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QUARTERLY PROGRESS REPORT

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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 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

During the third quarter of this year, we coprocessed an Illinois #6 coal (moisture:8.0%, ash:14.3, V.M.:36.9, and F.C.:40.9) with an AMOCO VTR as received and after it had been pretreated in three different ways. One pretreatment involved reacting the oil in the presence of hydrogen gas at 440 C for two hours. A second pretreatment included hydrotreating the oil with Mo naphthenate (2000 ppm of Mo) at 440 C for two hours. The third pretreatment was performed in two steps; first was a hydrotreatment with Mo naphthenate and then the oil was further upgraded with a Ni/Mo/Al₂O₃ catalyst.

Coprocessing runs were performed in a micro reactor. The reactor was charged with 3 grams of coal and 6 grams of oil and pressurized with H₂ gas to 1000 psig. Coprocessing runs

were made with and without a catalyst. Two different catalysts were used; Mo/Fe₂O₃/SO₄ and Mo naphthenate. Elemental sulfur was added in the catalytic runs in excess of the amount required to sulfide the catalyst.

The reactor was heated by submerging it in a fluidized sand bath. A reaction temperature of 440 C was reached within 12 min. and after a 30 min. reaction period, the reactor was removed from the sand bath and rapidly cooled with water. Liquid and solid products were washed from the reactor with THF. Solids were separated from the liquid by pressure filtration, and THF was removed from the liquid by use of a rotovapor.

Coal conversion was calculated by the equation,

$$Y_t = (1-Y)*100$$

where,

$$Y = (W_i - W_c - W_{ash} - W_{coke-oil}) / W_{maf}$$

W_i = THF insoluble fraction

W_c = weight of catalyst (MoS₂ or pyrrhotite)

W_{ash} = weight of ash in coal (14.3%)

$W_{coke-oil}$ = amount of coke produced from oil as estimated from runs made in absence of coal.

W_{maf} = moisture and ash free coal weight (77.8%)

Tables 1 and 2 summarize results of the coprocessing runs. Thermal coprocessing of the

coal with untreated AMOCO VTR resulted in 58 % coal conversion. Products comprised 41.1 % oils (pentane soluble), 19.7 % asphaltenes, 22.1 % gases, and 17.1 % coke. Yields were based on moisture and ash-free coal.

When the coal was thermally coprocessed with the AMOCO VTR after it had been hydrotreated with 2000 ppm Mo as Mo naphthenate, coal conversion increased to 79 % (this is an average of 2 runs- 78% and 80%). The quality of the products was also improved as determined by a higher oil yield of 58.9 %. The increase in oil yield was accompanied by lower gas and coke production.

When the AMOCO oil that had been upgraded in two steps was thermally coprocessed with the coal, a conversion of 85.4% was achieved. Oil yield was also higher for this run, at 67.2%, and gas yield was lower at 8.4%.

Coprocessing the coal with the AMOCO oil after it had been thermally (i.e., no catalyst) hydrotreated resulted in a coal conversion of 78%, which is similar to the conversion achieved when using the catalytically (Mo naphthenate) hydrotreated oil. This result was surprising and indicated that both oils worked equally well at facilitating coal dissolution. However, the products from the coprocessing run with the thermally treated oil had a lower oil and higher gas yield as compared to the coprocessing run with the catalytically treated oil (46.4% vs 58.9% and 21.2% vs 15.7%, respectively).

Adding the catalyst precursor Mo/Fe₂O₃/SO₄ at a concentration of 1 % (wt.) of the coal/oil mixture, resulted in little improvement in coal conversion (only 5 % for coprocessing with pretreated oil) or oil yield.

However, the catalyst precursor, Mo naphthenate, at a concentration of 1000 ppm of Mo

was effective in increasing both coal conversion and oil yield. For example, when the coal was catalytically coprocessed with the untreated AMOCO oil a coal conversion of 85 % was achieved. This compared to 58 % coal conversion without the catalyst. When the pretreated oil was used in place of the untreated oil, coal conversion was increased even further, to 90 %. This is over 20% higher than that achieved without the Mo catalyst. Coprocessing with Mo naphthenate also improved the oil yields over thermal coprocessing; the oil yield for the coprocessing run with the pretreated oil increased from 58.9 % to 61.6%.

In all coprocessing experiments, the pretreated oils gave better coal liquefaction conversions as compared to the untreated AMOCO VTR.

One important property of a liquefaction solvent is its ability to donate hydrogen. One measure of this property can be obtained by dehydrogenating the solvent and measuring the amount of hydrogen gas that is evolved or donated to an acceptor molecule. The untreated AMOCO VTR was dehydrogenated over a Pd/calcium carbonate catalyst in boiling phenanthridine (bp=350 C) at atmospheric pressure. At the end of 60 min., 20.9 cc of H₂ gas was evolved from the oil. This is equivalent to removal of 0.85 g of hydrogen per 100 g. of oil, which is about 8.3 % of the total hydrogen content of the oil, which had a hydrogen content of 10.2%.

Proton NMR analysis of the AMOCO VTR made before and after dehydrogenation indicated that hydrogens bonded to carbon atoms in polycyclic compounds at alpha and beta positions to aromatic carbons (i.e., hydroaromatic hydrogens) were removed. This is demonstrated in Figure 1. Based on NMR data, hydroaromatic hydrogen atoms present in the original AMOCO VTR totaled 0.92 g or 9 %. This number assumes that only half of the alpha

and beta hydrogen atoms are removed during dehydrogenation. The remaining alpha and beta hydrogen atoms are found in the newly formed aromatic rings. There is good agreement between the amount of hydrogen that was removed during the dehydrogenation experiment and the amount of available alpha and beta hydrogens predicted by proton NMR.

Based on proton NMR data, it was determined that the available hydrogen content of the AMOCO oil that had been pretreated with Mo naphthenate was 13.7% of the total hydrogen content of the oil. The pretreated oil that was upgraded in two steps had a removable hydrogen content of only 4.1 %. This is probably due to overhydrogenation of aromatic ring structures and/or cracking of naphthenic structures attached to aromatic rings. The percentage of removable hydrogen present in the thermally pretreated oil was 8%. This also was determined by proton NMR experiment. These results suggest that the percentage of available hydrogen was reduced as a result of severe hydrotreatment of the AMOCO VTR. Nevertheless, the pretreated oil that showed the lowest percentage of alpha and beta hydrogens (i.e., the oil pretreated in two steps) performed best as a coprocessing solvent. This suggests that other properties of the solvent, such as viscosity and its ability to transfer and shuttle hydrogen to coal, may play a more important role in the coprocessing of coal.

The ability of a solvent to transfer hydrogen to coal can be investigated in our dehydrogenation experiment by adding a hydrogen acceptor to the liquid, such as stilbene, and measuring the amount of the acceptor converted to saturated product. These experiments are being planned.

FUTURE WORK

Future plans include hydrotreating 500 to 1000 ml of the AMOCO VTR in a 1 liter autoclave reactor using Mo-naphthenate. Part of the upgraded oil will be treated with Shell- 324 catalyst to further upgrade the oil. Products from both pretreatment experiments will be evaluated by elemental analysis, vacuum distillation, proton NMR and catalytic dehydrogenation. The oils will also be coprocessed with coals so as to evaluate each as a coprocessing solvent.

Table 1 Coprocessing coal conversion for various catalysts and petroleum derived solvents.
(Conversions as % of maf Illinois #6 coal)

Catalyst	Untreated AMOCO VTR	Pretreated with (Mo-naphthenate	Pretreated thermally at 440 C	Pretreated step 1 Mo-naphthenate step 2 Shell 324
Thermal	58, 58	78, 80	78	85
Mo/Fe ₂ O ₃ /SO ₄	58	86	--	--
Mo naphthenate	85	90	--	--

Conditions: 440 C, 1000 psig H₂ (cold), 30 min.reaction, oil:coal=2:1
tubing bomb reactor, 200 rpm shaker speed.

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Table 2 Coprocessing yields (% of moisture and ash free coal and oil)

Oils (pentane sol.)

Catalyst	Untreated AMOCO VTR	Pretreated with (Mo-naphthenate)	Pretreated thermally at 440 C	Pretreated step 1 (Mo-naphthenate) step 2 (Shell 324)
Thermal	41.1	58.9	46.4	67.2
Mo/Fe ₂ O ₃ /SO ₄	35.0	60.1	---	---
Mo naphthenate	48.5	61.6	---	---

Gas

Catalyst	Untreated AMOCO VTR	Pretreated with (Mo naphthenate)	Pretreated thermally at 440 C	Pretreated step 1 (Mo-naphthenate) step 2 (Shell 324)
Thermal	22.1	15.7	21.2	8.4
Mo/Fe ₂ O ₃ /SO ₄	31.2	16.2	---	---
Mo naphthenate	22.4	13.4	---	---

Asphaltenes

Catalyst	Untreated AMOCO VTR	Pretreated with (Mo naphthenate)	Pretreated thermally at 440 C	Pretreated step 1 (Mo-naphthenate) step 2 (Shell 324)
Thermal	19.7	19.9	25.6	19.9
Mo/Fe ₂ O ₃ /SO ₄	16.9	19.7	---	---
Mo naphthenate	23.6	22.1	---	---

Conditions: 440 C, 1000 psig H₂ (cold), 30 min., oil:coal=2:1
tubing bomb reactor, 200 rpm shaker speed

Figure 1 ^1H NMR AMOCO VTR before and after catalytic dehydrogenation
 (7.15-4.7ppm:aromatic, 4.7-2.5:cyclic alpha, 2.5-2.0:alkyl alpha,
 2.0-1.4:cyclic beta, 1.4-1.0:alkyl beta, 1.0-0.5: gama)

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