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QUARTERLY PROGRESS REPORT

Submitted to: Department of Energy

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 (1000° F+), 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 effect of the host oil on coprocessing with coal will be compared to that obtained using catalytically modified host oils. When appropriate, model compounds will be used to study specific reactions brought about by the pretreatments.

EXPERIMENTAL WORK

To better characterize products from resid pretreatment as well as coprocessing runs, we have developed a distillation procedure, which is illustrated in Figure 1. After a reaction, a gas sample is collected for GC analysis, and the remaining gases are vented from the reactor. Next, a glass adapter and collection flask is fitted to the reactor, via a vent line, and light oils (b.p. < 380° F) are distilled and collected from the reactor under atmospheric pressure. The remaining heavier oils and solids are washed from the reactor using THF. Solids are separated by pressure filtration using a 10 micron filter, and liquids are

Figure 1 Product separation method

recovered after distilling off the THF. Since THF boils at 150 °F, it can be removed without loss of products, all of which now boil at temperatures above 380° F.

The liquids can be fractionated by boiling point using a small vacuum distillation unit, shown in Figure 2.

By this method the oil is divided into the following cuts;

IBP- 380 °F	gasoline range (from reactor)
380- 650 °F	diesel fuel range
650- 800 °F	middle oil
+ 800 °F	vacuum gas oil & resid

To test this new product workup procedure we coprocessed an Illinois # 6 coal with the untreated AMOCO resid at a oil:coal ratio of 2:1. The reaction was carried out in a 300 ml autoclave reactor at 425° C for 30 min under hydrogen gas at an average reaction pressure of 2,106 psig. When the AMOCO resid was reacted without coal it had the following product yields, based on MAF starting material;

Coprocessing Yields By Distillation Range

	Resid alone	Expected if coal is inert	Actual
Gas	5.2%	3.7%	10.9%
IBP-421°F	7.0%	5.0%	3.6%
421-650°F	12.7%	9.1%	11.7%
650-800°F	13%	9.4%	7.6%
800°F+	61%	43.9%	53.2%
Coke	1.1%	28.76%	13.0%

Figure 2 Micro distillation unit

The second column in the above table represents a hypothetical yield of products that assumes the added coal acted as an inert solid during coprocessing. The last column contains the experimental results from the coprocessing run. As expected, the coal did not act as an inert solid during coprocessing, but reacted. The yield data suggests that part of the coal (57% based on the remaining solids) was converted to gases and heavy liquids since the yield of these products was greater than that expected from oil alone.

In an attempt to determine the contribution of coal-derived products in the four liquid fractions, we plan to analyze each fraction for its -OH content. Petroleum resids are poor in oxygen containing compounds while coal contains an appreciable amount of oxygen (e.g., Illinois #6 contains 13.5 wt% oxygen) mostly in the form of phenolic compounds. We plan to react the oils with a reagent that converts the -OH to trimethylsilyl ethers, which can be readily identified by IR or mass spectroscopy.

FUTURE WORK

We have seen that pretreatments of the AMOCO resid with 1000 ppm of Mo naphthenate at 440°C and +1500 psig H₂ pressure resulted in removal of about 50% of the sulfur and partial conversion of the resid to gases and lighter liquids, a result of cracking. However, the pretreatments conducted so far have not resulted in any appreciable increase in the liquid's hydrogen content or H:C ratio, even though hydrogen gas was consumed during the pretreatment runs.

One of the original goals of this project was to treat the AMOCO resid so as to increase its hydrogen content from 10.2% to 11.5%. It is hoped that the hydrogenated oil would contain more hydroaromatic hydrogen atoms and would serve as a better liquefaction solvent than the untreated resid.

Future pretreatments of the resid will be designed to hydrogenate aromatic compounds with minimal cracking. If half of the aromatic carbon atoms are hydrogenated, for example, the hydrogen content of the oil will be increased to 11.3% for both the AMOCO and CITGO resids.

Accordingly, we plan to conduct the following reactions on the resids;

1. Pretreat with Mo naphthenate and Ni/Mo/Al₂O₃ catalyst at or below 400°C, to minimize cracking, for long reaction times (i.e., 5 to 10 hr.). At these conditions hydrogenation reactions may out pace cracking reactions.

2. Pretreat with metal carbonyl + CO/H₂ at low reaction

temperatures (less than 200°C). Friedman et al.¹ showed that anthracene can be almost completely converted to dihydroanthracene in the presences of $\text{Co}_2(\text{CO})_8$ and CO/H_2 gas at 135°C and 2900 psig pressure.

3. Pretreat with iodine compounds (HI and CH_3I) + H_2 . Iodine compounds have been shown to promote coal liquefaction. In the presence of hydrogen, iodine-produced radicals promote aromatic ring hydrogenation in coal.

4. We also plan to pretreat the resids with Mo and iron catalyst and small amounts (10% or so) of coal, similar to a CANMET hydrocracking additive.

We are in the process of installing a simulated distillation unit that will allow us to determine the boiling curve of products from coprocessing and liquefaction experiments. This tool should prove to be valuable for evaluating the quality of liquid products.

¹ Friedman, S., Metlin, S., Svedi, A., and Wender, I., J. Org. Chem., Vol 24, 1287 (1959).

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