoclave screening data that have been obtained in the first phase of our program. We will relate viscosity, sulfur content and conversion to the mineral content of the feed coals.

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EXPERIMENTAL

The coals used in the autoclave screening studies are listed in Table 1. They were pulverized to minus 100 mesh and stored under argon in polyethylene containers. Each sample was thoroughly homogenized prior to use. Proximate, ultimate and sulfur forms analyses are given in Table 2, and the petrographic (maceral) composition of each sample is shown in Table 3. All of the coals used in this study were high volatile bituminous, with widely varying sulfur and ash contents. Most of the samples had high (>80%) vitrinite contents and were relatively low in fusinite and micrinite. It was felt that these coals would provide a valuable test matrix for studying mineral matter effects because they were all of similar rank, geological origin and petrographic composition, but varied considerably in ash content.

Mineral matter content was determined by x-ray diffraction analysis of low temperature ash.⁶⁻⁷ The samples were prepared by ashing the coals at a low temperature (<100°C) in a radiofrequency field, using a Tracerlab Low Temperature Asher (LTA 600). The RF power was 200-250 watts, the oxygen flow rate 60-80 cm³/min and the total ashing time 48-96 hours. Calibration curves for the quantitative analysis of quartz, calcite and pyrite were prepared, using nickel oxide as an internal standard. The clays were analyzed by using talc as an internal standard. Kaolinite was distinguished from the mixed layer clays by expanding the basal layers of the latter with ethylene glycol. Results of these analyses are given in Table 4 as a weight percent of the coal on a dry basis. Also included in this table for comparison, are values for pyrite that were computed from the pyritic sulfur content shown in Table 2.

The solvent (vehicle) used for the liquefaction runs in this study was creosote oil (No. 4 cut), which was obtained from the Reilly Tar and Chemical Co. This oil had a specific gravity of 1.12 and a boiling range of 270-400°C.

All of the experiments were carried out in a one-liter (Autoclave Engineers, Inc.) magne-drive autoclave, equipped with a turbine agitator. A stainless steel liner, with an effective working volume of approximately 0.7 liter, was used in order to facilitate loading and unloading, and to improve the material accountability. The inside surface of this liner was cleaned by bead-blasting after each run. The temperature was monitored and controlled by dual chromel-alumel thermocouples; the pressure was monitored with a 0-5000 psig transducer. The temperature and pressure were recorded continuously.

In a typical experiment, the autoclave (with steel liner in place) was charged with 50.0 g (daf basis) of coal and 115.0 g of creosote oil, and the mixture was stirred at 500 rpm. The system was purged with inert gas and leak tested at 2000 psig. The system was then purged with hydrogen, charged to the desired initial (cold) pressure, which was controlled to ± 2 psig, and leak tested again. The autoclave contents were heated to the desired operating temperature (nominally 430°C) over a period of approximately one hour. The temperature during the (30 min.) run was manually controlled to ± 3 °C. No additional hydrogen was added during the run, and the pressure dropped gradually as the hydrogen was consumed. At the end

Table 1
Coals Used in the Autoclave Screening Study

Sample No.	State	Seam	Mine
G98-76	Kentucky	No. 11	Fies
G98-64	Kentucky	No. 11	Homestead
G98-54	West Virginia	Pittsburgh	Ireland
G98-57	Illinois	No. 6	Orient 4
G98-82	Pennsylvania	Pittsburgh	Bruceton
G98-71	Kentucky	Elkhorn No. 3	Guaranty

Table 2

Analyses of Coals Used in the Autoclave Screening Study^a

	Kentucky No. 11 (Fies)	Kentucky No. 11 (Homestead)	West Virginia	Illinois No. 6	Pennsyl- vania	Kentucky Elkhorn No. 3
<u>Proximate Analysis</u>						
Volatile Matter	39.01	39.24	41.32	36.69	38.11	36.83
Fixed Carbon	43.80	47.87	48.73	52.60	58.19	58.81
Ash	17.19	12.89	9.95	10.71	3.70	4.36
<u>Ultimate Analysis</u>						
Carbon	64.77	68.80	72.64	71.48	81.71	80.36
Hydrogen	4.65	4.78	5.19	4.89	5.35	5.45
Nitrogen	1.24	1.43	1.27	1.45	1.64	1.88
Sulfur	6.11	4.88	4.44	3.00	1.05	0.78
Oxygen (difference)	5.95	7.22	6.45	8.47	6.49	7.17
Ash	17.19	12.89	9.95	10.71	3.70	4.36
<u>Sulfur Forms</u>						
Pyritic	3.68	2.41	1.48	1.27	0.30	0.08
Sulfate	0.11	0.11	0.41	0.09	0.02	0.00
Organic	2.32	2.36	2.55	1.64	0.73	0.70
Total	6.11	4.88	4.44	3.00	1.05	0.78

^aAll data are on a dry basis.

Table 3

Petrographic Composition of Coals Used in the Autoclave Screening Study^a

Sample	Macerals ^a (volume %)							
	V	PV	F	SF	MM	GM	E	R
Kentucky No. 11 (Fies)	86.9	4.1	2.1	3.1	0.6	1.4	1.8	0.0
Kentucky No. 11 (Homestead)	87.7	3.6	3.1	3.0	0.4	1.2	1.0	0.0
West Virginia	85.7	3.6	2.9	3.3	0.8	2.3	1.4	0.0
Illinois No. 6	89.8	4.3	1.9	0.9	0.2	1.6	1.2	0.1
Pennsylvania	81.9	4.9	2.8	4.3	1.6	1.8	2.7	0.0
Kentucky Elkhorn No. 3	74.7	9.3	1.4	2.5	0.9	5.4	5.3	0.5

^aIn these columns, V = vitrinite, PV = pseudovitrinite, F = fusinite, SF = semifusinite,

MM = massive micrinite, GM = granular micrinite, E = exinite, R = resinite.

Table 4

Mineral Composition of Low Temperature Ash

Sample	% Dry Basis							Pyrite calculated from pyritic sulfur (% dry basis)
	mm ^a	Pyrite	Quartz	Calcite	Kaolinite	Mixed Layer Clays		
Kentucky No. 11 (Fies)	20.90	5.43	3.34	n.d. ^b	0.21	11.92	6.88	
Kentucky No. 11 (Homestead)	15.70	4.55	2.50	1.10	0.32	7.23	4.51	
West Virginia	13.82	3.26	1.46	n.d.	1.19	7.91	2.77	
Illinois No. 6	12:95	2.80	2.20	0.78	0.82	6.35	2.37	
Pennsylvania	5.18	0.53	0.54	n.d.	0.33	3.78	0.56	
Kentucky Elkhorn No. 3	5.62	n.d.	trace	n.d.	2.00	3.50	0.15	

^a mm = mineral matter

^b n.d. = not detected by x-ray diffraction techniques

of the experiment the furnace was lowered. Stirring was continued, and the contents of the autoclave were allowed to cool to room temperature overnight. The overhead gases were slowly vented through two caustic scrubbers, and the system was purged with inert gas. The reaction products were removed and weighed. A summary of the operating conditions used in all of the autoclave screening experiments is given in Table 5.

The liquid product from each run was filtered hot (60-100°C) under nitrogen (80-120 psig), using a jacketed (brass) pressure filter. In some cases, due to the high viscosity of the liquid or the gelatinous consistency of the residue, it was not possible to filter the product. In these situations, centrifugation (40 min at 2500 rpm) was used to accomplish solids separation, but this was not as effective for ash removal as was filtration.

The filter cake (residue), consisting of unreacted coal and mineral matter, was washed several times with acetone. It was then dried overnight in a vacuum oven at 105°C. The resulting dry residue, a freely flowing powder, was ashed at 775°C. The extent of conversion to liquid products, on a dry, ash-free (daf) basis, was then calculated by means of a forced ash balance.⁸

The viscosity of the filtered liquid product was measured at 60°C with a Brookfield viscometer that was equipped with a small sample adapter. The estimated precision, based on replicate measurements on certified standards, was $\pm 5\%$.

The sulfur content of the filtered liquid product was obtained with a Leco automatic sulfur analyzer, using a combustion iodometric procedure. Replicate analyses were carried out on samples whose sulfur contents had been independently determined by the standard Eschka method (ASTM D271-70). The Leco results were within $\pm 0.05\%$ (absolute) of the Eschka data.

RESULTS AND DISCUSSION

The data from the autoclave screening experiments are shown in Table 6. All of the liquid products were filterable except for the one obtained from the Kentucky Elkhorn coal, in which case centrifugation was required for solids separation. The viscosities of the liquid products varied by more than an order of magnitude. The observed increases in viscosity appeared to correlate well with the marked decreases in the mineral content of the feed coals (Table 6). Since the coals had similar maceral compositions (Table 3) and all autoclave runs were carried out under closely controlled conditions, it may be concluded that the variations in product viscosity were the result of a mineral matter effect. Thus, changes in mineral composition had a substantial effect on the quality (e.g., pumpability) of the resulting liquid product.*

*Ancillary experiments have shown that the product viscosity was strongly dependent upon the preasphaltene (pyridine soluble-benzene insoluble) content,⁹ which, in turn, was related to the mineral content of the feed coals.

Table 5

Conditions Used in the Autoclave Screening Experiments

Coal charge	:	50.0 g (daf basis)
Solvent (creosote oil) charge	:	115.0 g
Coal particle size	:	through 100 mesh
Initial (cold) pressure	:	1000 psig H ₂
Heatup time	:	≈ 60 min
Temperature (nominal)	:	430°C
Reaction time (nominal)	:	30 min
Mixing speed	:	500 rpm

Table 6

Results of Autoclave Screening Study^a

Run No. G98-	76	64	54	57	82	71
Coal	Kentucky No. 11 (Fies)	Kentucky No. 11 (Homestead)	West Virginia	Illinois No. 6	Pennsylvania	Kentucky Elkhorn No. 3
Mineral matter ^b (%)	20.90	15.70	13.82	12.95	5.18	5.62
Pyrite ^b (%)	5.43	4.55	3.26	2.80	0.53	0.15
Organic sulfur ^b (%)	2.32	2.36	2.55	1.64	0.73	0.70
Temperature (°C)	432	430	429	429	429	433
Initial pressure (psig, 25°C)	999	1000	1000	1001	1000	999
Operating pressure ^c (psig)	1701	1758	1730	1779	1761	1839
Conversion ^d (%)	93	94	88	87	84	62
Filtered liquid product						
Sulfur (%)	0.65	0.68	0.69	0.55	0.43	0.44 ^e
Viscosity (cps @ 60°C)	75	108	124	278	456	761 ^e
Organic Sulfur Removed ^f (%)	72	71	73	66	41	37

^aAll runs in creosote oil solvent; solvent : coal = 2.3.

^bFeed coal, dry basis; mineral matter and pyrite from low temperature ash data, except for Kentucky Elkhorn where pyrite was calculated from pyritic sulfur content.

^cMaximum pressure at operating temperature.

^dDry, ash-free (daf) basis.

^eCentrifuged liquid product.

^f $\left[\frac{S_{\text{product}}}{S_{\text{coal}}} \right] / S_{\text{coal}} \text{ (organic)}$.

It may be assumed that the sulfur in the liquid product was primarily organic sulfur, since the inorganic forms (pyritic and sulfate) were concentrated in the insoluble residues. From the data shown in Table 6, it can be seen that the liquids with the lowest sulfur contents were obtained from the coals that had the lowest organic sulfur contents. The fractional decrease in organic sulfur, however, was highest for the Kentucky No. 11, West Virginia and Illinois No. 6 coals. Thus, the coals with the highest mineral contents appeared to be the most reactive ones with respect to organic sulfur removal. This observation is in agreement with the work reported by Tarrer, *et al.*, where it was shown that certain coal minerals catalyzed the hydrodesulfurization of creosote oil.⁵ Our data (Table 6) would suggest that pyrite could have been active in this respect, but other work has shown that pyrite may not be active for desulfurization.^{5,10} Further experimental work will be required to establish these ideas in a more quantitative manner.

The percent conversion to liquid products were, with the exception of the Kentucky Elkhorn coal, fairly high (Table 6). Since coal dissolution is very rapid under the conditions of temperature, pressure and residence time used in this study,⁸ and since high-vitrinite coals are reactive in liquefaction processes,² it is not surprising that the conversions were high. The somewhat greater conversion for the Kentucky No. 11 coals could have been a result of the increased mineral content, but it is not clear that the observed differences were statistically significant. The extremely low reactivity of the Elkhorn coal, however, was probably due to the considerably lower vitrinite content.

The autoclave screening study has provided data that show a good correlation between mineral composition of the feed coal and product quality (sulfur content and viscosity). In order to pursue these concepts in greater detail, several experiments have been initiated with coals (Illinois No. 6 and Kentucky No. 11) in which the mineral content has been purposefully altered. This was accomplished by: (1) adding pure mineral constituents to the feed coal; and (2) removing mineral matter by both chemical (acid extraction) and physical (froth flotation) techniques. Preliminary data have confirmed several of the tentative conclusions reached in the autoclave screening study. These results will be documented when complete.

SUMMARY

Several high-volatile bituminous coals were hydrolized, in a one-liter autoclave, at a temperature of 430°C, initial (cold) H₂ pressure of 1000 psig and residence time of 30 min. All experiments were carried out in creosote oil as the solvent, at a solvent:coal ratio of 2.3:1. The feed coals ranged in mineral content from 21% to 5%, and in sulfur content from over 6% to under 1%. The coals had similar maceral distributions, and most were vitrinite-rich (>85%). Conversions, calculated by an ash balance on the acetone-washed residues, varied from 62 to 94%. The liquid products were assessed in terms of sulfur content and (Brookfield) viscosity. The sulfur contents ranged from 0.43 to 0.69%; the viscosities (at 60°C) varied from 75 to 761 cps. A good correlation was found between the mineral content of the feed coal and the extent of organic sulfur removal and product viscosity. The highest conversions were found for the coals having the highest mineral contents.

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