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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 through June 30, 1994

by

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July 1, 1994

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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 and hydrocracking. 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

During the 1st quarter of 1994 we concentrated on hydrotreating both the AMOCO and CITGO VTR with the aim of increasing their hydrogen contents through partial hydrogenation of polynuclear aromatic structures, which are present, to a limited extent, in heavy oils. Previous pretreatments with 1000 ppm of Mo naphthenate and added sulfur at a reaction temperature of 440 °C and + 1500 psig H₂ pressure resulted in removal of sulfur and conversion to lighter distillable products but only minimal increase in hydrogen content. In an attempt to hydrogenate the heavy oils with minimal cracking we conducted several experiments using Mo naphthenate at lower

temperatures and longer reaction times than had been previously used. Table I summarizes results of runs with the AMOCO VTR. It appears that best results were obtained by hydrotreating at 375°C for longer times. Under these conditions, minimal cracking of the oil resulted, as indicated by the low conversion to distillable products. However, available hydrogen content of the whole liquid product increased sharply, as indicated by the volume of gas evolved during catalytic dehydrogenation of the product (see Table I). Therefore, this pre-treated oil should contain more donatable hydrogen than the untreated heavy oil.

Similar results were observed for the CITGO VTR (see Table II). It appears that the temperature of the hydrotreatment is critical. Below 375°C cracking rates are reduced and perhaps are outpaced by hydrogenation reactions. Above 400°C cracking reactions dominate and probably result in destruction of hydroaromatic compounds, causing an overall drop in the available hydrogen content of the oil.

Another approach to increase hydrogen content involved treating the resids with catalysts that are only active for partially hydrogenating polynuclear aromatic compounds to form hydroaromatics. Table III shows results of two pretreatments of the CITGO VTR using $\text{Co}_2(\text{CO})_8$ and CO/H_2 gas at a ratio of 1:1. High CO pressure must be used to prevent dissociation of the catalysts. The results show that the cobalt catalyst was successful at adding available hydrogen even at the mild reaction temperatures used.

Table I. Hydrotreatment Experiments of AMOCO VTR With 1000 ppm of Mo Naphthenate (300 ml autoclave reactor)

Run #	54	72	73
Temp, °C	440	440	375
Press, psig	1855	1625	1690
Time, min	86	15	300
H ₂ Consump g-mol/100g	0.70	0.41	0.31
Conv, wt% (bp<800°F)	63	36	26
Catalytic Dehydrogen g-mol/100g	0.29	0.36	1.11 0.61

Untreated AMOCO VTR

Catalytic Dehydrogen = 0.42 g-mol/100g

Table II. Hydrotreatment Experiments of CITGO VTR (300 ml autoclave reactor)

Run #	36	74	78	81
Catalyst (amount)	Mo Naph. (500 ppm)	Mo Naph. (1000 ppm)	Mo Naph. (1000 ppm)+ Ill#6 coal (10% coal)	Mo Naph (1000 ppm)
Temp, °C	440	400	400	375
Press, psig	2087	1700	1870	1690
Time, min	120	545	545	300
H ₂ Consump g-mol/100g	1.1	0.77	0.77	0.23
Conv, wt% (bp<800°F)	71	35	45	22
Catalytic Dehydrogen g-mol/100g	0.49	0.48	0.51	0.60

Untreated CITGO VTR

Catalytic Dehydrogen = 0.35 g-mol/100g

Table III. Hydrotreatment Experiments of CITGO VTR in Toluene With $\text{Co}_2(\text{CO})_8$ and $\text{H}_2/\text{CO}=1:1$
(300 ml autoclave reactor)

Run #	77	80
Catalyst	$\text{Co}_2(\text{CO})_8$ (6.2%)	$\text{Co}_2(\text{CO})_8$ (6.7%)
Temp, °C	135	190
Press, psig	2650	3000
Time, min	120	120
H_2 Consump g-mol/100g	0.25	0.13
Conv, wt% (bp<800°F)	0	0
Catalytic Dehydrogen g-mol/100g	0.61	0.57

Untreated CITGO VTR

Catalytic Dehydrogen = 0.35 g-mol/100g

FUTURE WORK

The pretreated oils will next be characterized by elemental analysis to determine the extent to which hydrogen was added and sulfur and nitrogen removed. Selected pretreated oils may undergo additional characterization.

Based on preliminary results of these latest pretreatment experiments we believe that the chemical composition of the resids have been modified to significant extents. Except for a few repeat runs, this should conclude resid pretreatment experiments and we will next begin testing the pretreated oils in coprocessing.

Coprocessing experiments will be conducted in a microautoclave reactor. Initial testing will be conducted with an Illinois #6 coal. However, coprocessing experiments will also be conducted with a second coal, a Wyodak subbituminous sample.

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