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

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MASTER

IMPROVED PERFORMANCE IN COPROCESSING

THROUGH FUNDAMENTAL AND MECHANISTIC

STUDIES IN HYDROGEN TRANSFER

AND CATALYSIS

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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.   Elucidation 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, Subtask I.B.2., Evaluation of Enhanced Factors Prevalent in Pretreated Residua, Subtask II.A., Synthesis of Nonaromatic Hydroaromatics by Reduction with Metals and Electroreduction, and Subtask II.D., Chemistry and Reactivity of Nonaromatic Hydroaromatic Enriched Petroleum Solvents.

EXPERIMENTAL WORK

TASK I. ELUCIDATION OF HYDROGEN TRANSFER REACTIONS IN COPROCESSING

SUBTASK I.A. HYDROGEN TRANSFER FROM CYCLOALKANES

INTRODUCTION

The objective as stated in 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 coprocessing. This quarter reactions were conducted using the model compounds anthracene, pyrene, and perhydropyrene. A full-time technician was trained to perform various lab duties including conducting reactions, analyzing products using the gas chromatograph (GC), and organizing data using a computer spreadsheet program. The moisture and ash content of Illinois No. 6 coal was determined and perhydroanthracene synthesis was begun.

EXPERIMENTAL

Materials. The materials used this quarter included anthracene (ANTH), pyrene (PYR), and perhydropyrene (PHPYR) mentioned above, biphenyl (BIP) as the internal standard for GC analysis, and tetrahydrofuran (THF) as a solvent. The TET, ANTH, PYR, PHPYR, and BIP were all purchased from Aldrich Chemicals and had a purity of 99% or higher. The THF was Fisher certified.

Equipment. The equipment used for reactions consisted of 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 3/4 inch stainless steel tubing bomb microreactors (TBMRs). The TBMRs used for model reactions had a length of 4.5 inches and a volume of approximately 20 cm^3, while those used for synthesis reactions

had a length of 6.5 inches and volume of approximately 50 cm^3. A Model 3400 Varian gas chromatograph was used for GC analysis. A Lab-Line vacuum oven was used for moisture analysis. A Thermolyne high temperature furnace was used for ash analysis.

Determination of the Moisture Content of Coal. In preparation for the upcoming coal research, the moisture and ash content of Illinois No.6 coal was determined using the Auburn Vacuum Oven Method and the ASTM D-3174 Method for measuring the ash content of coal. The moisture analysis was performed previously and the results were in poor agreement with results from another laboratory. It was decided to perform this analysis again, drying the coal for the maximum amount of time. The procedure and results for both moisture and ash analysis are shown in Appendix I.A.A.

Synthesis of Perhydroanthracene. The perhydroanthracene needed for certain model compound reactions will have to be synthesized, because it is unavailable through commercial sources. It was decided to first try a synthesis using anthracene, with no solvent, and a presulfided nickel-molybdenum (NiMo) catalyst in a hydrogen atmosphere. The presulfided NiMo catalyst was chosen because of this research group's past experience with it.

Procedure and Analysis for Perhydroanthracene Synthesis. One gram of anthracene and 0.25 grams of NiMo catalyst were introduced into a 50 cm^3 TBMR and charged with 1200 psig of hydrogen. The reactor was tested to insure there were no leaks and then submerged in a 250°C fluidized sand bath, and agitated vertically for four hours. At the end of the reaction, the TBMRs were quenched in a water bath, the pressure was released, and products were extracted with THF. GC analysis indicated that this first synthesis reaction resulted in an array of products. The

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retention times of the different products were so similar, that it was impossible to identify them by comparing them to chromatograms of known hydrogenated forms of anthracene. In order to aid in the identification of these different products, samples will be analyzed by Auburn University's mass spectrometry center. Once product peaks are identified, GC analysis can be used to determine to what extent hydrogenation occurred. By knowing the extent of hydrogenation and the major products, the synthesis can be conducted so that the production of perhydroanthracene can be maximized.

Procedure and Analysis for Model Compound Reactions. The reactions conducted this quarter were with ANTH alone and with an ANTH/PHPYR mixture. ANTH was reacted for sixty minutes, while three different ratios of the ANTH/PHPYR mixture were reacted for sixty and ninety minutes. A measured amount of the compound or mixture to be reacted was introduced into a TBMR and then charged with 400 psig nitrogen. The reactor was tested to insure there were no leaks and then submerged in a fluidized sand bath at 430°C and agitated at a rate of 425 cpm. 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 Mike Bedell, a chemical engineering graduate student at Auburn University. The products were recovered by extracting with THF. BIP, the internal standard for gas chromatography analysis, was introduced into the product vials. The products were then analyzed using gas chromatography. The GC conditions for the ANTH, PYR, and PHPYR reactions are shown in Table I.A.1.

RESULTS AND DISCUSSION

GC analysis for earlier ANTH/PHPYR reactions (50/50 mixture by weight reacted for 60 minutes) had revealed an unknown product. Due to the location of the unknown product peak on

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the chromatogram, and the fact that the recovery of the ANTH was less than that of the of the PHPYR, it was postulated that the unknown product was a hydrogenated form of anthracene. Mass spectrometry analysis revealed that the unknown peak was probably 9,10-dihydroanthracene (DHA). The mass spectrum for the unknown peak agreed with the published DHA spectra. GC analysis for these same reactions also revealed that small amounts of PYR were being formed.

To investigate this phenomenon further, ANTH/PHPYR reactions were conducted in which the reaction time and/or weight ratio was varied. Reactions with weight ratios of 2/1, 1/1, and 1/2, were conducted at both sixty and ninety minutes. Reactions were duplicated and in some cases triplicated. As with the earlier reactions, GC analysis revealed that DHA and PYR were formed. To insure that these compounds were not the result of contaminated materials, the purity of the THF, BIP, and all reactants was confirmed with GC analysis. Table I.A.2 shows the results of all the ANTH/PHPYR reactions conducted thus far.

As can be seen from Table I.A.2, the trend for the percent DHA generated is as follows:

2/1 (60) < 2/1 (90) < 1/1 (90) < 1/1 (60) = 1/2 (60) < 1/2 (90)

The trend for the percent PYR generated is:

1/2 (60) < 2/1 (60) < 1/2 (90) < 1/1 (60) < 1/1 (90) < 2/1 (90)

The data indicates that the optimum conditions for DHA generation are not the same as for PYR generation. A reaction mechanism study may reveal the reason(s) for these trends.

The recoveries of the starting components, ANTH and PHPYR will be calculated as soon as the new response factors have been determined. A check of the previously calculated response factors indicated that the response factors have changed over the last few months. Obviously, it is absolutely necessary to use correct response factors in order to get accurate results. Several more samples will be analyzed by the mass spectrometry center in order to confirm the presence of DHA and PYR, and to determine if there are any additional products present.

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The single component ANTH reactions conducted this quarter proved to be stable at the reaction conditions used (430°C, 400 psig nitrogen, 60 minutes) with no products being formed.

CONCLUSIONS

This quarter experiments were conducted with ANTH alone, and with ANTH in a mixture with PHPYR. The ANTH/PHPYR reactions were conducted at several different ratios for both 60 and 90 minutes. The percentage of DHA and PYR generated depended on the weight ratio and the reaction time. Further analysis of ANTH/PHPYR reaction products will reveal if any other compounds are formed. Reactions with ANTH alone proved to be stable with no products being formed. This is in agreement with an earlier ANTH reaction.

The moisture content of Illinois No.6 coal was again determined, and this time the results were in fairly good agreement with earlier results found for this coal. In this second analysis the drying time was increased to sixteen hours, the upper range limit of drying time. The sample from the moisture analysis was used to determine the ash content of Illinois No.6 coal.

The reaction to synthesize perhydroanthracene yielded an array of products. In order to obtain a "fingerprint" of the different hydrogenated forms of anthracene produced, samples have been sent to the mass spectrometry center to be analyzed. Once the different GC peaks have been identified, the reaction can be conducted in a way that will maximize the amount perhydroanthracene produced.

Table I.A.1.   **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

Table I.A.2.   **Product Percentages for ANTH/PHPYR Reactions**

Reaction Time	Weight Ratio	Sample Number	%DHA *	%PYR **
60 minutes	2/1	97	2.66	1.06
		98	3.42	1.23
	1/1	90	9.20	2.15
		91	7.97	1.73
	1/2	95	8.03	0.66
		96	9.20	0.77
90 minutes	2/1	100	5.29	2.38
		109	5.57	2.66
		110	6.49	3.02
	1/1	99	5.35	2.30
		101	7.32	2.26
	1/2	102	10.2	1.31
		111	8.33	1.02
		112	7.14	1.30

*   %DHA = DHA peak area/(DHA peak area + ANTH peak area)
**   %PYR = PYR peak area/(PYR peak area + PHPYR peak area)

SUBTASK I.B.1. PRETREATMENT OF PETROLEUM RESIDUA FOR ENHANCED HYDROGEN TRANSFER

INTRODUCTION

During this quarter, the effect of pretreated Maya residuum, which was hydrogenated with a presulfided powdered nickel-molybdenum/alumina ($NiMo/Al_2O_3$) catalyst, on thermal coprocessing reactions with Illinois No. 6 coal was examined. In addition, the contents of molybdenum (Mo), nickel (Ni) and several other trace metals in the tetrahydrofuran (THF) soluble fractions of Maya, that were catalytically pretreated with Mo, Ni or vanadium (V) naphthenate in the presence of additional sulfur, were measured by atomic absorption and/or atomic emission spectrometry. The catalytic species of Mo sulfide from Mo naphthenate were produced from model hydrogenation reactions with excess sulfur, and the structural composition of these Mo sulfides was analyzed by X-ray diffraction spectrometry.

EXPERIMENTAL

Preparation of Presulfided NiMo/Al₂O₃ Catalyst. A commercial $NiMo/Al_2O_3$ catalyst (Shell 324 1/32 inch diameter extrudates: 2.72 wt% Ni and 13.16 wt% Mo) was dried and presulfided in a tubular furnace and pulverized to -150 mesh. First, ten grams of Shell 324 extrudates were packed between glass wool plugs in a one inch outside diameter borosilicate glass tube. The catalyst extrudates were dried at 300°C in a nitrogen (N_2) gas flow (30 Ml/min) for one hour. After the temperature was lowered to 225°C, the gas stream was switched to a hydrogen sulfide (H_2S)/hydrogen (H_2) gas mixture (10 vol% H_2S) flow of 20 Ml/min at 225°C. The catalyst extrudates were sulfided in this H_2S/H_2 mixture through a temperature-programmed procedure for two hours at 225°C, one hour at 315°C and two hours at 370°C. The sulfided catalyst was cooled to ambient temperature in N_2 gas flowing at 30 Ml/min for one hour to remove H_2S excessively adsorbed on the catalyst. During the sulfiding procedure, effluent gases were passed through a five

wt% lead nitrate (Pb(NO$_3$)$_2$) solution to remove H$_2$S from the outstream. The sulfided extrudates were pulverized to -150 mesh size and stored in a desiccator.

Pretreatment of Maya Residuum with a Presulfided NiMo/Al$_2$O$_3$ Catalyst. Twelve grams of Maya residuum were hydrogenated with 0.0270g of the powdered presulfided NiMo/Al$_2$O$_3$ catalyst (corresponding to the metal level of about 3000 ppm Ni and Mo) in a 56 cm^3 batch tubing bomb microreactor. The hydrogenation reaction conditions were the same as those described in the previous quarterly report, but elemental sulfur was not added. After the reaction, the pretreated Maya products were separated by a solvent extraction with THF. The THF-soluble fraction was recovered, and after evaporation of the THF, was used in the subsequent thermal coprocessing reactions.

Coprocessing of Illinois No. 6 Coal and Pretreated Maya Residuum. A mixture of 3g of Illinois No. 6 coal and 6g of the THF-solubles from Maya pretreated with NiMo/Al$_2$O$_3$ was thermally hydrogenated at 400°C for 1 hour. Reaction conditions, such as the reactor size, hydrogen pressure, agitation rate, solvent extraction procedure (using hexane, toluene and THF), and the H$_2$ consumption measured by gas chromatography (GC) were the same as described in the previous quarterly report.

Analysis of Metal Content in the THF-Solubles Fraction of Pretreated Maya Residuum. Amounts of metals contained in the original Maya residuum and the THF-solubles fraction of Maya residuum products pretreated with Mo, Ni and V sulfides were measured by graphite furnace atomic absorption spectrometry (AAS) and/or inductively coupled argon plasma (ICAP) atomic emission spectrometry. The original Maya contained only a negligible amount of THF-insolubles (less than

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0.2 wt%) and was directly analyzed without solvent extraction with THF. Pretreated Maya residua, that were hydrogenated with Mo, Ni and V naphthenates in the presence of additional elemental sulfur (0.018g of sulfur for Mo, 0.011g of sulfur for Ni, and 0.027g of sulfur for V) were fractionated into THF-solubles and insolubles. The THF-solubles fractions were analyzed for metals.

Structures of *in situ* Generated Mo and V Sulfides. Mo and V sulfides were generated *in situ* from Mo naphthenate and vanadium (III) acetylacetonate and vanadyl (IV) acetylacetonate, respectively, with excess sulfur from model hydrogenation reactions. The metal precursors at approximately 3000 ppm Mo or V were introduced in pure hexadecane or in a hexadecane solution containing 2 wt% naphthalene or 1 wt% indole. Elemental sulfur was added at three times the stoichiometric amount of sulfur required to form MoS_2 for Mo species and eighteen times the stoichiometric amount of sulfur required to form V_2S_3 for V species. Each metal sulfide was generated *in situ* during hydrogenation reactions at 380°C for 30 minutes under an atmosphere of approximately 2700 psig H_2. The black precipitates, possibly metal sulfides, were recovered by centrifugation after the reactions. Each Mo or V sulfide sample was washed with about 20 Ml of THF once a day for three weeks to dilute the concentration of organic species possible adsorbed and/or entrapped in the metal sulfides. After each THF washing, metal sulfides were dried under a flowing N_2 gas stream and stored in a vacuum desiccator. The structures of the metal sulfides were examined by X-ray diffraction spectrometry.

RESULTS AND DISCUSSION

Effect of Pretreated Maya Residuum on Thermal Hydrogenation of Illinois No. 6 Coal. Three types of thermal reactions were conducted with the THF-solubles fraction of Maya residuum pretreated with a $NiMo/Al_2O_3$ catalyst: (1) a hydrogenation reaction with the pretreated Maya alone, (2) a

coprocessing reaction with the pretreated Maya and Illinois No. 6 coal under a H_2 atmosphere, and (3) a coprocessing reaction with the pretreated Maya and Illinois No. 6 coal under a N_2 atmosphere. The overall product distribution based on the weight of each fraction extracted by hexane, toluene and THF (oils, asphaltenes, preasphaltenes and insoluble organic matter (IOM)) were summarized in Table I.B.1.1 using method A (explained in the previous quarterly report).

The thermal hydrogenation of the THF-solubles of the pretreated Maya alone (case 1) produced about 2.8 wt% gases, 76.7 wt% oil, 19.4 wt% asphaltenes, 0.7 wt% preasphaltenes and 0.4 wt% IOM. Compared to the original Maya (68.7 wt% oil, 31.1 wt% asphaltenes, and very little IOM), two step hydrogenation (catalytically with $NiMo/Al_2O_3$ and then thermally) produced more oil. But, at the same time, the two step thermal hydrogenation retrogressively produced an IOM fraction from the IOM-free reactant. Because the fraction distribution of Maya pretreated with the $NiMo/Al_2O_3$ catalyst has not yet been obtained, the effect of the two step thermal hydrogenation on the fraction distribution of the pretreated Maya cannot be examined in detail at this time.

The thermal coprocessing reactions of coal and the THF-solubles fraction of the pretreated Maya under a H_2 atmosphere (case 2) produced about 4.4 wt% gases, 50.2 wt% oil, 16.3 wt% asphaltenes, 18.4 wt% preasphaltenes and 10.7 wt% IOM. When the fractions produced from the pretreated Maya (corresponding to the results in case 1) were subtracted from the overall fractions, the fractions produced from coal were 7.6 wt% gases, -2.7 wt% oil, 10.1 wt% asphaltenes, 53.6 wt% preasphaltenes and 31.1 wt% IOM, and 68.3% of the coal was converted. Compared to the results with the Maya pretreated with Mo, Ni, and V catalysts and thermal hydrogenation (in the previous quarterly report), the Maya pretreated with $NiMo/Al_2O_3$ enhanced coal upgrading to some extent (Mo with S > Ni with S > $NiMo/Al_2O_3$ > V with S > thermal). However, it should be pointed out that results with Maya pretreated with the $NiMo/Al_2O_3$ catalyst were far less reproducible than the results of other reaction sets.

Thermal coprocessing reactions were conducted with coal and Maya residuum pretreated with a $NiMo/Al_2O_3$ catalyst under nitrogen conditions (case 3) for testing the possible transfer of hydrogen from the pretreated Maya to coal. The overall fraction distribution showed 4.2 wt% gas, 44.2 wt% oil, 12.8 wt% asphaltenes, 11.2 wt% preasphaltenes, and 27.8 wt% IOM. Compared to the results obtained under the H_2 condition (case 2), all of the fractions except for the IOM were substantially reduced as well as was coal conversion (coal conversion was only about 15% under the 850 psig N_2 condition at the reaction temperature). However, the reaction with pretreated Maya alone under the nitrogen condition needs to be completed to examine the possibility of hydrogen transfer from the pretreated Maya residuum to coal and to calculate the actual enhancement in coal upgrading by coprocessing under the nitrogen condition.

Analysis of Trace Metals in THF-Solubles Fraction of Pretreated Maya Residuum. The contents of Mo, Ni and other trace metals in the THF-soluble fractions of the Maya residuum, that were catalytically pretreated with Mo, Ni or V naphthenate, were measured using atomic absorption and/or atomic emission spectrometry. The vanadium content of the THF-soluble fractions of the Maya residuum could not be measured with the available instrumentation.

The original Maya residuum, which was reported to contain 118 ppm Ni and 680 ppm V by Amoco Oil Company, was shown to contain 240 ppm Ni and 4.1 ppm Mo (Table I.B.1.2). When Maya residuum was catalytically treated with Mo, Ni and V and extracted by THF, each THF-soluble fraction of Maya showed higher concentrations of catalyst metal but lower concentrations of other metals. For example, THF-solubles of Maya pretreated with Mo catalyst contained less Ni (170 ppm) but more Mo (1084 ppm) than the original Maya. The THF-solubles of Maya pretreated with Ni catalyst contained less Mo (2.7 ppm) but more Ni (650 ppm), and the THF-solubles of Maya pretreated with V contained less Mo (2.0 ppm) and Ni (210 ppm).

From this analysis, the high concentrations of catalyst species remaining in the THF-solubles fractions of pretreated Maya residuum was suspected to be at least partially responsible for upgrading the coal and the pretreated Maya during thermal coprocessing (as well as hydrogen transfer from pretreated Maya to coal). Actually, in the previous results, the effect of Maya, pretreated with Mo, Ni and V catalysts on subsequent thermal coprocessing was shown to be as high as the effect of each catalyst of 3000 ppm metal used in one-stage catalytic coprocessing reactions.

To test the activity of metals remaining in the THF-solubles fraction of pretreated Maya residuum, the following experiments have been designed. First, two more samples of Maya pretreated with Mo and Ni naphthenates will be prepared and extracted with hexane, toluene and THF to test which fraction(s) contain the metal species. Each fraction of hexane and toluene solubles are centrifuged twice to enhance the removal of possible colloidal suspension of catalyst species not soluble in each solvent. Next, the analyses for metals in each fraction are conducted using the same techniques used in this report. Coal conversion efficiencies of metal species at lower metal levels, such as 600, 300 or 150 ppm metal, in coprocessing will also be tested. Metal contents of the THF-solubles fraction of Maya residuum pretreated with solid NiMo/Al$_2$O$_3$ catalyst will also be tested to determine whether Mo and Ni naphthenate species remained in the THF-solubles fractions as organometallic species so that solvent extraction could not remove them from the THF-solubles fraction.

Structures of *in situ* Generated Mo and V Sulfides. Catalytic species of Mo sulfide and V sulfide were produced *in situ* in the model hydrogenation reactions in the presence of excess sulfur for the analysis of the structural composition of metal sulfides using X-ray diffraction spectrometry. Mo and V sulfides were generated *in situ* from Mo naphthenate and vanadium (III) acetylacetonate and vanadyl (IV) acetylacetonate with excess sulfur. Three Mo sulfide samples were prepared *in situ*

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from a model hydrogenation reaction at 380°C with additional elemental sulfur (three times stoichiometric amount of sulfur required to form MoS_2, a black precipitate). The metal sulfide samples were formed (1) from a reaction without a model compound reactant in hexadecane, (2) from a reaction with naphthalene in hexadecane, and (3) from a reaction with indole in hexadecane. By X-ray diffraction analysis, all samples showed similar patterns, but the patterns were not conclusively matched to those of the crystalline structures of Mo sulfides. These results indicated that the metal sulfide species of Mo and V were either amorphous, or that the metal sulfide samples possessed sufficient quantities of organic compounds to hinder the X-ray diffraction analysis.

CONCLUSIONS

The THF-solubles fraction of Maya residuum pretreated with a powdered $NiMo/Al_2O_3$ catalyst showed an ability to upgrade coal in the rank of Mo with S > Ni with S > $NiMo/Al_2O_3$ > V with S > thermal pretreating. In the coming quarter, more of the THF-solubles fraction of Maya residuum pretreated with a $NiMo/Al_2O_3$ catalyst will be prepared to further evaluate the effect of Maya residuum pretreated with a $NiMo/Al_2O_3$ catalyst on subsequent thermal coprocessing. The THF-solubles fraction prepared will be used in comparison of second-stage thermal coprocessing reactions under hydrogen and nitrogen conditions and in the second-stage thermal reaction of Maya residuum alone under nitrogen conditions. The pretreated Maya will also be fractionated into oil, asphaltenes, preasphaltenes and IOM, and this product distribution will be used as a reference for evaluating the effect of the second-stage hydrogenation of pretreated Maya residuum.

The THF-solubles fraction of catalytically pretreated Maya residuum contained high concentrations of catalyst metals, and these metals might act as catalysts during thermal coprocessing. To test whether the present solvent extraction procedure can remove metals from

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each solvent-solubles fraction and to analyze which fraction contains metals, two hydrogenation reactions of Maya residuum with Mo and Ni naphthenates will be conducted, and the hydrogenated products will be carefully extracted using double centrifugation. The contents of metals in the prepared fractions will be analyzed using atomic absorption and/or emission spectrometry. Several catalytic coprocessing reactions with low metal contents, such as 600, 300, or 150 ppm metal, will be performed to evaluate the critical amount of catalyst species necessary for upgrading coal and residuum.

The structure and composition of metal sulfides (Mo and V) will be analyzed by X-ray diffraction spectrometry using the samples which were carefully washed with THF for three weeks.

Table I.B.1.1.   **Thermal Reactions of Maya Pretreated with a NiMo/Al_2O_3 Catalyst**

Condition[1]	H_2 Used (%)	Overall Product Distribution[2] (wt%)					Coal Conv (%)	Toluene-Solubles
		Gas	Oil	Asp	Preasp	IOM		
A	6.5 ± 1.1	2.8 ± 0.1	76.7 ± 0.1	19.4 ± 0.0	0.7 ± 0.3	0.4 ± 0.3	-	96.1 ± 0.1
B	13.6 ± 2.6	4.4 ± 0.8	50.2 ± 1.7	16.3 ± 0.0	18.4 ± 0.2	10.7 ± 1.1	68.0 ± 2.3	66.5 ± 1.7
C		4.2 ± 0.6	44.2 ± 1.7	12.8 ± 0.1	11.2 ± 0.5	27.8 ± 0.8	NC[3]	56.9 ± 2.0

[1] A = Hydrogenation of pretreated Maya residuum alone.
 B = Coprocessing of pretreated Maya residuum and Illinois No. 6 Coal under a H_2 atmosphere.
 C = Coprocessing of pretreated Maya residuum and Illinois No. 6 Coal under a N_2 atmosphere.

[2] Overall product distribution produced from both coal and residuum.
 Asp (asphaltenes), Preasp (preasphaltenes), IOM (insoluble organic matter) and Toluene-Solubles (oil and asphaltenes).

[3] NC = not calculated

Table I.B.1.2.   **Metal Concentrations in Catalytically Pretreated Maya[1]**

Metal	Original Maya (ppm)	THF-Solubles of Pretreated Maya		
		with MoNaph (ppm)	with NiNaph (ppm)	with VNaph (ppm)
Mo	4.1	1084	2.72	1.98
Ni	240	170	650	210
Ca	0.74	0.45	0.61	0.26
K	-0.28	0.03	-0.1	-0.09
Mg	0.27	0.06	-0.2	-0.18
P	0.35	1.18	0.52	0.67
Cu	0.08	1.97	0.5	0.69
Fe	0.51	0.96	0.27	0.96
Mn	0.16	0.16	0.02	0.1
Zn	3.48	1.62	5.46	4.65
Al	1.54	5.28	3.85	-3.12
Ba	0.0	-0.02	-0.06	-0.06
Co	0.08	0.52	0.5	0.07
Cr	1.9	2.6	0.84	4.29
Pb	-0.1	0.42	0.11	0.11
Si	0.47	0.25	0.18	0.29

[1] Metals except for Ni were analyzed by inductively coupled argon plasma (ICAP) spectrometry. Ni was analyzed by graphite furnace atomic absorption spectrometry.

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

INTRODUCTION

During this quarter, the research concerning evaluation and characterization of untreated and hydropretreated residua was continued from the previous quarter. Quantitative analysis by Fourier transform infrared (FTIR) spectrometry was conducted by using a Nicolet 5SXC FTIR spectrometer for the examination and comparison of untreated residua with residua hydropretreated prior to coprocessing in order to determine chemical factors that make certain hydropretreated residua more effectual as coprocessing solvents. Additional work was conducted on the reactions of aromatic compounds such as those present in coal and hydroaromatic compounds such as those present in residua to investigate hydrogen transfer from hydrogen donor hydroaromatic compounds to hydrogen acceptor aromatic compounds.

This quarter, benzophenone was used as a hydrogen acceptor, and tetralin, dihydroanthracene, octahydroanthracene and fluorene were used as hydrogen donors. Products from these model compound reactions were analyzed by gas chromatography (GC). Response factors, required for GC analysis, were determined for benzophenone, diphenylmethane and naphthalene. The response factor for naphthalene will be determined again next quarter due to the unsatisfactory value (from previous experience) obtained this quarter.

EXPERIMENTAL

FTIR Analysis of Untreated and Hydropretreated Maya Residua. In the FTIR spectra of all samples, there are two aromatic regions: 3093 cm^{-1} to 2995 cm^{-1} (Ar1) and 920 cm^{-1} to 628 cm^{-1} (Ar2). For quantitative comparisons of all spectra, two kinds of peak area ratios were calculated using the data obtained from the Nicolet 5SXC FTIR spectrometer. They are (1) the 3093 cm^{-1} to 2995 cm^{-1} (Ar1) to the 2995 cm^{-1} to 2770 cm^{-1} aliphatic region (Al) and (2) the 920 cm^{-1} to 628 cm^{-1}

(Ar2) to the 2995 cm^{-1} to 2770 cm^{-1} (Al) peak area ratios. The peak area ratios of FTIR spectra of untreated Maya residuum and pretreated Maya residuum were compared and related to their efficiencies in coprocessing.

Procedure for Model Compound Reactions. The solvent, 1-methylnaphthalene, was thermally reacted alone and with tetralin to determine if 1-methylnaphthalene was involved in hydrogen transfer. Tetralin, octahydroanthracene, dihydroanthracene and fluorene were each reacted with benzophenone in a 1/5 mixture (by weight) using 1-methylnaphthalene as the solvent. Each reaction was conducted at least two times in a reactor with a volume of approximately 24mL. A weighed amount of the compound or mixture of compounds was introduced into a tubing bomb microreactor and then charged with 430 psig nitrogen. The reactor was tested to insure that there were no leaks and then submerged in a fluidized sand bath at 400°C. All reactions were conducted for one hour using 425 cpm horizontal agitation. At the end of each reaction, the reactor was quenched in a water bath. The gas pressure in the bomb was released and measured using a pressure determination apparatus. After the products were recovered by extracting with THF, biphenyl, the internal standard for GC analysis, was added to the product vials, and the reaction products were analyzed using GC. The recovery of benzophenone was calculated using the data from the GC analysis. A sample calculation for the recovery of benzophenone is shown in Appendix I.B.2.A. The GC conditions for the analysis of all products are shown in Table I.B.2.1.

Determination of Response Factors. In order to utilize the internal standard method in GC analysis, it was necessary to determine the response factors between the analyzed compounds and the internal standard, biphenyl. A sample calculation for response factors and results are shown in Appendix I.B.2.B.

RESULTS AND DISCUSSION

Table I.B.2.2. shows the FTIR peak area ratios for 3093 cm^{-1} - 2995 cm^{-1} (Arl) to 2995 cm^{-1} - 2770 cm^{-1} (A1) and 920 cm^{-1} - 628 cm^{-1} (Ar2) to Al for catalytically (nickel naphthenate (NiNaPh), molybdenum naphthenate (MoNaPh), and vanadium naphthenate (VNaph)) pretreated Maya asphaltene fractions. The aromatic character for both ratios give the same catalytic order: NiNaPh < MoNaPh < VNaph < Thermal (no catalyst).

Table I.B.2.3. and Table I.B.2.4. show the ratios of Ar1 to A1 and Ar2 to A1 for the asphaltene fraction products from the catalytic coprocessing reactions with untreated Maya residuum and for the asphaltene fraction products from thermal coprocessing reactions with catalytically pretreated Maya residuum. The aromatic characters of these products have the same catalytic order as hydropretreated Maya before coprocessing. The order is NiNaPh < MoNaPh < VNaph < Thermal. These data indicate that the products from the reaction with pretreated Maya residuum have lower aromatic characters (and, from previously reported data, higher coal conversion) than the products from reactions with untreated Maya residuum.

Table I.B.2.5. shows the FTIR peak area ratios for the untreated Maya residua THF-solubles and prehydrotreated Maya residuum THF-solubles. A lower aromatic character was observed for the THF-solubles from catalytically pretreated Maya with catalytic order, MoNaPh < NiNaPh $\leq$ Thermal (no catalyst). The highest aromatic character was observed for the original untreated Maya residuum. The catalytic order for coal conversion has been shown (see Table I.B.2.6.) to be NiNaPh $\geq$ MoNaPh > VNaph > Thermal. The aromatic character found in products from catalytic coprocessing and in catalytically pretreated Maya residua using these same catalysts agree well with the reactivity of these catalysts in coal conversion with Maya residuum. It was hypothesized that catalytic pretreatment of Maya residuum prior to coprocessing leads to the formation of hydroaromatic compounds having lower aromatic character (higher aliphatic character) than the

aromatic compounds originally present in the residuum. Further experimentation needs to be performed next quarter to test this hypothesis.

Table I.B.2.7. shows the result of the hydrogen donor/hydrogen acceptor model compound reactions. The 58.4 mole percent conversion of benzophenone to diphenylmethane in the reaction with dihydroanthracene and benzophenone indicated that dihydroanthracene was the strongest of the four hydrogen donor compounds tested. The calculated recoveries for benzophenone for most reactions studied are reasonable. For the lower recoveries in some reactions, error could have been caused by several factors. For instance, the yield for benzophenone would be slightly higher if hydrocracking was taken into account. Error may have also occurred during the GC analysis. Error could have also occurred if product gases escaped in the form of vapor during extraction with THF. There is always the possibility of instrumental as well as experimentalist error. All sources of experimental error will be investigated next quarter.

The GC analysis of products showed that anthracene was formed in the benzophenone and dihydroanthracene reaction. The same unknown product, thought to be a hydrogenated form of dihydroanthracene and octahydroanthracene, was formed in both the benzophenone/dihydroanthracene and benzophenone/octahydroanthracene reactions. Two other unknown products in the octahydroanthracene reaction were thought to be two hydrogenated forms of octahydroanthracene. The unknown products will be investigated further next quarter.

CONCLUSIONS

The coprocessing products formed from reactions with pretreated Maya residuum have lower aromatic character and give higher coal conversions than the coprocessing products formed from reactions with untreated Maya residuum. An inverse relation exists between aromatic character and coal conversion in catalytic order. For aromatic character, the catalytic order is NiNaPh < MoNaPh < VNaph ≤ Thermal.

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It is also important to note that naphthalene was formed in the reactions with 1-methylnaphthalene alone and with tetralin and 1-methylnaphthalene without benzophenone. Because the solvent, 1-methylnaphthalene, and tetralin both produce naphthalene in the tetralin-benzophenone reaction, a solvent such as hexadecane may be substituted for 1-methylnaphthalene next quarter.

Table I.B.2.1.   **Gas Chromatography Conditions for Product Analysis**

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

Table I.B.2.2   **FTIR Peak Area Ratios of Pretreated Maya Asphaltene Fractions Before Coprocessing**

Pretreating Catalysts	Areas			Ratios		
	Ar1	A1	Ar2	Ar2/Ar1	Ar1/A1	Ar2/A1
MoNaPh	3.7725	226.49	29.216	7.7445	0.0167	0.1289
NiNaPh	3.6035	212.71	28.369	7.8726	0.0169	0.1333
Thermal	4.1693	194.45	32.461	7.7857	0.0214	0.1669

Table I.B.2.3. FTIR Asphaltene Fraction Peak Area Ratios of Thermal Coprocessing Products with Catalytically Pretreated Maya Residuum

Pretreating Catalysts	Areas			Ratios		
	Ar1	A1	Ar2	Ar2/Ar1	Ar1/A1	Ar2/A1
MoNaPh	3.6627	122.10	28.194	7.6976	0.0300	0.2309
NiNaPh	2.651	108.17	20.315	7.6631	0.0245	0.1878
VNaph	3.781	122.98	29.031	7.6769	0.0307	0.2361
Thermal	3.1891	87.638	24.488	7.7686	0.0364	0.2794

Table I.B.2.4. FTIR Asphaltene Fraction Peak Area Ratios of Catalytically Treated Coprocessing Products with Untreated Maya Residuum

Coprocessing Catalysts	Areas			Ratios		
	Ar1	A1	Ar2	Ar2/Ar1	Ar1/A1	Ar2/A1
MoNaPh	2.2291	61.932	16.847	7.3977	0.0360	0.2720
NiNaPh	2.2405	65.156	17.041	7.7445	0.0344	0.2615
VNaPh	2.2028	55.059	16.108	7.3125	0.0400	0.2926
Thermal	2.1533	53.497	15.829	7.3510	0.0403	0.02959

Table I.B.2.5. FTIR Peak Area Ratios for THF-Soluble Fractions from Pretreated Maya and Original Maya Residua

Pretreating Catalysts	Area		Ratio
	Ar1	A1	Ar1/A1
MoNaPh	0.081	126.74	0.0006
NiNaPh	0.3683	204.95	0.0018
Thermal	0.2246	119.0	0.0019
Untreated	0.2609	130.51	0.0020

Table I.B.2.6. Coal Conversions of Coprocessing Reactions with Untreated Maya Residuum and with Pretreated Maya Residuum

Pretreating or Coprocessing Conditions	Coal Conversion (%)	
	Reactions with Original Maya	Reactions with Pretreated Maya*
NiNaph	82.8	89.7
MoNaph	66.9	92.1
VNaph	50.7	58.2
Thermal	37.4	41.2

*Coprocessing reactions with pretreated Maya were conducted under thermal conditions without catalysts.

Table I.B.2.7.   Model Compound Reactions[1]

Compound Name[2]	BNP		DPM Formed	BNP Conversion to DPM mole %	Recovery	
	before Rxn.	after Rxn.			BNP (%)	Total Sample
BNP	0.0803g	0.0637g	0.0	0.0	80	99.4%
BNP+TET	0.0814g	0.0718g	0.0144g	19.2	107	101.1%
BNP+DHA	0.0805g	0.0333g	0.0434g	58.4	99.8	102.5%
BNP+OHA	0.0804g	0.0600g	0.0149g	20.1	90	107%
BNP+FLR	0.0800g	0.0655g	0.0152g	20.6	103	97.2%

[1] 1-methylnaphthalene was used as the solvent in all reactions
[2] Abbreviations: BNP - benzophenone
                       TET - tetralin
                       DHA- dihydroanthracene
                       OHA- octahydroanthracene
                       FLR - fluorene

TASK II. DEVELOPMENT OF POTENT NONAROMATIC HYDROAROMATIC DONORS FOR COPROCESSING

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. Once successful methods have been developed using aromatic model compounds for the synthesis of nonaromatic hydroaromatics, their synthesis will be performed in real solvent materials such as atmospheric (or vacuum) residua and FCC Bottoms (Subtask II.C.). Because of the continued availability of additional manpower, research continued this quarter on the synthesis of nonaromatic hydroaromatic compounds both by Birch reduction with metals and by electroreduction methods.

EXPERIMENTAL

During the quarter, a Model 640 digital coulometer purchased from The Electrosynthesis Company Inc., East Amherst, New York, was thoroughly tested and calibrated for use in the synthesis of nonaromatic hydroaromatic compounds from their aromatic analogues using electroreduction methods similar to those employed by the Kariv-Miller research group at the University of Minnesota. A Model 6010A constant voltage/constant current autoranging power supply purchased from Hewlett Packard Company was also evaluated for use in the electroreduction synthesis.

An electrochemical cell of similar design to that described by the Kariv-Miller research group was also constructed this quarter. Platinum-platinum electrical connections for the electrochemical cell electrodes were made using a microarc welder made available by the Space Power Institute at Auburn University. Platinum-copper electrical connections for the

electrochemical cell electrodes were made using one-sixteenth inch outside diameter copper tubing. Teflon stoppers were machined to support the electrochemical cell electrodes and/or the anode chamber for divided cell operation.

A Cannon Instrument Company Model H1 constant temperature water bath was incorporated into the experimental setup for critical control of the electrochemical cell temperature during electroreduction. A magnetic stirring motor/teflon stirring bar combination was also included in the experimental setup as a means of renewing the mercury cathode surface of the electrochemical cell, and thus increasing the electroreduction efficiency. A Friedrichs condenser with a circulating ice water cooling bath was also included in the experimental setup to minimize the evaporation of the tetrabutylammonium hydroxide solution used as the electrolyte in the electrochemical cell.

The initial experimental setup for the synthesis of nonaromatic hydroaromatic compounds from their aromatic analogues with metals using a modified Birch reduction procedure from the chemical literature was also completed this quarter. The synthesis was begun, but problems with the published experimental design caused the synthesis to be terminated. Procedures for the safe neutralization and disposal of liquid ammonia were performed. The reaction flask design was changed to prohibit refluxing, caused by changes in pressure in the dry ice/acetone cooled condenser, of the liquid ammonia back into the dry ice/acetone cooled condenser. The design of the ammonia gas flow monitor was also altered to include a trap to prohibit contamination of the liquid ammonia in the reaction flask with potassium hydroxide and/or water. A new dry ice/acetone bath stand was constructed for the reaction flask. The new stand holds the 12 liter reaction flask, which had a tendency to float in the dry ice/acetone bath of the previous design, firmly in place. Also, the container for the dry ice/acetone mixture is made of polyethylene in the new design compared to the acetone soluble styrofoam of the initial design.

FUTURE WORK

Now that construction of the experimental setups for Birch reduction with metals and electroreduction have, for the most part, been completed, research during the next quarter will focus on (1) the synthesis of nonaromatic hydroaromatic compounds using both systems, and (2) evaluation of the yields and purities of nonaromatic hydroaromatics produced using both systems. If synthesis of nonaromatic hydroaromatic compounds from their aromatic analogues prove successful, then research will proceed with the synthesis of nonaromatic hydroaromatic compounds in real solvents (Subtask II.C.).

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

INTRODUCTION

Research this quarter consisted of the completion of the catalytic coprocessing studies with Maya residuum and Kentucky No. 9 coal employing both the Shell 324 (NiMo/Al$_2$O$_3$) and Amocat 1B (Mo/Al$_2$O$_3$) catalysts. The gas chromatography (GC) analyses for the two catalytic coprocessing studies and the thermal coprocessing studies under nitrogen were also completed. The net amount of hydrogen donated by the model compounds was calculated from the results obtained from the GC analysis for each coprocessing study.

EXPERIMENTAL

Two commercial hydrogenation catalysts, Shell 324 (NiMo/Al$_2$O$_3$) and Amocat (Mo/Al$_2$O$_3$), were employed for use in coprocessing reactions completed this quarter. Each catalyst was presulfided, pulverized, and sized to 100-200 mesh before use. The catalysts were charged at a total metal loading of 3000 ppm. The reactions were performed at 380°C and for a time of 30 minutes. Additional experiments were performed at a total metal loading of 12,000 ppm to further investigate catalyst effect on coal conversion.

RESULTS AND DISCUSSION

Table II.D.1 presents the results that were obtained in the catalytic coprocessing reactions for coal conversion to tetrahydrofuran (THF) solubles. In the reactions involving HHA and OHA at the two levels of total metal loading (3000 ppm and 12,000 ppm) there was no significant difference in the coal conversions obtained. This indicated that at 3000 ppm, reactivity was not hindered by the amount of catalyst that was present. For the reactions involving both catalysts, the cyclic olefin isotetralin (ISO) gave greater coal conversion than did its conventional hydrogen donor

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analogue, tetralin (TET). The cyclic olefin hexahydroanthracene (HHA) produced greater coal conversion than its analogue, octahydroanthracene (OHA). However, for the model compounds studied, dihydroanthracene (DHA) produced the greatest coal conversion to THF-solubles. Coal conversion decreased when comparing the Mo/Al_2O_3 catalyst to the $NiMo/Al_2O_3$ catalyst for DHA and HHA, while increasing, or remaining constant for OHA, ISO, TET and no added model compound. An anomalous point in Table II.D.1 is the TET reaction involving Mo/Al_2O_3. The conversion obtained with TET is lower than that obtained in the absence of any added model hydrogen donor. The reactions were repeated and the same results were again obtained. At this time it is not known why the conversion obtained with a hydrogen donor present, albeit a poor donor, was lower than that obtained with the residuum only present.

For each of the reactions performed, the THF-solubles fraction was further analyzed by gas chromatography. The results that were obtained for the anthracene series of compounds are presented in Table II.D.2, while the results for ISO and TET are presented in Table II.D.3.

For the anthracene series, e.g. DHA, OHA, and HHA, under both thermal and catalytic conditions, a significant amount (up to 75 weight percent) of OHA was formed. Both thermally and catalytically with OHA as the starting model compound, most of the OHA remained unreacted, and the primary product was DHA.

With HHA, thermally under nitrogen, the primary product was ANT with lesser amounts of DHA and OHA being formed. Thermally under hydrogen, HHA formed approximately equal amounts of OHA and DHA. With the $NiMo/Al_2O_3$ catalyst, equal amounts of OHA and DHA were formed with no ANT formed. With the Mo/Al_2O_3 catalyst, the primary reaction product was DHA with lesser amounts of OHA and ANT produced.

With DHA, approximately the same product distribution (weight percent) was obtained in either reaction with 1.2 g residuum or 3.0 g of residuum present. Thermally under nitrogen, the

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primary product was ANT. For the reactions under hydrogen, both thermally and catalytically, the primary product was OHA.

TET remained unreacted in the two catalytic systems. It reacted less than 10% under hydrogen and approximately 25% under nitrogen, with NAP being the only product. ISO, thermally under both nitrogen and hydrogen, formed mostly NAP and a small amount of TET. With the $NiMo/Al_2O_3$ catalyst the primary product was TET, while with the Mo/Al_2O_3 catalyst the primary product was NAP.

Based upon the results obtained from the GC analysis and the reaction product distribution, the net amount of hydrogen donated was determined. The results of these calculations are presented in Table II.D.4. A negative value in Table II.D.4 for the net amount of hydrogen donated implies a net increase in hydrogen from the initial model compound present. DHA in a hydrogen atmosphere had a net increase in hydrogen due to the large amount of OHA that it formed.

FUTURE WORK

Research next quarter will investigate the coprocessing reactions of Maya residuum with the Argonne series of coals to determine the generality of the reactivity of the nonaromatic hydroaromatic compounds and their conventional hydrogen donor analogues.

Table II.D.1. Catalytic Coprocessing Reaction Summary

Model Compound[1]	Coal Conversion[2]		
	NiMo/Al$_2$O$_3$[3]	NiMo/Al$_2$O$_3$[4]	Mo/Al$_2$O$_3$[3]
DHA (1.2 g resid)	> 3.2(0.1)		70.8(0.3)
DHA (3.0 g resid)	69.0(0.6)		64.8(1.4)
HHA	58.3(3.3)	58.7(0.2)	54.0 (2.8)
OHA	51.7(4.1)	55.8(2.0)	52.1(2.9)
ISO	42.6(1.5)		47.4(3.3)
TET	37.4(1.1)		37.6(1.1)
None	31.9(3.3)		39.4(1.8)

[1] DHA = dihydroanthracene, HHA = hexahydroanthracene, OHA = octahydroanthracene, ISO = isotetralin, TET = tetralin

[2] The percent coal conversion is followed by the standard deviation in percent in parentheses.

[3] 3000 ppm

[4] 12,000 ppm

Table II.D.2.   Analysis of Anthracene Series Model Compound Coprocessing Products by Gas Chromatography

Model Compound[1] Added	Reaction Conditions	Coal Conversion (Percent)	Weight Percent[*] of		
			OHA	DHA	ANT[2]
OHA	Thermal, N_2	38.2	52.7 (0.4)	39.0 (0.6)	8.3 (0.8)
	Thermal, H_2	45.4	77.0 (4.3)	23.0 (4.3)	-----
	NiMo/Al_2O_3	51.7	89.2 (0.7)	10.8 (0.7)	-----
	Mo/Al_2O_3	52.1	89.4 (0.3)	10.6 (0.3)	-----
DHA (1.2 g resid)	Thermal, N_2	66.2	15.6 (0.8)	18.7 (0.5)	65.7 (1.2)
	Thermal, H_2	73.61	52.0 (2.3)	26.5 (0.2)	21.5 (2.4)
	NiMo/Al_2O_3	73.2	68.1 (0.3)	26.1 (0.4)	5.8 (0.2)
	Mo/Al_2O_3	70.8	74.5 (0.5)	19.7 (0.3)	5.9 (0.2)
DHA (3.0 g resid)	Thermal, N_2	56.4	17.2 (1.1)	17.8 (0.4)	65.0 (1.3)
	Thermal, H_2	65.0	49.8 (4.2)	24.9 (0.7)	25.3 (3.5)
	NiMo/Al_2O_3	69.0	70.9 (0.3)	21.0 (0.2)	8.1 (0.3)
	Mo/Al_2O_3	64.8	72.2 (0.2)	20.2 (0.1)	7.6 (0.1)
HHA	Thermal, N_2	50.2	17.4 (0.6)	39.9 (1.2)	65.7 (1.2)
	Thermal, H_2	65.9	40.2 (1.6)	47.7 (0.3)	12.0 (1.6)
	NiMo/Al_2O_3	58.3	47.9 (1.4)	52.1 (1.4)	-----
	Mo/Al_2O_3	54.0	17.6 (0.3)	74.9 (0.8)	7.6 (1.0)

[1] OHA = octahydroanthracene, DHA = dihydroanthracene, HHA = hexahydroanthracene

[2] ANT = anthracene

[*] The weight percent is followed by the standard deviation in weight percent in parentheses.

Table II.D.3. Analysis of Naphthalene Series Model Compound Coprocessing Products by Gas Chromatography

Model Compound[1]	Reaction Conditions	Coal Conversion	Weight Percent* of	
			TET	NAP[2]
ISO	Thermal, N_2	28.1	14.9 (0.3)	85.1 (0.3)
	Thermal, H_2	44.8	21.0 (0.7)	79.0 (0.7)
	NiMo/Al_2O_3	42.6	68.0 (0.8)	32.0 (0.9)
	Mo/Al_2O_3	47.4	40.2 (0.5)	59.8 (0.5)
TET	Thermal, N_2	16.5	74.6 (0.5)	25.4 (0.5)
	Thermal, H_2	31.7	90.9 (0.4)	9.1 (0.4)
	NiMo/Al_2O_3	37.4	100.0	trace
	Mo/Al_2O_3	37.6	100.0	trace

[1] ISO = isotetralin, TET = tetralin

[2] NAP = naphthalene

* The weight percent is followed by the standard deviation in weight percent in parentheses.

Table II.D.4.   **Net Hydrogen Donated in Model Compound Reactions**

Reaction Conditions	Model Compound[1]	Coal Conversion (Percent)	Net Grams Hydrogen Donated (x100)
Thermal, N_2	DHA (1.2 g resid)	66.2	0.65
	DHA (3.0 g resid)	56.4	0.49
	HHA	50.2	1.92
	OHA	38.2	1.12
	ISO	28.1	1.28
	TET	16.5	0.37
	none	15.3	-----
Thermal, H_2	DHA (1.2 g resid)	73.6	-3.94
	DHA (3.0 g resid)	65.0	-3.37
	HHA	65.9	0.93
	OHA	45.4	0.51
	ISO	44.8	1.20
	TET	31.7	0.14
	none	24.3	-----
NiMo/Al_2O_3 Catalyst	DHA (1.2 g resid)	73.2	-5.86
	DHA (3.0 g resid)	69.0	-5.60
	HHA	58.3	0.58
	OHA	51.7	0.24
	ISO	42.6	0.48
	TET	37.4	0.00
	none	31.9	-----
Mo/Al_2O_3 Catalyst	DHA (1.2 g resid)	70.8	-6.43
	DHA (3.0 g resid)	64.8	-6.12
	HHA	54.0	1.55
	OHA	52.1	0.24
	ISO	47.4	0.91
	TET	37.6	0.00
	none	39.4	-----

[1] DHA = dihydroanthracene, HHA = hexahydroanthracene, OHA = octahydroanthracene, ISO = isotetralin, TET = tetralin

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Appendix I.A.A.

Auburn Vacuum Oven Method for Determining the Moisture Content of Coal. A porcelain crucible and cover was heated and then cooled in a desiccator. This was done until a constant weight was obtained for the crucible and cover. One gram of pulverized coal (approximately 150 mesh) was measured into the crucible. The sample was then placed in a 60°C oven and the cover removed. The sample was dried at constant temperature, under a vacuum of 25 inches of Hg, for 12 to 16 hours. After drying, the vacuum was slowly released to avoid losing particles, and the cover replaced. The covered crucible was cooled in a desiccator and then weighed. The percentage moisture was calculated as follows:

$$\% \text{ moisture} = (W_1 - W_2)/W_1 \times 100$$

where $\quad W_1$ = mass of original sample

$\qquad\qquad W_2$ = mass of sample after drying

ASTM D-3174 Method for Measuring the Ash Content of Coal. The sample in the covered crucible from the moisture analysis was placed in a cold furnace and uncovered. The controls of the furnace were set so that the temperature reached from 450 to 500°C the first hour, and 700 to 750°C after the second hour. The sample was ashed for two hours after attaining a temperature of 700 to 750°C. After four hours, the crucible was covered and removed from the furnace and allowed to cool in a desiccator. After insuring that the sample was completely ashed, the crucible was returned to the furnace and ashed until constant weight was attained. The crucible and cover were then cooled in a desiccator and weighed. The ash content was calculated as follows:

$$\% \text{ ash} = (W_3 - W_1)/W_2 \times 100$$

where
W_1 = mass of the empty crucible and cover

W_2 = mass of sample used (from moisture analysis)

W_3 = mass of crucible, cover and ash residue

For the experimental work done this quarter, the moisture and ash content of Illinois No.6 coal were determined. The results are shown in Table I.A.A.1.

Table I.A.A.1.   Percent Moisture and Ash Content of Illinois No. 6 Coal

Sample Number	Percent Moisture	Percent Ash
01	4.80	7.76
02	4.56	7.85
03	4.38	8.01

Appendix I.B.2.A.

Calculation for Recovery of Benzophenone. The recovery of benzophenone was calculated based on the following equation if only diphenylmethane and water were produced from benzophenone according to the following reaction:

$$Ph_2CO + H_2(g) = Ph_2CH_2 + H_2O.$$

Recovery of benzophenone = amount (g) of benzophenone after reaction + amount of diphenylmethane formed + amount (g) of oxygen in water - amount of hydrogen in diphenylmethane (DPM).

For the reaction with benzophenone and dihydroanthracene,

benzophenone before reaction = 0.0805g

benzophenone after reaction = 0.03327g

diphenylmethane formed = 0.04341g = 2.58×10^{-4} mol

oxygen in water = 2.58×10^{-4} mol x 16 = 0.00413g

hydrogen in DPM = 2 x 2.58×10^{-4} mol x 1 = 5.16×10^{-4}g

Recovery of benzophenone = 0.03327g + 0.04341g + 0.00413g - 5.16×10^{-4}g

= 0.08030g

0.08030g/0.0805g = 99.75%

Calculation of Response Factor for Benzophenone. The following equation was used to calculate

a response factor:

where $A_{BNP}/A_{BIP} = Rf\, W_{BNP}/W_{BIP} + Y_o$

A_{BNP} = peak area of benzophenone on GC

A_{BIP} = peak area of biphenyl on GC

W_{BNP} = weight of benzophenone

W_{BIP} = weight of biphenyl

Rf = response factor of benzophenone

Y_o = intercept of Y axis

Four standard solutions were prepared by adding a carefully weighed amount of biphenyl

internal standard to carefully weighed amounts of benzophenone. Each sample was injected into

the GC four times. The weights and the ratios of weights of benzophenone to biphenyl are shown

in Table I.B.2.B.1. The areas and average area ratio of benzophenone to biphenyl, and the standard

deviation and error are shown in Table I.B.2.B.2.

Table I.B.2.B.1.   Weights and Weight Ratios of Benzophenone to Biphenyl

Sample Number	1	2	3	4
weight of benzophenone	0.0114g	0.0200g	0.0304g	0.0419g
weight of biphenyl	0.0206	0.0199	0.0203	0.0203
W_{BNP}/W_{BIP}	0.5534	1.0055	1.4975	2.064

Table I.B.2.B.2   Area of GC Peaks and Area Ratios of Benzophenone to Biphenyl

Standard Number	1	2	3	4
Area of Benzophenone	23728 28432 26825	58386 22706 28340 22964	59738 69706 60368	48079 80443 71736 52417
Area of Biphenyl	36340 52369 45823	55734 20008 25059 21638	37698 45669 39422	21836 36889 33657 23905
A_{BNP}/A_{BIP}	0.6529 0.5429 0.5854	1.0470 1.1318 1.1309 1.0613	1.5846 1.5263 1.5317	2.2024 2.1819 2.1312 2.1927
Average of Area Ratios	0.5937	1.0930	1.5475	2.1770
Standard Deviation	0.0554	0.0389	0.0322	0.0317
Error (%)	9.3%	3.6%	2.08%	1.5%

Using the above peak area ratio and the weight ratios of benzophenone to biphenyl, a line was plotted to fit to the equation. The response factor was calculated. Rf is the slope of the analytical line, and Y is the intercept.

Table I.B.2.B.3. shows response factors for benzophenone and diphenylmethane.

Table I.B.2.B.3.   Response Factors and Y Intercepts for Benzophenone and Diphenylmethane

Compound	Rf	Y_o
Benzophenone	1.0523	-0.00011
Diphenylmethane	1.0033	-0.000073

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END

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4/19/94