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Effect of Pretreating of Host Oil on Coprocessing

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by

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INTRODUCTION

The principal objective of this research is to determine 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 oils 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, 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

A total of 18 pretreatment runs have been made on an AMOCO vacuum tower residuum, VTR, in an attempt to increase its hydrogen content from 10.2 wt % to a level of about 11.5 %. The conditions for the pretreatment runs are listed on Table 1. Reactions were performed using four different catalyst systems; 1) Shell 324 Ni/Mo/Al₂O₃; 2) Fe₂O₃/SO₄ with 1% Mo; 3) Fe₂O₃/SO₄ without Mo; and 4) Fe(CO)₅/Mo(CO)₆. For comparison, runs were

Table 1. Conditions for Pretreatment Runs

Catalyst	Run #	Gas	Max. Press psig	Average press.,psig	Average Temp.,°C	Temp Stdev.	Reaction Time.min
<u>None</u>	6	H ₂	1452	1442	403	1.9	60
	12	H ₂ /H ₂ S*	2964	2941	404	2.4	60
<u>Fe₂O₃/SO₄</u>	2	H ₂	1650	1630	403	2.9	60
	8	H ₂ /H ₂ S	3283	2888	413	2.6	60
	10	H ₂ /H ₂ S	2923	2879	402	1.1	60
	13	H ₂ /H ₂ S	2851	2786	432	9.4	60
	15	H ₂ /H ₂ S	3728	3640	404	3.7	120
<u>Fe(CO)₅/Mo(CO)₆</u>	4	H ₂	1935	1890	414	2.3	60
	11	H ₂ /H ₂ S	3035	2978	403	1.2	60
	17	H ₂ /H ₂ S	3689	3064	407	3.0	175
<u>Mo/Fe₂O₃/SO₄</u>	3	H ₂	1538	1491	405	5.9	60
	7	H ₂ /H ₂ S	2670	2532	399	3.0	60
	16	H ₂ /H ₂ S	3602	3344	405	2.5	200
	18**	H ₂ /H ₂ S	2628	2514	408	2.4	145
<u>Shell 324</u>	5	H ₂ /H ₂ S	2120	1852	399	3.5	60
	9	H ₂ /H ₂ S	2620	2253	398	9.4	60

Note: Run 1 and Run 14 were unsatisfactory and had to be repeated.

* 3% H₂S
 ** 20 wt % active carbon added to reactants

made using no catalyst. In all catalytic runs, sulfur was present in the system, both in the oil (the oil contains 4.6% sulfur) and as added H_2S gas or elemental sulfur. This was done to ensure that the catalyst would be converted to metal sulphides (pyrrhotites and the Mo to MoS_2) at reaction conditions.

The temperature for most of the runs was 400 °C; the average temperature was 398-408 for all but three runs. Hydrogen pressures were varied in different runs to explore the effect of pressure on hydrogenation of the heavy oil. In general, for a given catalytic system, the first reaction was at an average pressure between 1400 to 1900 psig. Subsequent runs were made at higher pressures in the range of 2000-3000 psig; some runs were made at pressures in the range of 3000-3700 psig. Most runs lasted for 60 min once the target temperature was reached. However, four runs were allowed to proceed much longer, 120 to 200 min.

During the pretreatment runs, reactor pressures and temperatures were recorded on a PC and the number of moles of gas calculated using the ideal gas law. Figure 1 shows a plot of the number of moles of gas vs time for Run 7. The decrease in number of moles of gas may indicate the amount of hydrogen taken up during the reaction, provided gas production is small. Figure 2 shows the gas-mole plot for Run 5. This pretreatment

resulted in a significant increase in the hydrogen content of the starting oil (10.2 wt % to 11.2%). During this run, the gas phase was reduced by 0.128 g-moles. The gas-mole plot for thermal Run 12 (Figure 3) shows that there was little change in the number of moles of gas during the 1 hr reaction period. Evidently, little or no hydrogen was taken up in this run. An elemental analysis of the liquid product from a previous thermal treatment, Run 1, indicated that the hydrogen content had decreased from 10.2 to 9.7 %.

Figure 1 Pretreatment Run 7 (Catalyst: Mo/Fe₂O₃/SO₄; Average hydrogen pressure=2532 psig; Average temperature= 399 °C)

Figure 2 Pretreatment Run 5 (Catalyst:Shell 324; Average hydrogen pressure=1852 psig; Average temperature= 399 °C)

Figure 3 Pretreatment Run 12 (no catalyst; Average hydrogen pressure=2941 psig; Average temperature=404 °C)

The change in moles of gas was estimated for pretreatment runs (see Table 2), and this information was used to judge the effectiveness of the run in increasing the hydrogen content of the starting oil. Based on runs with the Shell catalyst, a pretreatment run was considered to be effective if during the run the gas phase was reduced by 0.1 to 0.2 g-moles. As Table 2 shows, few of the pretreatment runs met this criterion and so were considered to be ineffective. Interpreting the change in the number of moles of gas for runs 17, 16, 13, and 15 was difficult since these runs produced significant amounts of gas (20 to 30 wt % of the starting oil).

Table 2. Change in Gas Moles During First Hour of Reaction Period

Catalyst	Run	Decrease in gas g-moles
<u>Fe₂O₃/SO₄</u>		
	10	0.038
	13	0.044
	15	-0.009
<u>Fe(CO)₅/Mo(CO)₆</u>		
	4	0.039
	11	0.041
	17	0.066
<u>Mo/Fe₂O₃/SO₄</u>		
	3	0.026
	7	0.113
	16	0.017
	18	0.050
<u>Shell 324</u>		
	5	0.128
	9	0.178

Following each run, solids were separated from the liquid product by extraction with THF followed by pressure filtration. Gas production was determined by difference. The liquid product from each run was separated into n-pentane insoluble (asphaltenes) and n-pentane soluble (oils) fractions. Table 3 lists the weights of solid (less starting catalyst weight), gas and liquid products from each pretreatment run based on 100 g of starting oil. The n-pentane soluble and insoluble fractions are also listed, again based on 100 g of starting oil. Run 9, with the Shell 324 catalyst, resulted in the largest reduction of asphaltenes. The starting oil had an asphaltene content of about 20.1 g/100 g; after Run 9 the asphaltenes had been reduced by almost 80%. It appears that increasing the severity of a run (i.e., increasing pressure and/or reaction time), resulted in less asphaltenes in the product. There seems to be a relationship between reaction time and gas production, with gas production increasing as reaction time is increased. For example, Run 16, with the catalyst $\text{Mo/Fe}_2\text{O}_3/\text{SO}_4$, had a reaction period of 200 min and produced almost 30 g of gas based on 100 g of starting oil. This is compared to Run 7, with the same catalyst, which had a shorter reaction period of 60 min and produced only 12 g of gas per 100 g of starting oil.

Table 3. Product Distribution of Pretreatment Runs With AMOCO VTR
Based on 100 g of starting oil

Catalyst	Run	Solid*	Gas	Liquid	C5 insol.	C5 sol.
<u>Thermal</u>						
	6	0.4	10.6	89.0	22.6	66.4
	12	0.5	8.1	91.4	18.7	72.7
<u>Fe₂O₃/SO₄</u>						
	2	0.6	5.2	94.2	19.2	75.0
	8	8.3	30.8	52.9	12.0	40.9
	10	0.5	4.5	95.0	16.8	78.2
	13	0.7	27.8	71.5	14.5	57.0
	15	0.6	20.0	79.4	13.8	65.6
<u>Fe(CO)₅/Mo(CO)₆</u>						
	4	----	<3.0	97.0	23.3	73.7
	11	1.7	7.0	91.3	12.9	78.4
	17	0.5	29.1	70.4	7.4	63.0
<u>Mo/Fe₂O₃/SO₄</u>						
	3	0.7	6.5	92.8	18.1	74.7
	7	0.6	12.0	87.4	16.2	71.2
	16	0.7	29.8	69.5	9.6	59.9
	18	7.1	14.3	78.6	-----	-----
<u>Shell 324</u>						
	5	----	<3.4	96.6	9.0	87.6
	9	2.0	12.2	85.8	4.0	81.8

* Solid = Weight of THF insol material less starting weight of catalyst.

Proton NMR spectra were obtained for the AMOCO starting heavy oil and liquid products from pretreatment Run 5 and Run 16. As shown by Figure 4, the NMR spectrum for the AMOCO heavy oil has six distinctive peaks. The following analysis was made of the oil based on this spectrum:

Peak ID	ppm range	% H
Aromatic-H	5 - 9	6.52
Alpha-H	2.2-5	14.54
Beta-H	1-2.2	57.99
Gamma-H	0.5-1	20.95

$$f(a) = 0.32 \text{ (by the Brown and Ladner (1960) method)}^1$$

The NMR spectrum for the liquid products from Run 5 and from Run 16 also had 6 distinctive peaks. However, for both spectra, the peak at 1 ppm was larger than the same peak for the starting oil. This suggests that the number of hydrogens bonded to carbons gamma or farther from an aromatic carbon increased as a result of the two pretreatment runs.

¹ Brown, J. K., and Ladner, W. R., Fuel, 39, 87 (1960).

Figure 4 ^1H NMR spectrum of AMOCO VTR

Further analyses of the spectra will be done in order to determine more precisely the distribution of hydrogen atoms in the liquid products. In addition, ^1H NMR and ^{13}C NMR data will be used to determine the concentration of possible functional groups in the starting oil and liquid products of pretreatment runs.

FUTURE WORK

The data presented above indicates that the dispersed iron based catalysts were not effective in hydrotreating the AMOCO VTR.

We plan to employ more active dispersed catalysts, such as $\text{Mo}(\text{CO})_6$ and Mo naphthenate, in the 100 to 1000 ppm range in future hydrotreatment runs of the AMOCO VTR and a second Venezuelan VTR obtained from the CITGO Co. With these more active catalyst we should be able to increase the hydrogen content of the starting oil to a level of 11.5% under more moderate conditions (i.e., 2000 psig hydrogen pressure and 1 hr reaction period) and thus minimize the amount of gas produced.

We plan to modify the 300 ml autoclave reaction system to improve temperature control of the furnace and to add data acquisition.

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