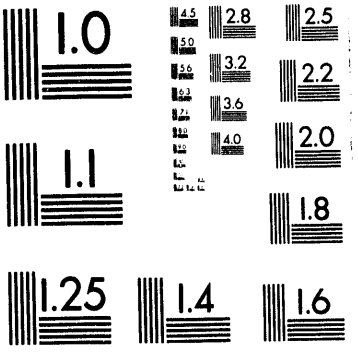
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DOE/PC/88801--T9

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

Contract No. DE-AC22-88PC88801

Quarterly Report

December 27, 1990 - March 26, 1991

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Submitted by

DEPARTMENT OF CHEMICAL ENGINEERING
AUBURN UNIVERSITY, ALABAMA

Dr. Christine W. Curtis, Principal Investigator

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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 hydoraromatics, 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 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 of Subtask I.A. is to investigate hydrogen transfer from cycloalkanes, such as those present in petroleum residua, to aromatics, such as those present in coal, during coprocessing. This quarter, reactions were conducted using the model compounds pyrene and perhydroanthracene.

EXPERIMENTAL

Materials. The materials used this quarter included anthracene (ANT), pyrene (PYR), perhydroanthracene (PHA), perhydropyrene (PHP), biphenyl (BIP) as the internal standard for gas chromatography (GC) analysis, and tetrahydrofuran (THF) and toluene (TOL) as solvents. The ANT, PYR, PHP, and BIP were all purchased from Aldrich Chemicals and had a purity of 99% or greater. The PHA was synthesized in the Auburn University Coal Laboratory, and had a purity of approximately 99%. The THF and TOL were 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 tubular microreactors (TMRs) with a length of 4.5 inches and a volume of approximately 20 cm^3. A Varian gas chromatograph, Model 3400, was employed for reaction product analysis.

Procedure and Analysis for Model Compound Reactions. Model compound reactions

were conducted this quarter using PHA alone and a 4:1 weight ratio of PYR to PHA. A measured amount of each compound was introduced into a TMR and then charged with 400 psig nitrogen. The reactor was leak tested, submerged in a fluidized sand bath at 430°C for sixty minutes, 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 extraction with THF. BIP, the internal standard for gas chromatography analysis, was added to the product vials. The products were then analyzed by GC. The GC instrumental conditions for the PYR and PHA reactions are shown in Table I.A.1. The GC results for the PYR and PHA reactions are shown in Table I.A.2.

Analysis of Products from Previously Conducted Coal and Residuum Reactions. The following is a complete list of coal and residuum reactions conducted for this study:

1 component:	coal residuum	2 component:	coal/ANT coal/PYR coal/PHP residuum/ANT residuum/PYR residuum/PHP
3 component:	coal/ANT/PHP coal/PYR/PHP residuum/ANT/PHP residuum/PYR/PHP	4 component:	coal/ANT/PHP/residuum coal/PYR/PHP/residuum

The reaction, extraction, and analytical procedures were described in detail in previous reports. A comprehensive list of the analytical results are shown in Table I.A.3.

RESULTS AND DISCUSSION

Due to the small amounts of PHA synthesized, the reactions using this compound were quite limited. PHA was reacted alone and in a 4:1 weight ratio of PYR to PHA. All reactions were duplicated. Gas chromatography analysis revealed an unknown product peak that analysis by mass spectrometry identified as ANT. As can be seen from Table I.A.2, the yield of ANT was greater in the reactions with PHA alone, than in the reactions with both PHA and PYR. No hydrogenated forms of PYR were present in the products from the PYR/PHA reaction. PYR appears to be very difficult to hydrogenate and might be acting as an inhibitor to PHA dehydrogenation.

A discussion of the results of all the coal and residuum reactions conducted for this study, shown in Table I.A.3, was presented in an earlier report.

CONCLUSIONS

- Overall, the conversion was greater for the residuum reactions than for the coal reactions, which is not surprising since residuum has a much higher hydrogen content. The residuum itself was degraded during these reactions. Residuum is 100% soluble in TOL; however, the products from the residuum reactions were never 100% TOL soluble.
- Coal and residuum reactions in which both ANT and PHP were used resulted in the formation of DHA, tetrahydroanthracene (THA), and PYR. DHA and THA were also formed in reactions in which no PHP was used. Likewise, PYR was formed in reactions in which no ANT was used.
- No products were formed in those coal and residuum reactions using PYR alone or PYR and PHP.

- The conversion was greater for ANT and PHP in those reactions in which both were used. It appears that systems in which both ANT and PHP are used are far more reactive than other systems. The higher yields of DHA, THA, and PYR in coal reactions may be attributed to trace metals in the coal acting as catalysts.
- The presence of ANT resulted in a higher insoluble organic matter (IOM) content than in the corresponding PYR or PHP system.
- The presence of PHP in a system resulted in much higher conversion than the corresponding ANT or PYR system.
- The presence of PYR seemed to have little effect on the upgrading of coal or residuum.
- By comparing the results of coprocessing reactions with the results of model reactions, it is evident that both the coal and residuum enhanced hydrogen transfer between model compounds.
- The addition of petroleum residuum to a coal system slightly enhances the coal conversion.

Table I.A.1
Instrumental Conditions for Product Analysis by GC

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 Distributions for PHA and PYR/PHA Sixty Minute Reactions**

Reactants	Product Distribution (mole %)		Product Distribution (mole %)		Reactant Recoveries (%)		
	ANT	PHA	PYR	PHP	PYR	PHP	PHA
PHA	16.46	83.54	---	---	---	---	91.8
	21.60	78.40	---	---	---	---	102.1
PHR/PHA	trace	100.00	100.00	---	69.1	---	79.7
	trace	100.00	100.00	---	70.9	---	80.4
	9.12	90.88	100.00	---	68.1	---	103.0

Table I.A.3. **Average Values for Coprocessing Reactions[1]**

System	TOL%	THF%	IOM%	Recovery (%)			Yield (%)			Conv.%	H_2 Eff.
				PHP	ANT	PYR	DHA	PYR	THA		
Coal/PHP	75.5	17.5	7.0	90.3				10.17		85.8	
Coal/ANT	50.0	14.0	36.0		58.3		7.33		3.12	13.4	
Coal/PYR	58.4	15.2	26.4			65.2				38.3	
Coal/ANT/PHP	83.3	8.2	8.0	79.0	61.2		19.15	15.74	24.66	73.0	49.7
Coal/PYR/PHP	87.7	7.1	5.2	101.5		81.6				83.4	
Resid/PYR	79.5	12.6	7.9			61.4				85.5	
Resid/ANT	77.8	9.4	12.8		73.8		13.47		3.76	78.7	
Resid/PHP	92.3	6.2	1.5	83.4				7.04		97.4	
Resid/ANT/PHP	96.1	3.0	0.9	101.7	84.4		17.42	10.37	16.10	97.6	60.6
Resid/PYR/PHP	94.8	4.1	1.1	90.6		100.3				97.1	
Resid/ANT/PHP/Coal	83.1	6.9	10.0	87.2	66.4		14.00	30.27	21.48	80.6	22.0
Resid/PYR/PHP/Coal	85.5	6.5	8.0	77.8		68.8				83.8	
Coal	4.0	31.2	64.8							30.4	
Resid	43.8	35.2	21.0							80.5	

[1] Moisture and Ash-Free Basis

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

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

INTRODUCTION

This quarter, oil fractions of pretreated Maya residuum, which were hydrogenated with various catalysts, were prepared. Thermal coprocessing reactions of Illinois No. 6 coal were conducted with these oil fractions of pretreated Maya residuum to test the effect of residuum pretreatment on thermal coal upgrading.

EXPERIMENTAL

Preparation of Oil Fractions of Pretreated Maya Residuum. Maya residuum was hydrogenated thermally and catalytically with a naphthenate paste of molybdenum (Mo), nickel (Ni) or vanadium (V), or a powder catalyst, presulfided nickel-molybdenum on alumina (NiMo/alumina), at 400°C for one hour. After the reaction, oil fractions were extracted with hexane, and the hexane was removed using a rotary evaporator. Six different oil fractions were prepared: oil from the original Maya residuum, oil from thermally pretreated Maya residuum, and oils from Maya residuum pretreated with molybdenum naphthenate (MoNaph), nickel naphthenate (NiNaph), vanadium naphthenate (Vnaph), and NiMo/alumina.

Thermal Coprocessing of Illinois No. 6 Coal with Pretreated Maya Residuum. Six oil fractions of Maya residuum prepared under different conditions were mixed with Illinois No. 6 coal, and the mixtures were thermally hydrogenated at 400°C for one hour. The weight ratio of the pretreated oil to coal reacted was 2:1. After the reaction, products were recovered and fractionated by solvent extraction using hexane, toluene, and tetrahydrofuran (THF) as solvents.

Each reaction was duplicated. The product distribution (fraction weight percent) and the coal conversion from each reaction were determined and compared.

RESULTS AND DISCUSSION

Effect of Pretreated Maya Residuum on Thermal Hydrogenation of Illinois No. 6 Coal. Illinois No. 6 coal was thermally hydrogenated with six different oil fractions from Maya residuum, and the effect of differently pretreated oil fractions on coal conversion was examined. The overall product distribution for each reaction based on the weight of each fraction extracted by hexane, toluene and THF (oils, asphaltenes, preasphaltenes and IOM) was summarized in Table I.B.1.1. The effect of differently pretreated oils on the product distribution and coal conversion was minimal. Coprocessing reactions of Illinois No. 6 coal with the oil fractions from pretreated Maya residuum produced coal conversions in the following order: original Maya residuum (45.9%) < thermally pretreated Maya residuum (47.4%) < Maya residuum pretreated with VNaph (50.7%) < MoNaph (52.0%) < NiMo/alumina (53.4%) < NiNaph (58.2%). These results indicated that pretreated Maya residuum, especially catalytically pretreated Maya residuum, appeared to enhance coal conversion to some extent. However, the extent of the effect of pretreated oils from Maya residuum on coal conversion was far smaller than that of the THF-solubles from Maya residuum pretreated with catalysts (quarterly report, September, 1990); coprocessing reactions of Illinois No. 6 coal with the THF-soluble fractions from pretreated Maya residuum produced coal conversions in the following order: original Maya residuum (37.4%) < thermally pretreated Maya residuum (41.2%) < Maya residuum pretreated with VNaph (58.2%) < NiMo/alumina (68.0%) < NiNaph (89.7%) < MoNaph (92.1%). As mentioned in the previous quarterly reports, the THF-solubles fractions from pretreated Maya

residuum contained high concentrations of catalyst metals, while the oil fractions contained nearly negligible amounts of these metals. Therefore, the oil fractions of catalytically pretreated Maya residuum showed far lower enhancing effects than the THF-soluble fractions. The oil fractions of original Maya residuum and thermally pretreated Maya showed somewhat higher enhancing effects than the THF-solubles fractions.

In all coprocessing reactions conducted with the oil fractions of pretreated Maya residuum, the amounts of oil produced were smaller than the amounts of the pretreated oil introduced as a reactant. This indicated that some portions of the oil fractions were converted to volatile materials, which vaporized during the extraction and weighing procedure, and some portions of the oil fractions were converted to heavier fractions by retrogressive reactions during the thermal coprocessing reactions.

With an assumption (1) that the oil was produced only from the oil fraction of Maya residuum, and that the coal was not upgraded to oil, oil loss has been expressed as a weight percentage of the amount of oil reacted (Table I.B.1.2.). The reactions with the oil fractions from original Maya residuum and the Maya residuum pretreated with VNaph showed the greatest oil loss.

With an assumption (2) that the oil fractions were produced only from the oil fraction of Maya residuum, the coal was not upgraded to oil, and the product was completely recovered (100% recovery in calculation) to compensate for a possible oil loss by vaporization, the oil loss was again expressed as a percentage of the amount of oil reacted (Table I.B.1.2.). Even though the weight difference between 100% recovery and the actual recovery was assumed to compensate for the volatile oil fraction, the oil recovered was still less than the oil added as a

reactant. The low oil recovery suggested that reacted oil fractions were converted to heavier materials, which could not be dissolved in hexane, and to volatile fractions.

CONCLUSIONS

Low metal content oil fractions of Maya residuum prepared under different conditions (original Maya residuum, Maya residuum hydrogenated thermally, and Maya residuum hydrogenated catalytically with MoNaph, NiNaph, VNaph and NiMo/alumina) were used in thermal coprocessing reactions of Illinois No. 6 coal to test the effect of residuum pretreatment on the thermal coal upgrading.

When compared to the product distribution from the reactions with the original Maya residuum, all of the rest of the reactions produced more oil and asphaltenes and higher coal conversion. Even though the differences in coal upgrading between different cases were not large, the coal conversion was affected by the oil fractions from differently pretreated Maya residuum in the following order: original Maya residuum < thermally pretreated Maya residuum < Maya residuum pretreated with VNaph < MoNaph < NiMo/alumina < NiNaph. These results suggested that the prehydrogenated Maya residuum, especially catalytically pretreated Maya residuum, might act as a hydrogen donor material, enhancing the hydrogenation reaction of coal in coprocessing. However, to confirm the pure effect of hydrogenated Maya residuum on coal conversion, it should be determined that the trace amount of catalytic species remaining in each pretreated oil fraction was insufficient to enhance the coal hydrogenation under the reaction conditions used.

Table I.B.1.1. **Thermal Coprocessing of Illinois No. 6 Coal with Oil Fractions from Pretreated Maya Residuum**[1]

Pretreated Maya	Overall Product Distribution (wt%)					Coal Conv (%)	Toluene-Solubles
	Gas	Oil	Asp	Preasp	IOM		
Original	2.1±0.1	63.5±0.6	8.6±0.2	8.3±1.7	17.5±1.1	45.9±2.9	72.1±0.4
Thermal	1.7±0.1	65.8±0.2	8.3±0.1	8.0±0.6	16.2±0.6	47.4±1.1	74.2±0.2
MoNaph	1.5±0.5	63.6±0.2	9.7±0.1	10.6±0.4	14.6±0.0	52.0±0.2	73.5±0.1
NiNaph	1.5±0.5	65.8±0.3	10.3±0.0	9.1±0.8	12.8±0.6	58.2±2.0	76.1±0.3
VNaph	1.6±0.6	64.5±0.1	9.8±1.3	7.7±1.0	16.4±0.2	50.7±0.6	74.3±1.4
NiMo/ Al_2O_3	1.6±0.1	66.2±0.1	8.4±0.2	9.6±0.5	14.1±0.3	53.4±0.5	74.6±0.1

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

Table I.B.1.2. Decrease of Oil Production from Coprocessing with Various Oil Fractions from Pretreated Maya Residuum

Pretreated Maya	(1) Overall Oil Loss, converting to Volatiles + Heavy Fractions (% ratio to reactant)	(2) Overall Oil Loss, converting to Heavy Fractions only (% ratio to reactant)	Product Recovery (%)
Original	−17.8±0.1	−5.0±1.4	91.9, 90.1
Thermal	−10.1±0.7	−4.4±0.5	97.7, 94.5
MoNaph	−12.0±0.1	−7.7±0.1	97.0, 97.2
NiNaph	−10.2±0.9	−4.3±0.3	95.4, 96.3
VNaph	−18.5±2.0	−2.5±1.4	86.3, 91.2
$NiMo/Al_2O_3$	−9.1±0.1	−4.2±0.4	96.8, 96.3

<Calculational Example>

Illinois No. 6 coal : 2.0095 g added; moisture, ash-free (maf) coal: 1.6860g
Oil of pretreated Maya (with NiNaph) : 4.6180 g added --- 4.0394 g Oil
0.5786 g Hexadecane
Hydrogen gas consumed during reaction : 0.0167 g
Oil from thermal reaction : 4.1685 g recovered --- 3.5899 g Oil
0.5786 g Hexadecane

Ideal overall product recovery = g maf coal + g oil added + g H_2 consumed
= 5.7421 g (100% recovery)

Actual overall product recovery = g oil + g asphaltenes + g preasphaltenes + g IOM + g H_2 consumed
= 5.4808 g (95.4% recovery)

(1) Oil Loss to Volatile Materials and Heavy Materials
$(Oil_{recovered} - Oil_{reacted}) / Oil_{reacted}$

$$((3.5899 - 4.0394) / 4.0394) * 100 = -11.1\ \%$$

(2) Oil Loss to Heavy Materials
Assume that the weight difference between 100% recovery and actual recovery compensates for the loss of volatile oil fraction.
$(Oil_{recovered} - Oil_{reacted} + Oil_{volatile}) / Oil_{reacted}$

$$(((3.5899 - 4.0394) + (5.7420 - 5.4808)) / 4.0394) * 100 = -4.7\ \%$$

TASK II. DEVELOPMENT OF POTENT NONAROMATIC HYDROAROMATIC DONORS FOR COPROCESSING

SUBTASK II.C. PRODUCTION OF NONAROMATIC HYDROAROMATICS IN REAL SOLVENT SYSTEMS

INTRODUCTION

The objective of this subtask is to produce nonaromatic hydroaromatic compounds in atmospheric or vacuum residua by electroreduction or reduction with metals. Due to the highly successful Birch reduction of naphthalene using sodium metal to produce high purity 1, 4, 5, 8-tetrahydronaphthalene (isotetralin), a modified Birch reduction designed to produce nonaromatic hydroaromatic compounds in petroleum residua was performed initially. If sufficient manpower exists in the future, research will continue on the synthesis of nonaromatic hydroaromatic compounds by electroreduction.

EXPERIMENTAL

The experimental conditions for the Birch reduction of the aromatic compound, naphthalene, to produce the nonaromatic hydroaromatic compound, isotetralin, were modified in the Birch reduction of Maya residuum. In addition, a relay activated, battery operated, exhaust fan assembly was constructed for purposes of safety to serve as a backup to exhaust ammonia, ether, and tetrahydrofuran (THF) vapors in case of fume hood failure during the modified Birch reduction of petroleum residua.

THF, a cyclic ether, was substituted for diethyl ether as a solvent in the modified Birch reduction of Maya residuum because of the low solubility of the residuum in diethyl ether. Subsequent to Birch reduction, the treated residuum did not separate from the reaction mixture when water was added; the treated residuum maintained its solubility in the THF, which was

completely miscible with water. The tendency to lose THF (b.p. = 67°C) from the reaction mixture after the reaction is complete was less than that of diethyl ether (b.p. = 34.6°C). Therefore, it was necessary to perform a distillation to remove the THF and recover the treated Maya residuum. The water-reaction product mixture was distilled to a minimum constant boiling temperature of 78°C, the boiling point of ethanol. The treated residuum-water suspension was cooled and filtered under nitrogen; the treated residuum was washed four times with distilled water and dried under partial vacuum (nitrogen purge) at room temperature.

RESULTS AND DISCUSSION

Most significantly during this quarter, Birch-pretreated Maya residuum was reacted with Pittsburgh No. 8, Western Kentucky No. 9, and Upper Freeport coals, with excellent results. The percent coal conversion to tetrahydrofuran (THF) solubles for each coal reacted with Birch-pretreated Maya residuum, original (untreated) Maya residuum and the nonaromatic hydroaromatic compound isotetralin (ISO), an excellent hydrogen donor, are presented in Table II.C.1.

The data indicated that Birch-pretreated Maya residuum performed in a highly efficient manner comparable to ISO (an increase in coal conversion of approximately 20 percent with reactive coals such as Pittsburgh No. 8 and Western Kentucky No. 9, and that Birch-pretreated Maya residuum also performed in manner similar to ISO with Upper Freeport, a coal that was found to be of low reactivity in coprocessing.

Preliminary comparisons of the Fourier transform infrared (FTIR) spectra of the original Maya residuum and the Maya residuum treated by the modified Birch reduction indicated that the aromatic character of the treated Maya residuum was decreased. Next quarter, more FTIR

spectra of the reaction products obtained from the modified Birch synthesis of petroleum residua will be compared. DAU Rock, a solid, easy to handle, high asphaltene content, well characterized residuum similar to Maya residuum, will be treated using the modified Birch reduction, and coal conversion yields will be reported.

Table II.C.1. Comparison of Percent Coal Conversion to THF Solubles Using Birch-pretreated Maya Residuum

Coal	Percent Coal Conversion		
	Pretreated Maya	Original Maya	Isotetralin
Pittsburgh No. 8	43.3 (2.6)[1]	20.1 (3.3)	41.5 (0.6)
W. Kentucky No. 9	43.7 (2.9)	24.3 (3.3)	44.8 (0.3)
Upper Freeport	16.9 (0.8)	14.0 (1.6)	16.5 (3.4)

[1] Percent coal conversion followed by percent standard deviation in parentheses.

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

INTRODUCTION

Research this quarter consisted of the completion of the GC analysis of the reaction products of the model compounds with Maya residuum and the Argonne premium coals. Coal conversion to tetrahydrofuran (THF) solubles obtained in these reactions was reported last quarter, and will not be repeated herein. Also completed this quarter, were the coprocessing reactions of Pittsburgh No. 8 coal and Alaskan North Slope and DAU Rock residua to determine coal conversion to THF solubles. Finally, work was begun to determine the kinetics and rate of hydrogen donation from the model compounds themselves.

RESULTS AND DISCUSSION

GC Analysis of the Reaction Products from the Model Compounds in Coprocessing Reactions

The THF soluble fractions for all the coprocessing reactions with the model hydrogen donors, Maya residuum, and the nine coals presented in Table II.D.1 were further analyzed by gas chromatography (GC) to determine the effect the coprocessing reactions had on the hydrogen donors that were initially present. The results of this analysis are also presented in Table II.D.1. In all of the reactions involving octahydroanthracene (OHA), OHA did not react substantially, with over 88% OHA being recovered from the reactions with Upper Freeport coal. For the reactions with Illinois No. 6 coal, where OHA showed the most conversion, nearly 36% was recovered. For all of the coprocessing reactions performed with OHA, the primary reaction product was dihydroanthracene (DHA), with anthracene (ANT) also being formed. Hexahydroanthracene (HHA) was completely converted to OHA, DHA, and ANT in all of the coprocessing reactions studied. For Western Kentucky No. 9, Upper Freeport, Pocahontas No. 3, Pittsburgh No. 8, Lewiston-Stockton, and Blind Canyon coals, the primary reaction product from HHA was DHA. With Wyodak-Anderson and Beulah-Zap coals, ANT was the primary reaction product; with Illinois No. 6 coal, OHA was the primary reaction product with nearly 74% being formed.

The primary product of DHA, in the presence of both 1.2 and 3.0g Maya residuum, was OHA for Western Kentucky No. 9, Illinois No. 6, and Upper Freeport coals. For Blind Canyon, Wyodak-Anderson, and Beulah-Zap coals, the primary reaction product from DHA was ANT. In the reactions with Pittsburgh No. 8 coal, nearly equivalent amounts of OHA and ANT were produced from the reaction of DHA in the presence of 3.0 g Maya residuum. For the reaction

of DHA with 1.2 g Maya residuum and Pittsburgh No. 8 coal, the primary reaction product was OHA; for the corresponding reaction with Lewiston-Stockton coal, ANT was the predominant product.

In all of the coprocessing reactions studied, isotetralin (ISO) was completely converted to naphthalene (NAP) and tetralin (TET). ISO was more than 92% dehydrogenated to NAP in the reactions with Beulah-Zap coal, and over 72% converted in the presence of Wyodak-Anderson coal, which produced the most TET of any of the reaction systems. For all of the reactions performed with TET, only a small amount of TET reacted, with NAP being the only product formed. In all of the coprocessing reactions studied, the most TET converted was approximately 25% in the reactions with Wyodak-Anderson coal. TET was completely unreactive in the Blind Canyon coal coprocessing reactions.

Net Hydrogen Donation from the Model Compounds During Coprocessing

The net amount of hydrogen released from the model compounds during the coprocessing reactions with the Argonne coals was determined from GC analysis, and the results of these calculations are also presented in Table II.D.1. Some trends that were observed with the model hydrogen donor present, regardless of the coal present, were 1) ISO always released more hydrogen than its conventional hydrogen donor analogue TET; 2) ISO also released more hydrogen than the conventional donor OHA, except for the reactions with Illinois No. 6 coal where nearly equivalent amounts of hydrogen were released; 3) The cyclic olefin, HHA, always released more hydrogen than OHA, except for the reactions with Illinois No. 6 coal. For the coprocessing reactions with Illinois No. 6 coal and HHA, there was a net hydrogen incorporation.

For the reactions with OHA, the most hydrogen released occurred in the reactions with Illinois No. 6 coal (0.01535 g), and the least donated occurred with Pittsburgh No. 8 coal (0.00225 g). With the reactions of HHA and Western Kentucky No. 9 coal, 0.00928 g of hydrogen were released, while the most hydrogen was released in the reactions with Beulah-Zap coal (0.01983 g). The reactions of DHA and Wyodak-Anderson coal, in the presence of both 1.2 and 3.0 g Maya residuum, had the least hydrogen incorporation. The reaction of DHA in the presence of 3.0 g Maya residuum and Illinois No. 6 coal had the most hydrogen incorporation, while the reactions for DHA and Western Kentucky No. 9 coal had the most hydrogen incorporation of the reactions in the presence of 1.2 g Maya residuum.

There were no clear trends with hydrogen incorporation in the reactions of DHA in the presence of 1.2 or 3.0 g Maya residuum. For Western Kentucky No. 9, Pittsburgh No. 8, and Beulah-Zap coals, more hydrogen was incorporated in the reactions with 1.2 g Maya residuum. For Illinois No. 6, Upper Freeport, Lewiston-Stockton, Blind Canyon, and Wyodak-Anderson coals, more hydrogen was incorporated for the reactions with 3.0 g Maya residuum.

For both ISO and TET, the most hydrogen was released in the coprocessing reactions with Beulah-Zap coal. In the reactions with ISO and Lewiston-Stockton coal, the least amount of hydrogen was released; for TET the least amount of hydrogen was released in the reaction with Western Kentucky No. 9 coal.

CONCLUSIONS

1) In all of the liquefaction and coprocessing reactions, the cyclic olefin ISO always produced greater coal conversion to THF solubles and released more hydrogen than its conventional hydrogen donor analogue, TET.

2) In all the liquefaction and coprocessing reactions, the cyclic olefin HHA always produced greater coal conversion and released more hydrogen than its conventional donor analogue, OHA.

3) In the liquefaction reactions performed, ISO always produced more coal conversion than OHA, except for those reactions with Western Kentucky No. 9 coal. For the coprocessing reactions, ISO produced more, or nearly equivalent conversions than OHA except for Upper Freeport and Blind Canyon coals.

4) TET produced lower conversions to THF solubles than the reactions of Upper Freeport, Blind Canyon, or Beulah-Zap coals with no added donor. For the coprocessing reactions, TET produced less conversion for these three coals, as well as for Lewiston-Stockton, than in the reactions with Maya residuum only.

5) In all of the liquefaction and coprocessing reactions, DHA produced more coal conversion than HHA.

6) For all the added donors in the coprocessing reactions, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8 coals were reactive; Pocahontas No. 3 coal was completely unreactive in the reaction system used, regardless of the donor present.

7) The cyclic olefins were completely converted in all of the coprocessing reactions that were performed. By contrast, their conventional hydrogen donor analogues all remained partially unreacted in every reaction system.

8) For the coprocessing reactions, Maya residuum acted as an inhibitor. This inhibition was indicated by the lower coal conversion obtained in the presence of 3.0 g residuum versus 1.2 g residuum with DHA at constant mass of donor present.

9) For all of the liquefaction and coprocessing reactions with DHA, there was a net incorporation of hydrogen through its conversion to OHA, a much poorer hydrogen donor compound for coal conversion.

Coprocessing Reactions with DAU Rock and Alaskan North Slope Residua

Research this quarter also consisted of the completion of the model compound coprocessing reactions of the DAU Rock residuum and the Alaskan North Slope residuum samples with Pittsburgh No. 8 coal. The results obtained for conversion of Pittsburgh No. 8 coal to tetrahydrofuran (THF) solubles using the cyclic olefins, isotetralin (ISO) and hexahydroanthracene (HHA), and their conventional hydrogen donor compounds, tetralin (TET),

octahydroanthracene (OHA), and dihydroanthracene (DHA), are presented in Table II.D.2.

For all reactions performed, more coal conversion to THF solubles was obtained with the DAU Rock residuum than with the Alaskan North Slope residuum. The cyclic olefin, ISO, produced more coal conversion that its hydroaromatic analogue, TET, for both residua. The cyclic olefin, HHA, produced more coal conversion than its analogue, OHA, but produced less conversion than its analogue, DHA. The reaction of Pittsburgh No. 8 coal, Alaskan North Slope residuum, and TET produced 28.0 percent coal conversion; the reaction of Pittsburgh No. 8 coal and Alaskan North Slope residuum with no model compound present produced 35.1 percent coal conversion.

Kinetics of Hydrogen Donation

One of the key aspects of obtaining a high degree of coal conversion is matching the rate of hydrogen donation to that of the hydrogen required by the coal generated free radicals. In order to investigate the rate of hydrogen donation, thermal reactions with the cyclic olefins and their conventional hydroaromatic analogues were begun. These experiments were designed so that reaction kinetics and rates of hydrogen donation could be determined, Arrhenius plots could be made, and the activation energies and pre-exponential factors could be determined. Analysis of the experimental results is ongoing and will be reported when completed.

Table II.D.1. GC Analysis of the Products from the Model Compounds in Coprocessing Reactions with the Argonne Premium Coals

Compound/Coal Reacted	WT% OHA	WT% DHA	WT% ANT	NET H DONATED
OHA				
KY #9	77.0(4.3)	23.0(4.3)	0.0	0.00511
IL #6	36.3(0.6)	47.9(0.4)	15.8(0.9)	0.01535
UP FREE	88.5(0.1)	11.5(0.1)	0.0	0.00255
POC #3	N/A	N/A	N/A	N/A
PITT #8	73.6(1.0)	24.7(0.6)	1.7(0.4)	0.00225
LEWIS	75.5(2.0)	24.5(2.0)	0.0	0.00544
B. CANYON	59.9(0.1)	35.4(0.1)	4.7(0.1)	0.00926
WYODAK	68.7(2.2)	25.5(1.2)	5.83(1.3)	0.00739
BEULAH	53.9(2.0)	32.7(0.4)	13.6(1.1)	0.01126
HHA				
KY #9	40.2(1.6)	47.7(0.3)	12.0(1.6)	0.00928
IL #6	73.5(0.5)	26.5(0.5)	0.0	-0.00180
UP FREE	37.8(0.5)	48.1(0.2)	14.1(0.4)	0.01021
POC #3	18.2(0.3)	51.7(1.1)	30.1(0.8)	0.01765
PITT #8	30.6(1.0)	52.0(1.0)	17.4(1.7)	0.01268
LEWIS	31.4(1.3)	39.8(0.2)	28.8(1.2)	0.01362
B. CANYON	17.9(0.4)	48.9(0.1)	32.2(0.3)	0.01806
WYODAK	19.3(1.2)	35.7(1.1)	45.1(2.4)	0.01886
BEULAH	15.7(2.0)	40.3(1.1)	44.1(1.3)	0.01983
DHA (3.0 g Maya resid)				
KY #9	49.8(4.2)	24.9(0.7)	25.3(3.5)	-0.03373
IL #6	57.2(1.7)	12.5(0.04)	30.3(1.7)	-0.04139
UP FREE	49.3(1.9)	23.8(0.3)	25.9(1.6)	-0.03543
POC #3	N/A	N/A	N/A	N/A
PITT #8	35.8(2.8)	27.1(0.5)	37.2(3.2)	-0.02030
LEWIS	34.3(2.5)	27.7(0.6)	38.0(3.1)	0.01869
B. CANYON	27.5(0.2)	21.5(0.1)	51.0(0.3)	-0.00863
WYODAK	28.6(0.4)	15.9(0.2)	55.5(1.1)	-0.00822
BEULAH	28.3(0.7)	15.7(0.7)	56.0(2.1)	-0.00837
DHA (1.2 g Maya resid)				
KY #9	52.0(2.3)	26.5(0.2)	21.6(2.4)	-0.03942
IL #6	47.1(2.3)	23.1(0.4)	29.8(2.6)	-0.03258
UP FREE	46.0(0.4)	24.9(0.1)	29.1(0.5)	-0.03182
POC #3	N/A	N/A	N/A	N/A
PITT #8	37.2(0.8)	29.4(0.2)	33.5(0.7)	-0.02268
LEWIS	31.9(1.0)	29.8(0.5)	38.4(1.3)	-0.01646
B. CANYON	26.4(0.4)	24.7(0.3)	49.0(0.2)	-0.00831
WYODAK	24.9(1.4)	20.2(0.7)	54.9(0.8)	-0.00512
BEULAH	33.3(1.3)	17.6(0.4)	49.1(1.2)	-0.01437

OHA = octahydroanthracene
DHA = dihydroanthracene
ANT = anthracene
HHA = hexahydroanthracene

Table II.D.1. (continued) GC Analysis of the Products from the Model Compounds in Coprocessing Reactions with the Argonne Premium Coals

Compound/Coal Reacted	WT% TET	WT% NAP	NET H DONATED
ISO			
KY #9	21.0(0.7)	79.0(0.7)	0.01195
IL #6	22.0(0.5)	78.0(0.5)	0.01179
UP FREE	21.9(1.1)	78.1(1.1)	0.01181
POC #3	N/A	N/A	N/A
PITT #8	19.8(1.2)	81.2(1.2)	0.01213
LEWIS	25.5(1.0)	74.5(1.0)	0.00778
B. CANYON	16.8(0.6)	83.2(0.6)	0.01258
WYODAK	22.7(1.1)	77.3(1.1)	0.01169
BEULAH	7.4(0.6)	92.6(0.6)	0.01400
TET			
KY #9	90.9(0.4)	9.1(0.4)	0.00135
IL #6	79.7(0.8)	20.3(0.8)	0.00307
UP FREE	84.2(4.6)	15.8(4.6)	0.00239
POC #3	N/A	N/A	N/A
PITT #8	78.7(1.6)	21.3(1.6)	0.00322
LEWIS	83.7(0.8)	16.3(0.8)	0.00246
B. CANYON	100.0	0.0	0.0
WYODAK	75.3(1.0)	24.7(1.0)	0.00373
BEULAH	68.7(1.1)	31.3(1.1)	0.00473

ISO = isotetralin
TET = tetralin

Table II.D.2. Percent Conversion of Pittsburgh No. 8 Coal to THF Solubles Using DAU Rock and Alaskan North Slope Residua

Model Compound	Percent Coal Conversion	
	DAU Rock	Alaskan North Slope
DHA (1.2 g resid)	65.6 (2.1)[1]	62.3 (0.9)
DHA (3.0 g resid)	66.5 (0.4)	58.8 (1.0)
HHA	55.1 (1.5)	51.4 (3.0)
OHA	47.6 (0.1)	39.5 (0.6)
ISO	45.6 (0.5)	40.4 (2.6)
TET	41.4 (0.1)	28.0 (0.5)
none	39.6 (1.9)	35.1 (1.9)

[1] Percent coal conversion followed by percent standard deviation in parentheses

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