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

Quarterly Report
October to December 1993

Contract No. DE-AC22-91PC91055

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Table of Contents

INTRODUCTION

The research performed this quarter focused upon reactions using resids, resid fractions, and those resid fractions with anthracene as a hydrogen acceptor. The method for analysis of the products from the reactions was also developed. The initial work performed was to obtain chromatographically the hexane soluble fraction from two different resids: FHC-362 and Maya. These fractions were reacted catalytically with a slurry-phase Mo catalyst with or without anthracene. These reactions were also performed without a catalyst. The reaction products were analyzed by gas chromatography by determining the relative retention times of the eluting peaks and comparing the amount of eluent at different retention times.

EXPERIMENTAL

Materials. The materials used during this quarter were Maya and FHC-362 resids which were donated by Amoco Corporation. Both of the resids were chromatographically separated using alumina as the absorbent and cyclohexane followed by chloroform as the eluting solvents. Both resids were also fractionated by a solvent fractionation scheme in which hexane and tetrahydrofuran (THF) were used as the solvents. The solvent fractionation resulted in three product fractions: hexane solubles; hexane insolubles, THF solubles; and THF insolubles or IOM which is insoluble organic matter and is ash-free. The results from the solvent fractionation are presented in Table 1. The FHC-362 resid contained much less toluene solubles than did Maya. Therefore, the resids used in this study were composed of considerably different components as evidenced by their different solubility characteristics.

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, hexahydroanthracene, and octahydroanthracene, were obtained from Aldrich Chemical Company. 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 this quarter 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 ~ 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 in order to evaporate the THF. For the reactions containing anthracene, 0.5 g of anthracene was charged to the microreactor. In the catalytic reaction, Mo naphthenate was introduced at a loading of 1000 ppm Mo on the basis of the grams of resid charged.

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 achieved for the reaction. 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 gas was captured and its volume determined. 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.

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. 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 H_2 accepted was equal to (1 x DHA mol% + 2 x THA mol% + 3 x HHA mol%) x 100%.

RESULTS AND DISCUSSION

The research this quarter focused upon determining if any hydrogen transfer occurred from whole resid or resid fractions during coprocessing. A hydrogen acceptor, anthracene, was introduced into the reactor to determine if hydrogen was donated during the high temperature and high H_2 pressure treatment. The reactions that were performed: (1) hexane soluble fraction of the resid in noncatalytic reactions; (2) hexane soluble fraction of resid in catalytic reactions; (3) hexane soluble fraction of resid with anthracene in noncatalytic reactions; and (4) hexane soluble fraction of resid with anthracene in catalytic reactions. These reactions were performed for both

FHC-362 resid and Maya resid as shown in Tables 2 and 3, respectively. Reactions of anthracene in the latter two reactions are given for reactions with FHC-362 Maya resids in Table 4.

The resids were analyzed by gas chromatography in which the fraction of resid eluting within different retention times was determined. The analysis and comparison of the fraction of the peaks eluting at given retention times gives a measure of the boiling point distribution of the reaction product. The shorter the retention time of each analyzed product, the lower the average boiling point is for that mixture.

Comparison of the GC analysis of the THF fraction of the unreacted resid with that for the hexane solubles of resid in Tables 2 and 3, for FHC-365 and Maya, respectively, show that the hexane soluble fractions have a lower average boiling point than their respective whole resids. This result is reasonable since in the solvent fractionation process, the hexane insoluble materials are removed. The components in the hexane soluble fraction are either nonpolar or have low polarity for them to be soluble in hexane, although some mutual solubility of more polar compounds may occur. The components in the hexane insoluble fraction are more polar and tend to have higher boiling points than the hexane soluble fraction.

Reactions of the hexane soluble resid material under catalytic and noncatalytic conditions showed a marked change in average boiling point compared to the untreated hexane soluble fractions. The FHC-365 hexane solubles showed increased amounts in the lower boiling point fractions in the noncatalytic fractions while the catalytic reaction gave even a higher fraction in the lower boiling point fractions. The hexane soluble fraction of Maya gave similar results compared to the untreated resid although the noncatalytic reaction gave a lower average boiling point than did the catalytic reaction.

The reactions with anthracene as a hydrogen acceptor were performed to determine how much hydrogen could be transferred by the hexane soluble resid fraction and hydrogen atmosphere to anthracene. The product distributions obtained by anthracene are given in Table 4. The products obtained from anthracene (ANT) were dihydroanthracene (DHA) and hexahydroanthracene (HHA). When FHC-365 was the resid used in the reaction, very similar amounts of ANT, DHA, and HHA were present after the reaction in both the catalytic and noncatalytic reaction. The predominant product was DHA at 51 to 53 mol%. Slightly more than one-fourth of the ANT remained unreacted. The production of HHA was between 20 and 22%. The amount of H_2 accepted by ANT was the same for both catalytic and noncatalytic reactions.

For the reactions with Maya, ANT reacted differently under noncatalytic and catalytic conditions. The reaction products produced were DHA and HHA, with DHA being the predominant product. In the catalytic reaction, substantially more DHA was produced under catalytic conditions and substantially less ANT remained than in the noncatalytic reaction. Under both reaction conditions nearly the same amount of HHA was produced. Under catalytic conditions, nearly twice as much hydrogen was accepted by ANT than under noncatalytic conditions. The product distribution from ANT obtained for the noncatalytic reaction with Maya was similar to that obtained from ANT when ANT was reacted with FHC-365. The catalyst only seemed to have an effect with Maya resid.

The catalyst also had a strong effect on the GC fraction obtained from the reaction using hexane solubles of Maya with ANT. The average boiling point showed a substantial shift toward low boiling constituents.

Summary and Future Work

The research this quarter focused on reacting and analyzing hexane soluble fractions of resid. The GC method developed allowed the determiination of the effect of different treatments on the hexane soluble resids. Other analyses such as NMR and mass spectrometry will be performed on selected reactions in order to determine the effect of the reactions on the chemical structures in the hexane soluble fraction. An updated experimental matrix is included for future work (Table 5).

Table 1. Solubility Fractions of FHC-362 and Maya Resid Prior to Reaction

Resids	Product Distribution (wt%)		
	Hexane Solubles	Toluene Solubles	THF Solubles
FHC-362	83.3 (1.1)	14.9 (0.4)	1.8 (0.8)
Maya	62.9 (1.1)	37.1 (1.1)	0.0 (0.0)

Table 2. GC Fraction Distributions from FHC-362 Resid Undergoing Different Treatments

Time for GC Fractions Obtained from THF Soluble Material	GC Fractions of THF Soluble Material					
	Untreated Resid	Hexane Solubles of Unreacted Resid	Noncatalytic Reaction with Hexane Soluble Resid Fraction	Catalytic Reaction with Hexane Soluble Resid Fraction	Noncatalytic Reaction with Hexane Soluble Resid and Anthracene	Catalytic Reaction with Hexane Soluble Resid and Anthracene
<45 min	0.201	0.251	0.657(0.04)[b]	0.708(0.05)	0.784(0.04)[c]	0.801(0.02)[c]
45 to 60 min	0.211	0.171	0.114(0.02)	0.103(0.03)	0.099(0.02)	0.074(0.00)
60 to 75 min	0.307	0.312	0.145(0.01)	0.114(0.02)	0.092(0.00)	0.078(0.01)
> 75 min	0.282	0.266	0.084(0.01)	0.075(0.00)	0.024(0.02)	0.048(0.01)
Increase in gas volume	NA	NA	yes	yes	yes	no
H_2 Accepted by ANT (mol)	NA	NA	NA	NA	0.0019	0.0019
Recovery, %	100	100	88.6	83.2	77.4	90.2

Note: [a]positive number = recovered gas is more than charged.
negative number = recovered gas is less than charged.
[b]mean (standard deviation).
[c]These analyses did not include any of the anthracene peaks.

Table 3. GC Fraction Distributions from Maya Resid Undergoing Different Treatments

	GC Fractions of THF Soluble Material						
GC Fraction Obtained from THF Soluble Material	Untreated Resid	Hexane Solubles of Unreacted Resid	Catalytic Reaction of Whole Resid	Noncatalytic Reaction of Hexane Soluble Resid Fraction	Catalytic Reaction of Hexane Soluble Resid Fraction	Noncatalytic Reaction of Hexane Soluble Resid Fraction with Anthracene	Catalytic Reaction of Hexane Soluble Resid Fraction with Anthracene
<45 min	0	0	0.654	0.793(0.02)[b]	0.777(0.06)	0.776[c]	0.912(0.04)[c]
45 to 60 min	0	0	0.127	0.094(0.01)	0.114(0.02)	0.084	0.055(0.03)
60 to 75 min	1	0.83	0.138	0.086(0.02)	0.09(0.04)	0.116	0.032(0.01)
>75 min	0	0.17	0.082	0.027(0.00)	0.017(0.00)	0.024	0.000(0.00)
Increase in gas volume	NA	NA	yes	yes	no	yes	yes
H_2 Accepted by ANT (mol)	NA	NA	NA	NA	NA	0.0019	0.0033
Recovery, %	100	100	81.9	79.2	85	87.6	86.3

Note: [a]positive number = recovered gas is more than charged.
negative number = recovered gas is less than charged.
[b]mean (standard deviation).
[c]These analyses did not include any of the anthracene peaks.

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

Resid	Donor/Reaction Condition	Product Distribution, (mol %)			H_2 Accepted by ANT x 10^3 (mol)
		ANT	DHA	HHA	
FHC-362	Catalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	26.3(6.0)	52.9(3.7)	20.8(2.3)	1.9(0.5)
FHC-362	Noncatalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	27.3 (4.5)[a]	51.3 (3.9)	21.5 (0.6)	1.9 (0.4)
Maya	Noncatalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	34.2 (12.6)[a]	45.4 (8.3)	20.3 (4.3)	1.9 (0.6)
Maya	Catalytic Reaction with Hexane Soluble Resid Fraction and Anthracene	10.1 (0.1)	68.1 (0.6)	21.8 (0.6)	3.3 (0.6)

[a] Mean (standard deviation).

Table 5. Experimental Matrix of Coal and Resids

H-Acceptor	Hydrogen Donor	
	Oil (Hexane Solubles)[b]	Starting Resid
ANT[a]	1	0
ANT	0	1
ANT	5	0
Coal	1	0
Coal	0	1
Coal	5	0
Coal	0	5

[a]ANT = anthracene.
[b]Loading: the ratio of anthracene or coal to the sum of oil and starting resid is 1:2.

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