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Role of the Resid Solvent in Catalytic Coprocessing with Finely Divided Catalysts

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Introduction

The research reported in this progress report describes the continuation of coal-resid coprocessing reactions that were discussed in the July to September 1994 Quarterly Report. During previous quarters, Maya and FHC-623 resids were evaluated in noncatalytic and catalytic reactions at 400 °C with Pittsburgh No. 8 and DECS-17 Blind Canyon coals. From the complete reaction matrix containing the two coals and two resids, it was found that the influence of resids on coprocessing depended on the type of coal used; for example, under catalytic reaction conditions, the hexane solubles of Maya resid increased coal conversion of Pittsburgh No. 8 coal but decreased that of DECS-17. In order to observe the intrinsic behavior of resids during coprocessing, another resid, Manji, and another coal, Illinois No. 6, are being tested. These reactions were begun this quarter. The results obtained are reported herein.

In order to evaluate the role of the different components in resids, the resids were separated into hexane soluble materials and hexane insoluble materials. The hexane solubles, which should contain the naphthenes present in the resid, and the untreated whole resids were reacted with coal at equivalent liquefaction conditions and at the same conditions as when the resids were reacted individually.

In the catalytic reactions, a Mo naphthenate catalyst precursor was used in the presence of sulfur. The catalyst generated in situ was MoS_2[1]. The effect of the reaction system on coal behavior during liquefaction was determined by coal conversion to THF solubles and solvent fractionation of the reaction products. Simulated distillations could not be performed this quarter because the laboratory was flooded from an overhead pipe that burst twice. The gas chromatograph, computer, and integrator were drenched twice with cold water. The equipment is now undergoing repair.

Experimental

Materials. The materials used during the quarter were Maya and Manji resids which were supplied by Amoco. The resids were used as whole resids or as the hexane soluble fractions of the resids in the reactions performed. The resids were dissolved in hexane and the hexane phase was decanted separating the hexane solubles from the hexane insolubles. In Table 1, the resids were fractionated into three solvent fractions: hexane solubles; toluene solubles, hexane insolubles; toluene insolubles, THF solubles; and THF insolubles or IOM which is insoluble organic matter and is ash free. The coprocessing solvents fractionated from the three solvents were quite different from one another. The two resids, FHC-623, which was used previously, and Manji were alike in solubility fraction contents, but these two resids contained less toluene solubles and more hexane solubles than did Maya resid as shown in Table 1.

The solvent fractionation procedure performed on the three resids involved dissolving 10 g of each resid in 150 ml of hexane and sonicating for 15 min. The sample was then centrifuged for 30 min and the hexane solubles were decanted from the hexane insolubles. Another 150 ml of hexane were added to the insolubles and the procedure was repeated a second and third time. The remaining solids were subjected to fractionation by toluene and THF sequentially following the same procedure as was used for hexane. The toluene solubles, hexane insolubles and THF solubles, toluene insolubles fractions were obtained along with the THF insolubles. The solvents used in this study were hexane, toluene and THF; all of which were HPLC grade and obtained from Fisher Scientific Co.

The coals used in this study were Pittsburgh No. 8 and Illinois No. 6 bituminous coals which were obtained from the Argonne Premium Coal Sample Bank and Blind Canyon (DECS-17) bituminous coal from the Penn State Coal Sample Bank. The coal particle size was 200 mesh. Proximate and ultimate analyses for the three coals are presented in Table 2.

The catalyst precursor used in this study was molybdenum (Mo) naphthenate, a slurry phase catalyst precursor. Molybdenum naphthenate was obtained from Shepherd Chemical and contained 6 wt% Mo. The Mo naphthenate was reacted in the presence of excess sulfur which was obtained from Aldrich.

Reaction Procedure. The reactions performed involved the reaction of resids with coal under noncatalytic and catalytic conditions. All of the reactions were performed in stainless steel tubular microreactiors of ~20 cm^3 volume. For each reaction, approximately 1 g of resid (weighed accurately to 0.0001 g) dissolved in 3 ml of THF was introduced into the reactor. The THF was evaporated by placing the microreactor in a vacuum oven overnight; coal was added to the system after the THF evaporated. In the catalytic reactions, Mo naphthenate was introduced at a loading of 1000 ppm Mo on total reactor charge. Elemental sulfur was added to the reactor at 3:1 S to Mo stoichiometric ratio assuming that MoS_2 was produced from Mo naphthenate.

The microreactor was pressurized with hydrogen three times to purge any air present. A hydrogen pressure of 1250 psig at room temperature was introduced for the reaction. The reaction conditions were 400 °C for 30 min with horizontal agitation of 400 cpm. After the reaction was completed, the tubular microreactor was immersed in cold water immediately quenching the reaction. All of the reactions were duplicated. The reaction products were removed from the reactor by washing the microreactor with several 10 ml aliquots of THF. The sample was then stored in a vial for further analysis. The reaction products dissolved in THF were subjected to gas chromatographic analysis to evaluate the temperature distribution of the resid products. The recovery of the reaction products was achieved by evaporating the THF solvent and drying the products in the oven over night at 50 °C.

Gas Chromatographic Analysis. The reaction products were analyzed using a Varian 3300 gas chromatograph equipped with a 25 m fused silica HT-5 capillary column and FID detection. For analysis of the resid reaction products, a temperature program starting at 100 °C increasing to 320 °C at a program rate of 2.5 °C/min was used. The GC output was automatically recorded and stored in a computer using a software named Peak96 from Hewlett Parkard. (Simulated distillation was not performed in quarter).

Calculations. The calculations performed to describe the coprocessing reactions are given in the following:

$$\text{conversion} = \left(1 - \frac{g(IOM)_{maf}}{g(coalcharged)_{maf}}\right) x\ 100\%$$

where IOM is the insoluble organic material and maf is moisture and ash free.

For Pittsburgh No. 8 as described in Table 2, the simplified equation is

$$\text{conversion} = \left(1.102 - 1.20 x \frac{g(IOM)_{maf}}{g(coalcharged)_{maf}}\right) x\ 100\%$$

For Blind Canyon DECS-17, the simplified equation is:

$$\text{conversion} = \left(1.070 - 1.112 x \frac{g(IOM)_{maf}}{g(coalcharged)_{maf}}\right) x\ 100\%$$

For Illinois No. 6 coal, the simplified equation is:

$$\text{Coal conversion} = \left(1.183 - 1.286 x \frac{g(IOM)_{maf}}{g(coalcharged)_{maf}}\right) x\ 100\%$$

Results and Discussion

The research performed this quarter focused on coprocessing a highly reactive coal, Illinois No. 6 coal, in conjunction with Maya and Manji resids. Selection of the third coal was prompted by the inconsistent results that were obtained previously when Pittsburgh No. 8 and Blind Canyon DECS-17 coals were used with Maya and FHC-623 resids. Manji was introduced into the sample matrix for the same reason since the two other resids were quite different in composition and gave substantially different results.

Previous results using Maya and FHC-623 resids showed that the interaction between resid and coal was affected by the composition of the resid or resid fraction. For example, the saturate fraction of Maya resid when reacted with Pittsburgh No. 8 coal resulted in decreased conversion to THF solubles, but when the Maya saturates were reacted with Blind Canyon coal, coal conversion to THF solubles increased. These two coals showed substantial differences in their inherent reactivity; Pittsburgh No.8 was much more reactive than Blind Canyon coal under equivalent reaction conditions and the same type of resid solvent. A highly reactive coal may provide valuable information concerning the interaction between the resid fraction and the coal, since the reactive coal may be more responsive to the chemical composition and characteristics of the resid.

The liquefaction of Illinois No. 6 coal is presented in Table 3. The reactions that were performed included reacting coal by itself, with a relatively inert solvent, hexadecane, with Maya whole resid, and with Manji hexane solubles. Both thermal and catalytic reactions were performed. The catalyst used was Mo naphthenate and sulfur. The reaction matrix is not complete at this time but will be completed during the next quarter. The thermal and catalytic reactions of coal alone yielded very similar conversion results. This effect was most probably caused by the slurry phase catalyst being ineffectual because the catalyst was not dispersed in a solvent medium and, hence, was not as accessible. Hexadecane as a solvent in the thermal reaction, served as an antisolvent and decreased the amount of coal conversion compared to the coal alone thermal reaction. The catalytic reaction with hexadecane increased the amount of coal conversion compared to the coal alone reaction. In the thermal reaction, hexadecane decreased coal conversion, while in the catalytic reaction hexadecane increased mass transfer between the dissolving coal molecules and the slurry phase catalyst. This increased contact resulted in increased conversion.

The thermal and catalytic reactions with Illinois No. 6 and whole Maya resid yielded suspect results, particularly for the catalytic reactions. These reactions gave low coal conversions and a substantial amount of error in the amount of conversion between the two reactions. These reactions will be repeated during the upcoming quarter to verify the results.

The last reactions performed were with the hexane soluble fraction of Manji resid. The thermal reaction of Illinois No. 6 and Manji hexane solubles resulted in 53.7% coal conversion. This thermal conversion was greater than either of the other two coals with the hexane soluble resid fraction (Table 4). The catalytic reaction with Manji hexane soluble fraction and coal increased coal conversion by 10% compared to the thermal reaction yielding 65.3%. However, the conversion of Illinois No. 6 coal was lower by 10% than the conversion either of the other two coals at equivalent reaction conditions. Some of the results with Blind Canyon and Pittsburgh No.8 coals and Manji hexane soluble fraction as the solvent had large error and will be repeated.

Conclusions

A compilation of the thermal and catalytic coprocessing reactions performed is presented in Table 5. All of the thermal reactions converted less than the catalytic reactions except for the thermal and catalytic reactions of Illinois No. 6 with whole Maya resid. The different types of solvents used had varying effects depending on their composition and interactions with coal. Pittsburgh No.8 coal seemed to respond most favorably to the presence of a solvent and catalyst. Substantially higher coal conversions were obtained than in the thermal reactions. Blind Canyon coal also responded favorably to the solvent and catalyst, but not to the same extent as Pittsburgh No. 8. Coprocessing of Illinois No. 6 with the resids tested to date was not favorable. The solvent hexadecane promoted the most favorable results; neither Maya nor Manji enhanced coal conversion. Further experiments will be performed to determine the interactions of Illinois No. 6 with the other resids and resid fractions. Also Manji whole resid and saturates will be reacted with all three coals to determine their effect and interaction.

Simulated distillations will be performed next quarter as soon as the water damaged equipment is repaired.

References

Kim, H., Curtis, C.W., Cronauer, D.C. and Sajkowski, D.J. "Characterization of Catalysts from Molybdenum Naphthenate," *ACS Fuel Div. Prep. 34,* 4, 1989, 1431.

Table 1. Fractions of FHC-362, Maya and Manji Resid

	Hexane Solubles (wt%)	Toluene Solubles (wt%)	THF Solubles (wt%)	Recovery (wt%)
FHC-623	83.3±1.1	14.9±0.4	1.8±0.8	99.9±0.9
Maya	62.9±1.1	37.1±1.1	0±0	99.8±0.9
Manji	86.2±0.7	13.9±0.7	0±0	99.9±0.7

Table 2. Analysis of Pittsburgh No. 8, Blind Canyon DECS-17 and Illinois No. 6 Coals[a]

	Pittsburgh No. 8	Blind Canyon (DECS-17)	Illinois No. 6
Proximate Analysis, % (As Received)			
Moisture	1.65	3.74	7.97
Ash	9.1	6.32	14.25
Volatile Matter	37.2	45.0	36.86
Ultimate Analysis (maf basis), wt%			
Carbon, %	83.2	82.1	77.67
Hydrogen, %	5.3	6.2	5.00
Nitrogen, %	1.6	1.4	1.37
Chlorine, %	0.12	0.12	0.06
Pyritic Sulfur, %	1.4	0.02	2.81
Sulfate Sulfur, %	0.01	0.01	0.01
Organic Sulfur, %	0.8	0.41	2.01
Oxygen, %	8.83	NA[b]	13.51
H/C ratio	0.77	0.91	0.77
Dry Btu	13629	13826	11951
Rank	HVB	HVBA	HVB
Fe, % (Calculated from FeS_2)	1.23	0.01	2.46

[a] Analyses of coal were obtained from Argonne Premium Coal Sample Bank and the Penn State Coal Sample Bank.
[b] NA = Not available

Table 3. Liquefaction Reactions of Illinois No. 6 Coal at 400 °C[a]

Reactant	Reaction Condition	THF Solubles (%)	IOM (%)	Coal Conversion (%)	Recovery (%)
Coal	Thermal	56.8±0.6	43.2±0.6	62.8±0.8	84.2
Coal	Catalytic	56.0±1.3	44.0±1.3	61.8±1.6	88.6
Hexadecane + Coal	Thermal	44.3±0.7	55.7±0.7	46.7±0.9	79.4
Hexadecane + Coal	Catalytic	64.5±0.6	35.5±0.6	72.7±0.8	82.0
Maya Whole Resid + Coal	Thermal	55.8±1.1	44.2±1.1	61.4±1.3	86.9
Maya Whole Resid + Coal	Catalytic	54.3±4.2	45.7±4.2	59.5±5.4	88.5
Manji Hexane Solubles + Coal	Thermal	49.7±1.3	50.3±1.3	53.7±1.6	86.7
Manji Hexane Solubles + Coal	Catalytic	58.8±1.3	41.2±1.3	65.3±1.8	81.0

[a] Reaction Conditions: 400 °C, 30 min, 8.7 MPa H_2 pressure at ambient temperature, agitated at 400 rpm, 1000 ppm of Mo introduced as Mo naphthenate plus elemental sulfur.

Table 4. Coal Conversion in the Coprocessing Reactions of Pittsburgh No. 8, DECS-17 Blind Canyon and Illinois No. 6 Coals with Manji Resid[a]

Reactant	Condition	THF Solubles (%)	IOM (%)	Coal Conversion (%)	Recovery (%)
Hexane Soluble + Pittsburgh No. 8	Thermal	27.8±0.3	72.2±0.3	29.3±0.4	96.6
Hexane Soluble + Pittsburgh No. 8	Catalytic	70.8±3.0	29.2±3.0	77.5±3.3	100.6
Hexane Soluble + DECS-17	Thermal	48.9±9.9	51.1±9.9	50.1±11.2	85.3
Hexane Soluble + DECS-17	Catalytic	74.6±3.2	25.4±3.2	78.7±3.5	91.2
Hexane Soluble + Illinois No. 6	Thermal	49.7±1.3	50.3±1.3	53.7±1.6	86.7
Hexane Soluble + Illinois No. 6	Catalytic	58.8±1.3	41.2±1.3	65.3±1.8	81.0

[a] Reaction Conditions: 400 °C, 30 min, 8.7 MPa H_2 pressure at ambient temperature, agitated at 400 rpm, 1000 ppm of Mo introduced as Mo naphthenate plus elemental sulfur.

Table 5. Coal Conversion in Coprocessing with Three Resids[a]

Reactions	Coal Conversion (%)					
	Pittsburgh No. 8		Blind Canyon DECS-17		Illinois No. 6	
	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
Coal	44.8±2.1[a]	61.7±4.2	26.4±0.4	45.3±0.8	62.8±0.8	61.8±1.6
Coal+Hexadecane	59.1±4.7	84.9±3.3	31.9±0.6	48.4±1.1	46.7±0.9	72.7±0.8
Maya Complete Reaction Matrix						
Coal+Whole Resid	56.2±5.2	89.3±1.1	31.8±2.2	64.0±2.3	61.4±1.3	59.5±5.4
Coal+Hexane Solubles	49.2±2.2	82.9±2.2	40.5±0.7	49.2±0.2	NYP[b]	NYP
Coal+Saturate Fraction	37.2±1.4	59.8±1.4	37.7±1.8	57.7±7.4	NYP	NYP
FHC-623 Complete Reaction Matrix						
Coal+Whole Resid	68.4±4.1	77.9±1.8	49.2±0.2	72.9±1.4	NYP	NYP
Coal+Hexane Solubles	44.3±4.4	77.8±6.6	43.6±0.7	63.4±0.6	NYP	NYP
Coal+Saturate Fraction	29.9±5.1	56.9±5.6	27.7±3.0	53.9±2.1	NYP	NYP
Manji Complete Reaction Matrix						
Coal+Whole Resid	NYP	NYP	NYP	NYP	NYP	NYP
Coal+Hexane Solubles	29.3±0.4	77.5±3.3	50.1±11.2	78.7±3.5	53.7±1.6	65.3±1.8
Coal+Saturate Fraction	NYP	NYP	NYP	NYP	NYP	NYP

[a] Reaction Conditions: 400 ℃, reaction time 30 min, agitated at 400 rpm, 8.7 MPa H_2 pressure at ambient temperature, 1000 ppm of Mo introduced as Mo naphthenate plus elemental sulfur.

[b] NYP = not yet performed