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THE ROLE OF THE RESID SOLVENT IN COPROCESSING WITH FINELY DIVIDED CATALYSTS

Quarterly Report
January to March 1994

Contract No. DE-AC22-91C91055

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Introduction

The research reported in this progress report describes the continuation of coal-resid coprocessing reactions which were begun last quarter (October to December 1993). During last quarter, Maya and FHC-623 resid were evaluated as whole resids and as the hexane soluble fraction in noncatalytic and catalytic reactions at 400°C. During this current quarter, reactions were performed using Pittsburgh No. 8 bituminous coal and several different solvents including Maya and FHC-623 resids.

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 naphthene present in the resid, and the untreated whole resids were reacted with coal at the same liquefaction conditions as when the resids were reacted individually.

In the catalytic reactions, a Mo naphthenate precursor was used in the presence of sulfur. The catalyst generated in situ was MoS_2 (1). The effect of different reaction conditions on the resid was monitored by gas chromatography in which the retention times of the eluting peaks were determined. The amount of eluent present at different retention times was determined and compared. 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.

Experimental

Materials. The materials used during this quarter were Maya and FHC-623 resids which were supplied by Amoco. The resids were used as whole resids or as the hexane soluble fraction of the resids in the reactions performed. Both resids were dissolved in hexane to obtain hexane solubles and 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 solvents fractionated from FHC-623 were

quite different from those obtained from Maya resid. The FHC-623 resid contained less toluene solubles and more hexane solubles than did Maya resid as shown in Table 1. Hence, these two resids were composed of considerably different components as evidenced by their different solubility characteristics.

The solvent fractionation procedure performed on Maya and FHC-623 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 the 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 coal used in this study was Pittsburgh No. 8 bituminous coal which was obtained from the Argonne Premium Coal Sample Bank. The coal particle size was 200 mesh. An proximate and ultimate analysis for Pittsburgh No. 8 is presented in Table 2.

The model compound anthracene was also used in this study. Anthracene was used as a model hydrogen acceptor in the resid reactions. Anthracene (98% purity) and its partially saturated analogues, dihydroanthracene (DHA), hexahydroanthracene (HHA), and octahydroanthracene (OHA), were obtained from Aldrich Chemical Company. The partially saturated anthracenes were used as gas chromatography standards. Biphenyl, which was used as an internal standard in the gas chromatographic analyses of anthracene and its reaction products, was also obtained from Aldrich. All model compounds were used as received.

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.

Reaction Procedures. The reactions performed involved the reaction of resids under noncatalytic and catalytic conditions. In some of the reactions, a hydrogen acceptor, anthracene was present while in other reactions, anthracene was not present. All of the reactions were performed in stainless steel tubular microreactors of $\sim 20\text{ cm}^3$ 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. For the reactions containing anthracene, 0.5 g of anthracene was charged to the microreactor. 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 to sulfide the catalyst.

In preparing the microreactor for reaction, the microreactor was pressurized with hydrogen three times to purge any air present. A hydrogen pressure of 1250 psig at room temperature was introduced. The reaction conditions were 400°C for 30 min with horizontal agitation of 400 cpm. After the reaction was complete, the tubular microreactors were immersed in cold water immediately quenching the reaction. All of the reactions were duplicated. The reaction products were removed from the reaction by washing the microreactor with 10 ml 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 resid from the reaction was achieved by evaporating the THF solvent.

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 Packard. When anthracene was present in the reaction as a hydrogen acceptor, quantitation was performed using the internal standard method. Biphenyl (obtained from Aldrich) was used as the internal standard. Response factors were obtained for anthracene and for each of the partially saturated anthracene reaction products: dihydroanthracene (DHA), tetrahydroanthracene (THA) and hexahydroanthracene (HHA). The response factors were checked every 10 days and updated as necessary. The hydrogen accepted by anthracene was calculated on the basis of the reaction products produced. The H₂ accepted was equal to (1 x DHA mol% + 2 x THA mol% + 3 x HHA mol%) x 100%.

Coprocessing Reactions. In the coprocessing reactions utilizing coal and resid or the hexane soluble fraction of resid, 1 g of coal and 1 g of resid were charged into the reactor along with Mo naphthenate at 1000 ppm Mo on a total charge basis and elemental sulfur. The reactor was purged with H₂ three times and then pressurized with H₂ to 1250 psig at ambient temperature. The reactions were performed at 400°C for 30 min. The solid products were scrapped from the reactor and the remaining material was recovered by washing with 150 ml of THF until the THF from the bomb was clear. The recovered material was centrifuged for 60 min after which the soluble material was decanted and the undissolved solids were washed twice again with 150 ml of THF. The THF was removed by rotary evaporation. The products were dried in a vacuum oven at 50°C overnight.

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

$$\text{Total Recovery} = \frac{\text{g Recovered Solubles} + \text{g IOM}}{\text{g Coal and g Resid Charge}} \times 100\%$$

The following assumptions were made to determine coal conversion. Coal and resid were recovered equally while IOM was derived exclusively from coal.

$$\text{Coal Conversion} = \left(1 - \frac{g(\text{IOM})_{\text{maf}}}{g(\text{coal charged})_{\text{maf}}}\right) \times 100\%$$

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

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

$$\text{Coal Conversion} = \left(1.102 - 1.120 \times \frac{g\text{IOM}}{g \text{ coal charge}}\right) \times 100\%$$

Analysis of Resid by Gas Chromatography

Historically, the application of gas chromatography to the analyses of petroleum and petroleum fractions centered on the light distillate fraction¹. The compounds in these reactions could be described by their relative retention times and their corresponding boiling point curve as simulated by the boiling points of known compounds.

The gas chromatographic method of analysis relies on the phenomenon that hydrocarbon, as present in petroleum fractions, elute from a nonpolar GC column in order of their boiling points. Because of the regularity of the elution order of hydrocarbon components, retention times can be converted to equivalent boiling points, i.e. simulated distillation temperatures. The peak area obtained as an accumulated detector response can be related to the amount of sample distilled². This simulated distillation method has been standardized as ASTM D 2887-89.

In simulated distillation, the hydrocarbon sample is introduced into a GC column that separates hydrocarbons in order of increasing boiling point. The column temperature is raised at a reproducible rate and the accumulated peak area is recorded throughout the analysis. Boiling points are assigned to the retention time axis from a calibration curve which was developed by analyzing a known mixture of hydrocarbons covering the expected boiling point range. Both the analysis and the calibration curve must be performed under equivalent GC conditions. From the data obtained, the boiling point range distribution of the hydrocarbon sample can be obtained³.

In the current work, the concept of simulated distillation was applied to the reacted and virgin resids and resid fractions. At this time, the application of a boiling point range has not been applied to the retention time axis. Therefore, the data presented in the results tables are given in terms of time. Since the method appears to be able to distinguish between different reaction conditions, a boiling point scale based on resid compound types will be investigated next quarter.

The resid analysis performed in the research reported herein was accomplished according to the following procedure. The products recovered from resid or coprocessing (resid plus coal) reactions, were dissolved in THF. Approximately 0.5 μ l of THF soluble product was injected. The GC column (HT-5 fused silica capillary column from SGE) was programmed from 100°C to 320°C at a program rate of 2.5°C/min. The injected sample volume of 0.5 μ l was used on the basis of the number of peaks that were detectable above the threshold. Lower injection volumes resulted in some sample peaks not being detected while higher injection volumes did not show any additional peaks. The upper column temperature was selected on the basis of the resid boiling point range provided by Amoco. The analysis was performed carefully and each injection was carefully synchronized with the initiation of the temperature program. Baseline GC experiments were performed daily by running the temperature program without a sample injection.

The simulated distillation curves for the resids were subdivided into five groups according to retention time. A sample chromatogram is presented in Table 1. The cut points were 25, 45, 60 and 75 min. The normal paraffin, hexadecane, which has been used as a model solvent in some of these experiments, has a boiling point of 289°C and elutes at 25 min. Hence, the cut point of 25 min separates the boiling range into two broad categories: (1) boiling points less than 290°C for peaks eluting before 25 min. and (2) boiling points greater than 290°C for peaks eluting after 25 min. This next quarter's research will be performed to establish corresponding boiling points for peaks eluting at 45, 60 and 75 min.

Products from coal liquefaction reactions not containing resid were also analyzed by the simulated distillation method. Only one peak and occasionally two were visible in the chromatogram. These peaks were deducted from the resid peak areas.

Results and Discussion

This quarter's research focused upon performing coprocessing reactions with coal and whole resid or the hexane soluble fraction of resid. In addition, analysis of the resid reactions performed last quarter were also performed. The gas chromatographic distillation curve was subdivided further than was reported last quarter. Last quarter the cut point started at 45 min. The time before 45 min has been subdivided into two fractions: < 25 min and 25 to 45 min. This subdivision allows better differentiation of the upgrading occurring among the different products.

In Table 3, the reactions of Maya whole and Maya hexane soluble fractions gave similar distributions of the resid. However, when anthracene was present in the reactions substantial differences were observed in the GC distribution between those reactions and the ones without anthracene. The noncatalytic and catalytic reactions gave different amounts at times less than 25 min with the noncatalytic being much less. The next fraction 25 to 45 min fraction for both reactions using anthracene was higher than without anthracene. By contrast, the FHC-623 resid showed substantial differences in the $t < 25$ min among the reactions. The catalytic reactions tended to have less in that fraction than did the noncatalytic reactions (Table 4). As with the Maya resid, the FHC-623 resid had a higher amount in the 25 to 45 min range when anthracene was present than in those without anthracene.

Conversion of the Coal During Coprocessing. Reactions were performed using both Maya and FHC-623 resids and their hexane soluble fraction with Pittsburgh No. 8 coal (Tables 5 and 6). These reactions were performed under noncatalytic and catalytic conditions. For both resids more

coal conversion was obtained in the catalytic reactions than in the noncatalytic reactions. For both resids more coal conversion was obtained noncatalytically with the whole resid than with the hexane soluble fraction. Noncatalytic reaction with Maya and FHC-623 resid showed differences between the coal conversion in the whole resid and hexane soluble resid. The whole Maya resid achieved 56.2% coal conversion noncatalytically while the hexane soluble fraction yielded 49.2% coal conversion. The FHC-623 resid showed even larger differences in coal conversion in the noncatalytic reaction: 68.4% conversion with the whole resid and 44.3% conversion with the hexane soluble fraction. The chemical composition of the whole resid was more favorable solvent for Pittsburgh No. 8 coal than the hexane soluble fraction. The composition of the whole Maya resid compared to the hexane solubles affected the catalytic reaction with the whole resid being more effective; however, the FHC-623 resid composition did not (whole versus hexane soluble) affect the catalytic reaction with conversions being nearly the same.

In Table 7, reactions were performed with Pittsburgh No. 8 coal with and without a solvent under noncatalytic and catalytic conditions. The reaction solvent used was hexadecane, a straight chain hydrocarbon, which only provides a fluid medium and does not react with coal. The presence of the fluid medium increases coal conversion under both noncatalytic and catalytic conditions by providing a means of mass transport for the reacting H_2 molecules. The solvent also allowed better contact between the slurry phase catalyst and the dissolving coal molecules.

Table 8 presents a comparison of the coal conversions achieved under noncatalytic and catalytic conditions. If the coal conversion in hexadecane is taken as the benchmark value where the solvent aids in mass transport but does not participate in the reaction, then the relative effect of the other resid solvents can be ascertained under both catalytic and noncatalytic conditions.

The benchmark value under noncatalytic conditions was $59.1 \pm 4.7\%$ conversion. The coal conversion achieved with Maya whole resid of $56.2 \pm \%$ fell within experimental error of the

benchmark value, indicating that Maya whole resid neither promoted nor inhibited coal conversion. By contrast, Maya hexane soluble yielded a noncatalytic coal conversion of 49.2%, suggesting that the removal of Maya asphaltenes decreased the solvent power. For FHC-623 noncatalytic reactions, the whole resid promoted coal conversions yielding a coal conversion of 68.4% which is higher than the benchmark. The hexane soluble fraction of FHC-623 gave the least coal conversion of 44.3%. Comparison of the coal conversions achieved by the whole resid and hexane solubles of FHC-623 evinced that the FHC-623 asphaltene fraction strongly promoted coal conversion. This promotion may have resulted from the chemical or metal composition of the asphaltenes. We are planning to obtain an ultimate analysis and a metals analysis of the two resids and their hexane solubles fraction.

Under catalytic reaction conditions, the effect of the resids changed. The benchmark value using hexadecane was $84.9 \pm 3.3\%$. The whole Maya resid achieved a coal conversion of 89.3%, promoting coal conversion while the hexane soluble fraction was within experimental error. The presence of asphaltenes seemed to promote the catalytic reaction and did not poison the catalyst. The FHC-623 resid behaved differently. Both the whole resid and the hexane soluble fraction achieved the same coal conversion of 77.9%, both of which were below the benchmark. The reasons for their behavior may have been different. Analyses of their composition will help elucidate the reasons.

Reaction of the Resids During Coprocessing. The resids, Maya and FHC-623, used in this study showed very different levels of reactivity as shown in Tables 3 and 4. The degree of reaction was expressed in terms of retention time in a simulated GC distillation. The GC fraction with a retention time of less than 25 min corresponded to a boiling point fraction of 290°C or less. Likewise, retention times above 25 min corresponded to higher boiling points.

On the basis of the amounts eluted at different retention times the resids behaved quite differently in the resid reactions without coal. Maya resid eluted at later retention times than did FHC-623. When Maya resid was reacted in both noncatalytic and catalytic reactions, both

hydrotreatments resulted in substantial upgrading of the resid. At both conditions, the resids eluted at substantially shorter reaction times than the unreacted resid. By contrast, when anthracene as a hydrogen acceptor was introduced into either noncatalytic or catalytic reactions, differences in the amount of material eluted at different retention times was obtained. More upgrading of Maya resid occurred in the catalytic anthracene reaction than in the noncatalytic reaction, while for FHC-623 less upgrading of the resid occurred catalytically. The anthracene presence appeared to compete for gaseous hydrogen with the resid and served as a hydrogen sink, effectively reducing the amount of gaseous hydrogen being accepted by the resid. Anthracene may have also accepted hydrogen from the resid.

When coprocessing reactions of Maya resid with coal were performed, the effect of catalyst addition was apparent. Both coal and resid were upgraded simultaneously. However, coal like anthracene changed the amount of upgrading that the resid underwent during the reaction. Comparing the coprocessing reaction to that of the resid alone showed that the fraction between 25 and 45 min was less with the coprocessing reaction than with resid alone.

The FHC-623 resid, when reacted alone, was quite sensitive to catalyst. However, the noncatalytic reaction yielded more of the resid at eluting lower retention time than did the catalytic reaction. The same behavior was observed when anthracene was present although the differences in the amount was less. The catalyst, Mo naphthenate plus sulfur, decreased the amount of the light fraction present. Perhaps the catalyst helped to reduce the amount of hydrocracking occurring. Similar results were obtained with noncatalytic and catalytic coprocessing reactions although substantial differences in retention times were observed between the whole resid as the solvent and the hexane soluble resid.

Future Work

The GC method for analysis of resids provided a means for determining the effect of the reaction conditions on the reaction of the resid. Next quarter further calibration of the retention times against known boiling points of n-paraffin and aromatic species will be undertaken.

Two primary experiments will be performed next quarter. First, the same reaction sequence of whole and hexane soluble Maya resid and whole and hexane soluble FHC-623 resid with DECS-17 coal will be performed. Secondly, either Pittsburgh No. 8 or DECS-17 coal will be reacted with the saturate fraction of the hexane soluble portion of Maya and FHC-623 resid. The saturate fractions of the resids will also be reacted alone and with anthracene.

References

1. Camin, David L., History of Chromatography in Petroleum Analysis, Chapter 1, Chromatography in Petroleum Analysis, Marcel Dekker, Inc., 1979.
2. Butler, Ronald C. Simulated distillation by gas chromatography. Chapter 4, Chromatography in Petroleum Analysis, Marcel Dekker, Inc., 1979.
3. ASTM Designation: D 2887-89.

Table 1. Fractions of FHC-362 and Maya Resid

	Hexane Solubles (wt%)	Toluene Solubles (wt%)	THF Solubles (wt%)
FHC-623	83.3(1.1)*	14.9(0.4)	1.8(0.8)
Maya	62.9(1.1)	37.1(1.1)	0(0)

*mean (standard deviation)

Table 2. Pittsburgh No. 8 Coal Proximate and Ultimate Analysis

Proximate Analysis (wt%)	
Moisture	1.65
Ash	9.1
Volatile Matter	37.2
Ultimate Analysis (wt%)	
C	83.0
H	5.3
O	9.0
S	2.2

Formula: $C_{100}H_{76.7}O_{8.0}N_{1.7}S_{0.4}$ based on 100 C atoms.

Source: Users Handbook for the Argonne Premium Coal Sample Program.

Table 3. Gas Chromatographic Fraction Distributions from Maya Resid Reacted Under Different Conditions

GC Fractions of THF Soluble Material								
GC Fractions Obtained from THF Soluble Material	Untreated Resid	Hexane Solubles of Unreacted Resid	Non-catalytic Reaction of Whole Resid	Catalytic Reaction of Whole Resid	Non-catalytic Reaction of Hexane Soluble Resid Fraction	Catalytic Reaction of Hexane Soluble Resid Fraction	Non-catalytic Reaction of Hexane Soluble Resid Fraction with Anthracene	Catalytic Reaction of Hexane Soluble Resid Fraction with Anthracene
t < 25 min	0	0.111	0.569 ^a (0.055)	0.540 (0.085)	0.513 (0.047)	0.505 (0.059)	0.345 ^b (0.171)	0.570 ^b (0.088)
25 to 45 min	0	0	0.274 (0.035)	0.224 (0.034)	0.280 (0.02)	0.284 (0.102)	0.463 (0.074)	0.363 (0.074)
45 to 60 min	0	0	0.085 (0.010)	0.094 (0.016)	0.094 (0.01)	0.109 (0.006)	0.169 (0.065)	0.042 (0.013)
60 to 75 min	1	0	0.057 (0.014)	0.107 (0.018)	0.086 (0.02)	0.087 (0.037)	0.023 (0.033)	0.026 (0.00)
> 75 min	0	0.889	0.016 (0.003)	0.035 (0.050)	0.027 (0.00)	0.016 (0.001)	0.000 (0.000)	0.000 (0.00)
Recovery, %	100	100	86.9	81.9	79.2	85.0	87.6	86.3

^amean (standard deviation).

^bThese analyses did not include any of the anthracene peaks.

Table 4. Gas Chromatographic Fraction Distributions from FHC-623 Resid Reacted Under Different Conditions

GC Fractions of THF Soluble Material								
Time for GC Fractions Obtained from THF Soluble Material	Untreated Resid	Hexane Solubles of Untreated Resid	Non-catalytic Reaction with Whole Resid	Catalytic Reaction with Whole Resid	Non-catalytic Reaction with Hexane Soluble Resid Fraction	Catalytic Reaction with Hexane Soluble Resid Fraction	Non-catalytic Reaction with Hexane Soluble Resid and Anthracene	Catalytic Reaction with Hexane Soluble Resid and Anthracene
<25 min	0	0.090	0.519 ^a (0.046)	0.306 (0.016)	0.485 (0.002)	0.194	0.397 ^b (0.039)	0.263 ^b (0.025)
25 to 45 min	0.201	0.161	0.164 (0.033)	0.203 (0.065)	0.172 (0.042)	0.387	0.387 (0.041)	0.556 (0.098)
45 to 60 min	0.211	0.171	0.105 (0.021)	0.219 (0.028)	0.114 (0.02)	0.087	0.099 (0.02)	0.111 (0.064)
60 to 75 min	0.307	0.312	0.134 (0.016)	0.162 (0.011)	0.145 (0.01)	0.186	0.092 (0.00)	0.050 (0.001)
> 75 min	0.282	0.266	0.078 (0.013)	0.110 (0.024)	0.084 (0.01)	0.146	0.024 (0.02)	0.020 (0.007)
Recovery, %	100	100	91.2	87.2	88.6	83.2	77.4	90.2

^amean (standard deviation).

^bThese analyses did not include any of the anthracene peaks.

Table 5. Reactions of Maya Resid and Pittsburgh No. 8 Coal

Reaction	Coal Product Distribution (%)			Resid Product Distribution (%)					Recovery (%)
	THF Solubles	THF Insolubles	Coal Conversion ^a	t < 25 ^c	25 < t < 45	45 < t < 60	60 < t < 75	t > 75	
Whole Resid + Coal Thermal Reaction	46.8 ^b (4.2)	53.2 (4.2)	56.2 (5.2)	0.569 (0.055)	0.115 (0.041)	0.221 (0.038)	0.082 (0.020)	0.013 (0.018)	90.4
Whole Resid + Coal Catalytic Reaction	80.0 (1.7)	20.0 (1.7)	89.3 (1.1)	0.910 (0.031)	0.062 (0.015)	0.028 (0.017)	0.000 (0.000)	0.000 (0.000)	96.7
Hexane Soluble Resid + Coal Thermal Reaction	41.4 (3.5)	58.7 (3.5)	49.2 (2.2)	0.248 (0.030)	0.321 (0.006)	0.233 (0.006)	0.140 (0.011)	0.059 (0.007)	92.9
Hexane Soluble Resid + Coal Catalytic Reaction	75.5 (3.1)	24.5 (3.1)	82.9 (2.2)	0.692 (0.122)	0.070 (0.062)	0.116 (0.027)	0.090 (0.018)	0.031 (0.016)	88.9

^amoisture and ash free basis

^bmean (standard deviation)

^ct is GC retention time

Table 6. Reactions of FHC-623 Resid and Pittsburgh No. 8 Coal

Reaction	Coal Product Distribution (%)			Resid Products Distribution (%)					Recovery (%)
	THF Solubles	THF Insolubles	Coal Conversion ^a	t < 25°	25 < t < 45	45 < t < 60	60 < t < 75	t > 75	
Whole Resid + Coal Thermal Reaction	54.2 ^b (1.5)	45.8 (1.5)	68.4 (4.1)	0.221 (0.033)	0.328 (0.024)	0.213 (0.003)	0.176 (0.024)	0.062 (0.051)	81.2
Whole Resid + Coal Catalytic Reaction	69.9 (1.4)	30.1 (1.4)	77.9 (1.8)	0.190 (0.044)	0.325 (0.011)	0.183 (0.002)	0.198 (0.001)	0.104 (0.011)	96.1
Hexane Soluble Resid + Coal Thermal Reaction	32.9 (6.0)	67.1 (6.0)	44.3 (4.4)	0.516 (0.030)	0.137 (0.013)	0.180 (0.039)	0.120 (0.039)	0.047 (0.013)	87.8
Hexane Soluble Resid + Coal Catalytic Reaction	69.7 (5.9)	30.3 (5.9)	77.8 (6.6)	0.503 (0.059)	0.121 (0.053)	0.136 (0.011)	0.159 (0.006)	0.081 (0.036)	95.1

^amoisture and ash free basis

^bmean (standard deviation)

^ct is GC retention time

Table 7. Coal Reactions at Different Reaction Conditions

Coal Reactions	Coal Product			Recovery (%)
	THF Solubles	THF Insolubles	Coal Conversion ^a	
Coal Extraction	3.4 ^b (0.4)	96.6 (0.4)	0.55 (0.49)	101
Coal Thermal Reaction	39.1 (1.3)	60.9 (1.3)	44.8 (2.1)	95.9
Coal Catalytic Reaction	55.3 (5.9)	44.7 (5.9)	61.7 (4.2)	96.9
Hexadecane + Coal Thermal Reaction	46.1 (3.3)	53.9 (3.3)	59.1 (4.7)	84.7
Hexadecane + Coal Catalytic Reaction	76.6 (0.3)	23.4 (0.3)	84.9 (3.3)	98.1

^amoisture and ash free basis

^bmean (standard deviation)

Table 8. Coal Conversion at Different Reaction Conditions

Reaction	Coal Conversion (%)	
	Thermal	Catalytic
Coal	44.8	61.7
Coal + Hexadecane	59.1	84.9
Coal + Maya Whole Resid	56.2	89.3
Coal + Maya Hexane Soluble	49.2	82.9
Coal + FHC-623 Whole	68.4	77.9
Coal + FHC-623 Hexane Soluble	44.3	77.8
Coal Extraction with THF	0.55	

$$\text{Coal Conversion} = (1.102 - 1.120 \times \frac{\text{g Insoluble}}{\text{g Coal Initial Charge}}) \times 100\%$$

Appendix A. Response to Questions Concerning October to December Report

The information given in this appendix is in response to questions raised about some of the data contained in the October to December Quarterly Report. The request was made that the data be given for the moles of H_2 accepted per mole of anthracene. The information has been given in Appendix Table 1 which corresponds to the quarterly report Table 4.

In order to compare the reactivity of anthracene under these reaction conditions in the presence of resid to a baseline reaction under the same reaction conditions, anthracene (ANT) was reacted alone and in the presence of hexadecane. Both noncatalytic and catalytic reactions were performed. The catalytic reactions using MoNaph + S resulted in more conversion of ANT to partially saturated products. For both the noncatalytic and catalytic reactions, ANT accepted slightly more hydrogen when hexadecane was present. When the amount of H_2 accepted per mole of ANT is compared between Tables 1 and 2, more H_2 was accepted by ANT in the presence of the hexane soluble fractions of resid under both noncatalytic and catalytic reaction conditions. These results indicate that both Maya and FHC-623 hexane soluble fractions of the resid promote hydrogen transfer to ANT.

Appendix Table 1.

Table 4. Product Distribution of Anthracene Reacted with FHC-362 and Maya Resid.

Resid	Donor/Reaction Condition	Product Distribution, (mol %)			Moles of H ₂ Accepted per mole of Anthracene
		ANT	DHA	HHA	
FHC-623	Noncatalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	27.3(4.5) ^a	51.3(3.9)	21.5(0.6)	1.158
FHC-623	Catalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	26.3(6.0)	52.9(3.7)	20.8(2.3)	1.153
Maya	Noncatalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	34.2(12.6) ^a	45.4(8.3)	20.3(4.3)	1.066
Maya	Catalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	10.1(0.1)	68.1(0.6)	21.8(0.6)	1.335

^aMean (standard deviation).

Appendix Table 2.

**Baseline Reactions of Anthracene in Hexadecane
Under Catalytic and Noncatalytic Conditions**

Reaction	Catalyst	Anthracene Product Distribution (mol %)			H ₂ accepted per mol ANT
		ANT ^a	DHA	HHA	
Anthracene	None	23.45 ^b (4.74)	70.65 (4.17)	5.90 (0.57)	0.8835
Anthracene + Hexadecane	None	28.05 (2.05)	66.55 (2.76)	5.40 (0.71)	0.8275
Anthracene	MoNaph + S ^c	19.75 (3.32)	69.05 (3.18)	11.20 (0.14)	1.0265
Anthracene + Hexadecane	MoNaph + S	18.10 (1.41)	75.75 (2.62)	6.15 (1.20)	0.9420

^aANT = anthracene, DHA = dihydroanthracene

^bmean (standard deviation)

^cMoNaph = Mo naphthenate introduced at 1000 ppm of total charge

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