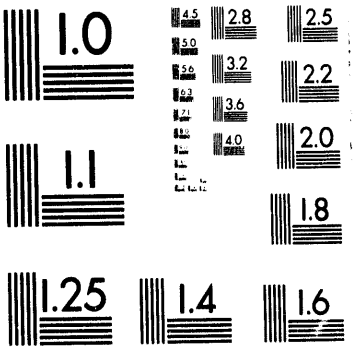
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2.8
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1 of 1

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IMPROVED PERFORMANCE IN COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

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TABLE OF CONTENTS

	Page
Objective	1
Major Subtasks and Their Objectives	1
Introduction	1
Experimental Work	2
Subtask I.A. Hydrogen Transfer from Cycloalkanes	2
Introduction	2
Experimental	2
Results and Discussion	4
Conclusions	7
Subtask I.B.1. Pretreatment, Fractionation and Reactivity of Petroleum Residua	7
Introduction	7
Experimental	8
Results and Discussion	11
Conclusions	13
Subtask I.B.2. Evaluation of Enhanced Factors Prevalent in Pretreated Residua	17
Introduction	17
Experimental	17
Results and Discussion	19
Conclusions	20
Subtask II.A. Synthesis of Nonaromatic Hydroaromatics	21
Introduction	21
Experimental	21

Nb28/Copr

Subtask II.D. Chemistry and Reactivity of Nonaromatic Hydroaromatic Enriched Petroleum Solvents 22

Introduction 22

Experimental 23

Results and Discussion 23

Appendix A 31

Appendix B 34

Nb28/Copr

IMPROVED PERFORMANCE IN COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

OBJECTIVE

To gain a fundamental understanding of the role and importance of hydrogen transfer reactions in thermal and catalytic coprocessing by examining possible hydrogen donation from cycloalkane/aromatic systems and by understanding the chemistry and enhanced reactivity of hydrotreated residuum, as well as by enriching petroleum solvent with potent new donors, nonaromatic hydroaromatics, thereby promoting hydrogen transfer reactions in coprocessing.

MAJOR TASKS AND THEIR OBJECTIVES

Task I. Elucidations of Hydrogen Transfer Reactions in Coprocessing

Objective. To attain a fundamental understanding of the hydrogen transfer reactions which occur during coprocessing and to elucidate their role and importance in achieving upgraded products.

Task II. Development of Potent Nonaromatic Hydroaromatic Hydrogen Donors for Coprocessing

Objective. To generate petroleum solvents enriched with nonaromatic hydroaromatics by metal or electrochemical reduction and to evaluate their reactivity and selectivity.

INTRODUCTION

Research continued this quarter on Subtask I.A., Hydrogen Transfer from Cycloalkanes, Subtask I.B.1., Pretreatment, Fractionation, and Reactivity of Petroleum Residua, and Subtask II.D., Chemistry and Reactivity of Nonaromatic Hydroaromatic Enriched Petroleum Solvents. New research was initiated this quarter on Subtask I.B.2., Evaluation of Enhanced Factors Prevalent in Pretreated Residua, and Subtask II.A., Synthesis of Nonaromatic Hydroaromatics by Reduction with Metals and Electroreduction.

EXPERIMENTAL WORK

SUBTASK I.A. HYDROGEN TRANSFER FROM CYCLOALKANES

INTRODUCTION

The objective of Subtask I.A. is to investigate hydrogen transfer from cycloalkanes, such as those present in petroleum residua, to aromatics, such as those present in coal, during thermal coprocessing. This quarter, response factors were determined for analysis of anthracene, pyrene, and perhydropyrene by gas chromatography (GC). Reactions were also conducted using the model compounds, tetralin, decalin, anthracene, pyrene, and perhydropyrene.

EXPERIMENTAL

Reagents. The reagents used this quarter included the model compounds, tetralin (TET), decalin (DEC), anthracene (ANTH), pyrene (PYR), and perhydropyrene (PHPYR) mentioned above, the internal standard biphenyl (BIP) for GC analysis, and the solvent tetrahydrofuran (THF). TET, DEC, ANTH, and PYR were purchased from Aldrich Chemicals and had a purity of 99% or higher. DEC was a mixture of cis and trans isomers. PHPYR, purchased from Pfaltz and Bauer Research Chemicals, had a purity of 99% or higher and was a mixture of seven observable isomers. BIP, obtained from Eastman Kodak, also had a purity of 99% or higher. The THF was Fisher certified.

Apparatus. The apparatus used this quarter consisted of 3/4 inch stainless steel tubing bomb microreactors (TBMRs), with a length of three inches and a volume of approximately 20 mL, a fluidized sand bath equipped with a horizontal agitation device, a volume determination device consisting of a series of gas sampling cylinders equipped with a pressure meter and corresponding transducer, and a Varian gas chromatograph, Model 3400, with FID detection.

Determination of Response Factors. In order to incorporate the internal standard method in the GC analysis, it was necessary to determine the response factor between the compounds used and the internal standard, biphenyl. The procedure and results are shown in Appendix A.

Procedure and Analysis. The work performed this quarter consisted of verifying results obtained using TET and DEC in earlier reactions, conducting reactions with ANTH, PYR, and PHPYR alone, and conducting reactions with a 50/50 weight percent mixture of PYR and PHPYR.

A measured amount of the compound or mixture to be reacted was introduced into a TBMR and then charged at 400 psig with nitrogen. The reactor was tested to insure that there were no leaks, submerged in a fluidized sand bath at 430°C, and agitated at a rate of 425 cpm. The DEC and TET were reacted for 30 minutes. The ANTH, PYR, and PHPYR were reacted for 60 minutes.

At the end of the reaction, the reactor was quenched in a water bath. The gas pressure in the bomb was released and measured using the volume determination apparatus designed and constructed by Michael Bedell, a chemical engineering graduate student at Auburn University. The products were recovered by extracting with three 5mL portions of THF. BIP, the internal standard for gas chromatographic analysis, was introduced into the product vials. The products were then analyzed using gas chromatography. The GC conditions for the TET and DEC reactions are shown in Table I.A.1.

Table I.A.1. Gas Chromatography Conditions for Product Analysis

Gas Chromatography	Varian 3400
Column	SGE HT-5 Al-clad
Split Ratio	50:1
Injector Temperature	300°C
Detector Temperature	310°C
Initial Column Temperature	80°C
Final Column Temperature	180°C
Temperature Programming	10°C/min

Because of the similar retention times of the PHPYR isomers, the temperature program was changed to produce sharper peak resolution. The GC conditions for the ANTH, PYR, and PHPYR reactions are shown in Table I.A.2.

Table I.A.2. Gas Chromatography Conditions for Product Analysis

Gas Chromatograph	Varian 3400
Column	SGE HT-5 Al-clad
Split Ratio	50:1
Injector Temperature	340°C
Detector Temperature	350°C
Initial Column Temperature	80°C
Final Column Temperature	240°C
Temperature Programming	3°C/min

RESULTS AND DISCUSSION

A comparison of the final pressure of the TBMR and the results of GC analysis for DEC and TET reactions are shown in Table I.A.3. The reactions in run 1 were conducted the previous quarter. The reactions in run 2 were conducted this quarter.

Table I.A.3. Recoveries and Average Final Pressures

Compound Name	Run 1			Run 2		
	Sample Number	Recovery[1] (%)	Average[2] Pressure	Sample Number	Recovery (%)	Average Pressure
Decalin	015	75.5	543 psig	030	77.4	518 psig
	016	79.3		031	78.3	
	017	70.0		032	78.5	
	018	86.0				
Tetralin	023	86.8	485	027	80.6	481
	024	81.6		028	73.7	
				029	80.3	

[1] $\% \text{ Recovery} = \frac{\text{grams reactant} - \text{grams product}}{\text{grams reactant}} \times 100\%$

[2] Pressures measured subsequent to cooling.

As can be seen from Table I.A.3, the results from decalin reactions were similar for runs 1 and 2. The gas chromatograms for the decalin reactions for both runs indicated that the ratio of trans- to cis-decalin increased slightly during the reactions. The decalin purchased from Aldrich Chemicals contained 40.3% trans isomers and 59.7% cis isomers. The decalin portion of the products contained 41.4 to 43.0% trans isomers and 57.0 to 58.6% cis isomers, for run 1, and 41.5 to 41.9% trans isomers and 58.1 to 58.5% cis isomers, for run 2. There were no significant products other than the trans- and cis-decalin. However, a small amount of hydrocracking may have occurred, helping to explain the low recoveries of the decalin. It is possible that the detection limit of the GC was set too high to detect hydrocracked products present in small quantities.

The results of the tetralin reactions were also similar for runs 1 and 2. For every reaction, the GC chromatograms indicated that naphthalene had been formed and that hydrocracking had occurred. The amount of naphthalene was only about 5% of the tetralin present but was significant. Another peak, of about the same area as the naphthalene peak, was present on each of the GC chromatograms. Very small peaks were also present in the vicinity of cis- and trans-decalin. Further analysis is necessary to identify these unknown peaks.

Table I.A.4 shows the results of the ANTH, PYR, and PHPYR reactions. In the reactions with ANTH alone, PYR alone, and PHPYR alone, the compounds were stable and no products were formed. No evidence of hydrocracking was detected. The PYR and PHPYR mixture seemed to be fairly stable also, but some very small unidentified peaks did occur near the pyrene peak. It is possible that the very small amounts of the PHPYR gave up hydrogen to form lesser hydrogenated compounds. Further analysis may reveal the identities of these compounds.

Table I.A.4. Recoveries and Average Final Pressures

Compound Name	Sample Number	Recovery (%)	Average Pressure
ANTH	056	91.4	504 psig
PYR	044	88.7	386
	045	89.7	
PHPYR	047	82.0	562
	057	92.8	
PYR + PHPYR (50/50 mixture by weight)	048	86.5 (PHR)	469
		82.0 (PHPYR)	
	049	99.1 (PYR)	511
		93.4 (PHPYR)	

Errors may have originated from several sources this quarter. The recoveries of the decalin reactions were lower than expected. This could have been caused by undetected hydrocracked products. Error may have also occurred if decalin escaped in the form of vapor when the TBMR was depressurized. There is always the possibility of experimentalist error. The yields for the tetralin reaction may be higher than first calculated, depending on the densities of the unknown peaks. The presence of hydrocracked products would also have led to a lower calculated recovery. The fact that runs 1 and 2 are similar for both tetralin and decalin reactions indicates that reproducibility exists. The recoveries for the ANTH, PYR, and PHPYR reactions were fairly reasonable. Since these are higher boiling compounds, less chance of products being lost in depressurizing the TBMRs exists. Error probably occurred during the GC analysis because high boiling compounds are more likely to adhere to the GC column and give erroneous results. For this same reason, a high experimental error probably occurred in determining GC response factors. For the reactions with the PYR and PHPYR mixture, several small unknown peaks did occur. The identification of these products may be important to the understanding of hydrogen transfer from cycloalkanes, even

though the presence of these products only slightly affects the recoveries. Further analysis may reveal the identities of these compounds.

CONCLUSIONS

This quarter experiments were conducted with several compounds of interest; ANTH, PYR, and PHPYR. When reacted alone, these compounds were found to be stable. However, GC analysis indicated that small amounts of products, other than PYR and PHPYR, were formed in the reactions with a PYR/PHPYR mixture. These products, believed to be less saturated forms of PHPYR, will be identified by further analysis. The work done this quarter with TET and DEC demonstrated the reproducibility of experimental results. The GC analysis of the TET reactions revealed several unknown peaks, which will be further investigated.

Also during this quarter, response factors necessary for GC analysis of ANTH, PYR, and PHPYR reaction products were determined. The high boiling points of these compounds made them more likely to adhere to the GC column. This, along with the temperature limitations of the GC, made the determinations of the response factors difficult. The installation of a septumless injector may be of great benefit by allowing higher temperatures to be used and, therefore, allowing response factors to be determined more easily with greater accuracy and precision.

SUBTASK I.B.1. PRETREATMENT, FRACTIONATION, AND REACTIVITY OF PETROLEUM RESIDUA

INTRODUCTION

During this quarter Maya residuum and Illinois No. 6 coal were selected as coprocessing feed materials, and their compositions were evaluated by solubility testing using different solvents. Different transition metals in organometallic species, Mo, Ni and V as naphthenates, and a commercial

supported bimetallic catalyst, $NiMo/Al_2O_3$, were selected as catalysts. Thermal and catalytic hydrogenation reactions of Maya residuum and Illinois No. 6 coal were performed. These reactions will provide a reference by which to evaluate the effect of hydrotreating Maya prior to coprocessing reactions.

EXPERIMENTAL

A petroleum residuum and a coal were selected as the feed materials for coprocessing, and their physical and chemical properties were determined. Hydrogenation reactions of the residuum and coal were performed thermally and catalytically with different catalysts in order to establish background information on the product slates which will be used to evaluate the effect of hydrotreating the residuum with different catalysts on the products obtained from coprocessing.

Materials

Maya heavy petroleum residuum and Illinois No. 6 were selected for coprocessing. Both materials were supplied by Amoco Oil Company. Maya was used as received, but Illinois No. 6 coal was pulverized to 100 mesh before use. The composition of each material presented in Table I.B.1. was determined by Amoco Oil Company. The moisture and ash contents of Illinois No. 6 coal were measured again in this laboratory, and the values were slightly different from those supplied by Amoco Oil Company; the moisture and ash contents obtained in Auburn were utilized in the calculations of experimental results.

Table I.B.1. Characterization of Maya Residuum and Illinois No. 6 Coal

	Maya	Illinois No. 6 Coal	
		Amoco	Auburn
Moisture (wt%)	0.0	7.5	6.3
Ash (wt%)	0.0	8.27	9.8
C (wt%)	83.7	68.67	
H (wt%)	9.76	4.49	
S (wt%)	5.4	0.94	
N (wt%)	ND[1]	1.61	
O (wt%)	ND	8.14	
Ni (ppm)	118	9,100	
V (ppm)	680	43,000	
Fe (ppm)	ND	40,000	
Co (ppm)	ND	3,600	

[1]ND: not detected
The sepecific gravity of Maya is 1.0535 g/cc.

Oil soluble naphthenates of Mo, Ni and V, and a supported bitmetallic commercial catalyst, $NiMo/Al_2O_3$, were selected as the coprocessing catalysts in this study. Naphthenates of Mo, Ni and V were supplied by Shepherd Chemical Company, and their metal contents in each paste were 6 wt% Mo, 12 wt% Ni, and 3 wt% V. Each catalyst paste was diluted by n-hexadecane to enhance its fluidity; the concentrations of metals in the diluted catalyst pastes were 3 wt% of Mo or Ni and 1.5 wt% of V. A solid catalyst, Shell 324 $NiMo/Al_2O_3$, was presulfided in a gas stream of 10 vol% H_2S in H_2 and then pulverized to 150 mesh before use.

Thermal and Catalytic Reactions. The coprocessing reactions were performed in a 56 cm^3 tubing bomb microreactor which was horizontally oriented during reactions and made of 316 stainless steel. Each coprocessing reaction was conducted with 3g of coal and 6g of Maya under reaction conditions of 1250 psig H_2 charged at ambient temperature (about 2820 psig H_2 at reaction

temperature), 400°C reaction temperature, one hour reaction time, and 550 cpm vertical shaking. In catalytic reactions, each catalyst paste or solid catalyst was introduced at the level of 3000 ppm metal content. Elemental sulfur was added in an amount sufficient to produce metal sulfide from the organometallic paste during the reaction; in thermal ractions, however, no additional sulfur was added.

Analysis. Maya alone (9g), a mixture of coal (3g) and Maya (6g), as well as the coprocessing products from 3g coal and 6g residuum were fractionated by three different solvents: first, the oil fraction was extracted using hexane; next, the asphaltene fraction was extracted using toluene; finally, the preasphaltene fraction was extracted using tetrahydrofuran. About 9g of whole reactants or products were dissolved in 450 mL of each solvent: sample materials were dissolved in 150 mL solvent, sonicated for 4 minutes, centrifuged to separate liquid and undissolved materials, and then all of these procedures were repeated twice with the same solvent. The amount of each fraction was compared in terms of oil (hexane soluble), asphaltene (hexane insoluble but toluene soluble), preasphaltene (toluene insoluble but tetrahydrofuran soluble), and insoluble organic matter (IOM - tetrahydrofuran insoluble) on a moisture, ash and catalyst free basis. The amount of gas product produced from the reaction was determined by H_2 analysis using a gas chromatograph with thermal conductivity detection.

RESULTS AND DISCUSSION

Fractionation of Maya and Coal. Maya alone (9g) and a mixture of Maya (6g) and Illinois No. 6 coal (3g) were fractionated. Extraction of each sample was duplicated. Maya was composed of 68.7 wt% oil, 31.1 wt% asphaltenes, and a negligible amount of IOM (Table I.B.2.a); this result will serve as background

information for the products fractionated from Maya residuum hydropretreated with different catalysts. From the mixture of Maya and coal, 46.4 wt% oil, 23.7 wt% asphaltenes, 1.6 wt% preasphaltenes, 28.3 wt% IOM, and 70.1 wt% toluene solubles (oil + asphaltenes) were obtained on an ash free basis (Table I.B.2.b); this result will serve as background information for the coprocessing products fractionated from reactions using prehydrogenated Maya residuum with coal and different catalysts.

Using the above two results, the solubility of coal was calculated by assuming that coal has no oil fraction and by subtracting the amounts of fractions produced from Maya alone (6g basis) from the total amount of each fraction produced from the mixture (Table I.B.2.c). Illinois No. 6 coal was shown to be composed of 6.8 wt% asphaltenes, 5.0 wt% preasphaltenes and 88.2 wt% IOM on an ash free basis. This calculated composition will be compared to that obtained from direct dissolution of Illinois No. 6 coal using each solvent in sequence in the following experiments.

Hydrogenation of Illinois No. 6 Coal. Three grams of coal were introduced in the reactor with 6g of n-hexadecane, which was assumed to be nonreactive at the reaction temperature, to test the extent of hydrogenation of coal without a hydrogen-transferable solvent. With an assumption that n-hexadexcane was not involved in any reaction, such as hydrocracking, gasification or polymerization, the weight percents of fractionated products from thermal and catalytic hydrogenation reactions of Illinois No. 6 coal were calculated and are summarized in Table I.B.3.

Thermal reaction with excess sulfur showed an activity mainly in converting the IOM fraction to preasphaltenes and in producing slightly more gaseous products. The negative value in the oil fraction arose because of the subtraction of n-hexadecane from the hexane solubles. In the catalytic

reaction with Mo naphthenate and excess sulfur, more IOM in coal was converted to preasphaltenes, asphaltenes and oil.

Coprocessing of Maya and Illinois No. 6 Coal. A mixture of 6g Maya and 3g Illinois No. 6 coal was hydrogenated thermally and catalytically with different catalysts under equivalent conditions. The fractionated products were calculated in two ways: in the first, the weight percent of each fraction was calculated based on the total product amount recovered (method A); in the second, the weight percent of each fraction was calculated based on the assumption of 100% product recovery in which the oil fraction was determined by subtracting the other recovered fractions from 100% (method B). Reactions were at least duplicated, and the results by method A are summarized as the averaged values and standard deviations of $X + \sigma_n$ by (Table I.B.4); the original data including the results summarized by method B are presented in Appendix B.

Catalytic reactions converted more of the IOM fraction to lighter fractions and consumed more H_2 than thermal reactions. The order of activity in producing useful fractions of oil and asphaltenes was MoNaph > $NiMo/Al_2O_3$ ≥ NiNaph > Thermal ≥ VNaph. The order of activity in coal conversion was slightly different: NiNaph > $NiMo/Al_2O_3$ > MoNaph > VNaph > Thermal. VNaph was the least active catalyst for producing oil and asphaltenes but was most active in producing gaseous products; VNaph seemed to enhance the retrogressive reaction producing higher molecular weight products. The hydrogen consumption in each reaction generally followed the activity of the catalyst used: more hydrogen consumption with MoNaph, NiNaph and $NiMo/Al_2O_3$ than with VNaph and without catalyst. Reactions with NiNaph and powdered $NiMo/Al_2O_3$ catalysts were less reproducible than the other reactions. The low reproducibility with $NiMo/Al_2O_3$ seemed to be caused by the poor dispersion of

the solid catalyst in the feed materials, but the reason for low reproducibility with NiNaph has not been determined.

A comparison of the catalytic coprocessing products from Maya and coal reactions just performed can be made with products achieved from planned coprocessing reaction using upgraded Maya. The amount of coal upgraded to different product fractions as well as the activities and selectivities of the different catalysts for coal conversion and upgrading can be determined through this comparison. In addition, the coal hydrogenation in coprocessing with different catalysts can be compared to that in the reaction of coal in n-hexadecane; the difference will show the efficacy of residua as coprocessing solvents.

CONCLUSIONS

Coprocessing of Maya heavy petroleum residuum and Illinois No. 6 coal was performed thermally and catalytically with different catalysts. The results obtained provided background information for the effect of prehydrogenating Maya with different catalysts prior to coprocessing reactions of Illinois No. 6 coal and Maya residuum.

MoNaph, NiNaph and powdered NiMo/Al_2O_3 showed high activities in producing oil and asphaltenes as well as in converting coal. But VNaph showed very low catalytic activity; the amount of each product was similar to that achieved in the thermal reaction. VNaph only slightly enhanced coal conversion and promoted the retrogressive reaction from oil and asphaltenes to preasphaltenes.

Table I.B.2. Fractionated Maya and Illinois No. 6 Coal

(a)Maya[1]

Sample No.	Extracted Products (wt%) Oil	Asp	Preasp	IOM	Recovery (%)
1.	68.7	30.9	0.0	0.4	104.8
2.	68.7	31.2	0.0	0.1	104.0
Average	68.7±0.0	31.1±0.2	0.0±0.0	0.2±0.2	

(b) Mixture of Maya and Illinois No. 6 Coal[2]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)[4]
3.	46.7	23.5	1.7	28.1	101.8
4.	46.0	23.9	1.5	28.6	101.2
Average	46.4±0.3	23.7±0.2	1.6±0.1	28.3±0.2	

(c) Calculated Fractions in Illinois No. 6 Coal[3]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)[4]
3.	0.0	7.2	5.2	87.6	104.3
4.	0.0	6.3	4.8	88.9	103.7
Average	0.0	6.8±0.5	5.0±0.2	88.2±0.7	

[1]9g of Maya
[2]6g of Maya and 3g of Illinois No. 6 Coal
[3]Values were calculated by subtracting the amounts of Maya fractions (6g basis) from the total amounts of products shown in (b).
[4]Recovery of coal including ash: recovery of Maya was 100.6% for #3 sample and 100.0% for #4 sample.
Asp = asphaltenes; Preasp = preasphaltenes; IOM = Insoluble Organic Matter

Table I.B.3. Hydrogenation of Illinois No. 6 Coal in Hexadecane[1]

Reaction Condition	H_2 Used(%)	Product Distribution (wt%)*					Coal Conversion (%)	Toluene-Solubles
		Gas	Oil	Asp	Preasp	IOM		
Thermal[2]	3.2	1.8	-0.1[4]	6.7	29.4	62.2	47.1	6.6
Catalytic[3]	16.8	2.0	9.0	23.0	35.1	30.9	72.2	32.0

*Method A
[1]3g Illinois No. 6 Coal in 6g n-Hexadecane.
[2]Thermal Reaction with Elemental Sulfur: S=0.0368g.
[3]Catalytic Reaction with Mo Naphthenate: Mo=2946 ppm, S=0.058g.
[4]Negative value was obtained because of the subtraction of the amount of n-hexadecane from the hexane solubles recovered.
Asp = Asphaltenes; Preasp = Preasphaltenes; IOM = Insoluble Organic Matter

Table I.B.4. Coprocessing of Maya and Illinois No. 6 Coal

Reaction Condition	H_2 Used(%)	Product Distribution (wt%)					Coal Conversion (%)	Toluene-Solubles
		Gas	Oil	Asp	Preasp	IOM		
Thermal[1]	7.7- 9.3	2.4±0.1	49.9±0.6	18.7±0.4	9.9±0.2	19.1±0.1	37.4±0.2	68.5±0.2
MoNaph[2]	15.8-24.1	2.2±0.2	56.7±0.1	23.7±0.1	7.0±0.1	10.4±0.1	66.9±0.1	80.4±0.2
NiNaph[2]	19.9-22.3	2.6±0.1	51.1±1.7	23.1±1.4	17.8±1.0	5.3±1.2	82.8±4.1	74.2±2.0
VNaph[2]	11.5-13.3	4.0±0.1	45.6±0.3	21.5±0.6	13.4±0.4	15.5±0.3	50.7±1.4	67.5±0.2
$NiMo/Al_2O_3$[1]	18.6-19.0	2.3±0.2	52.2±3.2	24.3±2.2	11.0±0.5	10.2±1.2	67.7±3.5	76.5±0.9

[1]No Extra Sulfur
[2]Additional sulfur as much as required to produce metal sulfide: S=0.019g for MoS_2, S=0.010g for Ni_3S_2, and S=0.027g for V_2S_3.
Asp = Asphaltenes; Preasp = Preasphaltenes; IOM = Insoluble Organic Matter

SUBTASK I.B.2. EVALUATION OF ENHANCED FACTORS PREVALENT IN PRETREATED RESIDUA

INTRODUCTION

The purpose of this subtask is to chemically evaluate and characterize the hydrotreated residua and residuum fractions produced in Subtask I.B.1. The ultimate goal is to to determine the chemical factors that make particular hydrotreated residua more effectual as coprocessing solvents than others. Once these factors are determined, then the hydrotreatment of different residua can be optimized to produce those desired characteristics.

EXPERIMENTAL

During the quarter, alternate means of quantitatively analyzing residua, coal, and various fractions extracted from coprocessing reactions by conventional Fourier transform infrared (FTIR) spectrometry were investigated. Maya and Khafji whole residua were analyzed to determine if differences in their observed efficacy as coprocessing solvents could be correlated to differences observed in the FTIR spectra of these residua. Illinois No. 6 coal was analyzed by FTIR to determine if its infrared spectrum was different from the residua utilized. Oil fractions (hexane extractables) and asphaltene fractions (toluene extractables) from reaction products were analyzed by FTIR to determine if differences in the reaction conditions shown in Table I.B.2.1 and their corresponding differences in efficiency of coal conversion could be observed in the FTIR spectra of these fractions.

Table I.B.2.1. Infrared Analysis of Oil Samples from Coprocessing

Materials: Khafji Residuum (6g) + ILL No. 6 Coal (3g)

Oil Sample	Reaction Conditions		
	Catalyst	Reaction Temperature (^{o}C)	Sulfur
A	No reaction		
B	Thermal	400	without
C	Thermal	400	x3
D	Mo-Naph	400	without
E	Mo-Naph	400	x3
F	Vl-AcAc	400	without
G	Vl-AcAc	400	x3
H	Ni-Oct	400	without
I	Ni-Oct	400	x3
R	$NiMo/Al_2O_3$	400	without
S	Mo-Ni (1500 ppm)	400	x3
T	Mo-V (1500 ppm)	400	x3
U	Ni-V (1500 ppm)	400	x3

Oil fractions were quantitatively weighed and prepared using a conventional demountable infrared cell with KBr windows and CCl_4 as the solvent. Because of problems associated in the preparation of the solid asphaltenes fraction using a conventional demountable infrared cell with KBr windows and CS_2 as the solvent, asphaltenes fractions were prepared using a KBr pressed pellet technique with KSCN added as an internal standard.

Viscosity measurements were included as a portion of this subtask for the reasons detailed in the November 1989 monthly report. A Haake cone and plate

viscometer was made available from the Department of Civil Engineering at Auburn University for use in this subtask.

RESULTS AND DISCUSSION

The alternate means used during the quarter to analyze the data resulting from FTIR analysis included background ratioing, background subtraction, comparison of integrated peak intensities from five different spectral regions (see November 1989 monthly report), comparison of integrated individual peak areas, comparison of individual peak absorbances, and ratioing of individual peak absorbances. Overall, it appears that background subtraction methods are superior to background ratioing methods commonly used in FTIR spectrometry, particularly when high analyte concentrations and solvents with very large molar absorptivities (e.g. CCl_4 and CS_2) are utilized. Also, it appears necessary to compare individual peak areas or absorbances as opposed to comparing integrated peak areas from different spectral regions in order to observe subtle changes in FTIR spectra.

In general, the Maya and Khafji whole residua were very similar in terms of their FTIR spectra. Both were of predominantly aliphatic character, with only a slight amount of aromatic character. The Illinois No. 6 whole coal showed substantial amounts of aliphatic and aromatic character. The oil fractions (hexane extractables) from the coprocessing products derived from the reactions shown in Table I.B.2.1 were of nearly pure aliphatic character, as indicated by their FTIR spectra. Indeed, the aromatic character of the oil fractions was so slight that it was nearly impossible to ratio the aromatic and aliphatic FTIR peaks; the ratio, however, was quite consistent for the various reaction product oil fractions. It was postulated that the asphaltene fractions from the reaction products may be more aromatic in character than he oil fractions. Further, it was felt that the increase in the intensities of

the aromatic peaks might provide a more sensitive, reliable means of detecting differences in the ratios of reaction products as determined by FTIR spectrometry. Indeed, preliminary results indicate that more subtle differences can be detected in examination of the FTIR spectra of the asphaltene fractions than could be detected using the oil fractions.

A portable intelligent data logger (Omega Engineering, Inc., Model OM-160) will be utilized with the Haake cone and plate viscometer because an A/D converter interface is no longer manufactured by Haake. As its name implies, the data logger can collect data from the viscometer and store the data for later manipulation by an IBM PC or compatible computer via the built-in RS-232C port. A data logger, available in the Department of Chemical Engineering, Auburn University was tested during the quarter to determine its compatibility with departmental computers, and was found to operate satisfactorily.

CONCLUSIONS

FTIR spectrometry appears to be a potentially effective analytical technique for use in determining chemical factors that make certain hydrotreated residua more effectual as coprocessing solvents than others. More FTIR spectrometry work must be performed in the examination and comparison of untreated residua with hydrotreated residua prior to coprocessing. Residua hydrotreated using different techniques (e.g. H_2, catalysts) should also be compared using FTIR spectrometry prior to coprocessing. Multiple internal reflectance - Fourier transform infrared (MIR-FTIR) spectrometry should also be investigated for use in this research because MIR-FTIR tends to minimize problems associated with requirements for reproducible short cell path lengths and solvents with very large molar absorptivities used in quantitative FTIR spectrometry methods.

Now that the portable intelligent data logger has been found to be compatible with departmental computers, it should be evaluated for its compatibility with the Haake viscometer available in the civil engineering department.

SUBTASK II.A. SYNTHESIS OF NONAROMATIC HYDROAROMATICS

INTRODUCTION

The objective of this subtask is to synthesize high yield and essentially pure nonaromatic hydroaromatic compounds from their aromatic analogues by reduction with metals and/or electroreduction. Review of the chemical literature associated with Birch reductions, modified Birch (Benkeser) reductions and electroreduction methods was undertaken during this quarter. Contact was made with the Kariv-Miller research group, Department of Chemistry, University of Minnesota, Minneapolis, MN to obtain recommendations for equipment and techniques to be used in the electroreduction portion of this subtask. The decision was made to postpone Birch and modified Birch reductions for approximately six months to evaluate electroreduction initially, because of the reported greater extent of control of the reactions in terms of products produced, the relative simplicity, and the lesser degree of risk in terms of handling hazardous materials inherently involved.

EXPERIMENTAL

Most activity during the quarter involved gathering additional information on electroreduction experimental methods, yields, separations and purification procedures, instrumentation, and sample cells used in the synthesis of nonaromatic hydroaromatics. A 1985 publication, "Electroreduction in Aqueous Media, Saturation of Polycyclic Aromatics" by E. Kariv-Miller and R. I. Pacut, Department of Chemistry, University of

Minnesota, was reviewed. It was concluded that a flow cell may be required to produce sufficient quantities of nonaromatic hydroaromatics rather than the conventional cell described, that a method of extraction not using diethyl ether be developed to isolate the crude product from the electrolyte, and that a series of column chromatographies could be used to separate and purify the various components of the reduction products.

Information on constant current power supplies utilized in electroreductions was obtained from Hewlett Packard and Electronic Measurements Inc. Information on potentiostatic controllers, commercially available laboratory scale flow cells designed after successful industrial scale flow cells, and glass H-type electrochemical cells was obtained from Electrosynthesis Company, Inc. Equipment necessary for synthesis of nonaromatic hydroaromatics using electroreduction will be specified and ordered.

SUBTASK II.D. CHEMISTRY AND REACTIVITY OF NONAROMATIC HYDROAROMATIC ENRICHED PETROLEUM SOLVENTS

INTRODUCTION

The research concerning the efficacy of nonaromatic hydroaromatic compounds (NAHA's) as hydrogen donating species in coprocessing reactions was continued from the previous quarter. NAHA's are hydroaromatic species which do not contain an aromatic ring. The NAHA's under study are 1,4,5,8-tetrahydronaphthalene, also known as isotetralin (ISO), and 1,4,5,8,9,10-hexahydroanthracene (HHA). The results obtained for the NAHA's are also being compared to those obtained with their conventional hydrogen donor analogues, 1,2,3,4-tetrahydronaphthalene (TET), 9,10-dihydroanthracene (DHA), and 1,2,3,4,5,6,7,8-octahydroanthracene (OHA).

EXPERIMENTAL

The reactivity of the NAHA's and their conventional hydroaromatic analogues in coprocessing reactions was tested under the following reaction conditions: 1" stainless steel tubing bomb reactor with approximate volume of 50 mL, mounted horizontally and agitated vertically at a rate of 700 cpm; 1250 psig (ambient) nitrogen or hydrogen atmosphere; 30 minute reaction time; 6.0 grams total reaction mixture which included 2.0 grams Western Kentucky No. 9 coal, 0.5 weight percent donable hydrogen of the model compounds, with the balance being Maya residuum.

RESULTS AND DISCUSSION

A series of reactions using ISO, HHA, TET, DHA, and OHA with Maya residuum and Western Kentucky No. 9 coal, in both hydrogen and nitrogen atmospheres, was performed. The results for the preliminary reactions were detailed in a previous quarterly report; however, they will also be reviewed here. Table II.D.1 presents the results of the reactions in a nitrogen atmosphere.

Table II.D.1. Coprocessing Study I: Kentucky No. 9 Coal, Maya Residuum, N_2, 380°C, 30 Min

Model Compound	Coal Conversion	g Residuum Present	g H_2 Released
DHA (1.2)	66.2 (3.7)	1.2	0.00650
DHA (3.0)	56.4 (2.1)	3.0	0.00486
HHA	50.2 (0.9)	3.1	0.01924
OHA	38.2 (3.6)	3.3	0.01121
ISO	28.1 (2.5)	3.5	0.01285
TET	16.5 (1.4)	3.5	0.00371
NONE	15.3 (1.2)	4.0	-

As was previously reported, it is important to note from Table II.D.1 that ISO produced approximately 12% greater coal conversion than did its conventional analogue, TET. The NAHA HHA also gave greater conversion (approximately 13%) than its analogue OHA. Table II.D.1 also lists the number of grams of residuum present during the reactions. As explained above, the experiments were configured to maintain a constant level of potentially donable hydrogen, 0.5 wt%, as well as a total mass of reaction mixture. Table II.D.1 also shows that all of the reactions, with the exception of the one with DHA, contained approximately the same quantity of residuum (3-4 g), while DHA only has approximately 1.25 g of residuum present. DHA gave greater coal conversion than did HHA. A possible explanation for this phenomenon is that it is a solvent effect, i.e. the residuum may be inhibiting the reactions, and because of the lower amount of residuum present with DHA, the inhibiting effect is lessened. Therefore, an experiment employing 3.0 g of residuum with DHA was performed to determine the coal conversion with an amount of residuum more in line with that present for the other reactions. This result is also presented in Table II.D.1. As can be seen in Table II.D.1, when comparing the two reactions involving DHA, the residuum is an inhibitor as illustrated by the lower coal conversion obtained when 3.0 g residuum was present. Because of this solvent effect, future coprocessing studies will include two DHA reactions, one at standard conditions, and one at the higher loading of residuum.

For each of the reactions, the tetrahydrofuran soluble (THFS) fraction was then further analyzed to determine the effect of the reaction on the amount of model hydrogen donor compound that was present in the reaction products. The results that were obtained are presented in Table II.D.2.

Table II.D.2. Coprocessing Study I: Kentucky No. 9 Coal, Maya Residuum, N_2, 380°C, 30 Min

Model Compound	Coal Conversion	Weight%		
		OHA	DHA	ANT
OHA	38.2	52.69 (0.37)	38.95 (0.60)	8.37 (0.82)
HHA	50.2	17.35 (0.60)	39.92 (1.17)	42.74 (1.34)
DHA (1.2)	66.2	15.57 (0.79)	18.70 (0.53)	65.74 (1.22)
DHA (3.0)	56.4	17.165(1.12)	17.81 (0.39)	65.03 (1.29)

Model Compound	Coal Conversion	Weight%	
		TET	NAP
ISO	28.1	14.92 (0.26)	85.08 (0.26)
TET	16.5	74.60 (0.46)	25.41 (0.46)

It is important to note that when OHA was the model hydrogen donor compound added, it dehydrogenated to form DHA and anthracene (ANT). When HHA was the model compound added, it dehydrogenated to form DHA and ANT, as well as being hydrogenated to form OHA. When DHA was the model compound added, it primarily dehydrogenated to form ANT. However, a significant amount (78%) of the hydrogen released by DHA was utilized in forming OHA (> 15 weight percent). While DHA produced a high overall coal conversion, it also produced a significant amount of OHA, a poorer hydrogen donor compound. Therefore, DHA appears to be a good hydrogen donor compound; i.e. DHA gave a high overall coal conversion to THFS; it is not an efficient donor, utilizing donable hydrogen to form a less effective donor species. When TET was the model compound added to the coprocessing reaction system, it remained relatively unreacted, with approximately 25% dehydrogenated to naphthalene, (NAP). When

ISO was the model compound, it was first converted to TET, which was then dehydrogenated to form NAP (85 weight percent).

Data are also presented in Table II.D.1 regarding the net grams of hydrogen released by the model compound during the reaction. Based upon the final product distribution, these values were obtained in the following manner: Net grams of hydrogen released = (grams of hydrogen donated from model compound) - (grams of hydrogen going to form other hydrogen donor species). For these calculations, the only other hydrogen donor species formed was OHA. Figure I presents a plot of coal conversion versus grams of hydrogen donated. The solid line is the linear best fit to the data points.

Table II.D.3. Coprocessing Study II: Kentucky No. 9 Coal, Maya Residuum, H_2, 380°C, 30 Min

Model Compound	Coal Conversion	g Residuum Present	g H_2 Released
DHA (1.2)	73.6 (0.7)	1.2	- .03942
HHA	65.9 (0.7)	3.1	.00928
DHA (3.0)	65.0 (1.6)	3.0	- .03373
OHA	45.4 (1.0)	3.3	.00511
ISO	44.8 (0.3)	3.5	.01195
TET	31.7 (2.6)	3.5	.00135
NONE	24.3 (3.3)	4.0	-

Table II.D.3 presents the results that were obtained when the same series of reactions was repeated in a hydrogen, as opposed to a nitrogen, atmosphere. It is important to note from Table II.D.3 that ISO produced over 13% greater coal conversion to THFS than did its conventional analogue, TET. The NAHA HHA produced almost 20% greater conversion that did its analogue, OHA. HHA also produced the same coal conversion as the DHA reaction, which involved 3.0 g of

residuum. Also, the conversion obtained for a given compound in a hydrogen atmosphere was greater than the corresponding one obtained in a nitrogen atmosphere.

The results of the gas chromatographic analysis of the THFS fraction for the experiments performed in a hydrogen atmosphere are presented in Table II.D.4.

Table II.D.4. Coprocesing Study II: Kentucky No. 9 Coal, Maya Residuum, H_2, 380°C, 30 Min

Model Compound	Coal Conversion	Weight%		
		OHA	DHA	ANT
OHA	45.37	76.95	23.05	
HHA	65.86	40.23	47.74	12.04
DHA (1.2)	73.61	51.97	26.45	21.59
DHA (3.0)	64.95	49.83	24.89	25.30

Model Compound	Coal Conversion	Weight%	
		TET	NAP
ISO	44.83	21.02	78.98
TET	31.69	90.93	9.07

In a hydrogen atmosphere, the reaction products are generally shifted toward the more hydrogenated compounds, as compared to the dehydrogenated products being favored under a nitrogen atmosphere. OHA remained 77% unreacted, with the only product being DHA. When HHA was the donor species present, it hydrogenated to form OHA (40 weight percent) and dehydrogenated to form DHA (48 weight percent) and ANT (12 weight percent). When DHA was reacted, it primarily formed OHA (50 weight percent) and also dehydrogenated to form ANT (22 weight percent). TET remained greater than 90% unreacted,

with the balance being NAP. ISO was converted to TET, which dehydrogenated to form NAP (79 weight percent).

Table II.D.3 also presents data for the net grams of hydrogen released by the model compound during the reaction. A negative value implies a net gain of donable hydrogen from the gaseous hydrogen by the model compounds and their products present at the end of the reaction. Figure II presents a plot of coal conversion versus net grams of hydrogen released. The solid line is the linear best fit to the data points.

CONCLUSION

It is important to note that in both nitrogen and hydrogen atmospheres, the NAHA ISO produced a greater coal conversion to THFS than did its conventional hydrogen donor analogue, TET. Also, the NAHA HHA produced a higher coal conversion than its analogue OHA, under both nitrogen and hydrogen atmospheres. The amount of residuum present can have an inhibiting effect on the conversion obtained, as illustrated with the lower conversion employing DHA and 3.0 g residuum in comparison with DHA and 1.2 g residuum. While DHA is a good hydrogen donor compound, as evidenced by the coal conversion obtained, it is an inefficient donor, in that it produces a significant amount of a relatively poor donor compound, OHA. The results obtained this quarter illustrate the benefits of using NAHA's rather than conventional hydrogen donor compounds in model coprocessing reactions.

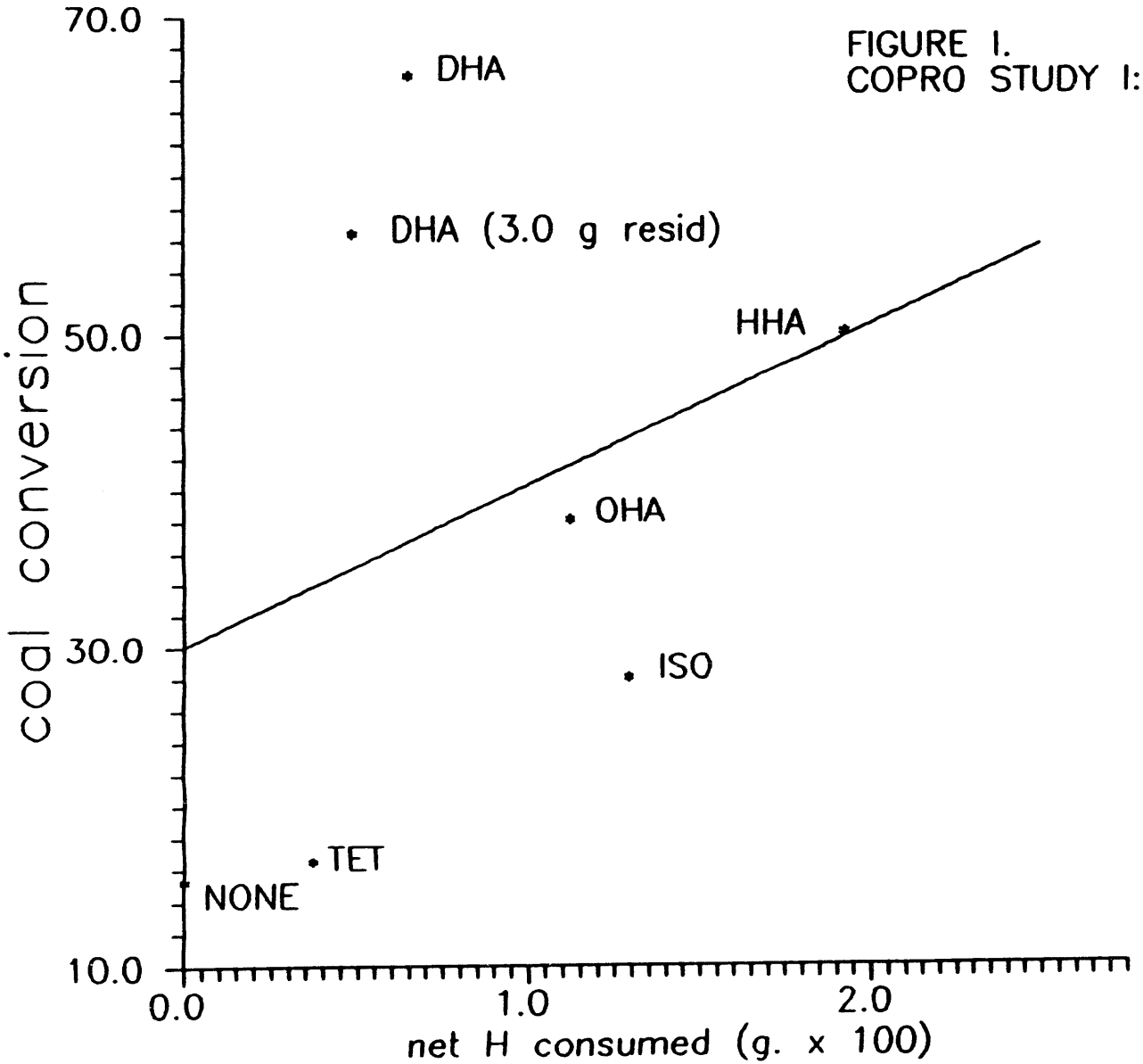

FIGURE I.
COPRO STUDY I: NITROGEN,
MAYA RESID

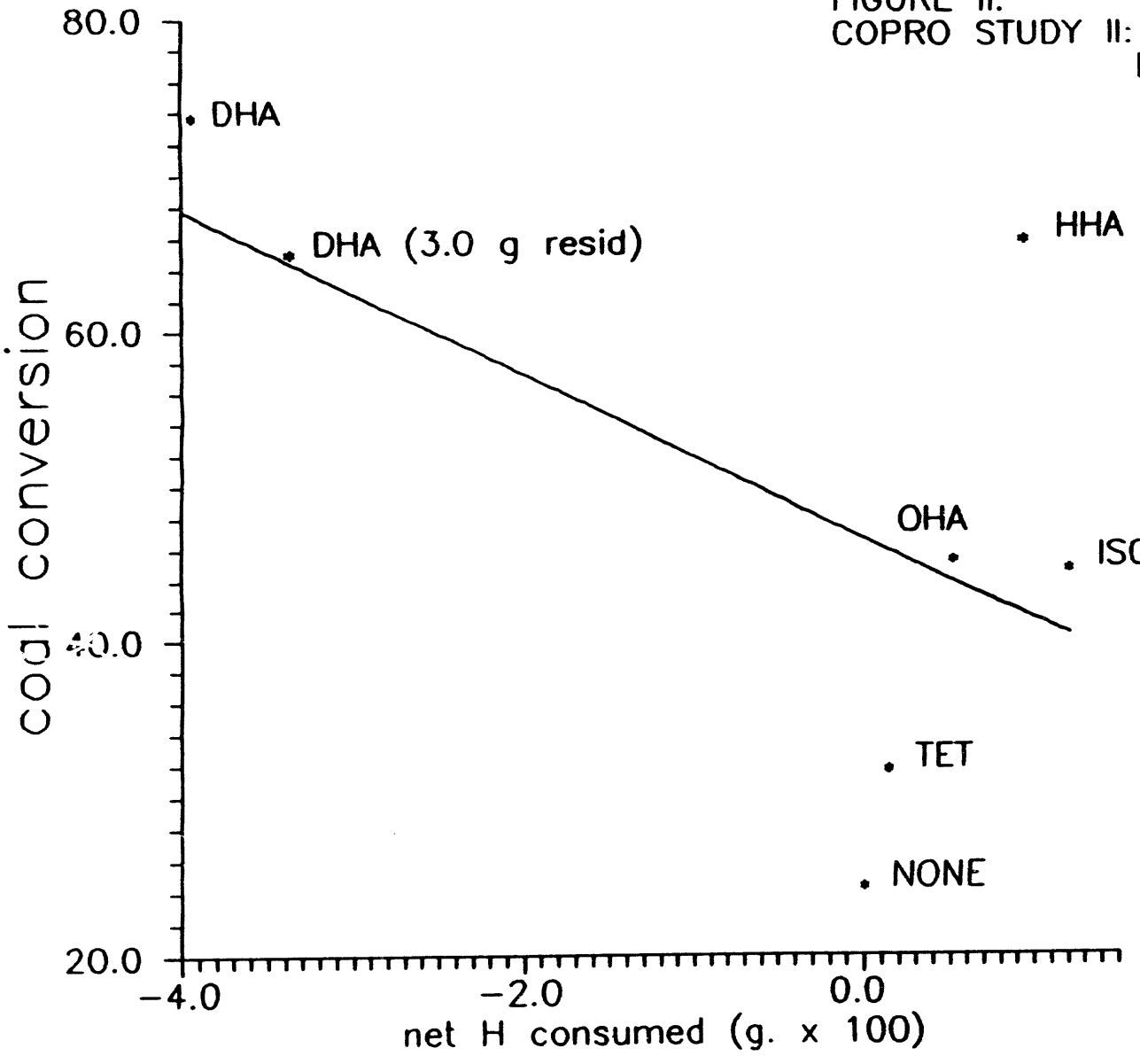

FIGURE II.
COPRO STUDY II: HYDROGEN,
MAYA RESID

APPENDIX A

Determination of Response Factors

The following equation A1 was used:

$$A_i/A_{BIP} = R_F\, W_i/W_{BIP} + Y_o \qquad (A1)$$

where A_i = peak area of compound of interest

A_{BIP} = peak area of biphenyl

W_i = weight of compound of interest

W_{BIP} = weight of biphenyl

R_F = response factor for the compound of interest and the biphenyl

Y_o = intercept of y axis

For the experimental work done this quarter, the compounds of interest were ANTH, PYR, and PHPYR. The peak area of the PHPYR was considered to be the total area of the seven isomers.

Samples were made by taking a carefully weighed amount of each compound, introducing it into a vial, adding approximately 15 mL of THF as a solvent, and then adding a carefully weighed amount of the biphenyl standard. The ratios of the weights of the compounds to the BIP are shown in Tables A1 - A3.

Each sample was injected into the GC five times and the average area ratio of the compound to the biphenyl, and the standard deviation were calculated. The experimental error was calculated by dividing the standard deviation by the average area ratio. The average area ratios and the corresponding standard deviation and error are also shown in Tables A1-A3.

Table 1. Weight Ratios and Corresponding Average Area Ratios of Anthracene to the Internal Standard Biphenyl

Sample Number	W_{ANTH}/W_{BIP}	Average A_{ANTH}/A_{BIP}	Std. Dev.	% Error
034	0.8800	0.7762	0.077	10.0
036	0.3922	0.3387	0.023	6.9
037	0.6060	0.5220	0.056	10.8
050	0.5651	0.6525	0.080	4.4
051	0.7438	0.7197	0.077	10.1

Table A2. Weight Ratios and Corresponding Average Area Ratios of Pyrene to the Internal Standard Biphenyl

Sample Number	W_{ANTH}/W_{BIP}	Average A_{ANTH}/A_{BIP}	Std. Dev.	% Error
033	0.7367	0.6339	0.098	15.4
036	1.0832	0.8684	0.056	6.5
037	0.5222	0.4136	0.059	14.2
051	0.6648	0.6089	0.100	16.5
053	0.8277	0.9029	0.061	6.7

Table A3. Weight Ratios and Corresponding Average Area Ratios of Perhydropyrene to the Internal Standard Biphenyl

Sample Number	W_{ANTH}/W_{BIP}	Average A_{ANTH}/A_{BIP}	Std. Dev.	% Error
033	1.0760	0.8366	0.076	9.0
036	0.8028	0.6323	0.025	3.9
037	1.6368	1.3137	0.103	7.8
054	0.9037	0.7862	0.036	4.6

Four or five samples were used to find each response factor. Using the average peak area ratios and the corresponding weight ratios of each compound to biphenyl, a line was fitted to equation A1 to yield the response factors. The calculated response factors and y intercepts are shown in Table A4.

Table A4. Response Factors and Y Intercepts for Anthracene, Pyrene, and Perhydropyrene Using Biphenyl as the Internal Standard

Compound	R_f	Y_o
Anthracene	0.864	0.052
Pyrene	0.850	0.033
Perhydropyrene	0.775	0.037

APPENDIX B

Original Data

The following are the data obtained from the coprocessing of Maya heavy petroleum residuum and Illinois No. 6 coal during this quarter. The data were analyzed in two ways. Data shown in the Method A were determined by the weight percent of each fraction dissolved in each solvent on the basis of the amount of whole fractions recovered. Data shown in the Method B were determined by calulating the weight percent of each fraction (except for the oil fraction), assuming the products to be completely recovered. The weight percent of the oil fraction is then obtained by subtracting the total weight percent of the other fractions from 100%.

Table B.1. Hydrogenation Reaction of Illinois No. 6 Coal[1]

Reaction No.	1-1103	2-1103
Reaction Condition	Thermal S=0.0368 g	Catalytic MoNaph Mo=2946 ppm S=0.0580 g
H_2 consumption (%)	3.2	16.8
Product Distribution (wt%)		
-Method A		
Gas	1.8	2.0
Oil	-0.1	9.0
Asphaltenes	6.7	23.0
Preasphaltenes	29.4	35.1
IOM	62.2	30.9
-Method B		
Gas	1.5	1.7
Oil	15.2	19.6
Asphaltenes	5.7	20.4
Preapshaltenes	24.9	31.0
IOM	52.7	27.3
Coal Conversion (%)	47.1	72.2
Recovery (%)	84.8	88.3

[1] 3g Illinois No. 6 Coal in 6 g n-Hexadecane

Table B.2. Coprocessing of Maya Heavy Petroleum Residuum and Illinois No. 6 Coal[1]

Reaction No.	1-1127	73-1127	2-1127	74-1127
Reaction Condition	Thermal S=0.0 g	Thermal S=0.0 g	Catalytic MoNaph Mo=2726 ppm S=0.0188 g	Catalytic MoNaph Mo=2772 ppm S=0.0192 g
H_2 Consumption (%)	9.3	7.7	15.8	24.1
Production Distribution (wt%)				
-Method A				
Gas	2.3	2.5	2.0	2.3
Oil	50.5	49.2	56.7	56.6
Asphaltenes	18.3	19.1	23.8	23.6
Preasphaltenes	9.8	10.1	7.1	7.0
IOM	19.0	19.1	10.4	10.5
-Method B				
Gas	2.3	2.4	1.9	2.2
Oil	51.6	50.6	58.7	59.0
Asphaltenes	17.9	18.6	22.7	22.3
Preasphaltenes	9.6	9.8	6.8	6.6
IOM	18.6	18.6	9.9	9.9
Coal Conversion (%)	37.3	37.6	66.7	66.8
Recovery (%)	98.0	97.4	95.5	94.5

(continued)

[1] 3g Illinois No. 6 Coal and 6 g of Maya at 400°C for 1 hour.

Table B.2. Coprocessing of Maya Heavy Petroleum Residuum and Illinois No. 6 Coal[1]

(continued)

Reaction No.	4-1204	12-1204	2-1212	73-1212
Reaction Condition	Catalytic VNaph V=2605 ppm S=0.0275 g	Catalytic VNaph V=2660 ppm S=0.00270 g	Catalytic $NiMo/Al_2O_3$ NiMo=2747 ppm S=0.0 g HXD=0.0309 g[2]	Catalytic $NiMo/Al_2O_3$ NiMo=2801 ppm S=0.0 g HXD=0.9130 g
H_2 consumption (%)	11.5	13.3	19.0	18.6
Product Distribution (wt%)				
-Method A				
Gas	4.0	4.1	2.6	2.1
Oil	46.8	44.3	49.0	55.4
Asphaltenes	20.9	22.0	26.5	22.0
Preasphaltenes	13.1	13.8	10.5	11.5
IOM	15.2	15.8	11.4	9.0
-Method B				
Gas	3.7	3.8	2.4	2.0
Oil	50.1	48.3	52.2	57.2
Asphaltenes	19.6	20.4	24.8	21.1
Preasphaltenes	12.4	12.8	9.9	11.1
IOM	14.2	14.7	10.7	8.6
Coal Conversion (%)	52.1	49.3	64.2	71.2
Recovery (%)	93.9	92.7	93.5	96.2

(continued)

[1] 3g Illonois No. 6 Coal and 6 g of Maya at 400°C for 1 hour.
[2] HXD (n-hexadecane) was introduced to balance the amount of n-hexadecane and the organic species of organometallic pastes used in the other catalytic reactions.

Table B.2. Coprocessing of Maya Heavy Petroleum Residum and Illinois No. 6 Coal[1]

(continued)

Reaction No.	3-1204	11-1204	1-1212
Reaction Condition	Catalytic NiNaph Ni=2765 ppm S=0.0097 g	Catalytic NiNaph Ni=2763 ppm S=0.0104 g	Catalytic NiNaph Ni=3340 ppm S=0.0110 g
H_2 consumption (%)	19.9	22.3	20.6
Product Distribution (wt%)			
-Method A			
Gas	2.6	2.6	2.7
Oil	53.5	49.6	50.2
Asphaltenes	23.0	24.9	21.5
Preasphaltenes	17.3	16.9	19.3
IOM	3.6	6.0	6.2
-Method B			
Gas	2.5	2.5	2.7
Oil	54.9	50.9	50.2
Asphaltenes	22.3	24.3	21.5
Preasphaltenes	16.8	16.5	19.3
IOM	3.5	5.8	6.2
Coal Conversion (%)	88.7	80.6	79.3
Recovery (%)	96.9	97.5	99.9

[1] 3g Illinois No. 6 Coal and 6 g of Maya at 400°C for 1 hour.

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