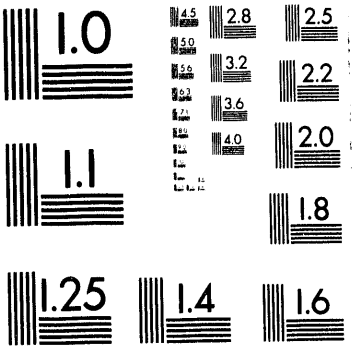
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IMPROVED PERFORMANCE IN COPROCESSING THROUGH FUNDAMENTAL AND MECHANISTIC STUDIES IN HYDROGEN TRANSFER AND CATALYSIS

Quarterly Report
for
Contract No. DE-AC22-88PC88801

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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. 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. Research initiated last 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 was also continued this quarter.

EXPERIMENTAL WORK

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 a technician was trained to use a new gas chromatograph that was set up this quarter, and response factors, required for gas chromatography (GC) analysis, were determined for anthracene, pyrene, and perhydropyrene using the new instrument. The moisture content of Illinois No. 6 coal was determined and preparations for synthesizing perhydroanthracene were made. Reactions were conducted using the model compounds, tetralin, anthracene, pyrene, and perhydropyrene.

EXPERIMENTAL

Materials. The chemicals used this quarter included tetralin (TET), 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, and PYR were purchased from Aldrich Chemicals and had a purity of 99% or higher. The PHPYR, purchased from Pfaltz and Bauer Research Chemicals, had a purity of 99% or higher and was mixture of seven isomers. The biphenyl also had a purity of 99% or higher and was used as received. The THF was Fisher certified.

Equipment. The equipment used for reactions 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, and a volume determination device

consisting of a series of gas sampling cylinders equipped with a pressure meter and corresponding transducer. A new Varian gas chromatograph Model 3400 was employed for GC analysis. A Lab-Line vacuum oven was used for moisture analysis.

Determination of Response Factors. In order to utilize the method of internal standards in GC analysis, it was necessary to determine the response factors for a new gas chromatograph between the compounds used and the internal standard, biphenyl. The procedure and results are shown in Appendix I.A.A.

Determination of the Moisture Content of Coal. In preparation for future coal research, the moisture content of Illinois No. 6 coal was determined using the Auburn Vacuum Oven Method. The procedure and results are shown in Appendix I.A.B.

Preparations for the Synthesis of Perhydroanthracene. The perhydroanthracene needed for future reactions must be synthesized because it is unavailable commercially. A literature search discussed several procedures. The older literature revealed a synthetic method in which Raney nickel was used as a catalyst to completely hydrogenate anthracene. Since Raney nickel is pyrophoric in nature and easily oxidized, it is thought that a further investigation of the literature for procedures involving other transition metals, e.g. platinum, rhodium, etc., may reveal a more simplified synthesis procedure.

It is expected that the synthesis of perhydroanthracene by the catalytic hydrogenation of anthracene will result in an array of products. In order to help to determine the different products and the extent of hydrogenation, chromatograms and retention times under set operating conditions have been generated for several different hydrogenated forms of anthracene:

dihydroanthracene, hexahydroanthracene, and octahydroanthracene. By knowing the extent of hydrogenation and the major products, the synthesis can be conducted so that the yield and purity of perhydroanthracene are optimized.

Procedure and Analysis. The work carried out this quarter consisted of verifying results obtained in earlier reactions. TET was reacted alone, while ANTH and PYR were each reacted with PHPYR in a 50/50 mixture (by weight).

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. TET was reacted for both 30 and 60 minutes, while the mixtures, ANTH/PHPYR and PYR/PHPYR, were reacted for 60 minutes only. 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. For selected reactions, the product gases were analyzed using a gas chromatograph equipped with a thermal conductivity detector. After the products were recovered by extracting with THF, the internal standard for gas chromatography analysis, BIP, was introduced into the product vials. The products were then analyzed using gas chromatography. The GC conditions for the TET reactions are shown in Table I.A.1. Because of the similar retention times of the PHPYR isomers, the temperature programming was changed to allow for sharper peak resolution. The GC high resolution product analysis conditions for the ANTH, PYR, and PHPYR reactions are shown in Table I.A.2.

RESULTS AND DISCUSSION

Reactions using tetralin were performed this quarter and compared to those performed previously. A comparison of the final pressure of the TBMR and the results of GC analysis for TET reactions are shown in Table I.A.3. The reactions in run 3 were conducted this quarter. The reactions in runs 1 and 2 were conducted during previous quarters. Unless otherwise indicated, reactions were conducted for thirty minutes.

As can be seen in Table I.A.3, the results of the thirty minute tetralin reactions were similar for runs 1, 2, and 3. For every reaction, the GC chromatograms indicated that naphthalene had been formed and that a small amount of hydrocracking had occurred. It was reported earlier that for runs 1 and 2, the amount of naphthalene formed was approximately 5 weight percent of the tetralin present. It has since been determined that the tetralin used was contaminated with naphthalene. A third run was made using pure tetralin that was confirmed by GC analysis, and the amount of naphthalene formed was found to be 0.8 weight percent of the tetralin present for the thirty minute reactions, and 1.0 weight percent for the sixty minute reactions. Hydrogen analysis for all the reactions in run 3 indicated that hydrogen was not present in the product gases. The low recoveries for the sixty minute tetralin reactions may have been the result of the TBMRs leaking during the reaction, or the escaping of products during depressurization.

Table I.A.4 shows the results of the ANTH/PHPYR and PYR/PHPYR reactions. The reactions in runs 2 and 3 were conducted this quarter, while the reactions in run 1 were conducted last quarter.

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	300°C
Detector Temperature	310°C
Initial Column Temperature	80°C
Final Column Temperature	180°C
Temperature Programming	10°C/min

Table I.A.2

Gas Chromatography Conditions for High Resolution 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.3

Recoveries and Average Final Pressures
for Tetralin Reactions

Run Number	Sample Number	Recovery (%)	Average Pressure
1	023	86.8	485 psi
	024	81.6	
2	027	80.6	481
	028	73.7	
	029	80.3	
3	061	92.1	539
	062	76.3	
	063*	35.6	470
	060*	42.1	

* denotes sixty minute reactions

Table I.A.4

Recoveries and Average Final Pressures

Compound Name	Run Number	Sample Number	Recovery (%)	Average Pressure
ANTH + PHPYR (50/50 mixture by weight)	3	088	72.2 (ANTH) 85.6 (PHPYR)	553 psi
PYR + PHPYR (50/50 mixture by weight	1	048	86.5 (PYR) 82.0 (PHPYR)	490
		049	99.1 (PYR) 93.4 (PHPYR)	
	2	066	81.2 (PYR) 89.8 (PHPYR)	499
	3	087	90.7 (PYR) 93.4 (PHPYR)	588

GC analysis of the products of the ANTH/PHPYR reaction revealed the presence of an unknown product. Because of the location of the peak on the chromatogram and the fact that the recovery of the ANTH is 13 percent less than that of the PHPYR, it is believed that this product may be a hydrogenated form of anthracene. The peak area of this unknown product is approximately ten percent of the ANTH peak area. This sample has been submitted for GC/MS analysis to identify the species present. There was no evidence of hydrocracking in the ANTH/PHPYR reaction.

In the PYR/PHPYR reactions, GC analysis indicated that the compounds were stable with the exception of one very small peak occurring near the PYR peak. The area of this peak was 1.5 percent of the total product area. It is possible that the PHPYR gave up a small amount of hydrogen to form a lesser hydrogenated compound or that a different isomer of PHPYR was formed uring thermal processing. Hydrogen analysis for the reactions in run 2 revealed no hydrogen in the product gases. If hydrogen was released by PHPYR, then it was either an amount too small to be detected or perhaps it hydrogenated the

pyrene. Earlier it was reported that there was also another unknown peak present in the reaction products. It is now believed that this peak belongs to tetracene, the contaminant which gives pyrene its yellow color. An authentic sample of tetracene has been purchased and its retention time will be compared to that of the species in question. Further analysis of the reaction products will yield more information. There was no evidence of hydrocracking in any of the PYR/PHPYR reactions.

Overall, the recoveries of the reactions in Table I.A.3 and I.A.4 are fairly reasonable and consistent, an indication that the experimental method is reproducible. For those reactions with low recoveries, there are several places where error may have occurred. The yields for the TET reactions would be slightly higher if hydrocracking was taken into account. The yields for the ANTH in the ANTH/PHPYR reactions would certainly be higher if the unknown product peaks were considered. Another place where error most likely occurred is during the GC analysis. ANTH, PHPYR, and PYR are fairly high boiling compounds and may adhere to the GC column and give erroneous results. The experimental error that occurred in calculating response factors was less than 5 percent for PHPYR, while it was substantially higher for ANTH and PYR. Error may have occurred if product gases escaped in the form of vapor when the TBMRs were depressurized. There is always the possibility of instrumental as well as experimental error.

Special Note. Several equipment problems hindered research this quarter. Ten TBMR reactions were lost due to the fluidized sandbath malfunctioning because the temperature could not be maintained. Several reactions were also lost when the contents of the TBMR were contaminated with copper sealant, a lubricant used to aid in removing reactor plugs. Before moisture analysis could be performed, a silicone gasket had to be purchased in order to make the

vacuum oven operable. The ash analysis of coal will commence upon the arrival and replacement of necessary hood exhaust filters.

CONCLUSIONS

This quarter experiments were conducted with several compounds of interest, TET, ANTH, PYR, and PHPYR. Reactions with TET were fairly stable with only very small amounts of hydrocracked compounds or naphthalene being formed. The ANTH/PHPYR and PYR/PHPYR reactions were both fairly stable with no hydrocracking occurring. GC analysis revealed that products were formed in both the ANTH/PHPYR and the PYR/PHPYR reactions. The unknown product for the ANTH/PHPYR reaction had a peak area of about 10 area percent that of the ANTH peak area and was thought to be a hydrogenated form of ANTH. The unknown product for the PYR/PHPYR reaction, thought to be a hydrogenated form of PYR, had a peak area of less than 2 area percent of the total product area. These products will be identified by further analysis.

Also during this quarter response factors necessary for GC analysis of ANTH, PYR, and PHPYR reaction products were determined using a new gas chromatograph. Due to the high experimental error that occurs when calculating these response factors, it is believed that the ANTH and PYR may have a tendency to adhere to the GC column. One solution to this problem may be to use higher temperatures. Presently, the temperature limits are determined by the type of septum being used. In the near future a high temperature septumless injector will be installed which will allow the gas chromatograph to be operated at higher temperatures.

The moisture content of Illinois No. 6 coal was determined, and the results did not agree with earlier results found for this coal. This test will be repeated with the drying time increased to sixteen hours, the upper

range limit of drying time. The sample from the moisture analysis will be used to determine the ash content of Illinois No. 6 coal.

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

INTRODUCTION

During this quarter, two experiments were conducted: a test of how coal solubility was affected by residuum and a test of how hydropretreated Maya residuum affected subsequent thermal coprocessing reactions.

In the first experiment, the solubility of Illinois No. 6 coal in different solvents was determined by extracting the coal by itself and in a coal-Khafji residuum mixture. These coal solubility results were compared with a coal-Maya residuum mixture obtained last quarter to examine the effect that petroleum residuum had on coal solubility. The analysis method used solvent extraction using hexane, toluene and tetrahydrofuran (THF).

In the second experiment, Maya residuum was hydrogenated thermally and catalytically with naphthenates of molybdenum (Mo), nickel (Ni), or vanadium (V). The hydrogenated residuum was then extracted with THF to remove the insoluble organic matter (IOM) and catalyst species from the hydropretreated Maya residuum. The IOM-free and catalyst-free THF soluble fractions of the pretreated Maya residuum were used in the subsequent thermal coprocessing reactions with coal to examine the effect that different prehydrotreated Maya residua had on thermally converting coal and upgrading the fractions from coal/residuum coprocessing. The IOM-free and catalyst-free THF soluble fractions of pretreated Maya residuum were also hydrogenated thermally without coal present under the same conditions as the coprocessing reaction. The thermally produced fractions from pretreated Maya were then subtracted from the overall coprocessing products to determine the extent of thermal

hydrogenation of coal effected by the different pretreatment conditions.

EXPERIMENTAL

Solubility of Coal at Room Temperature (No Reaction). Illinois No. 6 coal, Khafji residuum, and a mixture of Illinois No. 6 coal and Khafji residuum were each fractionated according to the solvent extraction procedure using hexane, toluene, and THF according explained in the previous quarterly report[1]. Illinois No. 6 coal was pulverized to 100 mesh before use, and Khafji residuum was obtained from Amoco Oil company and used as received. First, 9g of Illinois No. 6 coal was dissolved in 450 ml of each solvent to separate the fractions of oil, asphaltenes, preasphaltenes and IOM found in coal. Second, 9g of Khafji residuum was dissolved in 450 ml of each solvent to separate the fractions in Khafji residuum. Third, the mixture of 3g of Illinois No. 6 coal and 6g of Khafji was dissolved in 450 ml of each solvent to separate the fractions in the coal-Khafji residuum mixture. Each fractionation was duplicated. The portion of each fraction originating from coal in the coal/Khafji mixture was determined by subtracting the Khafji residuum fractions from those of the mixture.

Pretreatment of Maya Residuum. Maya residuum was hydrogenated thermally and catalytically with naphthenates of Mo, Ni, or V. Each hydrogenation reaction was performed with 12g of Maya residuum in a 56 mL batch tubing bomb microreactor which was made of 316 stainless steel and horizontally oriented. In thermal reactions, sulfur was not added. In catalytic reactions, elemental sulfur was added in the amount required to generate metal sulfide <u>in situ</u> from each catalyst paste, which was introduced at a concentration of 3000 ppm metal content: about 0.024g sulfur for Mo catalyst, 0.013g for Ni catalyst, and 0.034g for V catalyst. The pretreating reactions were conducted under the conditions of 1250 psig H_2 charged at ambient temperature, 400°C reaction

temperature, one hour reaction time, and 550 cpm vertical shaking. After the reaction, the pretreated Maya products were separated by extraction with THF into THF solubles and insoluble solids (including the IOM and catalyst species used in the reaction). The solvent, THF, was volatilized using a rotary evaporator. The solid materials from the THF solubles of the pretreated Maya residua were used in the subsequent thermal coprocessing reactions with coal.

Thermal Coprocessing Reactions with Pretreated Maya Residuum and Coal. The THF solubles of pretreated Maya residuum prepared thermally and catalytically were used in the subsequent thermal coprocessing reactions with Illinois No. 6 coal. In each coprocessing reaction, 6g of pretreated Maya residuum, 3g of coal and 1250 psig H_2 (at ambient temperature) were charged in the same type reactor used in the pretreatment of Maya residuum reaction. Sulfur was not added. The reactions were conducted at 400°C for one hour using 550 cpm vertical shaking. To determine the degree to which the thermally and catalytically pretreated Maya residuum was thermally hydrogenated, 6g of the pretreated Maya residuum were charged in the same reactor and hydrogenated under the same reaction conditions used for the above coprocessing reaction. After the reaction, the products from coprocessing reactions and hydrogenation reactions of pretreated Maya without coal present were fractionated into oil, asphaltenes, preasphaltenes, and IOM by using 450 mL each of hexane, toluene and THF. The amount of gas product produced from both reactions was determined by gas volume measurement and H_2 analysis using a gas chromatograph with thermal conductivity detection.

RESULTS AND DISCUSSION

Solubility of Coal. Illinois No. 6 coal (9g), Khafji residuum (9g), and a mixture of Illinois No. 6 coal (3g) and Khafji (6g) were each fractionated, and the fraction distribution was summarized as weight percents on an ash-free

basis (Table I.B.1.1). Because the moisture content in each fraction could not be clearly determined, the moisture amount was included in the calculation. In the fractionation of Illinois No. 6 coal, no hexane-soluble oil fraction was obtained, and toluene-soluble asphaltenes were obtained only in a negligible amount. The major fraction in coal was IOM. In contrast, Khafji residuum contained 82.4 weight percent oil as the major fraction but did not contain an IOM fraction. The coal and Khafji residuum mixture contained 57.5 weight percent oil, 13.3 weight percent asphaltenes, 2.0 weight percent preasphaltenes, and 27.2 weight percent IOM. With the assumption that the solubility of Khafji was unaffected by the coal used, the solubility of the coal and Khafji combination was calculated by subtracting a proportional amount of the Khafji residuum fraction from the total amount of the same fraction in the mixture. In Table I.B.1.1, the solubility of coal alone and that combined with different residua are compared. The coal fractions calculated from the coal-Khafji mixture and the coal-Maya mixture were not consistent with each other or with those determined experimentally by direct dissolution. Compared to the dissolution of coal alone, the coal combined with residua showed greater fractions of oil and asphaltenes and less undissolved coal (IOM). These results may indicate that the residua in the mixture enhanced the coal dissolution in each extracting solvent by dissolving the coal in the residua.

Hydropretreatment of Maya Residuum. Maya residuum (12g) was hydrogenated thermally and catalytically with naphthenates of Mo, Ni and V each at a concentration of approximately 3000 ppm metal. After the reaction, the IOM fraction and the generated catalyst species were separated from the reaction products by extraction with THF. From each reaction, about 2 weight

Table I.B.1.1. Extracted Fractions of Illinois No. 6 Coal[1]

Extraction System	Extracted Products from Coal (wt%)*			
	Oil	Asp	Preasp	IOM
Coal[2]	0.0±0.0	0.1±0.05	6.7±0.5	93.2±0.6
Coal-Khafji Mixture[3]	2.3±1.1	3.9±0.8	6.3±0.1	87.5±0.5
Coal-Maya Mixture[4]	0.0±0.0	4.3±0.4	5.1±0.3	90.6±0.6

[1]The fractions in coal directly measured or calculated by differentiation of coal from coal-residuum mixtures were summarized on the ash free basis.
[2]Directly measured coal solubility in different solvents.
[3]Calculated coal solubility by differentiation of coal-Khafji mixture.
[4]Recalculated data in the previous quarterly report (Dec. 1989).
*Asp (asphaltenes, Preasp (preasphaltenes)

percent of gaseous products and a negligible amount of IOM (zero to 0.6 weight percent, mainly 0.1-0.2 weight percent IOM) were produced. The THF solubles of the different hydropretreated Maya residua were used in the subsequent thermal coprocessing reactions with coal.

Coprocessing of Illinois No. 6 Coal and Pretreated Maya. A mixture of 3g Illinois No. 6 coal and 6g pretreated Maya residuum pretreated under different conditions were hydrogenated thermally under equivalent reaction conditions. The fractionated products were calculated in two ways: in method A, the weight percent of each fraction was calculated based on the total product amount recovered; in method B, the weight percent of each fraction was calculated based on the assumption of 100 percent product recovery in which the oil fraction was determined by subtracting the other recovered fractions from 100 percent. Reactions were at least duplicated and the results were summarized as the averaged values and standard deviations of $X + \sigma_n$ by method A (Table I.B.1.2); the original data including the results summarized by method B are presented in Appendix I.B.1.2.

Table I.B.1.2. Thermal Coprocessing Reactions with Illinois No. 6 Coal and Pretreated Maya Residua

Maya Pretreating Condition	H_2 Used (%)	Overall Product Distribution (wt%)[1]					Coal Conversion (%)	Toluene-Solubles (wt%)[2]
		Gas	Oil	Asp	Preasp	IOM		
Thermal[3]	6.3-13.5	3.1±0.3	44.4±0.4	16.1±0.2	17.3±0.1	19.1±0.9	41.2±0.9	60.4±0.7
MoNaph[4]	15.3-22.7	2.7±0.3	59.3±0.2	23.4±0.9	11.6±0.2	3.0±0.5	92.1±1.8	82.7±0.7
NiNaph[4]	9.4-15.1	2.4±0.3	55.5±1.4	20.0±0.2	19.0±1.9	3.1±0.5	90.7±1.7	75.4±1.7
VNaph[4]	2.0-10.3	2.3±0.3	47.2±1.7	18.3±0.8	19.1±2.2	13.1±0.0	61.1±0.3	65.4±2.6

[1]The product distribution was determined by the method A (Appendix B.2) using overall products obtained from a mixture of coal and pretreated Maya. Asp (asphaltenes), Preasp (preasphaltenes), IOM (insoluble organic matters)
[2]Toluene solubles (oil and asphaltenes)
[3]No additional sulfur
[4]Additional sulfur as much as required to produce metal sulfide <u>in situ</u> in the pretreatment of Maya residua (12g): S=0.024g for MoS_2, and S=0.034g for V_2S_3

Nb32/EXPWRK.IA

Maya residuum pretreated under different conditions showed differenc activities in thermal coprocessing reactions. The THF soluble fractions of Maya residuum pretreated with active coprocessing catalysts, in situ generated Mo and Ni species[1], showed high activity in producing toluene solubles and in converting coal. The THF solubles of Maya pretreated thermally or catalytically with the less active coprocessing catalyst, the V naphthenate species, showed low activity in converting coal (Table I.B.2). However, it is important to note that the THF solubles of Maya residua pretreated under different conditions already contained different amounts of each fraction before they were used in the thermal coprocessing reaction. The THF solubles of Maya possessed more oil and asphaltenes when pretreated with Mo or Ni species than with V species or without a catalyst.

The degree of coal upgrading in thermal coprocessing reactions with Maya pretreated thermally and with different catalysts was determined by calculation. To differentiate the contribution from coal to each fraction from that of the pretreated Maya, the following assumptions were adopted: (1) the degree of hydrogenation of pretreated Maya residuum in thermal coprocessing reactions was not affected by coal and (2) the recovery of the coprocessing products was evenly distributed in both coal and residuum products. In Table I.B.1.3, the activity of pretreated Maya residuum for converting coal and upgrading coal products in the thermal coprocessing reaction was compared (using the calculational method explained in Appendix I.B.1.C). The order of activity of the different pretreated Maya residua for coal upgrading was the same as shown in the overall upgrading of the mixture: the order of activity related to the pretreatment condition was MoNaph > NiNaph > VNaph > thermal, where Maya pretreated with Mo naphthenate and sulfur

Table I.B.1.3. Fractions from Illinois No. 6 Coal Produced from Thermal Coprocessing Reactions with Pretreated Maya Residuum[1]

Maya Pretreating Condition	Overall Product Distribution (wt%)[2]					Coal Conversion (%)	Toluene-Solubles (wt%)[2]
	Gas	Oil	Asp	Preasp	IOM		
Thermal[4]	2.5±0.9	0.0±0.0	3.1±1.4	38.3±0.1	56.1±2.4	41.2±3.5	3.1±1.4
MoNaph[5]	2.2±1.0	8.8±1.3	46.8±3.1	34.1±0.9	8.1±1.6	92.1±1.8	55.5±1.8
NiNaph[5]	3.9±1.0	5.1±5.0	27.1±0.7	55.2±6.2	8.7±1.6	90.7±1.7	32.2±5.6
VNaph[5]	3.6±1.0	3.5±3.5	4.3±4.3	51.3±6.8	37.3±0.1	61.1±0.3	7.8±7.8

[1]Coal products were differentiated from the products of pretreated Maya residuum used the thermal coprocessing reaction (assumption: the degree of hydrogenation of pretreated Maya residuum was not affected by coal during the coprocessing reaction; Appendix B.3).
[2]The coal product distribution was determined by subtracting the fractions of pretreated Maya from the overall fractions produced from the coprocessing reaction (method A in Appendix B.2). Asp (asphaltenes), Preasp (preasphaltenes, IOM (Insoluble organic matters).
[3]Toluene solubles (oil and asphaltenes).
[4]No additional sulfur
[5]Additional sulfur as much as required to produce metal sulfide <u>in situ</u> in the pretreatment of Maya residuum (12g): S=0.024g for MoS_2, S=0.013g for Ni_3S_2, and S=0.034g for V_2S_3.

showed the greatest activity and Maya pretreated thermally without a catalyst showed the least activity.

The effect of pretreated Maya on coal conversion and upgrading of coal products appears to be related to the residuum pretreating condition and the pretreating catalyst used. However, it is questionable whether the metal naphthenate catalysts used to pretreat the Maya residuum were completely converted to THF insoluble solids during the pretreatment reaction. All of the insoluble catalyst species generated during the pretreatment reaction were thought to be subsequently removed by extraction with THF. However, the possibility exists that some finely divided catalyst materials were not separated completely from the THF solubles. Some techniques to detect any catalyst species possibly remaining in the THF solubles of pretreated Maya are under study. In the next quarter, a solid $NiMo/Al_2O_3$ catalyst, which is originally THF insoluble, will be used for pretreating the Maya residuum. The THF solubles of this pretreated Maya, which are free of $NiMo/Al_2O_3$, will be used in the subsequent thermal coprocessing reaction, and the results will be compared to those reported in this quarterly report. More samples of Maya residuum that are hydropretreated under different catalytic and thermal conditions will be prepared. The effect of pretreated Maya residuum on the hydrogenation of coal in the coprocessing reactions will be examined under a N_2 atmosphere to investigate the possibility of hydrogen transfer from the pretreated Maya to coal.

CONCLUSIONS

The effect of residuum on the solubility of coal in the extracting solvents was examined. The enhanced coal dissolution in each solvent was possibly due to the dissolution of the coal in the residua. Maya residuum was hydropretreated thermally and catalytically with naphthenates of Mo, Ni, and

V. The THF solubles of pretreated Maya were used in the thermal coprocessing reactions. The Maya residuum pretreated with Mo naphthenate and Ni naphthenate converted more coal and upgraded more coal products to the lighter fractions than did Maya pretreated with V naphthenate or without a catalyst. The THF solubles of Maya pretreated with naphthenate of Mo or Ni contained more oil than THF solubles of Maya pretreated with V naphthenate or without catalyst. The thermal hydrogenation of the THF solubles of Maya pretreated with Mo or Ni also showed more oil production than THF solubles of Maya pretreated with V or without a catalyst.

REFERENCE

1. Curtis, C. W., Quarterly Report for DOE Contract No. DE-AC22-88PC88801, Sep.-Dec. 1989. Chemical Engineering Department, Auburn University.

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 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.

The research concerning evaluation and characterization of untreated and hydrotreated residua and residuum fractions was continued from the previous quarter. Analysis by Fourier transform infrared (FTIR) spectrometry and proton nuclear magnetic resonance (^{1}H-NMR) spectrometry were performed for the examination and comparison of untreated residua with residua hydrotreated prior to coprocessing in order to determine chemical factors that make certain

hydrotreated residua more effectual as coprocessing solvents. Additional work was conducted on the reactions of model acceptors and residua to investigate hydrogen transfer from residua and coprocessing solvents to model acceptors thought to be similar to those found in coal. During this quarter, the investigation of benzophenone as a model acceptor was initiated.

EXPERIMENTAL

Near the beginning of this quarter, thirteen (13) Khafji asphaltene coprocessing products were rerun using FTIR spectrometry in order to obtain detailed information and FTIR spectra appropriate for quantitative analysis. These asphaltene fractions were further compared with their corresponding oil fractions described in the last quarterly report. Most of work in this quarter concentrated on the analysis of untreated and hydrotreated Maya residuum and the products from the coprocessing of Maya residuum and coal. For all solid samples, potassium bromide (KBr) disks were prepared from a mixture containing 600 mg KBr and 30 mg of sample. The KBr used in this work contained 3.2 weight percent potassium thiocyanate (KSCN) as internal standard for quantitative analysis. A SPEX mixer/grinder was used to prepare solid samples in the latter portion of this quarter. All FTIR spectra were baseline corrected using the on-line minicomputer in the Nicolet 5SXC FTIR spectrometer.

For ^{1}H-NMR work, about 0.1 mg of sample in 2.5 g of carbon tetrachloride (CCl_4) or carbon disulfide (CS_2) with tetramethylsilane (TMS) as internal standard was used. The ^{1}H NMR spectra were obtained using a Varian EM-390 spectrometer.

Near the end of this quarter, the model acceptor compound, benzophenone, was reacted with residuum at coprocessing conditions. The products were examined by FTIR spectrometry.

RESULTS AND DISCUSSION

The asphaltene and preasphaltene fractions from the coprocessing products obtained from the thermal and catalytic reactions of Khafji residuum and Illinois No. 6 coal were analyzed by conventional FTIR spectrometry. The aromatic C-H stretch was ratioed to the aliphatic C-H stretch. Significant differences, though small, were more readily observed in the FTIR spectra of the asphaltenes and preasphaltenes than had previously been observed in the oil fractions of these coprocessing products. Coprocessing products from the thermal and catalytic reactions of Maya residuum and Illinois No. 6 coal were also analyzed by conventional FTIR spectrometry. Again, more significant differences in the spectra of the asphaltene and preasphaltene fractions were observed than had been observed previously in the oil fractions of these coprocessing products.

Because of the above observations involving coprocessing products, the decision was made to proceed with analysis by FTIR spectrometry of untreated and hydropretreated residua reacted without coal at coprocessing conditions. Subsequently, the differences observed in the FTIR spectra of these residua, untreated and hydropretreated under different experimental conditions, were compared with the differences in percent coal conversion achieved with these variously treated residua and Illinois No. 6 coal.

Again, the tetrahydrofuran solubles (oil + asphaltene + preasphaltene) fraction from the various Maya residua reacted at coprocessing conditions showed only small differences, possibly due to the predominance of oil in the THF solubles. However, the asphaltene fractions (toluene solubles) showed significant differences in their spectra. ^{1}H-NMR spectra were also collected from the various Maya residua asphaltene fractions. As with FTIR, significant differences were observed in the ^{1}H-NMR spectra. Moreover, significant

differences were observed between variously treated Maya residua resulting in high coal conversion and variously treated Maya residua resulting in low coal conversion. Unfortunately, time did not permit conclusive peak assignments to be completed during the quarter. FTIR and ^{1}H-NMR peak assignments will be reported during the next quarter.

Preliminary experiments with model acceptor compounds and residua were also initiated near the end of the quarter. Benzophenone was used as the hydrogen model acceptor compound. Because of equipment failure, experimental reproducibility could not be determined. Research with model acceptors and residua will continue next quarter.

CONCLUSIONS

FTIR spectrometry and ^{1}H NMR spectrometry appear to be a potentially effective analytical techniques for use in determining chemical factors that make certain hydrotreated residua more effectual as coprocessing solvent than others. More FTIR and ^{1}H NMR spectrometry work must be performed in the examination and comparison of untreated residua with hydrotreated residua 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 conventional quantitative FTIR spectrometry methods.

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. While it had previously been decided to postpone the Birch and modified Birch reductions associated with this subtask for approximately six months, it was decided to proceed with the syntheses of nonaromatic hydroaromatic compounds with metals during this quarter because of the availability of additional manpower. Plans for synthesis of nonaromatic hydroaromatics using electroreduction methods also continued this quarter.

EXPERIMENTAL

During the quarter, the Electrosynthesis Company Inc. was consulted regarding the synthesis in aqueous media of nonaromatic hydroaromatics from their aromatic analogues. It was recommended that a constant current power supply similar to that described by the Kariv-Miller research group, Department of Chemistry, University of Minnesota, be purchased rather than a potentiostatic controller-power supply combination. A versatile autoranging constant current power supply was purchased and received during the quarter from Hewlett Packard Company. A digital coulometer which will be used to integrate the amount of charge passed through the electrochemical cell during electroreduction was purchased and received late in the quarter from Electrosynthesis Company. The performance of both electronic instruments will be evaluated next quarter to determine if they satisfy the synthesis requirements of nonaromatic hydroaromatics from their aromatic analogues using electroreduction techniques.

Also during the quarter, most of the glassware and other related equipment required for the modified Birch synthesis of isotetralin from naphthalene using metals was ordered and received from Chemglass, Inc. Chemicals required for the synthesis were ordered from Fisher Scientific. Anhydrous ammonia and a regulator for corrosive gases were ordered from Air Products and Chemicals,

Inc. As an additional safety precaution, a Class D fire extinguisher for use with metals such as sodium was ordered, received, and installed in the laboratory. The modified Birch chemical synthesis will serve as a back-up for the electrochemical synthesis to assure success in the synthesis of nonaromatic hydroaromatics from their aromatic analogues.

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

INTRODUCTION

Work this quarter consisted of the investigation of the catalytic coprocessing reactions utilizing the Shell 324 ($NiMo/Al_2O_3$) catalyst. Both Shell 324 ($NiMo/Al_2O_3$) and Amocat 1B (Mo/Al_2O_3) hydrogenation catalysts were chosen to be investigated.

EXPERIMENTAL

The catalysts were presulfided in a heated flowing stream of 10% H_2S in H_2 for several hours, pulverized, and sized between 100-200 mesh before use. The catalysts were charged at a total metal loading of 3000 ppm. Table II.D.1. presents the results that were obtained for coal conversion to THF solubles. Also presented in Table II.D.1., for comparison purposes, is the coal conversion obtained in a hydrogen atmosphere that had been previously reported.

RESULTS AND DISCUSSION

Important to note from this Table II.D.1. is that the cyclic olefin (CLO) isotetralin (ISO) produced greater coal conversion than its conventional hydrogen donor analogue tetralin, and that the CLO hexahydroanthracene (HHA) produced greater conversion than octahydroanthracene (OHA). Also of note is

Table II.D.1. Comparison of Thermal and Catalytic Coprocessing Reactions*

Model Compound	Thermal Coal Conversion	Catalytic** Coal Conversion
DHA (1.2 g resid)	73.6(0.7)	73.2(0.1)
HHA	65.9(0.7)	58.3(3.3)
DHA (3.0 g resid)	65.0(1.6)	69.9(0.6)
OHA	45.4(1.0)	51.7(4.1)
ISO	44.8(0.3)	42.6(1.5)
TET	31.7(2.6)	37.4(1.1)
None	24.3(3.3)	31.9(3.3)

*Conditions: Maya resid, 1250 psig H_2 at ambient temperature, 380°C, 30 min. reaction time.

**Shell 324 ($NiMo/Al_2O_3$)

that the overall conversion of the conventional hydrogen donors tetralin (TET), OHA and dihydroanthracene (DHA) increased in the catalytic system when compared to the thermal systems. However, the CLOs, ISO and HHA, produced less coal conversion in the catalytic system. It is postulated that the CLOs are releasing their donable hydrogen in the catalytic system faster than the acceptor sites of the coal matrix can utilize the hydrogen.

Also, additional experiments at a higher total metal loading (12,000 ppm versus 30,000 ppm) are planned to investigate this further. Work next quarter will include the continuation of catalytic coprocessing reactions, but employing Amocat 1B (Mo/Al_2O_3) catalyst. Gas chromatographic analyses of the products produced from the hydrogen donors in the thermal and catalytic

reactions will also be completed. Reactions involving different coals and resid combinations will also be initiated.

Special Note

Due to a family crisis, Mr. Michael W. Bedell, a doctoral candidate in chemical engineering, was unable to complete as much research during the quarter as was initially planned. Research on this subtask will resume during the month of April.

APPENDICES

Appendix I.A.A.

Determination of Response Factors

The following equation A1 was used:

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

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 the adding a carefully weighed amount of the biphenyl standard. The ratios of the weights of the compounds to the biphenyl are shown in Tables I.A.A.1 to I.A.A.3.

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 I.A.A.1 to I.A.A.3.

Table I.A.A.1

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

Sample Number	Average W_{ANTH}/W_{BIP}	Average A_{ANTH}/A_{BIP}	Std. Dev.	% Error
070	2.0938	2.3568	0.245	10.4
071	0.9541	1.1106	0.058	5.2
072	2.9718	3.3463	0.175	5.2

Table I.A.A.2

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

Sample Number	Average W_{PYR}/W_{BIP}	Average A_{PYR}/A_{BIP}	Std. Dev.	% Error
070	1.0574	1.0629	0.082	7.7
071	2.6380	3.0400	0.467	15.4
072	2.0455	2.0825	0.197	9.5

Table I.A.A.3

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

Sample Number	Average W_{PHPYR}/W_{BIP}	Average A_{PHPYR}/A_{BIP}	Std. Dev.	% Error
070	1.1510	0.9960	0.046	4.6
071	1.4984	1.3267	0.019	1.4
072	2.7327	2.4214	0.018	0.8

Three 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 I.A.A.4.

Table I.A.A.4

Response Factors and Y intercepts for Anthracene, Pyrene, and Perhydropyrene Using Biphenyl as the Internal Standard

Compound	R_f	Y_o
Anthracene	1.107	0.049
Pyrene	1.228	-0.289
Perhydropyrene	0.897	-0.029

Appendix I.A.B.

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 W_1 = mass of original sample

W_2 = mass of sample after drying

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

Table I.A.B.1

Percent Moisture Content of Illinois No. 6 Coal

Sample No.	W_1	W_2	% Moisture
01	1.00064	0.99104	0.959
02	1.00168	0.99530	0.637
03	1.00064	0.99394	0.670

Appendix I.B.1.A
Original Data of the Solubility of Coal and Residuum

The following are the data obtained from the dissolution of Illinois No. 6 coal, Maya and Khafji residua, and the mixtures of coal and these residua in hexane, toluene, and tetrahydrofuran. In the first table, coal solubility was directly measured by the degree of coal dissolution in different solvents in sequence. In the next tables, the solubilities of Khafji or Maya alone and mixtures of coal and residuum combined were measured. For the purpose of calculation, the solubility of residuum in the mixture in the extracting solvents was assumed to be unaffected by the coal. Then he solubility of coal combined with residuum was calculated by subtracting a proportional amount of the fraction of residuum from the total amount of the same fraction in the mixture. The extraction results were summarized as weight percents of the fraction dissolved in each solvent on the ash free basis.

Table I.B.1.A.1
Coal Solubility Determined by Direct Dissolution of Illinois No. 6 Coal[1]

Sample No.	Extracted Products (wt%)*				Recovery (%)*
	Oil	Asp	Preasp	IOM	
1	0.0	0.1	6.1	93.8	102.0
2	0.0	0.2	7.2	92.6	103.2
Average	0.0±0.0	0.1±0.0.5	6.7±0.5	93.2±0.6	

[1]9g of 100 mesh Illinois No. 6 coal
*Weight percents on the ash free basis
Asp (asphaltenes), Preasp (preasphaltenes)

Table I.B.1.A.2. Coal Solubility Calculated from the Coal-Khafji Mixture

(a)Khafji Residuum[1]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)*
1	82.5	17.5	0.0	0.0	104.0
2	82.3	17.7	0.0	0.0	103.4
Average	82.4±0.1	17.6±0.1	0.0±0.0	0.0±0.0	

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

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)*
3	57.9	13.1	2.0	27.0	101.2
4	57.1	13.5	2.0	27.4	101.9
Average	57.5±0.4	13.3±0.2	2.0±0.0	27.2±0.2	

(c) Calculated Solubility of Illinois No. 6 Coal from Mixture of (b)[3]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)*
3	3.5	3.1	6.4	87.0	101.2
4	1.2	4.6	6.2	88.0	101.9
Average	2.3±1.1	3.9±0.8	6.3±0.1	87.5±0.5	

[1]9g of Khafji residuum
[2]#3: 5.9939g Khafji, 2.9973g coal; #4: 5.9976g Khafji, 2.9978g coal.
[3]Values were calculated by subtracting the proportional amounts of Khafji fractions referring to (a) from the total amounts of products shown in (b). As an example of the sample #3, in which a mixture of 5.9939g residuum and 2.7036g ash-free coal was extracted, the calculated coal fractions were determined as follows:

fraction	overall(g) -	Khafji x recovery x fraction(g)	=	coal(g)	coal(wt%)
Oil	5.0952	5.9939 x 1.012 x 0.824		0.0969	3.5
Asp	1.1519	" 0.176		0.0843	3.1
Preasp	0.1742	" 0.0		0.1742	6.4
IOM	2.3817	" 0.0		2.3817	87.0
			total ·	2.7371	

*Ash free basis. Asp (asphaltenes), Preasp (preasphaltenes)

Table I.B.1.A.3. Coal Solubility Calculated from the Coal-Maya Mixture[1]

(a) Maya Residuum[2]

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 Illinois No. 6 Coal and Maya Residuum[3]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)*
3	45.7	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 Solubility of Illinois No. 6 Coal from Mixture of (b)[4]

Sample No.	Extracted Products (wt%)* Oil	Asp	Preasp	IOM	Recovery (%)*
3	0.0	4.6	5.4	90.0	101.8
4	0.0	3.9	4.9	91.2	101.2
Average	0.0±0.0	4.3±0.4	5.1±0.3	90.6±0.6	

[1]Data in the previous quarterly report (Dec. 1989).
[2]9g Maya
[3]#3: 6.0058g Maya, 3.0052g coal; #4: 5.9989g Maya, 3.0002g coal.
[4]Values were calculated by subtracting the proportional amounts of Khafji fractions referring to (a) from the total amounts of products shown in (b). To evenly split the recovery between Maya and coal, the summed amount of oil and asphaltene fractions from Maya was subtracted from the summed amount of overall oil and asphaltenes. For example, in the case of #3 with 6.0058g Maya and 101.8% recovery (Maya x recovery = 6.1139g)

fraction	overall(g)	- Maya x fraction(g)	= coal(g)	coal'(g)	coal(wt%)
Oil	4.1465	6.1139 x 0.687	-0.0537	0.0	0.0
Asp	2.0827	x 0.311	0.1813	0.1276	4.6
Preasp	0.1477	x 0.0	0.1477	0.1477	5.4
IOM	2.4993	x 0.002	2.4871	2.4871	90.0

*Ash free basis: Asp (asphaltenes), Preasp (preasphaltenes)

Appendix I.B.1.B
Original Data of the Thermal Coprocessing Reactions with Pretreated Maya Residuum

The following data were obtained from the thermal coprocessing reactions with Illinois No. 6 coal and the pretreated Maya residuum prepared under different conditions. The THF solubles of each pretreated Maya residuum used in coprocessing reactions were also thermally hydrogenated separately. The results were summarized in two ways. Data shown in 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 method B were determined by calculating the weight percent of each fraction except for 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%.

Coal conversion was determined by the degree in which the moisture and ash free (maf) coal was converted during the reaction. Because THF solubles of pretreated Maya produced IOM fraction during the second-stage thermal coprocessing reaction, the percent coal conversion was determined by the following equation:

$$100 \times \{ 1 - [(IOM)_t - (IOM)_r \ 1/\text{maf coal} \} = \% \text{ coal conversion}$$

where $(IOM)_t$: overall IOM produced from the thermal coprocessing reaction with coal and pretreated residuum
$(IOM)_r$: IOM produced from the thermal hydrogenation reaction pretreated residuum (6g)

Table I.B.1.B.1 Thermal Coprocessing Reaction with Illinois No. 6 Coal and Maya Residuum Pretreated Under Different Conditions[1]

Reaction No.	1-0216	12-0222	2-0216	12-0222
Pretreatment Reaction & Condition	1-0202 Thermal S=0.0 g	73-0208 Thermal S=0.0 g	2-0216 Catalytic MoNaph Mo=2996 ppm S=0.0248 g	74-0208 Catalytic MoNaph Mo=2944 ppm S=0.0242 g
Coal (g)	3.0404	3.0076	3.0096	3.0056
Maya Pretreated (g)[2]	6.0258	6.1053	6.0843	6.2294
Hexadecane (g)[3]	0.0	0.0	0.6603	0.6631
H_2 consumption (%)	13.5	6.3	15.3	22.7
Product Distribution (wt%)				
-Method A				
Gas	2.8	3.4	3.1	2.4
Oil	43.9	44.8	59.5	59.1
Asphaltene	15.8	16.3	22.5	24.3
Preasphaltene	17.4	17.3	11.4	11.8
IOM	20.1	18.2	3.5	2.4
-Method B				
Gas	2.7	3.1	3.0	2.3
Oil	47.0	49.7	61.6	61.7
Asphaltene	14.9	14.9	21.3	22.8
Preasphaltene	16.4	15.7	10.8	11.0
IOM	19.0	16.6	3.3	2.2
Coal Conversion (%)[4]	37.7	44.7	90.4	93.9
Recovery (%)	94.4	91.3	94.6	93.8

[1]Thermal coprocessing reactions at 400°C for 1 hour without additional sulfur.
[2]Actual THF solubles of pretreated Maya residuum (after subtraction of hexadecane amount from the overall THF solubles from the first-stage residuum pretreating reaction).
[3]Hexadecane remaining in the overall THF solubles recovered from the Maya pretreating reaction (used for diluting catalyst pastes).
[4]Coal conversion determined by the equation of

$$100 \times \{ 1 - [(IOM)_t - (IOM_r \ 1/maf \ coal \}$$

where $(IOM)_t$: overall IOM produced from the thermal coprocessing reaction with coal and pretreated residuum

$(IOM)_r$: IOM produced from the thermal hydrogenation reaction pretreated residuum (6g)

Table I.B.1.B.1. (continued)
Thermal Coprocessing Reaction with Illinois No. 6 Coal and Maya Residuum Pretreated Under Different Condition[1]

Reaction No.	3-0216	77-0222	4-0216	78-0222
Pretreatment Reaction & Condition	3-0202 Catalytic NiNaph Ni=2824 ppm S=0.0134 g	11-0208 Catalytic NiNaph Ni=3230 ppm S=0.0143 g	4-0202 Catalytic VNaph V=2559 ppm S=0.0359 g	12-0208 Catalytic VNaph V=2603 ppm S=0.0356 g
Coal (g)	3.0012	3.0027	3.0048	3.0078
Maya Pretreated (g)[2]	6.1354	5.9973	6.0897	6.1058
Hexadecane (g)[3]	0.5164	0.5848	1.2142	1.2424
H_2 consumption (%)	9.4	15.1	2.0	10.3
Product Distribution (wt%)				
-Method A				
Gas	2.8	2.1	2.7	2.0
Oil	54.0	56.9	45.4	48.9
Asphaltene	19.7	20.2	17.4	19.1
Preasphaltene	20.9	17.1	21.4	16.9
IOM	2.6	3.7	13.1	13.1
-Method B				
Gas	2.7	2.0	2.5	1.8
Oil	55.8	59.4	48.9	52.8
Asphaltene	18.9	19.0	16.3	17.7
Preasphaltene	20.1	16.1	20.0	15.6
IOM	2.5	3.5	12.3	12.1
Coal Conversion (%)[4]	92.4	89.0	60.9	61.4
Recovery (%)	95.9	94.1	93.6	92.4

[1]Thermal coprocessing reactions at 400°C for 1 hour without additional sulfur.
[2]Actual THF solubles of pretreated Maya residuum (after subtraction of hexadecane amount from the overall THF solubles from the first-stage residuum pretreating reaction).
[3]Hexadecane remaining in the overall THF solubles recovered from the Maya pretreating reaction (used for diluting catalyst pastes).
[4]Coal conversion determined by the equation of

$$100 \times \{ 1 - [(IOM)_t - (IOM)_r]/\text{maf coal} \}$$

where $(IOM)_t$: overall IOM produced from the thermal coprocessing reaction with coal and pretreated residuum
$(IOM)_r$: IOM produced from the thermal hydrogenation reaction pretreated residuum (6g)

Table I.B.1.B.2. Thermal Coprocessing Reaction with Maya Residuum Pretreated Under Different Conditions[1]

Reaction No.	1-0305	2-0305	3-0305	4-0305
Pretreatment Reaction & Condition	1-0202 73-0208 Thermal S=0.0 g	2-0202 74-0208 Catalytic S=0.024 g	3-0202 11-0208 Catalytic S=0.014 g	4-0202 12-0208 Catalytic S=0.0340 g
Maya Pretreated (g)[2]	6.1437	6.0150	6.5618	5.9675
Hexadecane (g)[3]	0.0	0.6461	0.5939	1.2050
H_2 consumption (%)	13.7	11.5	6.7	5.0
Product Distribution (wt%)				
-Method A				
Gas	3.4	3.0	1.7	1.7
Oil	67.6	84.0	80.4	69.6
Asphaltene	21.4	12.0	16.4	24.2
Preasphaltene	6.9	0.6	1.1	3.3
IOM	0.7	0.4	0.4	1.2
-Method B				
Gas	3.1	2.7	1.6	1.6
Oil	69.9	85.3	81.5	71.7
Asphaltene	19.9	11.1	15.4	22.5
Preasphaltene	6.4	0.6	1.1	3.1
IOM	0.7	0.3	0.4	1.1
Recovery (%)	93.3	82.4	94.0	93.0

[1]Thermal coprocessing reactions at 400°C for 1 hour without additional sulfur.
[2]Actual THF solubles of pretreated Maya residuum (after subtraction of hexadecane amount from the overall THF solubles from the first-stage residuum pretreating reaction).
[3]Hexadecane remaining in the overall THF solubles recovered from the Maya pretreating reaction (used for diluting catalyst pastes).

Appendix I.B.1.C.
Calculation of Coal Products Produced from Thermal Coprocessing Reaction with Pretreated Maya Residuum

To differentiate the fractions produced from coal from the fractions of pretreated Maya in the thermal coprocessing reactions, the following were assumed: (1) hydrogenation of the pretreated Maya residuum in thermal coprocessing reactions were unaffected by coal, (2) the recovery of the coprocessing products was evenly distributed in coal products and residuum products, (3) in case of a negative value in oil, that amount was involved in the next fraction, asphaltenes. The fractions of coal products were calculated as described in the following examples.

(a) Coprocessing with thermally pretreated Maya residuum (sample # 1-0216)

	reactant(g)		recovery		recovered(g)
coal	3.0404	x	0.944	=	2.8701
Maya	6.0158	x	0.944	=	5.6789

	weight percent		weight(g)					coal
	coproc.	Maya	coproc.	Maya from		coal products		product
fraction	mixture	alone	mixture	coprocessing		I	II	(%)
Gas	2.8%	3.4%	0.2394 -	5.6789 x 0.034	=	0.0463	0.0463	1.6
Oil	43.9	67.6	3.7531 -	" x 0.676	=	-0.0858	0.0	0.0
Asp	15.8	21.4	1.3507 -	" x 0.214	=	0.1354	0.0496	1.7
Preasp	17.4	6.9	1.4875 -	" x 0.069	=	1.0957	1.0957	38.2
IOM	20.1	0.7	1.7183 -	" x 0.007	=	1.6785	1.6785	58.5
						total	2.8701	

(b) Coprocessing with catalytically pretreated Maya residuum (sample # 2-0216)

	reactant(g)		recovery		recovered(g)
coal	3.0096	x	0.946	=	2.8471
Maya	6.0843	x	0.946	=	5.7557

	weight percent		weight(g)				coal
	coproc.	Maya	coproc.	Maya from		coal product	product
fraction	mixture	alone	mixture	coprocessing		I	(%)
Gas	3.1%	3.0%	0.2667 -	5.7557 x 0.030	=	0.0940	3.3
Oil	59.5	84.0	5.1187 -	" x 0.840	=	0.2839	10.0
Asp	22.5	12.0	1.9356 -	" x 0.120	=	1.2449	43.7
Preasp	11.4	0.6	0.9807 -	" x 0.006	=	0.9462	33.2
IOM	3.5	0.4	0.3011 -	" x 0.004	=	0.2781	9.8
					total	2.8471	

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