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QUARTERLY PROGRESS REPORT

Submitted to : Department of Energy

Effect of Pretreating of Host Oil on Coprocessing ,

Contract DE-AC22-91PC91054

April 1, 1993 through June 30, 1993

by

Chemical and Petroleum Engineering Department

University of Pittsburgh

Irving Wender, Principal Investigator

John W. Tierney, Co-Principal Investigator

August 16, 1993

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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 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 progress report for January, 1993, through March, 1993, we concluded that the dispersed iron based catalysts were not effective in hydrotreating the AMOCO VTR at 400°C. During the second quarter of this year, several pretreatment runs were conducted at 440°C using molybdenum naphthenate, a known active hydrotreatment catalyst. The reaction time was increased from one hour to two hours, during which time the reaction pressure leveled off. Table 1 lists reaction conditions for Runs 26-36, all of which were made at 440°C. Conditions for Runs 2-18 were reported in the last progress report. Details for Runs 19-25 are not being reported at this time because they were made below 440°C and for less than 2 hrs and appeared to be ineffective at hydrotreating the oil.

Table 2 lists the product distribution from Runs 26-36. The products are defined as

follows. Solids are insoluble in THF, liquids are soluble in THF and gases are determined by difference. Liquid products comprise asphaltenes, which are insoluble in pentane, and oils. Hydrogen uptake was determined by taking the difference between the amount of hydrogen gas loaded in the reactor and the amount of hydrogen gas remaining after the run. The amount of hydrogen gas remaining was estimated based on a GC analysis of the gas products. The H₂ uptake values are reported as wt. % of the starting oil.

A non-catalytic hydrotreatment of the AMOCO oil at 440°C resulted in about 12 % of the oil being converted to coke, while 54.6% remained as a liquid. By difference, 33.5% of the oil was not recovered and presumed to be converted to gas. The asphaltene content of the starting oil was reduced from 20.1 to 8.7 g/100g of starting oil. Hydrogen uptake was estimated at 1.4 % (wt). Adding 1% of the catalyst Mo/Fe₂O₃/SO₄ resulted in little change to the products and this catalyst was not effective in suppressing coke production.

When Mo naphthenate was added at a concentration of 500 ppm of Mo, coke production was drastically reduced, to less than 3%. Gas production was also reduced which resulted in higher oil (pentane soluble) yields.

At a higher catalyst loading of 2,000 ppm of Mo there was little change to the products, the asphaltene content decreasing slightly. This indicates that a catalyst loading of 500 ppm of Mo is probably sufficient for hydrotreating the AMOCO VTR, and there is little benefit in increasing the loading to 2000 ppm. In future hydrotreatments of the AMOCO oil we plan to use a catalyst concentration of 1000 ppm of Mo.

An elemental analysis of products from a hydrotreatment of the AMOCO oil made with 500 ppm Mo (Run 26, Table 3) indicated that the liquid product had a higher hydrogen

content (10.7%) and a higher atomic H/C ratio (1.5) than that of the starting AMOCO VTR, which had a H/C ratio of 1.45. This result indicated that the pretreatment with Mo increased the hydrogen content of the starting oil.

Run # 29 was performed using 2.5% (wt) of an additive consisting of 70% Ill #6 coal and 30% Mo/Fe₂O₃/SO₄ ("CANMET like" additive). As Table 2 shows, a significant amount of coke was produced (14.9 % excluding the weight of the additive). This additive will have to be investigated further to evaluate its potential for hydroprocessing heavy oil.

We began working on a second residue obtained from the CITGO Co. (a Venezuelan heavy oil). Table 4 lists the properties of both the Venezuelan and AMOCO oil. The Venezuelan oil contains about twice as much metallic compounds, and has a higher asphaltene content. Based on this, the Venezuelan oil might be more difficult to upgrade than the AMOCO oil. Indeed, pretreatment of the Venezuelan oil made with 500 ppm Mo resulted in a higher asphaltene content in the liquid product as compared to similar runs made with the AMOCO oil.

FUTURE WORK

Based on the favorable results obtained using the Mo naphthenate catalyst at 440°C for 2 hours we plan to hydrotreat 1 to 1.5 liters of the AMOCO oil for subsequent upgrading using a supported hydrotreating catalyst (e.g., Shell 324) and then to make coprocessing runs with coal. To better accomplish this task, we are in the process of setting up a 1 liter autoclave reactor system.

To determine the boiling range of liquid products from future pretreatment and

coprocessing runs we are constructing a micro (10-50 ml) vacuum distillation apparatus. The data obtained from this apparatus will help to characterize the liquid products. Other characterization methods such as elemental analysis, catalytic dehydrogenation and NMR will also be used.

Table 1 Pretreatments of AMOCO and Venezuelan VTR

Run #	Catalyst	Amount-ppm	Oil	Press.(cold)-pig	Max. Press-pig
28	None	0	AMOCO	1130	2780
27	Mo/Fe ₂ O ₃ /SO ₄	10,000	AMOCO	1100	2210
29	Fe + Coal additive *	2.5 %	AMOCO	1080	2875
26	Mo Naphthenate	500	AMOCO	1120	1940
30	Mo Naphthenate	500	AMOCO	1130	2080
31	Mo Naphthenate	500	AMOCO	1080	1955
33	Mo Naphthenate	2000	AMOCO	1140	2090
35	Mo Naphthenate	2000	AMOCO	1540	2290
32	Mo Naphthenate	500	CITGO (Venezuelan)	1170	2080
36	Mo Naphthenate	500	CITGO (Venezuelan)	1190	2125

Conditions: 440°C, 2 hr reaction

* 70% coal / 30% Mo/Fe₂O₃/SO₄ additive

Note: Run 34 was aborted because of a leak.

Table 2 Product Distribution of Pretreatment Runs
Based on 100 g of starting oil

Run	Catalyst	Solid THF- insols	Gas	Liquids (Asphaltene +Oil)	Asphaltenes C5-insols.	Oil	H ₂ uptake %(wt)
28	None	11.9	33.5	54.6	8.7	45.9	1.4
27	Mo/Fe ₂ O ₃ / SO ₄	11.3	32.7	56.0	8.9	47.1	N.D.
29	Fe+coal additive	14.9	-----	-----	-----	---	1.5
26	Mo Naphthenate	2.5	24.5	73.0	8.5	64.5	N.D.
30	Mo Naphthenate	1.3	19.4	79.3	9.0	70.3	1.7
31	Mo Naphthenate	9.8*	36.1	54.1	----	---	1.9
33	Mo Naphthenate	3.2	19.4	77.4	7.8	69.6	2.1
35	Mo Naphthenate	2.9	27.7	69.4	6.0	63.4	2.9
32	Mo Naphthenate	2.0	9.2	88.8	16.4	72.4	1.2
36	Mo Naphthenate	2.3	23.5	74.2	12.3	61.9	2.2

* Run 31 is suspect due to high coke and gas production.

Table 3 Elemental Analysis of Products from Pretreatment of AMOCO VTR

Wt %, as determined	THF- soluble	THF- insoluble	n-pentane soluble	n-pentane insoluble
C	85.2	71.9	84.9	88.2
H	10.7	4.1	11.0	5.4
N	0.5	1.8	0.4	2.0
S	2.8	7.2	2.7	5.3
H/C	1.5	0.7	1.55	0.7

Pretreatment conditions: 440°C, 2 hr reaction, 1120 psig (cold) H₂, 500 ppm Mo.

Table 4 Properties of CITGO and AMOCO VTR

	CITGO VTR	AMOCO VTR
C	85.4	84.3
H	10.1	10.2
N	0.8	0.5
S	3.4	4.6
O	0.3	0
H/C	1.42	1.45
Ash	0.01	
Ni	110	57
V	560	251
Fe	12	13
Asphaltene (C5 sol)	27.3	20.1
f(a)-fraction*	0.33	0.32

* Aromatic fraction determined by ^1H NMR.

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