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Effect of Pretreating of Host Oil on Coprocessing

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INTRODUCTION

The principal objective of this research is to gain information on the role that host petroleum-derived oils (1000F+), as well as that of catalytically treated host oils, play when used as liquefaction solvents in coprocessing with coal. The host oil will be extensively characterized and then pretreated in a number of ways which involve catalytic reactions such as hydrogenation, hydrocracking, and isomerization. The pretreated oils will then be characterized by elemental analysis, catalytic dehydrogenation, distillation, GC-MS, and NMR. The effects of the host oil on coprocessing with coal will be compared to those obtained using catalytically modified heavy oils. When appropriate, model compounds will be used to study specific reactions brought about by the pretreatments.

EXPERIMENTAL WORK

In the last quarterly report we presented results of coprocessing runs made with an Illinois No. 6 coal and an AMOCO VTR (as received) and after the heavy oil had been pretreated a number of different ways. Coal conversions and product yields were presented for each coprocessing experiment. We have now further analyzed results from coprocessing experiments in order to estimate the yields of coal-derived gas, asphaltenes and oil products. Although coal-derived products can not be measured directly from the coprocessing experiments, since coal and petroleum products are commingled, they can be estimated based on repeat reactions with the petroleum solvent alone. This technique assumes that the petroleum solvent reacts to yield the same products whether coal is present or not.

Tables I-IV summarize results of these analyses of coprocessing products. When the coal was coprocessed with untreated heavy oil (Table I), 58% of coal (MAF) was converted to gas and liquid products. We estimated that 7% of coal was converted to oils (n-pentane solubles), 28% to asphaltenes (n-pentane insolubles) and 24% to hydrocarbon gases, mostly methane. When the same coal was coprocessed with AMOCO oil that had been pretreated with 1000 ppm (metal concentration) of Mo naphthenate (Table III), 81% of coal was converted; this is an average of two runs. Coal-derived oil yield remained nearly the same at 8% and gas yield remained at 23%. However, the asphaltene yield increased from 28% to 50%. The increase in asphaltenes accounted for the increase in coal conversion.

Table IV shows yields for the case where Illinois No. 6 coal was coprocessed with AMOCO oil that was first pretreated in two steps; step one with 1000 ppm of Mo naphthenate, step two with the catalyst Ni/Mo/Al₂O₃. As a result of this reaction, 85% of coal was converted to gas and liquids. Gas yield was 19%, oil yield was 10% and asphaltene yield was 56%. As in the previous run, most of the coal was converted to asphaltenes.

Table I Thermal Coprocessing Product Yields. Conditions: Untreated AMOCO VTR + Illinois No. 6 coal, 440°C, 1000 psig H₂ (cold), 2070 psig avg. pressure, 30 min reaction, oil:coal= 2:1, Micro reactor, 200 rpm shaker speed.

	Oil & Coal	Oil	Coal
Total, g.	8.07	5.74	2.33
Solid, g.	1.38	0.41	0.97
Gas, g.	1.78	1.23	0.55
Oil, g.	3.32	3.16	0.16
Asphalt, g.	1.59	0.94	0.65
Coal Conver, %			58
Gas Yield, %		21	24
Oil Yield, %		55	7
Asphalt Yield, %		16	28

Table II Coprocessing Product Yields. Conditions: Thermally Pretreated AMOCO VTR + Illinois No. 6 Coal, 440°C, 1000 psig H₂ (cold), 2250 psig avg. pressure, 30 min reaction, oil:coal= 2:1, Micro reactor, 200 rpm shaker speed

	Oil & Coal	Oil	Coal
Total, g.	8.4	6.07	2.33
Solid, g.	0.57	0.05	0.52
Gas, g.	1.78	0.95	0.83
Oil, g.	3.9	4.18	-0.28
Asphalt, g.	2.15	0.89	1.26
Coal Conver, %			78
Gas Yield, %		16	36
Oil Yield, %		69	-12
Asphalt. Yield, %		15	54

Table III Coprocessing Product Yields. Conditions: Mo Naph. Pretreated AMOCO VTR + Illinois No.6 Coal, 440°C, 1000 psig H₂ (cold), 2190 psig avg. pressure, 30 min reaction, oil:coal=2:1, Microreactor, 200 rpm shaker speed.

	Oil & Coal	Oil	Coal
Total, g.	6.94	5	1.94
Solid, g.	0.38	0.01	3.7
Gas, g.	1.09	0.65	0.44
Oil, g.	4.09	3.94	0.15
Asphalt, g.	1.38	0.4	0.98
Coal Conver, %			81
Gas Yield, %		13	23
Oil Yield, %		79	8
Asphalt. Yield, %		8	50

Table IV Coprocessing Product Yields. Conditions: Two step Hydrotreated AMOCO VTR+Illinois No.6, 440°C, 1000 psig H₂(cold), 2217 psig average press., 30 min, oil:coal=2:1, Microreactor, 200 rpm.

	Oil & Coal	Est. Oil	Est. Coal
Total, g.	8.39	6.06	2.33
Solid, g.	0.38	0.04	0.34
Gas, g.	0.7	0.26	0.44
Oil, g.	5.64	5.4	0.24
Asphalt, g.	1.67	0.36	1.31
Coal Conver, %			85
Gas Yield, %		4	19
Oil Yield, %		89	10
Asphalt. Yield, %		6	56

An interesting result was obtained when a thermally pretreated (no added catalyst) AMOCO oil was coprocessed with coal; Table II lists the results. This experiment resulted in a coal conversion of 78%, which was close to the coal conversion obtained in the experiment where coal was coprocessed with the Mo naphthenate pretreated oil. However, the combination of thermally pretreated oil and Illinois No. 6 coal had a negative effect on oil yield. The oil-alone run had a higher oil yield than the oil and coal coprocessing run.

During the fourth quarter of 1993, pretreatments of the AMOCO residuum were performed using a one liter autoclave batch reactor. Results are summarized in Table V. In one experiment, AMOCO heavy oil was hydrocracked with 1000 ppm (metal concentration) of Mo naphthenate at an average temperature of 445°C and an average pressure of 1885 psig. The reaction was carried out until the reactor pressure, which was rapidly decreasing, began to level off. The reaction took 90 mins. The pretreatment yielded 4% coke, 13.4% hydrocarbon gases (mostly methane), 9.2% asphaltenes, and 73.4% oils. Hydrogen uptake was calculated at 1.0 wt.% of the oil feed. Elemental analysis of liquid products from the pretreatment indicated that the H:C ratio had increased from 1.45 to 1.50 and sulfur content decreased from 4.6% to 3.29%; nitrogen remained level at about 0.5%. Proton NMR showed that hydrogen was distributed as follows;

Aromatic = 1.9%	Alkyl alpha= 0.0%
Cyclic alpha= 6.0%	Alkyl beta= 62.5%
Cyclic beta= 3.1%	Gamma= 22.2%

Table V AMOCO VTR Pretreatment Conditions and Product Yields.

Run	63	59
Catalyst	none	Mo Naph.
Conc., ppm	0	1,000
Avg. P, psig	2,700	1,885
Avg. T, C	435	445
Time, min	120	90
Oil Yield, %	59.3	73.4
Gas Yield, %	25.1	13.4
Asphaltene Yield, %	Inc. in oil yield	9.2
Coke Yield, %	15.6	4.0
H ₂ Uptake, %	n.d	1.0

Figure 1 GC/MS of AMOCO VTR following hydrocracking with Mo naphthenate at 440°C and 1885 psig total pressure.

When compared to the untreated heavy oil, this pretreated oil had fewer aromatic and hydroaromatic (cyclic alpha and cyclic beta) hydrogens and more alkyl beta hydrogens. The proportion of gamma hydrogens appears not to have been affected by this pretreatment.

By vacuum distillation of liquid products we estimated that 53.5 % of the residuum was converted to distillate products that boiled below 650°F. GC/MS analysis of liquid products from the pretreatment identified a large number of hydrocarbons. The GC/MS graph is shown in Figure 1. The larger peaks were identified by their mass as normal paraffins in the range of C8 to C24. Many of the smaller peaks that are between the larger n-paraffin peaks were identified as branched paraffins, alkylated aromatic compounds, and cyclic aliphatic compounds. A few sulfur containing benzothiophene-type compounds were also identified. These hydrocarbons were not present in the untreated heavy oil based on a GC/MS analysis of untreated oil that showed only a few peaks in this range.

In a different pretreatment experiment, the AMOCO heavy oil was thermally treated with hydrogen gas for 2 hr. at an average temperature of 435 C and an average pressure of 2700 psig. Again, the one liter autoclave reactor was used. As a result of this pretreatment, 15.6% of the starting heavy oil was converted to coke, 25.1% to hydrocarbon gas, and 59.3% to liquids; this includes asphaltenes and oils (Table V). This run demonstrated, once again, the effect of Mo naphthenate on suppressing coke production.

A sample of liquid product from this pretreatment run was dehydrogenated over a Pd/CaCO₃ catalyst that was first reduced with hydrogen gas for one hr. at 300°C. The experiment involved adding 0.2 g. of oil and 0.5 g. of catalyst to 3.0 g. of phenanthridine,

which acts as a vehicle to remove hydroaromatic hydrogen from the oil. The mixture was boiled at 350°C, the normal boiling point of phenanthridine, and the volume of gas evolved was measured. After 270 min. 16 cc of gas, presumably all hydrogen, was evolved from the pretreated oil. As reported previously, a similar experiment was conducted with untreated AMOCO heavy oil and resulted in evolution of 20.9 cc of gas from the same amount of sample. These results agree with proton NMR results and showed that the thermally pretreated oil contained less hydroaromatic hydrogens than the untreated oil did.

FUTURE WORK

We are currently reviewing preliminary results obtained to date and outlining future work on this project. Initially, we plan to make more pretreatments of AMOCO residuum in the one liter autoclave reactor until we have produced about 500 g of product for each different pretreatment (i.e., thermal and catalytic using Mo naphthenate and Ni/Mo/Al₂O₃). This amount of material is needed for proper characterization of products from pretreatment runs. Products from the pretreatment experiments will be separated into solid, distillate, oil and asphaltene fractions by distillation and extraction methods, shown in Figure 2. Solid samples will undergo elemental and metal analysis and liquid samples will receive elemental and proton NMR analysis in order to determine hydrogen content and distribution. Liquid samples will be dehydrogenated to measure donatable hydrogen content. Samples that are light enough will be analyzed by GC/MS in order to isolate and identify the compounds

present. Samples will also undergo GC simulated distillation to determine their boiling point range.

Depending on results of the initial pretreatment experiments, different types of pretreatments might be investigated, such as selective hydrogenation with a $\text{Co}_2(\text{CO})_8$ catalyst and CO/H_2 gas, or perhaps hydrocracking at different time/temperature conditions.

Figure 2 Product Separation Method

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