2. 2.

DOE/PC/91054-T5

QUARTERLY PROGRESS REPORT

Submitted to: Department of Energy

for Project

Effect of Pretreating of Host Oil on Coprocessing

Contract DE-AC22-91PC91054

July 1, 1992 through September 30, 1992

by

Chemical and Petroleum Engineering Department

University of Pittsburgh

Irving Wender, Principal Investigator

John W. Tierney, Co-Principal Investigator

January 25, 1993

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

BD
110 Inven
Se

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

INTRODUCTION

The principal objective of this research is to determine the role host petroleum-derived oils ($1000^{\circ}\text{F}+$), as well as that of catalytically treated host oils, play when used as liquefaction solvents in coprocessing with coal. The host oils will be extensively characterized and then pretreated in a number of ways which involve catalytic reactions such as hydrogenation, hydrocracking, isomerization, and dehydrogenation. The pretreated oils will then be characterized. 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. Highly dispersed iron catalysts modified by the addition of small amounts of other metals will be used to modify the chemical composition of the host oils.

EXPERIMENTAL PLAN

After discussion with Dr. A. Bose and Dr. M. Farcasiu the following experimental plan was outlined:

I. Selection of Heavy Oils

A heavy oil obtained from the Amoco Corporation will be the first oil to be investigated. This residuum is an Amoco Vacuum Bottoms ($1000^{\circ}\text{F}+$) heavy oil that is "real" in the sense that it is a blend of crudes obtained from several sources.

It had been hoped that the second oil to be studied, at a later date, would be a North Slope oil which we obtained from BP. However, the oil is too light ($725^{\circ}\text{F}+$), and may not be used. We have obtained a Venezuelan heavy oil, $>923^{\circ}\text{F}$ or $>495^{\circ}\text{C}$, from Citgo's Corpus Christi, Texas refinery. A decision on possible investigations of coprocessing using a second

oil will depend on results obtained with the Amoco oil.

II. Analyses and Characterization of the Starting Heavy Oil before Pretreatment

a. Hydroaromatic hydrogen content of the starting oils: This will be estimated by catalytic dehydrogenation and will be an indicator of hydrogen donor properties of the oil for coprocessing.

b. Elemental analysis: The H/C ratio, heteroatom and metal content are important properties.

c. Aromatic carbons and protons identified by ^1H and ^{13}C NMR.

d. Compound types determined by chromatographic separation.

f. Simulated distillation to obtain an approximate true point curve.

g. GC-MS analysis of the pentane solubles.

III. Pretreatment of Heavy Residua

Two main kinds of pretreatment will be used.

a. Partial hydrogenation: Heavy oils (one, perhaps two) will be treated with suitable hydrogenation catalysts such as $\text{Mo}(\text{CO})_6$ and $\text{Fe}_2\text{O}_3/\text{SO}_4$ to increase their hydrogen content from about 10-11 wt% to about 11.5 wt%. The treated oil will probably have a higher hydroaromatic hydrogen content. Multiple test runs will be needed to determine proper conditions.

b. Severe hydrogenation/hydrotreating: The hydrogen content can be further increased to over 12 wt% with this severe treatment, leading to almost complete saturation of aromatic moieties in the heavy oil. A well-known supported catalyst such as Shell 324 ($\text{Ni-Mo}/\text{Al}_2\text{O}_3$) will be used and reactions will be carried out under elevated pressure and in the presence of 3 wt% H_2S or added sulfur.

The objective of the pretreatment is to increase the hydrogen content of the starting oils with significant breakdown (cracking) of their structures. The reactions will be carried out in a 300 cc stainless steel stirred autoclave at temperatures of 375-425°C and pressures of 1500 to 2000 psi.

IV. Analysis and Characterization of Heavy Oils after Pretreatment

The analytical tests described above for the untreated oils will be used for the treated oils. Changes caused by the pretreatment will be determined.

V. Coprocessing Reactions

In these tests, a coal and a heavy oil will be reacted with hydrogen and a catalyst. Tentatively, the coals to be tested are Wyodak, a subbituminous coal, and either DECS-6 or 16, a high volatile bituminous coal obtained from the Penn State Coal Bank. The catalysts will include sulfated iron oxide and molybdated iron oxide. The heavy oils to be used are:

- i. As received (containing about 10-11 wt% H₂).
- ii. Partially hydrogenated (containing about 11.5 wt% H₂).
- iii. Severely hydrogenated (containing over 12 wt% H₂).

A 2:1 ratio of oil to coal will be employed. Reactions will be carried out at 400-425°C, 1500 to 2000 psi H₂ (1000 psi cold) for 30 to 60 minutes in a 300 cc stirred autoclave.

For each combination of coal, heavy oil and catalyst the following runs are planned:

- i. Oil + Coal. (Thermal reaction)
- ii. Oil + Catalyst.
- iii. Oil + Coal + Catalyst.

Each of the reactions above will be carried out for the untreated heavy oil and the pretreated heavy oils, a total of nine runs. Each will be repeated, to give a total of 18 reactions. If time permits and the results warrant it, a second heavy oil will be investigated.

VI. Characterization of Coal-Oil Coprocessing Products

Solvent extraction, filtration, and vacuum distillation will be used to determine the yield of light products, those boiling below 350°C.

EXPERIMENTAL WORK

A five gallon sample of the Amoco oil was heated while being shaken (work done at UPARC) to thoroughly mix the heavy oil. The five gallons of heavy oil were poured into one gallon cans for ease in further handling. Solid samples were taken from two of these gallon cans for elemental analysis. A third sample was removed from one of these gallon cans after warming. This is also being analyzed. The results will be compared to determine homogeneity of the samples.

To date, five different pretreatment reactions have been carried out on the Amoco oil. Table 1 list some properties of this oil. Details of the reaction conditions used are given in Table 2. An objective of the pretreatment reactions is to increase hydrogen content without too significant a breakdown (cracking) of the hydrocarbon structures. Severe cracking could produce a light hydrocarbon solvent which may not be suitable for coprocessing because of its low boiling point.

Table 1. Some Characteristics of Amoco Vacuum Residuum		
Property	Total	1000°F
Specific Gravity @ 60°F	1.028	1.039
Metals, ppm		
Vanadium	251	303
Nickel	57	68
Iron	13	14
Oil, wt%		20.0
Resin, wt%		63.7
Asphaltene, wt%		14.7
Ultimate Analysis, wt% *		
Carbon	84.0	84.1
Hydrogen	10.1	10.0
Nitrogen	0.5	0.6
Sulfur	4.5	4.9
* Source: Amoco Oil		

The following procedure was used for the pretreatment experiments.

1. Preheat reactor to 100-150°F using a muffle furnace placed below the reactor.
2. Add heavy oil and catalyst to reactor. Liquid occupies about 1/3 of reactor volume (300 ml).
3. Seal reactor and pressure test to anticipated maximum reaction pressure (in most cases 1500 psig) using H₂.
4. Bleed off gas to desired starting pressure and start stirrer at 500 rpm. Mix contents of reactor for at least 30 minutes.
5. At end of pre-mix period, check reactor pressure. Add additional gas if necessary.

Table 2. Conditions for Pretreatment Reactions					
Run Number	Run 1	Run 2	Run 3	Run 4	Run 5
Condition	Thermal	Partial Hydrogenation			Severe
Wt of Heavy Oil (g)	73.6	68.2	69.5	56.4	46.9
Catalyst	None	Fe ₂ O ₃ /SO ₄	Fe ₂ O ₃ /SO ₄ /Mo	Fe(CO) ₅ /Mo(CO) ₆	Shell 324 Presulfided
Wt of catalyst (g)	0	0.8	0.8	1.3/0.022	7.16
Temperature (°C)	396-417	399-405	389-408	408-416	393-406
Gas used	H ₂	H ₂	H ₂	H ₂	97% H ₂ 3% H ₂ S
Average Pressure, psig	1533	1630	1490	1890	1852
Initial Pressure, psig	1000	1000	1000	1000	1400
Reaction time, min	60	60	60	60	60

6. Increase stirrer speed to 1000 rpm. Raise muffle furnace around reactor and start heating. Record reactor temperature and pressure every five minutes during heating period.

7. After reaching the desired reaction temperature, maintain this temperature during the reaction. Continue to record temperature and pressure every five minutes.

8. After desired reaction time, shut off and lower furnace away from reactor and cool reactor with fan. Continue recording temperature and pressure as the reactor cools.

9. When reactor has approached room temperature, vent gases and open reactor.

10. Wash reactor with tetrahydrofuran (THF) and recover liquid and solid products.

This completes the reaction steps of the pretreatment experiments. The next step involves separating the products into oils, asphaltenes, and insoluble organic matter. Figure 1 illustrates the separation scheme used.

Solid liquid separation was achieved by pressure filtration using filter paper with 10 μ m

Figure 1. Separation Scheme for Reaction Products.

pores. All fractions were collected and weighed. Samples of the THF soluble, pentane soluble, and pentane insoluble fractions were saved for further analysis. Analysis and characterization of the reaction products and the starting oil will include:

1. Hydroaromatic hydrogen content. This will be estimated by catalytic dehydrogenation and will be an indicator of the hydrogen donor properties of the liquid for coprocessing.
2. Elemental analysis. The H/C, heteroatom and metal content are important properties.
3. Aromatic carbon and proton identification by ^1H and ^{13}C NMR.
4. Compound types identified by chromatographic separation.

5. Distillation.

RESULTS

The run using the Shell supported catalyst displayed the largest pressure drop (over 400 psi) during reaction. There was a small pressure drop (50 psi) when the sulfated iron catalyst (Run 2) was used. The pressure increased during the thermal reaction (no catalyst) suggesting that gas products were generated at a greater rate than hydrogen was consumed. The total reaction pressure alone, however, cannot be used to determine the change in hydrogen pressure since it is likely that gaseous products such as H_2S , H_2O , NH_3 and light hydrocarbons were produced during the reaction. In future runs, we plan to collect and analyze these gas products.

Table 3. Product Distribution from Pretreatment Experiments						
	Starting Oil	Run 1	Run 2	Run 3	Run 4	Run 5
THF Soluble	104	65.1	93.0	91.7	94.9	83.8
THF Insoluble	0.1	0.8	1.7	1.8	1.3	9.3
Gas + Loss	-4.5 [*]	34.1 ^{**}	5.2	6.5	3.8	6.9
Pentane Soluble, as % THF Soluble	74.7	67.6	72.3	76.2	76.0	80.3
Pentane Insoluble	20.1	23.1	20.4	19.5		9.3
Loss	5.2	9.3	7.3	4.3		10.4
[*] Apparent incorporation of THF in heavy oil. ^{**} High product loss occurred during product recovery step.						

Results of the separation steps are presented in Table 3. The products from the 5 runs were fractionated into the THF soluble and the THF insoluble fractions. The same fractionation was made for the starting heavy oil. The difference between the weight of starting reactants (neglecting hydrogen gas) and the weight of final products was taken to be the weight of gas

products , which were not recovered, and handling losses. In most runs, this value was less than 7%. However, during the product recovery step in Run 1, high losses resulted because the liquid products were foamy and bubbled out of the reactor when it was opened. This foaming problem was resolved in subsequent runs by allowing the products to come to room temperature before opening the reactor. We plan to repeat Run 1.

Based on the yield of the pentane soluble fraction, Run 5, with the Shell supported catalyst produced the highest yield of oils. Specifically, the oil content of the starting residuum was increased by more than five percentage points. The next step will be to analyze the products of the pretreatment runs to determine their hydrogen content and other chemical characteristics. The characterization tests will indicate whether the pretreatment reactions were successful in increasing the hydrogen content of the starting heavy oil to the desired levels. If necessary, different pretreatment reactions will be conducted.

END

DATE
FILMED

7 / 13 / 93