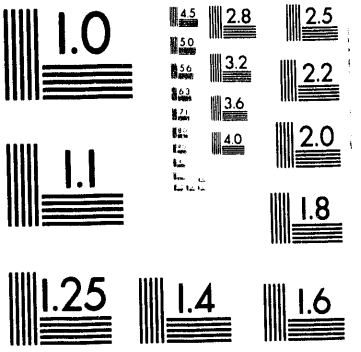

1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

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

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

September 26, 1989 - March 31, 1993

Christine W. Curtis

Chemical Engineering Department
Auburn University
Auburn, AL 36849-5127

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ACKNOWLEDGEMENTS

The research of the following individuals on this research project is gratefully acknowledged.

Ruth M. Owens
Shu-Li Wang
Michael W. Bedell
Honggon Kim
Kenneth W. Olson

The technical assistance of the following individuals is also gratefully acknowledged.

Janice Johnson
Patricia Sandlin
Franklin Bowers
Joseph Aderholdt
Crystal Chen

TABLE OF CONTENTS

Executive Summary 1

Objective 7

Major Tasks and Their Objectives 7

Task I. Elucidation of Hydrogen Transfer From Naphthenes During Coprocessing 8

Subtask I.A.1. An Investigation of Hydrogen Transfer from Naphthenes During Coprocessing 9

Subtask I.A.2. An Investigation of Hydrogen Transfer in Coprocessing Using Model Donors and Reduced Resids 32

Subtask I.B.1. Pretreatment, Fractionation, and Reactivity of Petroleum Residua 61

Subtask I.B.2. Evaluation of Enhanced Factors Prevalent in Pretreated Residua 114

Task II. Development of Potent Nonaromatic Hydroaromatic Hydrogen Donors for Coprocessing 121

Subtask II.A. Synthesis of Nonaromatic Hydroaromatics 122

Subtask II.B. Birch Reduction of Resids 126

Subtask II.C. Coprocessing of Pittsburgh No. 8 Coal with Reduced Resids 132

Subtask II.D.1. Chemistry and Reactivity of Nonaromatic Hydroaromatic Donors 144

Subtask II.D.2.a. Chemistry and Reactivity of Nonaromatic Hydroaromatic Donor Enriched Petroleum Solvents 169

Subtask II.D.2.b. Reactivity of Argonne Coal in the Presence Hydroaromatic Donor Enriched Petroleum Solvents 196

Subtask II.E. Kinetics and Reactivity of Nonaromatic Hydroaromatic Donors 221

Appendix A Isomerization of Decalin by Slurry-Phase Catalysts 257

EXECUTIVE SUMMARY

The overall objective of this research project was 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.

Two major tasks were involved in this research project. Task I involved the elucidation of hydrogen transfer reactions in coprocessing which evaluated the interactions of different hydrogen transfer compounds on coprocessing reactions. First, model systems involving naphthenes, cyclic olefins, and hydroaromatic donors were used to evaluate hydrogen transfer under a variety of coprocessing conditions. Secondly, hydrogen transfer resulting from the prehydrotreatment of resids in coprocessing was examined.

Task II investigated the development of potent nonaromatic hydroaromatic compounds (cyclic olefins) for coprocessing. In this task two approaches were taken for introducing nonaromatic hydroaromatic species into the coprocessing solvent. First, nonaromatic hydroaromatic species were generated in situ in the resid by reducing the resid using the Birch reduction method. Second, nonaromatic hydroaromatic compounds were introduced into the resid prior to coprocessing. In both cases, the effect of the added hydrogen donor species on coprocessing reactions was evaluated. The kinetics and reactivity of cyclic olefins at coprocessing reaction conditions were also determined.

The key results obtained from this research project are given below.

- Hydrogen transfer from naphthenes to aromatics, coal and resid occurred at coprocessing temperatures and in a N_2 atmosphere.

- Hydrogen donors ranked in reactivity as cyclic olefins (nonaromatic hydroaromatic compounds) > hydroaromatic compounds > naphthenes. This ranking held regardless of the type of atmosphere, hydrogen or nitrogen, used.

- Resids reduced by the Birch method transferred substantially more hydrogen to the aromatic acceptor than did the parent resids under coprocessing conditions.

- Hydropretreatment of resids resulted in enhanced coal conversion compared to the parent resid.

- Addition of hydrogen donors such as cyclic olefins or hydroaromatic donors increased the amount of coal conversion during coprocessing. Cyclic olefins and the active hydroaromatic donor, dihydroanthracene, showed the highest level of hydrogen donability. Tetralin and octahydroanthracene showed low reactivity.

- Reduced resids were more effective in coprocessing than the parent resids, in terms of enhanced coal conversion.

- Thermal and catalytic reactivity of cyclic olefins under nitrogen and hydrogen atmospheres was much higher than conventional hydroaromatic donors when no aromatic acceptor was present.

- Reactivity of hydrogen donors was dependent upon the reactivity of the acceptor as well as that of the donors.

- Three-ring hydrogen donors, dihydroanthracene and hexahydroanthracene, were most effective for transferring hydrogen to the Argonne coals while octahydroanthracene was the least reactive.

- The kinetics data obtained for thermal and catalytic reactions involving cyclic olefins and hydroaromatic donors were adequately modeled by pseudo-first order kinetics.

- ΔG values calculated for cyclic olefins and hydroaromatic donors based on kinetics data adequately represented the reactivity observed experimentally.

Hydrogen transfer from naphthenes to aromatics, coal, resid, and coal plus resid has been investigated at 430 °C in a N_2 atmosphere. The reaction of perhydropyrene with anthracene resulted in the formation of pyrene and dihydroanthracene. The weight percents of the products formed varied according to the initial ratio of anthracene:perhydropyrene with a minimum appearing at a 2:1 weight ratio. Increased reaction times and high anthracene:perhydropyrene

ratios also yielded tetrahydroanthracene. Reactions of Illinois No. 6 coal from the Argonne Premium Coal Sample Bank with perhydropyrene, anthracene, and pyrene resulted in higher coal conversion with perhydropyrene and lower with anthracene and pyrene. Reactions of perhydropyrene with resid resulted in less retrogressive reactions occurring in the resid than with either pyrene or anthracene. Apparent hydrogen transfer from coal or resid to anthracene was observed. Combining perhydropyrene with anthracene or pyrene with coal, resid or coal plus resid yielded higher conversions and less retrogressive reactions. Hydrogen transfer occurred from perhydropyrene to anthracene or pyrene and to the coal and resid as evinced by the increased conversion.

Hydrogen donor reactions in the coprocessing of coal and petroleum resids have been investigated using different hydrogen-rich model compounds and reduced resids as donors and aromatics as acceptors. Three hydrogen-rich donor species were compared: cyclic olefins, hydroaromatics, and cycloalkanes; the aromatic acceptors included pyrene and anthracene; and the resids were reduced by the Birch method. Hydrogen was transferred most readily at 380 °C by cyclic olefins, followed by hydroaromatics, and the least by cycloalkanes. Catalysis by thiophenol promoted the hydrogen transfer by the cycloalkanes at 380 °C but had little effect at 440 °C. Reduced resids transferred substantially more hydrogen to an aromatic acceptor than did the parent resids. In a tertiary system of resid, cycloalkane, and aromatic, the reduced resids yielded more hydrogen transfer and promoted hydrogen donation from the cycloalkanes in a N_2 atmosphere. Reduction of resids by the Birch method appeared to be an effective means of increasing the hydrogen donor ability of resids.

Hydropretreatment of petroleum residua prior to coprocessing was performed in order to determine whether adding hydrogen donating compounds to the resids by catalytic treatment

would improve their solvating ability in coprocessing. Active transition metal salts of molybdenum, nickel, and vanadium organic acids were used as catalysts for pretreatment, which included molybdenum naphthenate, nickel naphthenate, and vanadium naphthenate. A commercial hydrotreating catalyst, $NiMo/Al_2O_3$, which was presulfided, was also used. The prehydrotreated residua were then used in coprocessing reactions to evaluate the effect of the hydropretreatment. By comparing the product slates achieved from coprocessing reactions using the parent resid, the hydropretreatment with molybdenum naphthenate and nickel naphthenate had a definite positive effect on coal conversion. Thermal hydropretreatment or catalytic hydropretreatment with vanadium naphthenate did not have a positive effect. Some of the slurry-phase catalysts was entrapped in the resids after pretreatment which led to some of the improvement. However, Maya resid, pretreated with supported $NiMo/Al_2O_3$, also showed improvement in coal conversion which suggested that at least some of improvement resulted from changes in the chemistry of the residua.

In Task II, Pittsburgh No. 8 coal was coprocessed with five different resids to establish the effect of these resids on coal conversion at 380 °C in a H_2 atmosphere. The resids with the highest asphaltene content yielded the most conversion. The addition of hydrogen donor species like the cyclic olefins, 1,4,5,8-tetrahydronaphthalene (isotetralin) and 1,4,5,8,9,10-hexahydro-anthracene, and hydroaromatic species, 9,10-dihydroanthracene, 1,2,3,4,5,6,7,8-octahydro-anthracene, and tetralin, increased the amount of coal conversion obtained in the coprocessing systems regardless of the resid used as solvent. Dihydroanthracene and hexahydroanthracene had the greatest effect on coal conversion while both octahydroanthracene and isotetralin showed positive but lesser effects on coal conversion. Reduction of three resids with the Birch reduction method yielded resids with a greater hydrogen donor capacity which resulted in higher coal conversion than the parent resid and comparable coal conversion to that obtained with isotetralin

added to the resid at 0.5 wt% donable hydrogen level. Prehydrogenating the resid by the Birch method can change the role of the resid from being a diluent to being an active participant in the coal conversion process.

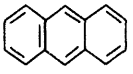
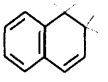
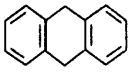
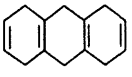
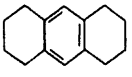
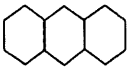
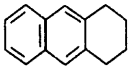
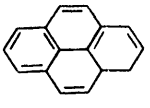
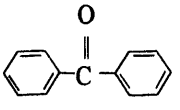
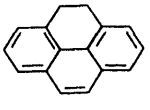
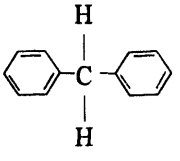
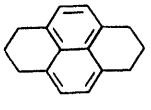
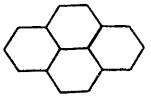
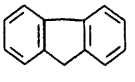
The hydrogen donating ability of cyclic oelfins and their effect on coal conversion during coprocessing was investigated. The cyclic olefins proved to be highly effective and efficient hydrogen donors. Dihydroanthracene also showed high reactivity under these conditions. Neither tetralin nor octahydroanthracene compared in reactivity to the cyclic olefins and dihydroanthracene when coal conversion was used as the criterion for determining donor effectiveness. For all of the reactions studied, the cyclic olefins were completely converted while the hydroaromatic donors remained at least partially unconverted. Lower severity (temperatures of 380 °C compared to 410 °C) resulted in more reactivity and hydrogen donor activity from the cyclic olefins. Longer residence time also promoted higher coal conversion.

The reactivity of eight coals from the Argonne Premium Sample Bank ranging in rank from lignite to low volatile bituminous coal was evaluated in the presence and absence of hydrogen donors. The effect of highly reactive cyclic olefins, isotetralin and hexahydroanthracene, on coal conversion to tetrahydrofuran soluble material was compared to that of more conventional hydroaromatic donors, tetralin, dihydroanthracene, and octahydroanthracene. The Argonne coals were ranked according to their reactivity in an inert solvent, hexadecane, and in Maya resid. These rankings, based on averages, agreed with those calculated by a computed signal-to-noise ratio which measures simultaneously average and variability of coal conversion. The high volatile bituminous coals, Illinois No. 6, Western Kentucky No. 9, Pittsburgh No. 8, and Blind Canyon, were the most reactive. The three-ring hydrogen donors, dihydroanthracene and hexahydroanthracene, were the most effective for transferring hydrogen to coal, whereas, octahydroanthracene and tetralin were the least effective. The reaction products obtained from

each of the hydrogen donors were different and specific to each reaction. The reactivity of the coal, the ease and effectiveness of hydrogen donation from the donor, and, to a lesser degree, the solvent medium present affected the extent of reaction occurring for each coal system.

The kinetic and thermodynamic properties of cyclic olefins as donors for coprocessing were investigated. The experimental data obtained for both thermal and catalytic reactions were adequately modeled by pseudo-first order reaction kinetics. For all of the thermal reactions, the rate constants increased with temperature. The thermal rate constants for the cyclic olefins were much greater than those for the hydroaromatic analogues. On the basis of the Gibbs free energy as a function of temperature, the ΔG values were calculated to be lower than for the hydroaromatic analogues. Since the more negative ΔG values indicate a more spontaneous reaction, the cyclic olefins should be more reactive than the hydroaromatic donors. This difference in reactivity was verified experimentally. The kinetic rate constants and Gibbs free energy values obtained for cyclic olefins under catalytic conditions clearly showed that cyclic olefins were considerably more reactive than their hydroaromatic analogues.

Table of Chemical Structures

Compound	Structure	Abbreviation	Compound	Structure	Abbreviation
Anthracene		ANT	1,2 Dihydronaphthalene		1,2-DHN
Dihydroanthracene		DHA	1,4 Dihydronaphthalene		1,4-DHN
Hexahydroanthracene		HHA	Hexahydronaphthalene		HHN
Octahydroanthracene		OHA	Isotetralin		ISO
Perhydroanthracene		PHA	Octahydronaphthalene		OHN
Tetrahydroanthracene		THA	Tetralin		TET
Pyrene		PYR	Benzophenone		BEN
Dihydropyrene		DHP	Diphenzlmethane		DPM
Hexahydropyrene		HHP			
Perhydropyrene		PHP	Fluorene		FL
Naphthalene		NAP	Hexadecane	$C_{16}H_{34}$	HEX

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 solvent enriched with nonaromatic hydroaromatics by metal or electrochemical reduction and to evaluate their reactivity and selectivity.

TASK I

ELUCIDATION OF HYDROGEN TRANSFER FROM NAPHTHENES DURING COPROCESSING

SUBTASK I.A.1.

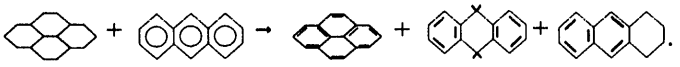
AN INVESTIGATION OF HYDROGEN TRANSFER FROM NAPHTHENES DURING COPROCESSING

INTRODUCTION

The coprocessing of coal with petroleum residuum involves the simultaneous conversion of coal to liquid products and the upgrading of resid to higher quality products. These two feedstocks are quite different in composition with petroleum resid being hydrogen rich with a hydrogen to carbon (H:C) ratio in the range of 1.4 to 1.6 while coal is hydrogen deficient with a H:C ratio of 0.6 to 0.8. The conversion of coal and the subsequent upgrading of coal liquids requires the transfer of hydrogen to coal. Many different sources of hydrogen are available to coal during typical coprocessing: hydrogen from hydrogen-rich portions of the coal, hydrogen from aliphatic, naphthenic, or hydroaromatic components in the resid, or hydrogen from the molecular hydrogen present in the reactor. Hydrogen from hydrogen-rich portions of coal or from hydroaromatic compounds in the coal is fairly labile and available for transfer; however, the hydrogen in saturated species such as naphthenes is held more tightly and is much more difficult to donate. If hydrogen were transferred from naphthenic components in the resid to coal during coprocessing, this hydrogen would provide a valuable hydrogen resource for coal and alleviate some dependence on molecular hydrogen.

This research investigates hydrogen transfer from naphthene-type structures in resid to hydrogen acceptors: aromatic species, coal, and the resid itself. Previous research by Clarke et al.[1] had pointed to the possibility that hydrogen transfer occurred between naphthenic components and coal resulting in increased conversion of coal and formation of aromatics from the naphthenes. In this work, a systematic set of experiments was performed using the naphthene,

perhydropyrene (PHP) reacted with the aromatic pyrene (PYR) or anthracene (ANT) to evaluate hydrogen transfer from naphthenes to aromatics in an inert atmosphere. The reaction being investigated then was



Reactions were also performed with perhydroanthracene synthesized in our laboratory and PYR. Reactions were then performed with both naphthenes and aromatics with Illinois No. 6 coal from the Argonne Premium Coal Sample Bank and with Maya resid. The model species were also reacted with the coal and resid together. Hydrogen transfer from both the naphthenes to the coal and resid and from the coal and resid to the aromatic was examined in terms of the conversion of coal to tetrahydrofuran (THF) solubles and the amount of resid remaining THF soluble.

EXPERIMENTAL

Materials. The chemicals used in this study included PYR and ANT from Aldrich Chemical with a purity of 99% or higher and PHP also from Aldrich at a purity of 97%. Perhydropyrene was synthesized by hydrogenating 1.0 g of hexahydroanthracene at 380 °C for 60 min in the presence of 1.0 g of presulfided $NiMo/Al_2O_3$. Analysis of the synthesized PHA by gas chromatography (GC) showed only that perhydroanthracene was present; no impurities were visible in the chromatogram. The coal used was Illinois No. 6 from the Argonne Premium Coal Sample Program whose properties are given the Table I.A.1.1. The residuum used was Maya resid from Amoco whose properties are shown in Table I.A.1.2. The solvents used for the extraction analyses were toluene and THF from Fisher Scientific.

Procedure. Model compound and coprocessing reactions were conducted in small tubular microreactors of $\sim 20\ cm^3$ charged with N_2 gas. The reaction conditions for the model reactions

were a reaction temperature of 430 °C, N_2 at 400 psig introduced at ambient temperature, and reaction times of 60, 90, and 180 min. The reactor was well agitated at 435 cpm. For the single-component model reactions, 0.1 g of reactant was charged. For the binary component model reactions, the amount of individual reactant used ranged from 0.1 to 0.6 g with the total amount of reactants charged ranging from 0.4 to 1.0 g. Following the reaction, the products were extracted with THF and analyzed by GC. The gaseous products from the reaction were analyzed using a Varian 3700 GC equipped with a thermal conductivity detector and a molecular sieve column. The liquid products were analyzed on a Varian 3400 GC using a HT-5 fused silica column from SGE and FID detection. The internal standard method with biphenyl as the internal standard was used for quantitation. Identification of the products was accomplished by GC mass spectrometry using a VG 70 EHF spectrometer.

The reactions containing coal and/or resid with model naphthenes, aromatic or both, which were conducted for 60 min only, were reacted at the same conditions as the model reactions. Each reactant was charged at a level of 1 g for the single-component reactions; while for the two-, three-, and four-component coprocessing reactions the amounts charged were 2.0, 3.0, and 4.0 g, respectively. After reaction the liquid and solid products were extracted with toluene to yield toluene solubles and with THF to yield THF solubles or THF insolubles which were insoluble organic matter and ash-free.

Definitions for Model Systems. The following definitions of hydrogenation, dehydrogenation, and hydrogen efficiency were employed for this work in order to compare readily the results of the different reaction conditions. Percent hydrogenation is defined as the moles of hydrogen required to produce the liquid as a percentage of the moles required to produce the most hydrogenated liquid product times 100%. The most hydrogenated product from ANT was defined

as 1,2,3,4-tetrahydroanthracene. One hundred percent hydrogenation is defined as ANT hydrogenating to a 100% yield of tetrahydroanthracene. One hundred percent dehydrogenation is defined as PHP dehydrogenation to a 100% yield of PYR; thus, the percent dehydrogenation is equal to the percent yield of PYR. Hydrogen efficiency is the moles of hydrogen accepted by the acceptor to form partially saturated species divided by the moles of hydrogen donated by the donor times 100%. For every mole of PYR formed from PHP, 8 mol of hydrogen were donated; for every mole of dihydroanthracene formed from ANT, 1 mol of hydrogen was accepted; and for every mole of tetrahydroanthracene formed from ANT, 2 mol of hydrogen was accepted. The amount of hydrogen present in the product gases was the difference in the amount donated and the amount accepted.

Definitions for Coal and Resid Systems. For this study, coal conversion is defined as moisture and ash free (maf) coal charged minus insoluble organic matter divided by maf coal charged and multiplied by 100. Resid conversion which is that portion of resid remaining THF soluble is defined as resid charged minus insoluble organic matter divided by resid charged and multiplied by 100. Coal and resid conversion is defined as maf coal plus resid charged minus insoluble organic matter divided by maf coal and resid charged and multiplied by 100. Liquid to solid ratio is defined as the amount of toluene solubles divided by the amount of toluene insolubles present. Another term, degree of upgrading to toluene solubles which describes the degree of upgrading or degrading of the system in terms of the amount of toluene solubles, was defined in order to provide a comparison among the different reactions with coal, resid, and coal plus resid. Degree of upgrading is defined as the toluene solubles in the product minus the toluene solubles in the reactant divided by the upgradable materials. Upgradable materials are defined as maf coal for coal reactions, resid for resid reactions, and maf coal plus resid for the combined reaction.

A positive number for degree of upgrading indicates that upgrading occurred while a negative number indicates that retrogressive reactions took place.

RESULTS AND DISCUSSION

Hydrogen Transfer in Thermal Coprocessing

A systematic set of experiments has been performed to evaluate whether hydrogen can be transferred directly from saturated naphthenes to coal and resid.[2] The experiments performed evaluated the hydrogen transfer from naphthenic PHP to aromatics ANT or PYR and from naphthenic perhydroanthracene to PYR. Both sets of reactions were performed in a N_2 atmosphere. Reactions were then conducted to evaluate the reaction of PHP with Illinois No. 6 coal, the reactions of aromatics, ANT and PYR, with coal, and the reaction of the combined system of naphthenes and aromatic with coal. The same set of reactions was performed with Maya resid: naphthenes with resid, aromatics with resid, and naphthenes and aromatic with resid. The final set of reactions performed involved naphthenes, aromatic, coal, and resid. Base line reactions were also performed with each individual reactant to evaluate the effect of the reaction conditions on the reactions occurring with the individual species.

Hydrogen Transfer in the Model Reactions

The model systems that were used included the binary combinations of ANT with PHP, PYR with PHP and PYR with perhydroanthracene. When reacted individually in N_2 at 430 °C, neither PHP, PYR, nor perhydroanthracene reacted; however, perhydroanthracene reacted, forming ~20% ANT under these conditions. For the PYR and PHP system, reactions were performed using only a 1:1 PYR:PHP weight ratio. Only PYR and PHP were detected in the

products and no H_2 was observed in the product gases. Hence, no net change was observed in that reaction system. The reactions of PYR with perhydroanthracene were quite limited, because of the small quantity of perhydroanthracene that was synthesized. For the PYR and perhydroanthracene system, reactions were conducted with PYR in excess using a 4:1 PYR:perhydroanthracene ratio. Although the PYR and perhydroanthracene reactions formed small amounts of ANT (less than 10%), the yield was less than with the perhydroanthracene reacted individually. Since no hydrogenated forms of PYR were observed in the products, PYR did not readily hydrogenate under these conditions and may even have served as an inhibitor to perhydroanthracene dehydrogenation.

The initial ANT and PHP reactions were performed with a 1:1 weight ratio of ANT:PHP in a N_2 atmosphere. Reactivity was observed as the production of the partially saturated dihydroanthracene from ANT and the formation of the unsaturated PYR from PHP. Hydrogen transfer occurred in this system since the only hydrogen available was from PHP. This reactive system was further investigated by performing three sets of experiments at 60, 90, and 180 min with weight ratios of ANT:PHP ranging from 0.14: ~ 10. The results from these reactions are presented in Tables I.A.1.3 through I.A.1.5 where the product distribution for the 60-, 90-, and 180-min reactions are given, respectively. Hydrogen transfer occurred at all of these conditions as evinced by the hydrogenated and dehydrogenated products formed from ANT and PHP, respectively. At 60-min reaction time, 10-12 mol% dihydroanthracene was formed at low weight ratios (0.14:0.5) of ANT:PHP but decreased by two-thirds at an ANT:PHP weight ratio of 2:1. The amount of dihydroanthracene formed increased somewhat to 5 and 6 mol% at higher ANT:PHP weight ratios, but at weight ratios of 5.0:10.0 the product of tetrahydroanthracene was also observed. At longer reaction times of 90 and 180 min tetrahydroanthracene appeared at

somewhat lower ANT:PHP weight ratios and more was formed. Pyrene was formed from PHP during these reactions; however, no partially saturated forms of PYR were observed. The amount of PYR formed increased almost linearly with increasing ANT:PHP ratios at all three reaction times. At the higher ANT:PHP ratios, the hydrogen donor PHP was limited while ANT was available in excess.

The production of tetrahydroanthracene only occurred when higher concentrations of dihydroanthracene were present. Dihydroanthracene has been shown to act both as a hydrogen donor and a hydrogen acceptor under liquefaction conditions.[3,4] A likely mechanism for tetrahydroanthracene production was that dihydroanthracene formed from ANT hydrogenation acted as a hydrogen acceptor and utilized hydrogen released from PHP to form tetrahydroanthracene.

The product distributions for ANT and PHP reactions as a function of reaction time are given in Table I.A.1.6. Two nominal weight ratios of ANT to PHP, 4 and 6, were used. Reaction times ranged from 5 to 120 min. The amount of dihydroanthracene formed increased with reaction time. Only trace amounts of tetrahydroanthracene were formed before 120 min. At 120 min and at both weight ratios tetrahydroanthracene was formed, although more tetrahydroanthracene was formed at the higher weight ratio. These results correspond to those obtained in Tables I.A.1.3-I.A.1.5. As the reaction time and weight ratio increased, more tetrahydroanthracene was produced in the reaction system.

The hydrogenation of ANT showed a dependence on the weight ratio of ANT to PHP as shown in Figure I.A.1.1. At low and high weight ratios, more hydrogenation of ANT occurred than at weight ratios of 2 to 3%. At weight ratios of 4 or higher, depending on the reaction time, production of tetrahydroanthracene occurred which manifested itself as an increase in the hydrogenation of ANT. By contrast, the dehydrogenation of PYR appeared to increase linearly

with increasing weight ratios of ANT to PHP as shown in Figure I.A.1.2. The shortest reaction time of 60 min on the average yielded less dehydrogenated PHP than the 90-min reaction which was less than in the 180-min reaction. Hence, the time of reaction affected the extent of dehydrogenation of PHP. Hydrogen efficiency presented in Table I.A.1.7 usually ranged from low to high with a minimum being present at a 2:1 ANT:PHP ratio for the 60-min reaction. The errors observed in the hydrogen efficiency were in part caused by the error due to small sample sizes as well as error involved in each aspect of the experiment, recovery, and analysis. Higher hydrogen efficiencies were observed at higher ANT to PHP ratios where the stoichiometric weight ratio was approximately 6.3:1. Since PHP donates 8 mol of hydrogen for every mole of PYR formed and ANT accepts 1 mol of hydrogen for every mole of dihydroanthracene formed, the most favorable condition for stoichiometric conversion would be an ANT:PYR weight ratio of 6.53:1. Observed high hydrogen efficiency were close to this ratio.

The product gases from the PHP/ANT reactions were analyzed, but no hydrogen was detected. The maximum amount of hydrogen that would be produced from the complete dehydrogenation of PHP at the largest amount of PHP charged was 4.4×10^{-2} g and at the least amount would be 7.4×10^{-3} g. However, when based on the products formed the amount of hydrogen present in the gas phase ranged from 0.0 to 2.4×10^{-3} g. Although hydrogen was present in the product gases, particularly with the systems with low hydrogenation efficiency, the hydrogen could not be detected.

These data indicate that hydrogen transfer occurred under these conditions, albeit only a small amount of the naphthenes and aromatic species reacted. These results strongly suggest that under certain reaction conditions, hydrogen transfer can occur from naphthenes to aromatic species. This result may have important implications for coprocessing where a substantial portion

of the resid solvent is composed of naphthenic type structures and coal is composed of aromatic species.

Hydrogen Transfer in Coal and Resid Reactions

Hydrogen transfer between naphthenes and aromatics was evaluated in the presence of coal and resid individually and combinatorially. As with the model studies, all reactions were performed thermally in an inert N_2 atmosphere so that hydrogen transfer resulted only because of interactions among the reactants. Twelve different reaction systems were employed to evaluate hydrogen transfer between naphthenes and aromatics as shown in Tables I.A.1.8 and I.A.1.9. The reactions were at least duplicated and the error observed is presented as standard deviations in these tables. In addition, Illinois No. 6 coal and Maya resid were reacted individually to provide base lines for their individual conversion and reactivity under the coprocessing conditions employed. It should be noted that the product distributions in terms of toluene solubles, THF solubles and THF insolubles are dependent upon the total number of components used in a reaction system. The product distributions should only be used for comparison among the set of components with the same number of reacting species.

Coal Reaction Systems. The binary coal systems ranked in reactivity in terms of coal conversion to THF solubles as coal/PHP > coal/PYR > coal/ANT. The reaction of coal with PHP gave the highest coal conversion of 86% as compared to the coal systems with PYR and ANT, which yielded 38 and 14%, respectively (Table I.A.1.8). Coal conversion obtained with coal alone, without either naphthene or aromatic present, was 30%; therefore, neither ANT nor PYR promoted coal conversion to any extent. In fact, ANT increased the amount of insoluble organic matter present substantially, resulting in the very low coal conversion which was less than coal by itself, while the coal/PYR system gave a conversion that was only slightly higher than coal by

itself. The substantial increase in coal conversion in the coal/PHP system resulted in part from hydrogen transfer from PHP to coal as evidenced by the production of PYR during the reaction (Table I.A.1.9).

Both the amount of THF soluble and toluene solubles produced during the reaction ranked the systems in the same order as the coal conversion (Table I.A.1.8). Tetrahydrofuran solubles were similar for the three systems, ranging from 14 to 17.5%, but the toluene solubles varied considerably more, ranging from 50% for the coal/ANT system to 75.5% for coal/PHP system. Since PYR, an aromatic, should have a higher solvating power for coal than PHP, a naphthene, the substantially higher conversion obtained with PHP, compared to PYR must involve hydrogen transfer. In the PHP/coal reaction, more than 10% PYR was produced (Table I.A.1.9) indicating that dehydrogenation of PHP occurred during the reaction. This PYR originated from PHP since the GC chromatogram of the coal reacted alone did not indicate any PYR peak. By contrast, the coal/PYR system did not show any reaction products from the PYR (Table I.A.1.9). Production of dihydroanthracene and tetrahydroanthracene in the coal/ANT system indicated that hydrogen was transferred from coal to ANT, since the coal present was the only source of hydrogen.

Ternary systems combined a naphthene and an aromatic with coal and were reacted under equivalent reaction conditions as the binary systems. Comparison of ternary systems showed higher coal conversion for the system of coal/PHP/PYR of 83% than for coal/PHP/ANT of 73%, although little difference was observed in their toluene-soluble or THF-soluble yields. Lower coal conversion with ANT in the system may result from a lower solvating power for coal than PYR or a higher propensity for retrogressive reactions. The addition of PHP to coal/ANT effectively blocked some of the retrogressive reactions of ANT and increased coal conversion from 13% for the binary system to 73% for the ternary system. Substantial hydrogenation of ANT occurred in

the coal/PHP/ANT system resulting in 19.2% dihydroanthracene and 24.7% tetrahydroanthracene. More than 15% PYR was formed from PHP during the reaction (Table I.A.1.9).

The ternary system of coal/PYR/PHP yielded substantial coal conversion, 83%, which was quite similar to that obtained for coal/PHP of 86% and much greater than the coal/PYR system of 38%. However, it is difficult to ascertain if hydrogen transfer occurred between PYR and PHP. An equal weight amount of each reactant was charged to the reactor, but no net change in their amounts was observed after reaction. However, the error observed in the amounts of PYR and PHP present after reaction was much higher than in other ternary and binary systems, indicating some variability in the products produced and some possible changes in the amounts of each product. The chemistry of this ternary system with PHP present was conducive for coal conversion while the coal/PYR system was not. Hence, the presence of PHP increased coal conversion by possibly transferring hydrogen to the system.

Resid Reaction System. The binary reactions of the model reactants with resid resulted in a substantial effect of the different reactants on the solubility of the resid. Without added reactants in the N_2 atmosphere, the resid underwent substantial retrogressive reactions causing 20% of the resid to become tetrahydrofuran insoluble (Table I.A.1.8). The addition of PHP resulted in 97% of the resid remaining tetrahydrofuran soluble which was much more than the resid reacted alone. Neither the addition of ANT nor PYR blocked the retrogressive reactions occurring in the N_2 atmosphere. However, the binary system with PYR kept more of the resid THF soluble (~86%) than did the ANT at 79%. These binary systems yielded less THF solubles but substantially more toluene soluble than the resid did alone. The ranking of the binary resid/model reactants in terms of maintaining THF and toluene solubles was resid/PHP > resid/PYR > resid/ANT.

In the binary system, PHP transferred hydrogen to the resid with 7% PYR being formed (Table I.A.1.9). In the resid/PYR system, neither the resid nor PYR showed any reactivity. But in the resid/ANT system, ANT underwent substantial hydrogenation, accepting hydrogen from resid and forming both dihydroanthracene and tetrahydroanthracene at 13.4 and 3.8%, respectively. The amount of the hydrogenated products present showed some variability in the two replicate reactions, but regardless, even in the reaction with the lower extent of reaction, more than 13% hydrogenated products were formed. Of the three binary resid reactions, the resid/ANT yielded the least amount of toluene solubles, intermediate amount of toluene solubles and the most THF solubles. The resid, in releasing some of its hydrogen to ANT, underwent changes that resulted in less THF solubility.

Ternary systems involving resid had similar resid conversions of 97% for resid/PHP/PYR and 98% for resid/PHP/ANT. These conversions were nearly equivalent to resid conversion obtained with the binary system of resid with PHP. Hence, regardless of the aromatic additive in the ternary system, addition of PHP to resid enhanced resid upgrading in the hydrogen atmosphere and helped to inhibit retrogressive reactions. The amount of toluene and THF solubles produced during these reactions were quite similar (Table I.A.1.8). In resid/ANT/PHP reaction more than 30% of ANT hydrogenated yielding 17.4% dihydroanthracene and 16.1% tetrahydroanthracene as products (Table I.A.1.9). More than 10% PYR was produced. The hydrogenation efficiency for this ternary system was quite high at 60.6% compared to the binary at 49.7% and quaternary system with resid/coal/ANT/PHP at 22.0%. Since ANT accepted ~60% of the hydrogen released by PHP, 40% of hydrogen released was available to the resid. The resid/PYR/PHP system, however, showed no net change in the quantity of PYR and PHP present, although substantial variability in these quantities was observed.

Coal Plus Resid Reaction System. Quaternary mixtures of resid/coal/PHP and PYR or ANT yielded similar coal conversions as the ternary system although reaction with ANT did increase somewhat (Table I.A.1.8). The amount of toluene and THF solubles present in both quaternary reactions was quite similar. Substantial hydrogenation of ANT to dihydroanthracene at 14.0% and tetrahydroanthracene at 21.5% occurred while 30% PYR was produced (Table I.A.1.9). Anthracene only accepted 22% of hydrogen released by PHP thereby leaving substantial hydrogen for uptake by coal and resid. In the quaternary systems with PYR and PHP, no net change in weight percents of PHP and PYR present after reaction was observed; however, a large variability in the quantities was again observed, which leaves open the possibility that some hydrogen transfer occurred during these reactions.

Degree of Upgrading. The effect of different added species on the system performance was evaluated by comparing the degree of upgrading, percent degree of upgrading, occurring in each system (Table I.A.1.8). The highest degree of upgrading occurred in coal systems in which PHP was present and the lowest with ANT present. Likewise, the least amount of degrading occurred in those resid systems that contained PHP and the most with ANT present. However, for the ternary systems with either coal or resid with PHP and PYR or ANT, very little difference was observed between degree of upgrading with PYR or ANT. For reactions with both coal and residuum, combined with either PYR or ANT, PYR had a slightly positive effect on the system compared to ANT.

SUMMARY AND CONCLUSIONS

The hydrogen donor and acceptor ability of both coal and resid has been demonstrated in this study. In a N_2 atmosphere and when no other donor was present, both coal and resid

transferred hydrogen to ANT, yielding partially saturated products. Reactions of PHP alone resulted in no conversion but PHP released hydrogen when reacted with hydrogen acceptors either as an aromatic or as compounds present in coal or resid in a N_2 atmosphere. Hence, a hydrogen acceptor was required in order for PHP to act as a donor. Hydrogen transfer from PHP to aromatics, coal, and resid occurred as shown by their respective conversion and the formation of PYR. Differences in the relative reactivity of ANT and PYR were observed in the model studies. Anthracene accepted hydrogen readily and quickly from whatever source (perhydropyrene, coal, or resid) was available while PYR was nearly unreactive.[5,6] The same order of reactivity was observed in the experiments performed in Subtask I.A.2. Hence, those coals and/or resids with reactive structures such as ANT can readily participate in hydrogen transfer reactions while those coal or resid materials that primarily contain nonreactive or stable species like PYR may not participate as readily in hydrogen transfer reactions. Under the conditions employed in this study, hydrogen transfer was observed from the naphthene PHP to an aromatic ANT, to Illinois No. 6 coal and to Maya resid.

NOMENCLATURE

PYR = pyrene ANT = anthracene PHP = perhydropyrene THF = tetrahydrofuran

REFERENCES

1. Clarke, J.W.; Rantell, T.D.; Snape, C.E. *Fuel, 63*, 1476 (1984).
2. Owens, R.M. Master's Thesis, Auburn University (1991).
3. Bermejo, J.; Canga, J.; Guillen, M.; Gayol, O.; Blanco, C. *Fuel Proc. Tech., 24*, 157 (1990).
4. Bedell, M.W.; Curtis, C.W. *Energy and Fuels, 5*, 469 (1991).
5. Chiba, K.; Tagaya, H.; Suzuki, T.; Sato, S. *Bull Chem. Soc. Jpm, 64*, 1034 (1991).
6. Fixari, B.; LePerchec, P. *Fuel, 60*, 218 (1989).

Figure 1. Hydrogenation of Anthracene as a Function of Anthracene to Perhydropyrene Ratio and Time.

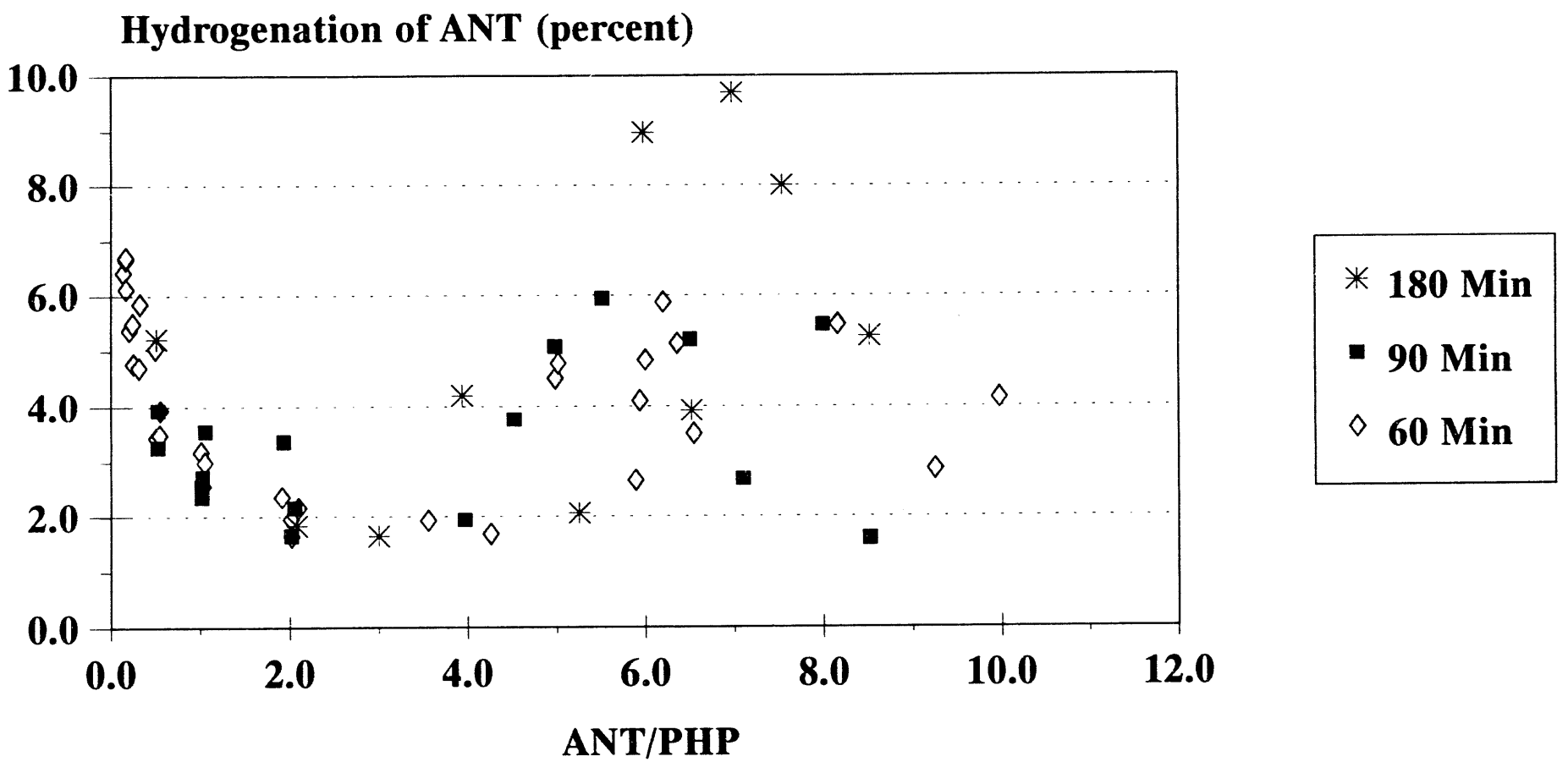


Figure 2. Dehydrogenation of Perhydropyrene as a Function of Anthracene to Perhydropyrene Ratio and Time.

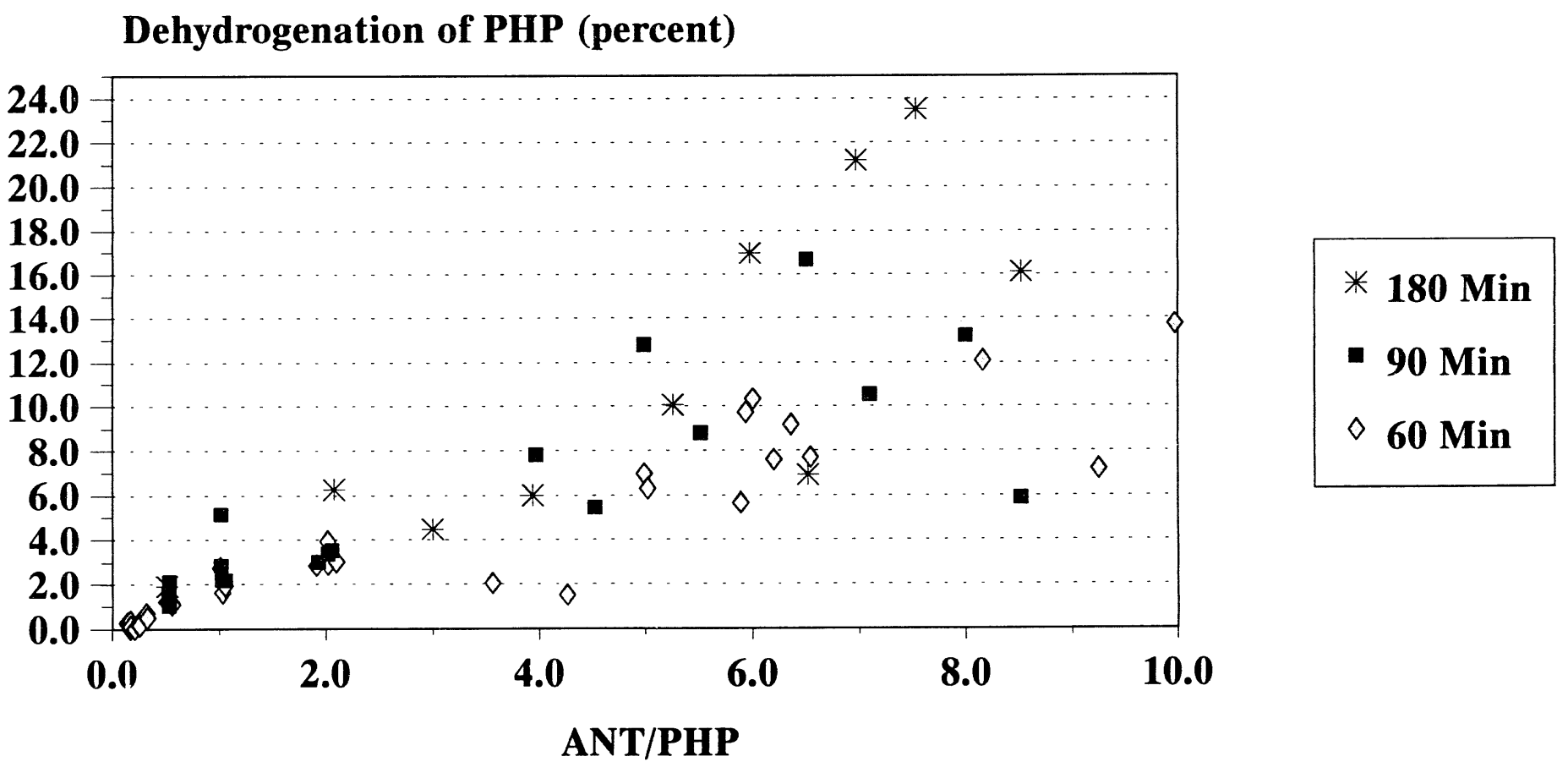


Table I.A.1.1. Properties Illinois No. 6 Coal

Moisture, %	8.0
Ash, %	15.5
Volatile Matter, %	36.9
Btu	10999
C, %	77.7
H, %	5.0
O, %	13.7
S, %	4.9

Table I.A.1.2. Properties of Maya Resid

Source of Resid	Mexico
Specific Gravity, g/cm^3	1.0535
Ramsbottom Carbon, wt%	26.38
C, wt%	83.7
H, wt%	9.8
S, wt%	5.4
N, wt%	ND[a]
Ni, ppm	118
V, ppm	680
Hexane Solubles, wt%	71.8
Hexane Insolubles, wt%	28.2
Toluene Insolubles, wt%	0

[a] ND = not determined.

Table I.A.1.3. Product Distribution for 60 Minute Anthracene and Perhydropyrene Reactions

ANT/PHP Weight Ratio	Product Distribution (mol%)				
	ANT[a]	DHA	THA	PHP	PYR
0.14	87.2	12.8	0.0	99.7	0.3
0.17	86.7	13.3	0.0	99.7	0.3
0.17	86.6	13.4	0.0	100.0	0.0
0.17	87.8	12.2	0.0	99.9	0.1
0.21	89.2	10.8	0.0	100.0	0.0
0.24	89.0	11.0	0.0	99.8	0.2
0.25	90.5	9.5	0.0	99.8	0.2
0.32	90.6	9.4	0.0	99.3	0.7
0.33	88.3	11.7	0.0	99.5	0.5
0.50	89.9	10.1	0.0	98.8	1.2
0.51	93.1	6.9	0.0	98.8	1.2
0.55	93.0	7.0	0.0	98.8	1.2
0.56	92.1	7.9	0.0	98.9	1.1
1.01	93.7	6.4	0.0	97.2	2.8
1.03	94.9	5.1	0.0	98.4	1.6
1.05	94.0	6.0	0.0	98.1	1.9
1.91	95.3	4.7	0.0	97.1	2.9
2.02	96.1	3.9	0.0	96.6	3.4
2.02	96.7	3.3	0.0	97.1	2.9
2.10	95.7	4.3	0.0	97.0	3.0
3.56	96.1	3.9	0.0	98.0	2.0
4.26	96.6	3.4	0.0	98.5	1.5
4.99	94.3	5.7	trace	93.0	7.0
5.02	91.9	6.6	1.5	93.7	6.3
5.89	94.7	5.3	0.0	94.3	5.7
5.94	94.6	5.4	trace	90.3	9.7
6.00	93.9	6.1	trace	89.7	10.3
6.20	93.3	6.7	trace	92.4	7.6
6.36	91.7	6.3	2.0	90.8	9.2
6.54	94.0	5.0	1.0	92.3	7.7
8.16	91.5	6.1	2.4	87.9	12.1
9.25	95.0	4.2	0.8	92.8	7.2
9.98	93.2	5.3	1.5	86.3	13.7

[a] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene
PHP = perhydropyrene; PYR = pyrene

Table I.A.1.4. Product Distribution for 90 Minute Anthracene and Perhydropyrene Reactions

ANT/ PHP Weight Ratio	Product Distribution (mol%)				
	ANT[a]	DHA	THA	PHP	PYR
0.52	93.5	6.5	0.0	98.4	1.6
0.53	93.5	6.5	0.0	100.0	1.0
0.53	92.1	7.9	0.0	97.9	2.1
1.02	94.9	5.2	0.0	97.5	2.5
1.02	95.3	4.7	0.0	97.1	2.9
1.03	94.5	5.5	0.0	97.8	2.2
1.06	92.9	7.1	0.0	97.8	2.2
1.93	93.3	6.7	0.0	97.0	3.0
2.02	96.7	3.3	0.0	96.6	3.4
2.06	95.7	4.3	0.0	96.5	3.5
3.97	96.1	3.9	0.0	92.2	7.8
4.53	93.6	5.2	1.2	94.5	5.5
4.99	91.9	6.1	2.0	87.2	12.8
5.52	90.3	7.5	2.2	91.2	8.8
6.50	92.1	5.5	2.4	83.3	16.7
7.10	95.7	3.2	1.1	89.5	10.5
8.00	91.5	6.0	2.5	86.8	13.2
8.52	96.8	3.2	0.0	94.1	5.9

Table I.A.1.5. Product Distribution for 180 Minute Anthracene and Perhydropyrene Reactions

ANT/PHP Weight Ratio	Product Distribution (mol%)				
	ANT[a]	DHA	THA	PHP	PYR
0.51	89.6	10.4	0.0	98.1	1.9
2.08	96.3	3.7	0.0	93.7	6.3
3.00	96.7	3.3	0.0	95.5	4.5
3.94	93.1	5.4	1.5	94.0	6.0
5.26	95.9	4.1	0.0	89.9	10.1
6.52	93.4	5.4	1.2	93.1	6.9
6.97	85.8	9.0	5.2	78.8	21.2
7.54	87.8	8.3	3.9	76.5	23.5
8.52	91.3	6.9	1.8	83.9	16.1

[a] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene
PHP = perhydropyrene; PYR = pyrene

Table I.A.1.6. Product Distributions for Anthracene and Perhydropyrene Reactions at Different Reaction Times[a]

Reaction Time (min)	ANT/PHP Weight Ratio	Product Distribution (mol%)				
		ANT[b]	DHA	THA	PHP	PYR
5	4.00	97.3	2.7	0.0	100.0	0.0
5	6.11	98.0	2.0	0.0	100.0	0.0
15	3.95	97.0	3.0	0.0	100.0	trace
15	6.13	96.4	3.6	0.0	100.0	trace
30	3.99	95.4	4.6	0.0	100.0	trace
30	5.26	95.8	4.2	0.0	100.0	trace
120	4.53	92.3	6.5	1.2	93.4	6.6
120	6.52	89.3	7.3	3.4	85.0	15.0

[a] Reaction Conditions: 430 °C, 60 min, N_2 atmosphere.
[b] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene
PHP = perhydropyrene; PYR = pyrene

Table I.A.1.7. Hydrogen Efficiency as a Function of Anthracene and Perhydropyrene Weight Ratio

ANT/PHP[a] Weight Ratio	Hydrogen Efficiency 60 Minutes	ANT/PHP Weight Ratio	Hydrogen Efficiency 90 Minutes	ANT/PHP Weight Ratio	Hydrogen Efficiency 180 Minutes
0.14	-	0.52	33.6	0.51	41.7
0.17	-	0.53	41.7	2.08	21.2
0.17	-	0.53	28.4	3.00	30.1
0.17	-	1.02	27.0	3.94	62.9
0.21	-	1.02	19.4	5.30	34.3
0.24	-	1.03	33.9	6.52	85.9
0.25	-	1.06	35.3	6.97	90.4
0.32	60.6	1.93	45.6	7.54	87.4
0.33	116.0	2.02	41.3	8.52	81.6
0.50	46.0	2.06	46.0		
0.51	38.1	3.97	33.0		
0.55	35.7	4.53	81.1		
0.56	40.2	4.99	72.2		
1.01	31.2	5.52	110.0		
1.03	51.1	6.50	74.5		
1.05	55.0	7.10	54.2		
1.91	33.3	8.00	108.2		
2.02	28.5	8.52	59.1		
2.02	27.5				
2.10	44.9				
3.56	95.6				
4.26	137.9				
4.99	104.2				
5.02	105.5				
5.89	73.4				
5.94	76.1				
6.00	88.2				
6.20	125.6				
6.36	106.5				
6.54	83.2				
8.16	111.3				
9.25	111.3				
9.98	104.0				

[a] ANT = anthracene; PHP = perhydropyrene.

Table I.A.1.8. Coal and Resid Reaction Products from Thermal Coprocessing Reactions[a]

System	TOL Solubles (%)	THF Solubles (%)	IOM (%)	Converison (%)	Degree of Upgrading (%)	Liquid to Solid Ratio
Coal/PHP[b]	75.5±2.2[c]	17.5±0.7	7.0±1.5	85.8±3.2	24.0±3.4	3.1
Coal/ANT	50.0±3.1	14.0±1.7	36.0±1.3	13.4±7.3	-9.0±1.1	1.0
Coal/PYR	58.4±1.6	15.2±2.7	26.4±1.1	38.3±3.7	7.6±4.6	1.4
Coal/ANT/PHP	83.8±1.0	8.2±0.9	8.0±0.1	73.0±1.3	26.8±19	5.2
Coal/PYR/PHP	87.7±1.3	7.1±0.7	5.2±0.5	83.4±1.2	29.1±8.7	7.2
Resid/PHP	92.3±0.3	6.2±0	1.5±0.2	97.4±0.5	-47.6±1.9	12.0
Resid/ANT	77.8±1.0	9.4±0.2	12.8±0.8	78.7±1.7	-69.1±2.8	3.5
Resid/PYR	79.5±3.6	12.6±3.2	7.9±0.5	85.5±1.3	-55.4±4.1	4.0
Resid/ANT/PHP	96.1±2.1	3.0±2.1	0.9±0.1	97.6	-46.5±1.3	24.6
Resid/PYR/PHP	94.8±0.5	4.1±0.3	1.1±0.2	97.1±0.5	-45.1±9.7	18.4
Resid/ANT/PHP/Coal	83.1±1.2	6.9±0.9	10.0±0.4	80.6±0.1	-6.4±6.5	5.0
Resid/PYR/PHP/Coal	85.5±0.8	6.5±0.5	8.0±0.4	83.6±0.9	6.7±18	5.9
Coal	4.0±1.6	31.2±0.7	64.8±2.3	30.4±3.8	4.3±1.7	0.4
Resid	43.8	35.2	21.0	80.5	-61.8±2.4	0.8

[a] Reaction Conditions: 430 °C, 60 min, N_2 atmosphere
[b] ANT = anthracene; PHP = perhydropyrene; PYR = pyrene
[c] Standard deviations

Table I.A.1.9. Reactive Products From Model Donor and Acceptor Reactions in Thermal Coprocessing[a]

System	ANT[b]	DHA	THA	PHP	PYR	Hydrogen Efficiency
Coal/PHP	--[c]	--	--	89.8±2.2	10.2±2.4	NA[e]
Coal/ANT	89.6±0.1[d]	7.3±0.1	3.1±1	--	--	NA
Coal/PYR	--	--	--	--	100.0±0	NA
Coal/ANT/PHP	56.2±1.0	19.2±2.3	24.7±1.4	84.3±0.9	15.7±0.8	49.7
Coal/PYR/PHP	--	--	--	55.4±8.0	44.6±8.0	NA
Resid/PHP	--	--	--	93.0±1.5	7.0±1.4	NA
Resid/ANT	82.8±4.2	13.4±4.4	3.8±0.2	--	--	NA
Resid/PYR	--	--	--	--	100.0±0	NA
Resid/ANT/PHP	66.5	17.4	16.1	89.6	10.4	60.6
Resid/PYR/PHP	--	--	--	47.8±5.3	52.4±5.4	NA
Resid/ANT/PHP/Coal	64.5±0.4	14.0±0.4	21.5±0.1	69.7±1.5	30.3±1.6	22.0
Resid/PYR/PHP/Coal	--	--	--	52.5±13.3	47.5±13.3	NA
Coal	--	--	--	--	--	NA
Resid	--	--	--	--	--	NA

[a] Reaction Conditions: 430 °C, 60 min, N_2 atmosphere.
[b] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene
PHP = perhydropyrene; PYR = pyrene
[c] None of the compound is present.
[d] Standard deviations.
[e] NA = not applicable.

SUBTASK I.A.2.

AN INVESTIGATION OF HYDROGEN TRANSFER IN COPROCESSING USING MODEL DONORS AND REDUCED RESIDS

INTRODUCTION

Hydrogen-donor reactions are important in the transfer of hydrogen from hydrogen-rich compounds to aromatic species in the liquefaction of coal. Different hydrogen-rich compounds have different propensities for donating hydrogen under liquefaction conditions; just as different hydrogen acceptors have different propensities for accepting hydrogen. In this study, the ability of three different hydrogen donors to donate hydrogen and the efficiency of their hydrogen transfer to aromatic species were compared under both hydrogen and nitrogen atmospheres.

The compounds compared were cyclic olefins, which have been shown to release their hydrogen quickly under liquefaction conditions,[1,2] hydroaromatics, that are typically present in coal liquids and are known hydrogen donors,[2-4] and cycloalkanes, that are present in resids[5] and do not readily donate their hydrogen.[6] Previous work by Clarke et al.[7] indicated that hydrogen transfer was occurring between naphthenic components and coal, resulting in increased conversion of coal and formation of aromatics from naphthenes. A study by Owens and Curtis[6] showed that hydrogen transfer occurred from naphthenes to aromatics, coal, and resid in a N_2 atmosphere, although the amount of hydrogen released from the naphthenes and transferred to the acceptors was small. Resid and coal were also capable of transferring hydrogen to the aromatic, anthracene (ANT). Promotion of hydrogen transfer from the hydrogen-rich cycloalkanes to aromatics is of special interest because these structures are prevalent in resids and offer an indigenous source of hydrogen during the coprocessing of coal with resid. Rudnick[8,9] has patented the process of catalyzing hydrogen transfer from the naphthenes by introducing an organic sulfur compound which promoted this type of hydrogen transfer.

In the current work, the reactions performed by Rudnick were repeated. In addition, catalytic reactions with organic sulfur were performed to evaluate the effect on the hydrogen transfer from cycloalkanes to aromatics at 380 and 440 °C under both N_2 and H_2 atmospheres. These results were compared to thermal reactions at the same conditions.

In the coprocessing of coal with resid, resids have limited ability to solvate coal and to donate hydrogen because of the predominance of indigenous saturated structures.[10,11] Increasing the hydrogen donability of the chemical species of resid should enhance the ability of the resid to solvate coal. This enhancement was induced by reducing resids by the Birch reduction method[12-14] which produces cyclic olefinic structures from aromatic species. Previous researchers have reduced resids by the Birch reduction method[15-17] and have shown improvement in the liquefaction of coal.[17] The ability of these reduced resids to transfer hydrogen to aromatics was determined and compared to the parent resids.

EXPERIMENTAL

Materials and Analysis. Reactions were performed using the following hydrogen-rich compounds: cyclic olefins, isotetralin (ISO) which was synthesized in our laboratory, and hexahydroanthracene from Aldrich; hydroaromatics, tetralin and 9,10-dihydroanthracene, both from Aldrich; and a cycloalkane, perhydropyrene (PHP), from Aldrich. The commercial compounds were all 99+% purity and ISO was more than 97% pure. The compounds used as hydrogen acceptors in these reactions were ANT and pyrene (PYR) both obtained from Aldrich. The reactions, performed to replicate the patents of Rudnick,[8,9] used PHP as the cycloalkane and benzophenone as the acceptor. Benzophenone was obtained from Aldrich with a purity of 99+% and was used as received. Thiophenol, also from Aldrich at 99+% purity, was used as a catalyst

for promoting the transfer of hydrogen from cycloalkanes to aromatics. The catalyst was introduced at a level of 2000 ppm of sulfur. The reaction products were analyzed by gas chromatography using a Varian 3300 gas chromatograph with flame ionization detection and biphenyl as the internal standard. Qualitative analysis of the products was conducted with a VG70 EHF GC-mass spectrometer.

Thermal and catalytic reactions were performed with the parent resids and treated resids which had been reduced by a modification of the Birch method.[13] The Birch reduction method reduces aromatics in the resid to cyclic olefins and other partially saturated forms by adding Na, alcohol, and ammonia to the resid which is dissolved in tetrahydrofuran as the solvent. Resids that were used in these reactions were Maya obtained from Amoco Oil Co., a deasphalted resid from a deasphalting resid unit from Exxon and south Louisiana resid also from Exxon; the hydrogen acceptor for the reactions was ANT; and the catalyst was 2000 ppm sulfur introduced at thiophenol. Analyses of the parent and reduced resids are given in Tables I.A.2.1 and I.A.2.2. The products from these resid reactions were analyzed by gas chromatography to determine the reaction products from both the model donors and acceptors and by solvent fractionation to determine the products from the resid. The solvents used in the extraction of the thermal products were toluene and tetrahydrofuran, but in the catalytic reactions, hexane was also used.

Reaction Procedures. Reactions were performed in 20 cm^3 stainless steel tubular micro-reactors with single reactants charged at 0.1 g and with binary reactants charged at 0.1 g aromatic and the hydrogen-rich compound introduced at a 1:1 or 5:1 weight ratio to the aromatic for thermal reactions. Reaction conditions for the thermal-model reactions were 380 °C, 30 min, nitrogen or hydrogen at 400 or 1250 psig at ambient, respectively, and horizontal agitation at 450 cpm.

For single component catalytic reactions, ~0.1 g of reactant was used; for binary component catalytic reactions, the amount of reactants was based on 0.1 g of ANT with 0.1 g of PHP added for the 1:1 weight ratio. For the 5:1 ratio, 0.5 g PHP and 0.1 g ANT were added. At both weight ratios, 2000 ppm sulfur from thiophenol was introduced. The catalytic reactions were performed at 380 and 440 °C, agitated horizontally at 450 cpm for 30 min and then quenched immediately after reaction. The catalytic reactions of PHP with benzophenone utilized 0.5 g PHP, 0.175 g benzophenone, 0.51 wt% catalyst, and hydrogen or N_2 at 400 psig or 1250 psig introduced at ambient temperature. The reactions were conducted at 380 and 440 °C.

The thermal and catalytic binary resid reactions employed 1 g resid and 0.2 g ANT which were charged in ~50 cm^3 stainless steel tubular microreactor. The ternary systems used 1 g resid, 1 g coal, and 0.2 g ANT. In the catalytic reactions, 2000 ppm sulfur was added as thiophenol. The reactions were conducted out at 380 °C with 1250 psig nitrogen or hydrogen for 30 min.

Definitions. The following definitions were used: percent hydrogenation, hydrogen efficiency, and amount of gaseous H_2 accepted. Percent hydrogenation is defined as the moles of hydrogen required to achieve the liquid products as a percentage of the moles of hydrogen required to produce the most hydrogenated product. In the case of ANT, octahydroanthracene was considered the most hydrogenated product; in the case of PYR, the most hydrogenated product was hexahydropyrene. Hydrogen efficiency is defined as the moles of hydrogen accepted by the hydrogen acceptor divided by the moles of hydrogen released by the hydrogen donor. The amount of gaseous H_2 that was accepted by the hydrogen donor is defined as the moles of hydrogen accepted by the hydrogen acceptor under a hydrogen atmosphere minus the moles of hydrogen accepted by the hydrogen acceptor under a N_2 atmosphere.

RESULTS AND DISCUSSION

Thermal Reactions of Hydrogen-Rich Compounds with Aromatics

Reactions of hydrogen-rich compounds, cyclic olefins, hydroaromatics, and cycloalkanes, with aromatic species, ANT and PYR, were performed in both nitrogen and hydrogen atmospheres. The purpose of these experiments was to determine how much hydrogen was released from the hydrogen donor and how much of that hydrogen was accepted by the aromatic species at coprocessing conditions.

The reaction of the cyclic olefin, ISO, with ANT produced naphthalene, 1,2- and 1,4-dihydronaphthalene, tetralin, and decalin as products with the amounts of each being dependent upon the weight ratio of ISO to ANT as shown in Table I.A.2.3. The type of atmosphere present had little effect. By contrast, the hydroaromatic isomer tetralin, when reacted with ANT, showed almost no reactivity, converting less than 1% to naphthalene. Likewise, PHP, when reacted with ANT, showed between 0.1 and 1.4% conversion to PYR, the amount of conversion depending upon the atmosphere and weight ratio of PHP to ANT.

In the reactions with PYR as the acceptor, presented in Table I.A.2.3, ISO formed the same products as in the reaction with ANT; however, with PYR present, the type of atmosphere and weight ratio of ISO:PYR affected the product distribution obtained. Tetralin again showed little reactivity. The cyclic olefin, hexahydroanthracene, reacted in the presence of PYR, formed the products of octahydroanthracene, tetrahydroanthracene, dihydroanthracene, and ANT. The product distribution was affected by the atmosphere and the weight ratio of hexahydroanthracene to PYR. The presence of PYR in the reaction also had a substantial effect on the product distribution obtained from hexahydroanthracene which was evident when the products from hexahydroanthracene reacted alone are compared to the products obtained with PYR. The

hydroaromatic dihydroanthracene gave slightly higher conversion with PYR present than without yielding ~10% with PYR and 6-8% without PYR. The cycloalkane perhydroanthracene showed no reactivity in either atmosphere or regardless of whether an acceptor was present.

The acceptors, ANT and PYR, showed different abilities to accept hydrogen from the hydrogen-rich species as illustrated by their product distributions given in Table I.A.2.4. When reacted alone in a hydrogen atmosphere, more than 11% ANT converted to form dihydroanthracene. With ISO, the reactions with a weight ratio of 5:1 ISO to ANT yielded almost 100% dihydroanthracene in hydrogen and nearly 92% conversion to dihydroanthracene and tetrahydroanthracene in N_2. Reactions at 1:1 weight ratio of ISO:ANT also showed substantial hydrogenation of ANT to dihydroanthracene in both atmospheres, 71% in hydrogen and 68% in N_2; tetrahydroanthracene was also produced. In the reactions of ANT with tetralin or PHP, dihydroanthracene and a trace amount of tetrahydroanthracene were formed but the increases above the base line cases were rather small, although the amount varied with atmosphere and weight ratio.

Pyrene, in contrast to ANT, did not hydrogenate in hydrogen; however, in the presence of ISO the hydrogenated products of dihydropyrene, tetrahydropyrene, and hexahydropyrene were formed as presented in Table I.A.2.5. More hydrogenated products were formed as the weight ratio of ISO to PYR increased and more donable hydrogen became available for hydrogenating PYR. With tetralin as the hydrogen donor, dihydropyrene was the only product which was formed in small amounts when tetralin was present at a 5:1 weight ratio. Hexahydroanthracene like ISO transferred substantial amounts of hydrogen to PYR, yielding dihydropyrene, tetrahydropyrene, and hexahydropyrene as products. The most hydrogenation of PYR occurred in a hydrogen atmosphere at 5:1 hexahydroanthracene to PYR ratio. Dihydroanthracene also donated hydrogen to PYR yielding the same three products but in lesser amounts than hexahydroanthracene. The

cycloalkane perhydroanthracene donated a small amount of hydrogen to PYR forming dihydropyrene as the product.

The amount of hydrogen released from an equivalent weight of hydrogen-rich compounds was in the order of cyclic olefins > hydroaromatics > cycloalkanes (Table I.A.2.5). This order held regardless of the acceptor present. The amount of hydrogen released from each species was dependent upon the type of atmosphere and acceptor present as well as upon the amount of hydrogen-rich compounds present. The amount of hydrogen released from the cyclic olefins, ISO and hexahydroanthracene, and from the hydroaromatic, dihydroanthracene, was substantially higher in the reactions with 5:1 weight of donor to aromatic compared to the 1:1 weight ratio.

The percent hydrogenation of the aromatic species in individual reactions and in binary reactions with hydrogen-rich species is presented in Table I.A.2.5. The most hydrogenation of the aromatic species occurred in the presence of the cyclic olefins and in a hydrogen atmosphere. The amount of hydrogen accepted by the hydrogen acceptor was also dependent upon the weight ratio of hydrogen donor to acceptor, particularly with the hydrogen donor species of ISO, hexahydroanthracene, and dihydroanthracene in hydrogen. A lesser effect was observed in N_2. ANT was more reactive than PYR in terms of the moles of hydrogen accepted when reacted with the same hydrogen-rich species and at the same conditions of atmosphere and weight ratio of hydrogen donor to acceptor. The moles of hydrogen accepted by the two aromatic species is also given on Table I.A.2.5.

The hydrogen efficiency of the systems which describes the ability of the acceptor to accept the hydrogen released by the donor is also compared in Table I.A.2.5. As the value for hydrogen efficiency approaches one, then the amount of hydrogen released becomes equal to the amount of hydrogen accepted. In N_2, the hydrogen efficiency was a true measure of the efficiency

of the hydrogen transfer since the only source of hydrogen was that from the hydrogen donor. The hydrogen efficiency of the systems in N_2 showed that the cyclic olefins were the least efficient of all of the hydrogen-rich species since they released substantially more hydrogen than the aromatic species was able to accept under the reaction conditions employed. The tetralin/ANT, PHP/ANT, and dihydroanthracene/PYR were efficient donor systems in N_2. Although these systems, particularly the first two, released very little hydrogen, the hydrogen that was released was accepted. In the hydrogen atmosphere, hydrogen efficiencies of greater than one were obtained which indicated that gaseous H_2 was participating in the reactions. The moles of gaseous H_2 incorporated into the reaction products from the hydrogen acceptor varied with the system as shown in the last column in Table I.A.2.5.

Reactions of Perhydropyrene and Benzophenone

Rudnick[8,9] performed a series of reactions in which the catalysis of hydrogen transfer from different hydroaromatic and alicyclic compounds by thiophenol was evaluated. Reactions at 440°C with an unspecified superatmospheric pressure with hydrogen-rich compounds such as decahydropyrene with benzophenone resulted in conversion to the aromatic PYR and several less hydrogenated hydroaromatics. The alicyclic, PHP, when reacted with benzophenone at 440°C and 1 hr did not convert, but in the presence of 0.51 wt% thiophenol, 94.7% diphenylmethane was formed from benzophenone. The reaction of PHP with benzophenone was repeated in this work at reaction temperatures of 440°C in the presence and absence of thiophenol. The reactions were conducted at an initial charge of 400 and 1250 psig in both N_2 and hydrogen. The thiophenol catalyst was introduced at 0.51 wt% and PHP to benzophenone mole ratio was 0.42.

The thermal and catalytic reactions in N_2 produced diphenylmethane from benzophenone. Although more diphenylmethane was produced from benzophenone in the catalytic reaction, only

5% was produced (Table I.A.2.6). In the thermal and catalytic reactions in hydrogen, more hydrogenation of benzophenone to diphenylmethane occurred than in N_2. The different hydrogen pressures were used: 400 and 1250 psig introduced at ambient temperature. The higher hydrogen pressure increased the amount of diphenylmethane formed. The highest conversion of benzophenone to diphenylmethane was 30 mol%, which was produced at 440 °C and 1250 psig hydrogen charged at ambient. None of the eight conditions used were able to replicate the 94% production of diphenylmethane observed by Rudnick.[9] The moles of hydrogen released by PHP, the moles of hydrogen accepted by benzophenone and the hydrogen efficiency of the system are presented in Table I.A.2.7. Substantial incorporation of molecular hydrogen occurred in the reactions conducted in hydrogen.

Catalytic Reactions of Hydrogen-Rich Compounds with Aromatics

Catalytic reactions were performed with a reaction system of PHP with ANT at a weight ratio of PHP to ANT of 1:1 and 5:1 in both nitrogen and hydrogen atmospheres at 400 and 1250 psig at reaction temperatures of 380 and 440 °C. The catalyst was 2000 ppm of sulfur introduced as thiophenol. The purpose of these reactions was to determine if the presence of sulfur as H_2S in the reactor promoted hydrogen transfer from the cycloalkane PHP and enhanced hydrogen acceptance by the aromatic ANT.

Thermal and catalytic reactions of PHP reacted individually showed no conversion under either a hydrogen or nitrogen atmosphere at either temperature (Table I.A.2.8). By contrast, ANT thermally produced 12% dihydroanthracene in hydrogen while a small amount, 0.5%, was observed in N_2 at 380 °C. In the catalytic reactions with thiophenol, the amount of dihydroanthracene produced increased to 16.7% in hydrogen and 1.9% in N_2 at 380 °C.

In the thermal reaction a small amount of hydrogen was transferred from PHP to ANT as evinced by the production of PYR and dihydroanthracene above that which was produced in the hydrogen atmosphere. The addition of thiophenol increased the amount of PHP reacted which formed both hexahydroanthracene and PYR as reaction products. The amount of hydrogen accepted by ANT also increased forming the product dihydroanthracene. The largest amount of dihydroanthracene produced, 44%, was at 380 °C in the catalytic reaction in hydrogen and a 5:1 PHP:ANT weight ratio.

The addition of sulfur catalyst increased the amount of hydrogen donation from PHP. The catalyst also increased the amount of hydrogen acceptance and, hence, hydrogenation of ANT to dihydroanthracene in both atmospheres (Table I.A.2.9). Under thermal conditions, PHP produced only PYR as the product while under catalytic conditions hexahydropyrene was formed in larger amounts than PYR. The catalysis of hydrogen donation and acceptance by sulfur was observed most in the PHP/ANT system at a 5:1 weight ratio at 380 °C in hydrogen and N_2 compared to the thermal reaction where a substantial increase in the hydrogenation of the aromatic was obtained compared to the thermal reaction.

The promotion of the reaction by sulfur was also observed in N_2 but not in hydrogen at 440 °C. The higher reaction temperature of 440 °C with hydrogen as the atmosphere seemed to have more effect on hydrogen donation and acceptance than did the catalyst, since the percent hydrogenations of ANT were equivalent in thermal and catalytic reactions (Table I.A.2.9).

The hydrogen efficiency in N_2 shown in Table I.A.2.9 was always less than one with the hydrogen efficiency of 5:1 PHP to ANT reaction systems frequently having a higher efficiency than the 1:1 ratio. The hydrogen efficiencies for the reactions in hydrogen were always greater than one indicating incorporation of gaseous H_2 into the reaction products. The number of moles

of gaseous H_2 incorporated was substantially higher for the higher temperature reactions at 440 °C than those at 380 °C.

Hydrogen Transfer from Resids

The purpose of this work was to evaluate the efficacy of hydrogen transfer from hydrogen-enriched reduced resids to an aromatic species and to compare that to the hydrogen transfer from the parent resid. The systems used were binary systems of reduced or parent resids with the aromatic acceptor ANT and ternary systems of a reduced or parent resid with ANT and the hydrogen-rich species, PHP.

The reactions of the reduced and parent resids with ANT in both nitrogen and hydrogen atmospheres are presented in Table I.A.2.10. All three of the reduced resids yielded substantially more moles of hydrogen accepted and, hence, hydrogenation of ANT to dihydroanthracene and tetrahydroanthracene than did the parent resids. The hydrogen atmosphere promoted more hydrogenation of ANT than did nitrogen regardless of whether the resid was reduced or was the parent. The product distributions from each of the resid reactions are given in Table I.A.2.11. The binary system of resid with ANT produced some tetrahydrofuran soluble material and insoluble organic material in each reaction regardless of resid or atmosphere. The reduced resids showed a slightly higher propensity for having tetrahydrofuran soluble materials in the presence of ANT than did the parent resids. Introduction of 2000 ppm sulfur as thiophenol had no effect on either the hydrogenation of ANT or the product distributions obtained from the resid.

When PHP was added to the resid/ANT system, the change observed was fairly small in terms of the hydrogenation of ANT. However, more hydrogen uptake appeared to be achieved from hydrogen transferred from hydrogen-rich species than from gaseous H_2, since the uptake of gaseous H_2 tended to be less with PHP present. The percent hydrogenation of ANT in N_2 was

higher in the systems with PHP present than in those without PHP which also suggests that some hydrogen was transferred from PHP to ANT during the reaction. Small increases in percent hydrogenation were also observed in the hydrogen atmosphere. The product distributions for the ternary systems (Table I.A.2.11) showed that all of the resids remained toluene soluble. The amount of hexane solubles produced was greater in the hydrogen atmosphere than in the nitrogen for all but one of the systems.

Synergism Between Perhydropyrene and Resid in the Resid/Perhydropyrene/Anthracene Systems

Since binary and tertiary reactions were performed using resid/ANT and resid/PHP/ANT, the effect of PHP addition on the moles of hydrogen accepted by ANT was examined. In a N_2 atmosphere the moles of hydrogen accepted by ANT was greater in the resid/PHP/ANT system than in the two individual systems resid/ANT + PHP/ANT summed together. Hence, ANT accepted more hydrogen when resid and PHP were present together in a reaction than the sum of the individual reactions which indicates a synergism between the resid and PHP for promoting hydrogen transfer. These results were consistent for both the parent and reduced resids, as shown in Table I.A.1.12.

In a hydrogen atmosphere, the effect of hydrogen on the binary and tertiary systems had to be considered to determine if synergism between PHP and ANT occurred. Synergism was evaluated by comparing the moles of hydrogen accepted for the resid/PHP/ANT system and for the combined systems of resid/ANT + PHP/ANT - ANT(H_2). For the latter combined systems in hydrogen, the hydrogen sources for ANT were resid and molecular hydrogen for resid/ANT while PHP and molecular hydrogen were for PHP/ANT. Since molecular hydrogen reacted with ANT in each of these reactions, the amount of hydrogen accepted by ANT from molecular

hydrogen was subtracted out once from the combined systems of resid/ANT and PHP/ANT. The hydrogen sources for the combined systems were then equivalent to the hydrogen sources for the ternary system. A comparison of the moles of hydrogen accepted by ANT in the ternary system and the combined binary system in a hydrogen atmosphere is also given in Table I.A.2.12. The moles of hydrogen accepted by ANT for a given resid/PHP/ANT system and the corresponding resid/ANT + PHP/ANT - ANT(H_2) system were the same regardless of whether the resid was reduced or the parent. Under a hydrogen atmosphere, the influence of molecular hydrogen was so great that the addition of PHP to the system had little effect on the amount of hydrogen accepted by ANT.

SUMMARY

Hydrogen donation from three types of hydrogen-rich species resulted in substantial hydrogen donation from cyclic olefins, less from hydroaromatic species, and a very small amount from cycloalkanes by comparison. The hydrogen transfer by cycloalkanes to aromatics was promoted by the presence of sulfur. This promotion, however, appeared to be condition specific with more catalysis apparent at 380 °C in N_2 than at any other condition. Reduced resids produced by the Birch method were more effective hydrogen donors than their parent resids. Hydrogen enrichment of these resids produced a solvent more effective for the thermal hydrogenation of aromatic species such as are present in coal.

NOMENCLATURE

ANT = anthracene ISO = isotetralin PHP = perhydropyrene PYR = pyrene

REFERENCES

1. Bedell, M.W.; Curtis, C.W. *Energy and Fuels*, *5*, 469-479 (1991).

2. Curtis, C.W.; Guin, J.A.; Kwon, K.C. *Fuel*, *63*, 1404-1409 (1984).

3. Neavel, R.C. *Fuel*, *55*, 237-242 (1976).

4. Bockrath, B. *Coal Science*; Academic Press: New York, Vol. 2 (1982).

5. Speight, J.G. Chemistry and Technology of Petroleum, Marcel Dekker, New York (1980).

6. Owens, R.M.; Curtis, C.W. Submitted to *Energy and Fuels* (1993).

7. Clarke, J.W.; Rantle, T.D.; Snape, C.E. *Fuel*, *63*, 1476-1479 (1984).

8. Rudnick, L.R. Mobile Oil Corporation, European Patent, 195,541 (1986).

9. Rudnick, L.R. Mobile Oil Corporation, European Patent, 195,539 (1986).

10. Curtis, C.W.; Tsai, K.J.; Guin, J.A. *Fuel Proc. Tech.*, *16*, 71-87 (1987).

11. Curtis, C.W. and Hwang, J.S. *Fuel Proc. Tech.*, *30,* 47-67 (1992).

12. Birch, A.J.; Rao, G.S. *Advances in Organic Chemistry, Methods and Results*, Vol. 8, Taylor, E.C., Ed.; Wiley Interscience, New York, NY (1972).

13. Olson, K.W.; Bedell, M.W.; Curtis, C.W. *Fuel Science and Technology International*, in press (1993).

14. Vogel, E.; Klu, W.; and Breuer, A. *Organic Synthesis*, *55*, 86-91 (1976).

15. Branthaver, J.F.; Sugihara, J.M. *Amer. Chem. Soc. Petrol. Chem. Div. Preprints*, 11(2):B-105-B-107 (1966).

16. Mochida, I.; Tomari, Y.; Maeda, K.; Takeshita, K. *Fuel*, *54*, 265-268 (1975).

17. Mochida, I.; Moriguchi, Y.; Korai, Y.; Fujitsu, H.; Takeshita, K. *Fuel*, *60*, 746-747 (1980).

Table I.A.2.1. Properties of the Resids Used in This Study

Properties	Maya	DAU[d]	SLA[d]
Source of Residuum	Mexico	Blend	Louisiana
Specific Gravity, g/cc	1.1	NA[b]	0.9848
API Gravity	NA	NA	12.2
Ramsbottom Carbon, wt%	26.4	NA	NA
Conradson Carbon, wt%	NA	NA	13.2
C, wt%	83.7	NA	NA
H, wt%	9.8	NA	NA
S, wt%	5.4	NA	1.89
N, wt%	ND[a]	NA	0.32
Ni, ppm	118	NA	19.6
V, ppm	680	NA	47.5
Hexane, Solubles, wt%	80.5(1.0)[c]	75.6(1.6)	93.2(0.5)
Hexane Insolubles, wt%	19.5(1.0)	24.4(1.6)	6.8(0.5)
Toluene Insolubles, wt%	0	0	0

[a] not detected
[b] not available
[c] Numbers in parentheses are standard deviations
[d] DAU = deasphalting resid unit; SLA = south Louisiana resid

Table I.A.2.2. Characteristics of Parent and Reduced Resids

Resid	Product Distribution, wt%			
	Oil	Asphaltenes	Preasphaltenes	IOM[e]
ANS[b,e]	82.6(0.1)	17.4(0.1)	0.0	0.0
Maya[b]	80.5(1.1)	19.5(1.1)	0.0	0.0
Reduced Maya[a,c]	35.1	31.2	20.1	13.6
DAU[b,e]	75.6(1.6)	24.4(1.6)	0.0	0.0
Reduced DAU[c]	68.4	31.6	0.0	0.0
SLA[b]	93.2(0.5)	6.8(0.5)	0.0	0.0
Reduced SLA[c]	93.8	6.2	0.0	0.0
Yates[b]	87.6(0.1)	12.4(0.1)	0.0	0.0
	Elemental Analysis, wt%[d]			
Resid	Carbon, %	Hydrogen, %	Nitrogen, %	
Maya	84.3	9.6	0.8	
Reduced Maya	75.8	10.0	<0.5	
DAU	85.3	9.0	0.8	
Reduced DAU	82.0	9.7	0.5	
SLA	87.2	11.3	0.5	
Reduced SLA	75.0	11.5	0.6	

[a]Product fractionations with reduced resids were performed only once because of limited amount of material.
[b][Bedell, 1991].
[c][Wang, 1992].
[d]Analyzed by Galbraith Laboratories, Knoxville, TN.
[e]ANS = Alaska North Slope; DAU = deasphalted resid; SLA = south Louisiana resid; IOM = insoluble organic matter

Table I.A.2.3. Product Distributions for Hydrogen-Rich Species in Reactions with Aromatic Acceptors

Product Distributions, mol%						
Isotetralin and Isotetralin with Anthracene or Pyrene						
Compound/ Conditions	**NAP[a]**	**1,2-DHN**	**1,4-DHN**	**TET**	**ISO**	**DEC**
ISO						
H_2	51.9(1.3)[b]	4.1(0.4)	34.1(0.9)	9.9(1.1)	0.0	0.0
N_2	57.5(0.2)	3.4(0.5)	32.3(0.3)	6.8(0.8)	0.0	0.0
ISO/ANT (1:1)						
H_2	63.5(0.1)	8.5(0.2)	16.1(0.1)	10.3(0.1)	0.0	1.6(0.1)
N_2	63.1(0.6)	8.7(0.2)	15.9(0.4)	10.8(0.14)	0.0	1.5(0.0)
ISO/ANT (5:1)						
H_2	51.5(0.7)	12.1(0.3)	11.1(0.3)	22.3(0.6)	0.3(0.0)	2.7(0.1)
N_2	51.4(0.4)	12.7(0.1)	12.7(0.7)	20.3(0.3)	0.2(0.1)	2.7(0.0)
ISO/PYR (1:1)						
H_2	56.9(0.7)	4.3(0.1)	30.0(0.4)	7.9(1.0)	0.0	0.9(0.1)
N_2	66.2(1.9)	3.7(0.1)	22.8(1.2)	6.4(0.6)	0.0	0.9(0.1)
ISO/PYR (5:1)						
H_2	57.6(1.5)	9.4(0.2)	12.4(2.5)	18.6(1.3)	0.0	2.0(0.2)
N_2	48.1(0.3)	9.4(0.2)	25.8(0.4)	14.9(0.3)	0.0	1.8(0.1)
Tetralin with Anthracene or Pyrene						
	NAP	**TET**				
TET						
H_2	0.4(0.1)	99.6(0.1)				
N_2	0.2(0.0)	99.8(0.0)				
TET/ANT (1:1)						
H_2	0.4(0.0)	99.6(0.0)				
N_2	0.1(0.1)	99.9(0.1)				
TET/ANT (5:1)						
H_2	0.2(0.0)	99.8(0.0)				
N_2	0.6(0.2)	99.4(0.2)				
TET/PYR(1:1)						
H_2	0.0	100.0(0.0)				
N_2	0.0	100.0(0.0)				
TET/PYR(5:1)						
H_2	0.1(0.0)	99.9(0.0)				
N_2	0.4(0.3)	99.6(0.3)				

[a] DEC = decalin; 1,2-DHN = 1,2-dihydronaphthalene; 1,4-DHN = 1,4-dihydroaphthalene; NAP = naphthalene; TET = tetralin; ANT = anthracene; PYR = pyrene; ISO = isotetralin.
[b] Numbers in parentheses indicate standard deviations.

Table I.A.2.3. Product Distributions for Hydrogen-Rich Species in Reactions with Aromatic Acceptors (Continued)

Product Distributions, mol%					
Perhydropyrene with Anthracene					
Compound/ Conditions	**PYR**	**PHP**			
PHP					
H_2	0.0(0.0)	100.0(0.0)			
N_2	0.0(0.0)	100.0(0.0)			
PHP/ANT (1:1)					
H_2	0.7(0.1)	99.3 (0.1)			
N_2	0.8(0.1)	99.2(0.1)			
PHP/ANT (5:1)					
H_2	0.1(0.0)	99.9(0.0)			
N_2	1.4(0.2)	98.6(0.2)			
Hexahydroanthracene and Hexahydroanthracene with Pyrene					
Compound/ Conditions	**ANT**	**DHA**	**THA**	**HHA**	**OHA**
HHA					
H_2	5.1(1.5)	80.9(0.6)	8.0(0.4)	4.4(0.7)	1.6(0.9)
N_2	7.4(0.4)	77.8(1.0)	8.5(0.7)	4.2(0.3)	2.1(0.3)
HHA/PYR(1:1)					
H_2	7.1(0.2)	76.1(0.2)	11.8(0.6)	3.0(0.2)	2.0(0.2)
N_2	18.5(0.9)	50.4(3.1)	23.3(2.8)	3.8(0.2)	4.0(0.7)
HHA/PYR(5:1)					
H_2	4.7(0.3)	51.4(1.0)	25.0(0.3)	9.2(0.5)	9.7(0.3)
N_2	26.2(2.5)	25.1(2.7)	38.2(0.5)	4.7(0.1)	5.8(0.4)

[a] PHP = perhyropyrene; DHA = dihydroanthracene; THA = tetrahydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene; TET = tetralin; ANT = anthracene; PYR = pyrene.

[b] Numbers in parentheses indicate standard deviations.

Table I.A.2.3. Product Distributions for Hydrogen-Rich Species in Reactions with Aromatic Acceptors (Continued)

Product Distributions, mol%					
Dihydroanthracene and Dihydroanthracene with Pyrene					
Compounds/ Conditions	**ANT[a]**	**DHA**	**THA**		
DHA					
H_2	6.9(0.7)[b]	92.8(0.5)	0.3(0.5)		
N_2	5.3(0.2)	94.7(0.2)	0.0(0.0)		
DHA/PYR(1:1)					
H_2	8.7(0.1)	90.6(0.4)	0.7(0.3)		
N_2	9.6(1.0)	90.2(1.1)	0.2(0.2)		
DHA/PYR(5:1)					
H_2	8.3(0.2)	90.5(0.2)	1.2(0.1)		
N_2	7.8(0.7)	91.1(0.9)	1.1(0.2)		
Perhydroanthracene with Pyrene					
	ANT	**PHA**			
PHA					
H_2	0.0(0.0)	100.0(0.0)			
N_2	0.0(0.0)	100.0(0.0)			
PHA/PYR (1:1)					
H_2	0.0(0.0)	100.0(0.0)			
N_2	0.0(0.0)	100.0(0.0)			
PHA/PYR (5:1)					
H_2	0.0(0.0)	100.0(0.0)			
N_2	0.0(0.0)	100.0(0.0)			

[a] ANT = anthracene; DHA = dihydroanthracene; PHA = perhydroanthracene; THA = tetrahydroanthracene; PYR = pyrene.
* Numbers in parentheses are standard deviations.

Table I.A.2.4. Product Distribution of Aromatic Acceptors in Reactions with Hydrogen-Rich Species

Anthracene with Isotetralin (mol%)				
	ANT[a]	DHA	THA	
ANT				
H_2	88.3(1.1)[b]	11.7(1.1)	0.0(0.0)	
N_2	99.5(0.8)	0.5(0.2)	0.0(0.0)	
ISO/ANT (1:1)				
H_2	25.8(1.1)	71.4(1.1)	2.8(0.1)	
N_2	29.5(0.5)	67.7(0.4)	2.8(0.1)	
ISO/ANT (5:1)				
H_2	1.2(0.3)	98.1(0.3)	0.7(0.1)	
N_2	7.9(0.7)	86.6(0.7)	5.5(0.1)	
Pyrene with Isotetralin (mol%)				
	PYR	DHP	THP	HHP
PYR				
H_2	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
N_2	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
ISO/PYR (1:1)				
H_2	82.7(0.7)	16.6(0.7)	0.7(0.0)	0.0(0.0)
N_2	87.7(0.9)	12.3(0.9)	0.0(0.0)	0.0(0.0)
ISO/PYR (5:1)				
H_2	57.2(0.6)	36.0(0.6)	4.6(0.2)	2.2(0.2)
N_2	67.4(1.5)	27.8(1.2)	2.6(0.3)	2.2(0.2)
Anthracene with Perhydropyrene (mol%)				
	ANT	DHA		
PHP/ANT (1:1)				
H_2	87.7(1.1)	12.3(1.1)		
N_2	98.2(0.7)	1.8(0.7)		
PHP/ANT (5:1)				
H_2	84.0(1.6)	15.9(1.7)		
N_2	97.5(0.1)	2.5(0.1)		
Anthracene with Tetralin (mol%)				
	ANT	DHA	THA	
TET/ANT (1:1)				
H_2	82.1(1.1)	17.6(1.0)	0.3(0.0)	
N_2	99.0(0.2)	1.0(0.2)	0.0(0.0)	
TET/ANT (5:1)				
H_2	82.7(0.8)	16.7(0.7)	0.6(0.2)	
N_2	96.3(0.2)	3.7(0.2)	0.0(0.0)	

[a] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; DHP = dihydropyrene; HHP = hexahydropyrene; PYR = pyrene; THP = tetrahydropyrene; ISO = isotetralin.
[b] Numbers in parentheses are standard deviations.

Table I.A.2.4. Product Distribution of Aromatic Acceptors in Reactions with Hydrogen-Rich Species (Continued)

Pyrene with Tetralin (mol%)				
	PYR[a]	DHP		
TET/PYR (1:1)				
H_2	100.0(0.0)[b]	0.0(0.0)		
N_2	100.0(0.0)	0.0(0.0)		
TET/PYR (5:1)				
H_2	98.8(0.3)	1.2(0.3)		
N_2	99.3(0.0)	0.7(0.0)		
Pyrene with Hexahydroanthracene (mol%)				
	PYR	DHP	THP	HHP
HHA/PYR (1:1)				
H_2	66.6(0.5)	28.5(0.6)	2.5(0.2)	2.4(0.1)
N_2	79.2(2.3)	18.7(1.8)	0.6(0.7)	1.5(0.2)
HHA/PYR (5:1)				
H_2	40.7(2.0)	39.3(1.5)	8.3(0.5)	11.7(0.4)
N_2	83.8(1.7)	8.9(1.5)	0.0(0.0)	7.3(2.9)
Pyrene with Dihydroanthracene (mol%)				
	PYR	DHP	THP	HHP
DHA/PYR (1:1)				
H_2	93.6(0.8)	5.7(1.6)	0.0(0.0)	0.7(0.8)
N_2	95.4(2.2)	4.6(2.2)	0.0(0.0)	0.0(0.0)
DHA/PYR (5:1)				
H_2	78.5(0.1)	15.1(0.5)	0.5(0.0)	5.9(0.5)
N_2	81.9(2.3)	14.1(0.3)	0.2(0.2)	3.8(2.1)
Pyrene with Perhydroanthracene (mol%)				
	PYR	DHP		
PHA/PYR (1:1)				
H_2	98.8(0.0)	1.2(0.0)		
N_2	99.1(0.1)	0.9(0.1)		
PHA/PYR (5:1)				
H_2	98.7(0.1)	1.3(0.1)		
N_2	99.4(0.0)	0.6(0.0)		

[a] DHA = dihydroanthracene; DHP = dihydropyrene; HHA = hexahydroanthracene; HHP = hexahydropyrene; PHA = perhydroanthracene: PYR = pyrene; THP = tetrahydropyrene; TET = tetralin.

[b] Numbers in parenthesis are standard deviations.

Table I.A.2.5. Thermal Reaction Systems

Reaction Conditions	Moles of Hydrogen Released x 10^4		Moles of Hydrogen Accepted x 10^4		Percent Hydrogenation (%)		Hydrogen Efficiency		Moles of H_2 From Gaseous H_2 Moles X 10^4
	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2
ISO	10.7(0.2)	11.4(0.1)							
ISO/ANT (1:1)	11.1(0.0)	17.0(0.1)	4.3(0.1)	4.1(0.0)	19.2(0.3)	18.3(0.1)	0.4(0.0)	0.2(0.0)	0.2(0.1)
ISO/ANT (5:1)	44.7(0.6)	45.4(0.1)	5.6(0.0)	5.5(0.0)	24.9(0.1)	24.4(0.9)	0.1(0.0)	0.1(0.0)	0.1(0.1)
TET	0.1(0.0)	0.0(0.0)							
TET/ANT (1:1)	0.1(0.0)	0.0(0.0)	1.0(0.1)	0.1(0.0)	4.5(0.3)	0.3(0.1)	19.8(2.9)	---[a]	1.0(0.1)
TET/ANT (5:1)	0.1(0.0)	0.4(0.0)	1.0(0.1)	0.2(0.0)	4.5(0.3)	0.9(0.1)	8.8(1.7)	0.5(0.1)	0.4(0.1)
PHP	0.0(0.0)	0.0(0.0)							
PHP/ANT (1:1)	0.3(0.0)	0.3(0.1)	0.7(0.1)	0.1(0.0)	3.1(0.3)	0.5(0.2)	2.6(0.2)	0.4(0.1)	0.6(0.1)
PHP/ANT (5:1)	0.2(0.0)	0.3(0.0)	0.9(0.1)	0.1(0.0)	4.0(0.4)	0.6(0.0)	4.9(0.8)	0.6(0.1)	0.7(0.1)
ISO/PYR (1:1)	11.0(0.1)	11.8(0.2)	0.9(0.0)	0.6(0.0)	6.0(0.3)	4.1(0.3)	0.1(0.0)	0.1(0.0)	0.3(0.1)
ISO/PYR (5:1)	49.5(0.8)	47.7(0.3)	2.6(0.0)	2.0(0.1)	17.3(0.3)	13.2(0.8)	0.1(0.0)	0.0(0.0)	0.6(0.2)
TET/PYR (1:1)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	---	---	0.0(0.0)
TET/PYR (5:1)	0.1(0.0)	0.3(0.2)	0.1(0.0)	0.0(0.0)	0.4(0.1)	0.2(0.0)	0.8(0.2)	0.2(0.1)	0.0(0.0)
HHA	10.0(0.3)	10.0(0.1)							
HHA/PYR (1:1)	9.9(0.0)	9.5(0.3)	2.0(0.3)	1.2(0.1)	13.6(0.2)	8.1(0.8)	0.2(0.0)	0.1(0.0)	0.8(0.2)
HHA/PYR (5:1)	35.8(0.5)	43.7(0.8)	4.5(0.1)	1.5(0.4)	30.4(1.0)	10.4(2.5)	0.1(0.0)	0.0(0.0)	3.0(0.5)
DHA	0.4(0.1)	0.3(0.0)							
DHA/PYR (1:1)	0.4(0.0)	0.5(0.1)	0.4(0.0)	0.2(0.1)	2.5(0.2)	1.6(0.9)	0.9(0.1)	0.4(0.2)	0.2(0.1)
DHA/PYR (5:1)	2.0(0.0)	1.8(1.0)	1.7(0.1)	1.3(0.3)	11.3(0.4)	8.6(2.2)	0.9(0.0)	0.7(0.2)	0.4(0.4)
PHA	0.0(0.0)	0.0(0.0)							
PHA/PYR(1:1)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.3(0.0)	0.3(0.0)	---	---	0.0(0.0)
PHA/PYR(5:1)	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.0(0.0)	0.4(0.1)	0.4(1.0)	---	---	0.1(0.0)

[a] --- means no hydrogen was released in that condition.
[b] ISO = isotetralin; TET = tetralin; PYR = pyrene; DHA = dihydroanthracene; HHA = hexahydroanthracene; PHA = perhydroanthracene; PHP = perhydropyrene; ANT = anthracene
[c] Numbers in parentheses are standard deviations.

Table I.A.2.6. Product Distributions for Reactions of Perhydropyrene with Benzophenone under Thermal and Catalytic Conditions[a]

Reaction Conditions	Atmosphere	Pressure (psig)	Product Distribution (mole %)				
			BENZ[b]	DPM	PHP	HHP	PYR
Thermal	N_2	400	98.8(0.5)[c]	1.2(0.5)	99.7(0.1)	0.3(0.1)	0.0(0.0)
Catalytic	N_2	400	95.2(1.2)	4.8(1.2)	99.1(0.1)	0.7(0.0)	0.2(0.0)
Thermal	N_2	1250	99.3(0.1)	0.7(0.1)	99.6(0.0)	0.4(0.0)	0.0(0.0)
Catalytic	N_2	1250	94.8(0.2)	5.2(0.2)	98.9(0.1)	0.9(0.1)	0.3(0.0)
Thermal	H_2	400	91.2(0.7)	8.8(0.7)	100.0(0.1)	0.1(0.1)	0.0(0.0)
Catalytic	H_2	400	83.6(0.8)	16.4(0.8)	99.4(0.2)	0.6(0.2)	0.0(0.0)
Thermal	H_2	1250	81.8(0.6)	18.2(0.6)	99.6(0.0)	0.4(0.0)	0.0(0.0)
Catalytic	H_2	1250	69.8(1.3)	30.2(1.3)	99.3(0.0)	0.6(0.0)	0.1(0.0)

[a] Reactions conditions: 440°C, 450 cpm, 400 or 1,250 psig H_2 or N_2 charged at ambient conditions.
[b] BENZ = benzophenone, DPM = diphenylmethane, PHP = perhydropyrene, HHP = hexahydropyrene, PYR = pyrene.
[c] Numbers in parenthese are standard deviations.

Table I.A.2.7. Thermal and Catalytic Reactions of Benzophenone and Perhydropyrene[a]

Reaction Conditions	Atmosphere	Pressure (psig)	Moles of Hydrogen x 10^4		Hydrogen Efficiency	Moles of H_2 From Gaseous H_2 x 10^4
			Released by PHP	Accepted by BENZ[b]		
Thermal	N_2	400	0.3(0.2)	0.1(0.1)[c]	0.4(0.2)	
Catalytic	N_2	400	1.2(0.2)	0.5(0.2)	0.4(0.2)	
Thermal	N_2	1250	0.5(0.1)	0.1(0.0)	0.1(0.0)	
Catalytic	N_2	1250	1.5(0.3)	0.5(0.0)	0.3(0.0)	
Thermal	H_2	400	0.2(0.1)	0.9(0.1)	5.3(1.3)	0.7(0.2)
Catalytic	H_2	400	0.7(0.3)	1.6(0.1)	2.2(0.8)	1.1(0.3)
Thermal	H_2	1250	0.4(0.1)	1.8(0.1)	4.1(0.8)	1.8(0.1)
Catalytic	H_2	1250	0.9(0.1)	2.9(0.2)	3.4(0.5)	2.4(0.2)

[a] Reactions conditions: 440°C, 450 cpm, 400 or 1,250 psig H_2 or N_2 charged at ambient conditions.
[b] BENZ = benzophenone, PHP = perhydropyrene.
[c] Numbers in parenthese are standard deviations.

Table I.A.2.8. Product Distributions for Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 380 and 440°C[a]

	Product Distribution (mole%)						
	ANT[b]	DHA	THA	OHA	PYR	HHP	PHP
Thermal Reactions at 380°C							
PHP							
H_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
N_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
ANT							
H_2	88.3(1.1)[b]	11.7(1.1)	0.0(0.0)	0.0(0.0)			
N_2	99.5(0.8)	0.5(0.2)	0.0(0.0)	0.0(0.0)			
PHP/ANT(1:1)							
H_2	87.7(1.1)	12.3(1.1)	0.0(0.0)	0.0(0.0)	0.7(0.8)	0.0(0.0)	99.3(0.7)
N_2	98.2(0.7)	1.8(0.7)	0.0(0.0)	0.0(0.0)	0.8(0.1)	0.0(0.0)	99.2(0.1)
PHP/ANT(5:1)							
H_2	84.1(1.7)	15.9(1.7)	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.0(0.0)	99.9(0.0)
N_2	97.5(0.8)	2.5(0.8)	0.0(0.0)	0.0(0.0)	1.4(0.0)	0.0(0.0)	98.6(0.1)
Catalytic Reactions at 380°C							
PHP							
H_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
N_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
ANT							
H_2	83.3(1.5)	16.7(1.5)	0.0(0.0)	0.0(0.0)			
N_2	98.1(0.6)	1.9(0.6)	0.0(0.0)	0.0(0.0)			
PHP/ANT(1:1)							
H_2	80.7(2.1)	19.3(2.1)	0.0(0.0)	0.0(0.0)	0.9(0.1)	1.9(0.1)	97.2(0.0)
N_2	96.2(0.1)	3.8(0.1)	0.0(0.0)	0.0(0.0)	0.5(0.1)	2.4(0.7)	97.1(0.1)
PHP/ANT(5:1)							
H_2	55.6(2.4)	44.4(2.4)	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.8(0.1)	99.1(0.1)
N_2	82.4(0.4)	17.6(0.3)	0.0(0.0)	0.0(0.0)	0.2(0.1)	1.0(0.1)	98.8(0.2)
Thermal Reactions at 440°C							
PHP							
H_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
N_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
ANT							
H_2	43.5(0.8)	54.1(0.8)	1.1(0.1)	1.3(0.0)			
N_2	99.3(0.1)	0.7(0.1)	0.0(0.0)	0.0(0.0)			
PHP/ANT(1:1)							
H_2	38.1(2.7)	61.9(2.6)	0.0(0.0)	0.0(0.0)	0.1(0.2)	1.0(0.7)	98.9(0.6)
N_2	98.8(0.2)	1.2(0.2)	0.0(0.0)	0.0(0.0)	1.0(0.2)	0.8(0.2)	98.2(0.3)
PHP/ANT(5:1)							
H_2	38.1(0.7)	61.9(0.7)	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.5(0.1)	99.4(0.1)
N_2	89.6(0.8)	10.4(0.8)	0.0(0.0)	0.0(0.0)	0.1(0.1)	0.6(0.1)	99.3(0.1)

[a] Reaction Conditions: 450 cpm, 400 psig N_2 or H_2 charged at ambient temperature.
[b] ANT = anthracene; DHA = dihydroanthracene; OHA = octahydroanthracene; THA = tetrahydroanthracene; HHP = hexahydropyrene; PHP = perhydropyrene; PYR = pyrene.
[c] Numbers in parenthesis indicate standard deviations.

Table I.A.2.8. Product Distributions for Thermal and Catalytic Reactions of Perhydropyrene with Anthracene at 380 and 440°C [a] (Continued)

	Product Distribution (mol%)						
	ANT[b]	DHA	THA	OHA	PYR	HHP	PHP
Catalytic Reactions at 440°C							
PHP							
H_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
N_2					0.0(0.0)	0.0(0.0)	100.0(0.0)
ANT							
H_2	39.3(1.0)[c]	57.5(1.3)	2.2(0.1)	1.0(0.0)			
N_2	98.5(0.1)	1.5(0.1)	0.0(0.0)	0.0(0.0)			
PHP/ANT(1:1)							
H_2	40.3(0.8)	59.7(0.8)	0.0(0.0)	0.0(0.0)	0.0(0.0)	2.7(0.2)	97.3(0.2)
N_2	94.1(0.5)	5.9(0.5)	0.0(0.0)	0.0(0.0)	0.5(0.5)	1.7(0.6)	97.8(0.9)
PHP/ANT(5:1)							
H_2	42.0(1.3)	58.0(1.3)	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.5(0.0)	99.5(0.1)
N_2	87.0(0.9)	13.0(0.9)	0.0(0.0)	0.0(0.0)	0.1(0.0)	0.8(0.2)	99.1(0.2)

[a] Reaction Conditions: 450 cpm, 400 psig N_2 or H_2 charged at ambient temperature.
[b] ANT = anthracene, DHA = dihydroanthracene, THA = tetrahydroanthracene, OHA = octahydroanthracene, PHP = perhydropyrene, PYR = pyrene
[c] Numbers in parenthesis are standard deviations.

Table I.A.2.9. Catalytic Reaction Systems

Reaction Conditions	Moles of Hydrogen Released x 10^4		Moles of Hydrogen Accepted x 10^4		Percent Hydrogenation (%)		Hydrogen Efficiency		Moles of H_2 From Gaseous H_2 Moles X 10^4
	H_2	N_2	H_2	N_2	H_2	N_2	H_2	N_2	H_2
380°C Thermal									
PHP/ANT (1:1)	0.3(0.0)	0.3(0.1)	0.7(0.1)	0.1(0.0)	3.1(0.3)	0.5(0.2)	2.6(0.2)	0.4(0.1)	0.6(0.1)
PHP/ANT (5:1)	0.2(0.0)	0.3(0.0)	0.9(0.1)	0.1(0.0)	4.0(0.4)	0.6(0.0)	4.9(0.8)	0.6(0.1)	0.7(0.1)
380°C Catalytic									
PHP/ANT (1:1)	0.8(0.0)	0.7(0.2)	1.1(0.1)	0.2(0.0)	4.8(0.5)	1.0(0.1)	1.4(0.2)	0.3(0.9)	0.9(0.1)
PHP/ANT (5:1)	1.1(0.1)	1.4(0.2)	2.5(0.1)	1.0(0.0)	11.1(0.6)	4.4(0.1)	2.4(0.3)	0.7(0.1)	1.5(0.1)
440°C Thermal									
PHP/ANT (1:1)	0.2(0.1)	0.6(0.1)	3.5(0.1)	0.1(0.0)	15.4(0.6)	0.3(0.0)	14.1(0.3)	0.1(0.0)	3.4(0.1)
PHP/ANT (5:1)	0.6(0.1)	0.8(0.2)	3.5(0.0)	0.6(0.0)	15.5(0.2)	2.6(0.2)	5.9(1.3)	0.8(0.2)	2.9(0.1)
440°C Catalytic									
PHP/ANT (1:1)	0.6(0.0)	0.6(0.3)	3.3(0.1)	0.3(0.0)	14.9(0.2)	1.5(0.1)	5.5(0.3)	0.8(0.5)	3.0(0.1)
PHP/ANT (5:1)	0.7(0.1)	1.2(0.2)	3.3(0.1)	0.7(0.1)	14.5(0.3)	3.3(0.2)	4.9(0.6)	0.6(0.2)	2.6(0.1)

[a] ANT = anthracene; PHP = perhydropyrene.
[b] Numbers in parentheses are standard deviations.

Table I.A.2.10. Resid Reaction Systems[a]

Reaction Conditions	Moles of Hydrogen Accepted x 10^4		Percent Hydrogenation (%)		Moles of H_2 From Gaseous H_2 Moles X 10^4
	H_2	N_2	H_2	N_2	H_2
Maya/ANT	3.2(0.2)[c]	1.6(0.1)	7.0(0.4)	3.6(0.2)	1.5(0.3)
Maya/ANT (Reduced)	8.0(0.3)	4.3(0.1)	17.9(0.6)	9.5(0.2)	3.8(0.2)
DAU/ANT[b]	4.7(0.2)	1.6(0.1)	10.0(0.5)	3.6(0.2)	3.1(0.3)
DAU/ANT (Reduced)	8.3(0.1)	5.1(0.2)	17.9(0.4)	11.3(0.3)	3.2(0.3)
S.LA/ANT	3.3(0.1)	1.0(0.1)	7.3(0.1)	2.2(0.2)	2.3(0.2)
S.LA/ANT (Reduced)	5.3(0.1)	3.3(0.2)	11.7(0.2)	7.2(0.4)	2.0(0.2)
Maya/PHP/ANT	5.0(0.2)	3.1(0.2)	11.1(0.4)	6.9(0.8)	1.9(0.5)
Maya/PHP/ANT (Reduced)	7.9(0.1)	5.8(0.2)	17.6(0.2)	13.0(0.5)	2.0(0.3)
DAU/PHP/ANT	4.7(0.2)	3.6(0.1)	10.5(0.5)	8.0(0.2)	1.1(0.3)
DAU/PHP/ANT (Reduced)	8.1(0.1)	5.9(0.0)	18.0(0.2)	13.1(0.1)	2.2(0.1)
S.LA/PHP/ANT	3.0(0.2)	2.0(0.1)	6.7(0.4)	4.4(0.3)	1.1(0.3)
S.LA/PHP/ANT (Reduced)	6.2(0.1)	5.1(0.1)	13.7(0.3)	11.3(0.3)	1.1(0.3)

[a] Reaction Conditions: 380°C, 1,250 psig H_2 charged at ambient temperature.
[b] DAU = deasphalted resid; SLA = south Louisiana resid; PHP = perhydropyrene; ANT = anthracene
[c] Numbers in parentheses are standard deviations.

Table I.A.2.11. Product Distribution from the Resid in Binary and Ternary Systems[a]

Reaction System	Product Distribution, wt%							
	H_2				N_2			
	HEX Solubles (%)	TOL Solubles (%)	THF Solubles (%)	IOM (%)	HEX Solubles (%)	TOL Solubles (%)	THF Solubles (%)	IOM (%)
Maya/ANT		98.7(0.2)[c]	1.3(0.2)	0.0(0.0)		97.9(1.2)	1.8(1.2)	0.3(0.1)
Maya/ANT (Reduced)		98.2(0.2)	1.4(0.1)	0.4(0.0)		95.8(0.4)	3.7(1.1)	0.5(0.6)
DAU/ANT[b]		96.9(0.3)	2.9(0.2)	0.2(0.1)		99.1(0.4)	0.9(0.4)	0.1(0.0)
DAU/ANT (Reduced)		96.3(0.6)	3.5(0.6)	0.2(0.1)		96.9(2.0)	2.9(2.0)	0.2(0.1)
SLA/ANT		98.7(0.3)	1.1(0.1)	0.2(0.1)		98.2(1.1)	1.7(1.0)	0.1(0.1)
SLA/ANT (Reduced)		98.3(0.7)	1.5(0.6)	0.2(0.1)		98.6(0.5)	1.4(0.5)	0.0(0.0)
Maya/ANT/PHP	76.8(1.2)	23.2(1.2)	0.0(0.0)	0.0(0.0)	73.7(0.9)	26.3(0.9)	0.0(0.0)	0.0(0.0)
Maya/ANT/PHP (Reduced)	78.1(2.1)	21.9(2.1)	0.0(0.0)	0.0(0.0)	81.9(0.0)	18.1(0.0)	0.0(0.0)	0.0(0.0)
DAU/ANT/PHP	81.1(1.4)	18.9(1.4)	0.0(0.0)	0.0(0.0)	76.6(0.6)	23.4(0.6)	0.0(0.0)	0.0(0.0)
DAU/ANT/PHP (Reduced)	88.4(6.1)	11.6(6.1)	0.0(0.0)	0.0(0.0)	83.0(0.3)	17.0(0.3)	0.0(0.0)	0.0(0.0)
SLA/ANT/PHP	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
SLA/ANT/PHP (Reduced)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)	100.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)

[a] Reaction Conditions: 380 °C, 1,250 psig H_2 charged at ambient temperature.
[b] DAU = deasphalted resid; HEX = hexane; SLA = south Louisiana resid; TOL = toluene; PHP = perhydropyrene; THF = tetrahydrofuran; ANT = anthracene; IOM = insoluble organic matter
[c] Numbers in parentheses are standard deviations.

Table I.A.2.12. Comparison of Moles of Hydrogen Accepted in Ternary and Binary Systems

Moles of Hydrogen Accepted x 10^4			
N_2 Atmosphere		H_2 Atmosphere	
Maya/ANT + PHP/ANT	1.8(0.1)	Maya/ANT + PHP/ANT - ANT (H_2)	3.4(0.3)
Maya/PHP/ANT	3.1(0.4)	Maya/PHP/ANT	5.0(0.2)
Reduced Maya/ANT + PHP/ANT	4.4(0.1)	Reduced Maya/ANT + PHP/ANT - ANT (H_2)	8.3(0.4)
Reduced Maya/PHP/ANT	5.8(0.2)	Reduced Maya/PHP/ANT	7.9(0.1)
DAU/ANT + PHP/ANT	1.8(0.1)	DAU/ANT + PHP/ANT - ANT (H_2)	4.9(0.3)
DAU/PHP/ANT	3.6(0.1)	DAU/PHP/ANT	4.7(0.2)
Reduced DAU/ANT + PHP/ANT	5.2(0.2)	Reduced DAU/ANT + PHP/ANT - ANT (H_2)	8.5(0.3)
Reduced DAU/PHP/ANT	5.9(0.0)	Reduced DAU/PHP/ANT	8.1(0.1)
SLA/ANT + PHP/ANT	1.1(0.1)	SLA/ANT + PHP/ANT - ANT (H_2)	3.5(0.2)
SLA/PHP/ANT	2.0(0.1)	SLA/PHP/ANT	3.0(0.2)
Reduced SLA/ANT + PHP/ANT	3.4(0.2)	Reduced SLA/ANT + PHP/ANT - ANT (H_2)	5.5(0.2)
Reduced SLA/ANT/PHP	5.1(0.1)	Reduced SLA/ANT/PHP	6.2(0.1)

[a] Reaction Conditions: 380 °C, 1,250 psig H_2 charged at ambient temperature.
[b] DAU = deasphalted resid; SLA = south Louisiana resid; PHP = perhydropyrene; ANT = anthracene
[c] Numbers in parentheses indicate standard deviations.

SUBTASK I.B.1.

PRETREATMENT, FRACTIONATION, AND REACTIVITY OF PETROLEUM RESIDUA

INTRODUCTION

Petroleum residua that have been hydrotreated show definite improvements in coal conversion and the product slate achieved.[1] Effectiveness of hydrogen donation from petroleum solvents in coprocessing was also shown to be dependent on the activities and selectivities of the catalysts used in the pretreatment of petroleum residua.[2] In this subtask, the effect of different catalysts on hydrotreatment of petroleum solvents prior to coprocessing was investigated. Active transition metal salts of Mo, Ni, and V organic acids were used to hydrotreat the residua prior to coprocessing. The catalysts used were molybdenum naphthenate (MoNaph), nickel naphthenate (NiNaph), and vanadium naphthenate (VNaph). A commercial $NiMo/Al_2O_3$ hydrotreating catalyst was also used. The prehydrotreated residua were then used in coprocessing reactions to evaluate the effect of the prehydrotreatment. Coprocessing reactions with coal and residua using the catalyst directly were also performed in order to compare the effect of the prehydrotreatment.

EXPERIMENTAL

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

Materials. Maya and Khafji heavy petroleum residua, and Illinois No. 6 coal were selected for coprocessing. The materials were supplied by Amoco Oil Company. Maya and Khafji residua were used as received, but Illinois No. 6 coal was pulverized to 100 mesh before use. Composition of each material presented in Table I.B.1.1 was determined by Amoco Oil Company. The moisture and ash contents of Illinois No. 6 coal were measured again in this laboratory, and the values were slightly different from those supplied by Amoco Oil Company; the moisture and ash contents obtained in Auburn were utilized in the calculations of experimental results.

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

Thermal and Catalytic Reactions. The coprocessing reactions were performed in 56 cm^3 tubular microreactors which were vertically oriented during reactions and made of 316 stainless steel. Each coprocessing reaction was conducted with 3 g of coal and 6 g of residuum under reaction conditions of 1250 psig hydrogen charged at ambient temperature (about 2820 psig hydrogen at reaction temperature), 400 °C reaction temperature, 1 hr reaction time, and 550 cpm vertical shaking. In catalytic reactions, each catalyst paste or solid catalyst was introduced at the level of 3000 ppm metal content. Elemental sulfur was added in an amount sufficient to produce metal sulfide from the organometallic paste during the reaction; in thermal reactions, however, no additional sulfur was added.

Analysis. The residuum alone (9 g), a mixture of coal (3 g) and residuum (6 g), as well as the coprocessing products from 3 g coal and 6 g residuum were fractionated by three different solvents: first, the oil fraction was extracted using hexane; next, the asphaltene fraction was extracted using toluene; finally, the preasphaltene fraction was extracted using tetrahydrofuran (THF). About 9 g of whole reactants or products were dissolved in 450 mL of each solvent: sample materials were dissolved in 150 mL solvent, sonicated for 4 min, centrifuged to separate liquid and undissolved materials, and then all of these procedures were repeated twice with the same solvent. The amount of each fraction was compared in terms of oil (hexane soluble), asphaltene (hexane insoluble but toluene soluble), preasphaltene (toluene insoluble but THF soluble), and insoluble organic matter (IOM - THF insoluble) on a moisture-, ash-, and catalyst-free basis. The amount of gas product produced from the reaction was determined by hydrogen analysis using a gas chromatograph (GC) with thermal conductivity detection. Each fractionation was duplicated. The portion of each fraction originating from coal in the coal/residuum 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 12 g of Maya residuum in a 56 mL tubular microreactor which was made of 316 stainless steel and vertically oriented. In thermal reactions, sulfur was not added. In catalytic reactions, elemental sulfur was added in the amount required to generate metal sulfide in situ from each catalyst paste, which was introduced at a concentration of 3000 ppm metal content: about 0.024 g sulfur for Mo catalyst, 0.013 g for Ni catalyst, and 0.034 g for V catalyst. The pretreating reactions were conducted under the conditions of 1250 psig hydrogen charged at ambient temperature, 400 °C reaction temperature, 1 hr reaction time, and 550 cpm vertical shaking. After

the reaction, 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 pretreated Maya residua were used in the subsequent thermal coprocessing reactions with coal.

Thermal Coprocessing Reactions with Pretreated Maya Residuum and Coal. 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, 6 g of pretreated Maya residuum, 3 g of coal and 1250 psig hydrogen (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 1 hr using 550 cpm vertical shaking. To determine the degree to which the thermally and catalytically pretreated Maya residuum was thermally hydrogenated, 6 g 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 hydrogen analysis using a gas chromatograph with thermal conductivity detection.

Preparation of Presulfided $NiMo/Al_2O_3$ Catalyst. A commercial $NiMo/Al_2O_3$ catalyst (Shell 324 1/32-in diameter extrudates: 2.72 wt% Ni and 13.16 wt% Mo) was dried and presulfided in a tubular furnace and pulverized to -150 mesh powders. First, 10 g of Shell 324 extradites were packed between glass wool plugs in a 1 inch outside diameter borosilicate glass tube. The catalyst extrudates were dried at 300 °C in a N_2 gas flow (30 mL/min) for 1 hr. After

the temperature was lowered to 225 °C, the gas stream was switched to a hydrogen sulfide (H_2S/H_2)/H_2 gas mixture (10 vol% H_2S) flow of 20 mL /min at 225 °C. The catalyst extrudates were sulfided in this H_2S/H_2 mixture through a temperature-programmed procedure for 2 hr at 225 °C, 1 hr at 315 °C, and 2 hr at 370 °C. The sulfided catalyst was cooled down to ambient temperature in N_2 gas flowing at 30 mL/min for 1 hr to remove H_2S excessively adsorbed on the catalyst. During the sulfiding procedure, effluent gases were passed through a 5 wt% lead nitrate ($Pb(NO_3)_2$) solution to remove H_2S from the outstream. The sulfided extrudates were pulverized to -150 mesh size and kept in a desiccator.

Pretreatment of Maya Residuum with a Presulfided NiMo/Al_2O_3 Catalyst. Twelve grams of Maya residuum were hydrogenated with 0.0270 g of the powdered presulfided NiMo/ Al_2O_3 catalyst (corresponding to the metal level of about 3000 ppm Ni and Mo) in a 56-cm^3 tubular microreactor. The hydrogenation reaction conditions were the same as those described in the previous section on thermal and catalytic reactions, but elemental sulfur was <u>not</u> added. After the reaction, the pretreated Maya products were separated by a solvent extraction with THF. The THF-soluble fraction was recovered, and after the evaporation of the THF, was used in the subsequent thermal coprocessing reactions.

Coprocessing of Illinois No. 6 Coal and Pretreated Maya Residuum. A mixture of 3 g Illinois No. 6 coal and 6 g of the THF solubles from Maya pretreated with NiMo/Al_2O_3 was thermally hydrogenated at 400 °C for 1 hr. Reaction conditions, such as the reactor size, hydrogen pressure, agitation rate, solvent extraction procedure (using hexane, toluene, and THF), and the hydrogen consumption measured by GC were the same as described previously.

Analysis of Metal Content in Tetrahydrofuran-Solubles Fraction of Pretreated Maya Residuum. Amounts of metals contained in the original Maya residuum and the THF-solubles

fraction of Maya residuum products pretreated with Mo, Ni, and V sulfides were measured by graphite furnace atomic absorption spectrometry and/or inductively coupled argon plasma atomic emission spectrometry. The original Maya contained only a negligible amount of THF insolubles (less than 0.2 wt%) and was directly analyzed without a solvent extraction with THF. Pretreated Maya residua, that were hydrogenated with Mo, Ni, and V naphthenates in the presence of additional elemental sulfur (0.018 g of sulfur for Mo, 0.011 g of sulfur for Ni, and 0.027 g of sulfur for V) were fractionated into THF solubles and insolubles. The THF-solubles fractions were analyzed for metals.

Structures of in situ Generated Molybdenum and Vanadium Sulfides. Mo and V sulfides were generated in situ from MoNaph and vanadium(III) acetylacetonate and vanadyl(IV) acetylacetonate, respectively, with excess sulfur from model hydrogenation reactions. The metal precursors at approximately 3000 ppm Mo or V were introduced in a pure hexadecane or a hexadecane solution containing 2 wt% naphthenates or 1 wt% indole. Elemental sulfur was added at three times the stoichiometric amount of sulfur required to form MoS_2 for Mo species and eighteen times the stoichiometric amount of sulfur required to form V_2S_3 for V species. Each metal sulfide was generated in situ during hydrogenation reactions at 380 °C for 30 min under an atmosphere of approximately 2700 psig hydrogen. The black precipitates, possibly metal sulfides, were recovered by centrifugation after the reactions. Each Mo or V sulfide sample was washed with about 20 ml of THF once a day for 3 weeks to dilute the concentration of organic species possibly adsorbed and/or entrapped in the metal sulfides. After each THF washing, metal sulfides were dried under a flowing N_2 gas stream and stored in a vacuum desiccator. The structures of the metal sulfides were examined by X-ray diffraction spectrometry.

Activity of Molybdenum, Nickel, and Vanadium Catalysts at Different Metal Loadings. Research was performed using two different coprocessing systems with different catalyst metal loadings: (1) Illinois No. 6 coal and Khafji residuum with MoNaph or NiOct and (2) Illinois No. 6 coal and Maya residuum with naphthenates of Mo, Ni, or V.

In the first coprocessing reaction, a mixture of 3 g of Illinois No. 6 coal and 6 g of Khafji residuum was hydrogenated with MoNaph at concentrations of 1500, 750, 300, and 150 ppm Mo, or with NiOct at a concentration of 1500 ppm Ni. In the second coprocessing reaction, a mixture of 3 g of Illinois No. 6 coal and 6 g of Maya residuum was hydrogenated with MoNaph or NiNaph at concentrations of 150 to 340 ppm metal. Elemental sulfur was added at a constant level of 0.018 g in both coprocessing reactions. Reactions were conducted at 400 °C for 1 hr under a hydrogen atmosphere at approximately 2,800 psig at reaction temperature. Other reaction conditions and analysis of samples, such as the reactor size, the agitation rate, the solvent extraction procedure (using hexane, toluene, and THF), and the analysis of hydrogen consumption by GC were the same as described previously.

Analysis of Metal Content in Oil and Asphaltene Fractions of Pretreated Maya Residuum. Concentrations of metals contained in the oil (extracted by hexane) and asphaltenes (extracted by toluene) fractions of the original Maya and the Maya products pretreated with Mo and Ni naphthenates were measured by graphite furnace atomic absorption spectrometry for Ni and/or inductively coupled argon plasma atomic emission spectrometry for other trace metals. For some samples, both the top and bottom portions of each extracted fraction were analyzed separately.

Size Exclusion Chromatographic Analysis. Size exclusion chromatography was performed to compare the different molecular size distributions in various fractions extracted from

thermal and catalytic coprocessing products. The liquid chromatograph used was equipped with a Waters 590 programmable HPLC pump, a Waters 484 UV absorbance detector, and four size exclusion columns connected in series, which were composed of one each 500 Å and 100 Å porosity Ultrastyragel columns (Waters), and one each 100 Å and 50 Å porosity 5μ-Phenogel columns (Phenomenex); each column was 30 cm in length and had a 0.74 mm inside diameter.

Oil, asphaltenes, and preasphaltenes from coprocessing reactions with Maya (6 g) and Illinois No. 6 coal (3 g) were prepared in previous experiments under the following different conditions: a mixture of Maya residuum and coal without reaction, thermal reactions and catalytic reactions with MoNaph, NiNaph, VNaph, and $NiMo/Al_2O_3$. Each fraction extracted from coprocessing products was dissolved in THF. The oil and preasphaltene fractions were diluted to 0.1 wt% for size exclusion chromotography analysis; however, the asphaltene fractions required dilution to 0.05 wt% for size exclusion chromotography analysis. Each sample solution was filtered using a Micron 0.2 μm polytetrafluoroethylene laminated membrane, and 25 μL of the filtered solution was injected into the size exclusion chromotography columns. Size separation was performed using the size exclusion chromotography columns at 50 °C in THF at a 1 mL/min flow rate. The eluting fractions were detected using a UV detector at 254 nm fixed wavelength.

X-Ray Diffraction of in situ Generated Molybdenum Sulfide. Mo-sulfur catalyst species were prepared in situ using tubular microreactors charged with 15 g n-hexadecane, 0.75 g MoNaph paste, and 0.09 g elemental S (three times the stoichiometric amount of sulfur required to form MoS_2) under a hydrogen atmosphere (1250 psig at ambient temperature). Two different conditions, (1) 380 °C for 30 min using a copper sealant for sealing the tubular microreactors and (2) 400 °C for 1 hr without using a copper sealant were used to prepare the Mo-sulfur catalyst. After the reaction, black precipitates were recovered and washed with 20 mL THF three times

a day for 3 weeks. After THF washing, the solids were dried using a dry N_2 gas purge. Structures in these in situ generated Mo samples were characterized using two different X-ray spectrometers. A Rigaku DMAXB X-ray spectrometer operated at a scanning rate of 1° 20/min was used to characterize the sample prepared using condition (1). A Philips X-Ray Spectrometer operated at a scanning rate of 2° 20/min equipped with XRG 3100 X-ray generator was used to characterize sample (2). A commercial molybdenum sulfide (MoS_2) powder (Alfa Chemical) was also characterized and used as a reference material.

RESULTS AND DISCUSSION

Fractionation of Maya and Coal

Maya residua alone (9 g) and a mixture of Maya residua (6 g) and Illinois No. 6 coal (3 g) were fractionated. Extraction of each sample was duplicated. Maya was composed of 68.7 wt% oil, 31.1 wt% asphaltenes, and a negligible amount of IOM (Table I.B.1.2.a); this result will serve as background information for the products fractionated from Maya residuum hydropretreated with different catalysts. From the mixture of Maya and coal, 46.4 wt% oil, 23.7 wt% asphaltenes, 1.6 wt% preasphaltenes, 28.3 wt% IOM, and 70.1 wt% toluene solubles (oil + asphaltenes) were obtained on an ash free basis (Table I.B.1.2.b); this result will serve as background information for the coprocessing products fractionated from reactions using prehydrogenated Maya residuum with coal and different catalysts.

Using the above two results, the solubility of coal was calculated by assuming that coal has no oil fraction and by subtracting the amounts of fractions produced from Maya alone (6 g basis) from the total amount of each fraction produced from the mixture (Table I.B.1.2.c). Illinois No. 6 coal was shown to be composed of 6.8 wt% asphaltenes, 5.0 wt% preasphaltenes

and 88.2 wt% IOM on an ash-free basis. This calculated composition will be compared to that obtained from direct dissolution of Illinois No. 6 coal using each solvent in sequence in the hydrogenation experiments.

Solubility of Coal. Illinois No. 6 coal (9 g), Khafji residuum (9 g), and a mixture of Illinois No. 6 coal (3 g) and Khafji (6 g) were each fractionated. The fraction distribution was summarized as weight percents on an ash-free basis (Table I.B.1.3). 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 wt% oil as the major fraction but did not contain an IOM fraction. The coal and Khafji residuum mixture contained 57.5 wt% oil, 13.3 wt% asphaltenes, 2.0 wt% preasphaltenes, and 27.2 wt% 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.1.3, the solubility of coal alone and that combined with different residua are compared. 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.

Hydrogenation of Illinois No. 6 Coal. Three grams of coal were introduced in the reactor with 6 g of n-hexadecane, which was assumed to be nonreactive at the reaction tempera-ture, to

test the extent of hydrogenation of coal without a hydrogen-transferable solvent. With an assumption that n-hexadexcane was not involved in any reaction, such as hydrocracking, gasification or polymerization, the weight percents of fractionated products from thermal and catalytic hydrogenation reactions of Illinois No. 6 coal were calculated and are summarized in Table I.B.1.4.

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

Coprocessing of Maya and Illinois No. 6 Coal. A mixture of 6 g Maya residuum and 3 g Illinois No. 6 coal was hydrogenated thermally and catalytically with different catalysts under equivalent conditions. The fractionated products were calculated in two ways: in the first, the weight percent of each fraction was calculated based on the total product amount recovered (method A); in the second, the weight percent of each fraction was calculated based on the assumption of 100% product recovery in which the oil fraction was determined by subtracting the other recovered fractions from 100% (method B). Reactions were at least duplicated, and the results by method A are summarized as the averaged values and standard deviations of $X + \sigma_n$ in Table I.B.1.5.

Catalytic reactions converted more of the IOM fraction to lighter fractions and consumed more H_2 than thermal reactions. The order of activity in producing useful fractions of oil and asphaltenes was MoNaph > NiMo/Al_2O_3 $\geq$ NiNaph > Thermal $\geq$ VNaph. The order of activity in coal conversion was slightly different: NiNaph > NiMo/Al_2O_3 > MoNaph > VNaph >

Thermal. VNaph was the least active catalyst for producing oil and asphaltenes but was most active in producing gaseous products; VNaph seemed to enhance the retrogressive reaction producing higher molecular weight products. The hydrogen consumption in each reaction generally followed the activity of the catalyst used: more hydrogen consumption with MoNaph, NiNaph, and NiMo/Al_2O_3 than with VNaph and without catalyst. Reactions with NiNaph and powdered NiMo/Al_2O_3 catalysts were less reproducible than the other reactions. The low reproducibility with NiMo/Al_2O_3 seemed to be caused by the poor dispersion of the solid catalyst in the feed materials, but the reason for low reproducibility with NiNaph was not determined.

Hydropretreatment of Maya Residuum. Maya residuum (12 g) 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 wt% of gaseous products and a negligible amount of IOM (zero to 0.6 wt%, mainly 0.1-0.2 wt% 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 3 g Illinois No. 6 coal and 6 g 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% product recovery in which the oil fraction was determined by subtracting the other recovered fractions from 100%. 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.1.6).

Maya residuum pretreated under different conditions showed different activities in thermal coprocessing reactions. The THF soluble fractions of Maya residuum pretreated with active coprocessing catalysts, in situ generated Mo and Ni species, 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 VNaph species, showed low activity in converting coal (Table I.B.1.6). 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 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.1.7, the activity of pretreated Maya residuum for converting coal and upgrading coal products in the thermal coprocessing reaction was compared. 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 MoNaph and sulfur showed the greatest activity and Maya pretreated thermally without a catalyst showed the least activity.

The effect of prehydrotreated 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 were used and will be described later in this section.

Effect of Pretreated Maya Residuum on Thermal Hydrogenation of Illinois No. 6 Coal. Three types of thermal reactions were conducted with the THF-solubles fraction of Maya residuum pretreated with $NiMo/Al_2O_3$ catalyst: (1) a hydrogenation reaction with the pretreated Maya alone, (2) a coprocessing reaction with the pretreated Maya and Illinois No 6 coal under a hydrogen atmosphere, and (3) a coprocessing reaction with the pretreated Maya and Illinois No. 6 coal under a N_2 atmosphere. The overall product distribution based on the weight of each fraction extracted by hexane, toluene, and THF (oils, asphaltenes, preasphaltenes, and IOM) is summarized in Table I.B.1.8 using calculational method A.

The thermal hydrogenation of the THF solubles of the pretreated Maya alone (case 1) produced about 2.8 wt% gases, 76.7 wt% oil, 19.4 wt% asphaltenes, 0.7 wt% preasphaltenes and 0.4 wt% IOM. Compared to the original Maya (68.7 wt% oil, 31.1 wt% asphaltenes, and very little IOM), two-step hydrogenation (catalytically with $NiMo/Al_2O_3$ and then thermally) produced

more oil. But, at the same time, the two step thermal hydrogenation retrogressively produced an IOM fraction from the IOM-free reactant.

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

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

Analysis of Trace Metals in Tetrahydrofuran-Solubles Fraction of Pretreated Maya Residuum. The contents of Mo, Ni, and other trace metals in the THF-soluble fractions of Maya residuum, that were catalytically pretreated with Mo, Ni, or V naphthenate, were measured using

atomic absorption and/or atomic emission spectrometry. The vanadium content of the THF-soluble fractions of the Maya residuum could not be measured with the available instrumentation.

The original Maya residuum, that was reported to contain 118 ppm and 680 ppm V by Amoco Company, was shown to contain 240 ppm Ni and 4.1 ppm Mo (Table I.B.1.9). When Maya residuum was catalytically treated with Mo, Ni, and V and extracted by THF, each THF-soluble fraction of Maya showed higher concentrations of catalyst metal but lower concentrations of other metals. For example, THF-solubles of Maya pretreated with Mo catalyst contained less Ni (170 ppm) but more Mo (1084 ppm) than the original Maya. The THF solubles of Maya pretreated with Ni catalyst contained less Mo (2.7 ppm) but more Ni (650 ppm), and the THF solubles of Maya pretreated with V contained less Mo (2.0 ppm) and Ni (210 ppm).

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

Activity of Molybdenum, Nickel, and Vanadium Catalysts at Different Metal Loadings. In the first set of experiments, the effect of catalyst metal concentration on coal upgrading was examined with a mixture of Illinois No. 6 coal, Khafji residuum, and MoNaph and NiOct catalysts at concentrations of 150 to 3000 ppm metal. As shown in Table I.B.1.10, both Mo and Ni catalysts at concentrations of over 1500 ppm showed the same activity (coal conversion) for coprocessing as they did at concentrations of 3000 ppm. With MoNaph, a Mo metal loading of 300 ppm continued to show a relatively high activity (approximately 84%) for

coal conversion (3000 ppm Mo results in a coal conversion of approximately 85%) compared to thermal coprocessing with sulfur (approximately 56%). At 150 ppm Mo, a coal conversion of 76-78% was obtained. With NiOct, both 3000 and 1500 ppm Ni showed 78% or higher coal conversion.

In the second set of experiments, the effect of metal concentration on the activity of Mo and Ni naphthenate catalysts was tested with a mixture of Illinois No. 6 coal and Maya residuum. Hydrogenation reactions were performed using 150 to 300 ppm Mo or Ni metal loadings with MoNaph and NiNaph as the starting materials (see Table I.B.1.11). Even though the metal contents were lowered to approximately 300, 200, and 150 ppm, both the Mo and the Ni catalysts continued to perform nearly as well as those at 3000 ppm for both oil and asphaltene production and coal conversion. The results with lower metal contents showed, however, larger deviations in the product distributions and coal conversions than those with 3000 ppm metal loadings. Compared to the Mo and Ni coprocessing results at a concentration of 3000 ppm metal (approximately 67 and 83%, respectively), the coal conversions with Mo and Ni at 300 ppm were approximately 92% and 87%, respectively, and that with 160 ppm Mo was approximately 87% and that with 200 ppm Ni was approximately 80%. However, when 160 ppm Ni was used, the activity was markedly reduced to approximately 56% coal conversion.

The results of these two sets of experiments indicated that Mo and Ni, even at low metal loadings such as 160 ppm to 300 ppm, could be catalytically active enough to upgrade coal and residuum at 400 °C and high hydrogen pressure. The Mo and Ni contents in the THF solubles of pretreated Maya (1080 ppm Mo and 650 ppm Ni) were discussed earlier. The high activities of Mo and Ni catalysts observed at concentrations as low as 160 ppm indicated that the THF-soluble fraction of Maya pretreated with Mo or Ni could contain sufficient amounts of catalytic

species to catalyze the subsequent thermal coprocessing reaction with the pretreated Maya and Illinois No. 6 coal.

Analysis of Metal Content in Oil and Asphaltene Fractions of Pretreated Maya. As mentioned before, the THF-extracted fraction of the pretreated Maya residuum contained catalyst metals far in excess of 150 ppm. In this experiment, the pretreated Maya was further extracted, and the distributions of metals in different fractions were determined. Maya residuum was pretreated with Mo and Ni naphthenates and extracted with hexane (oil fraction), toluene (asphaltene fraction), and THF (preasphaltene fraction). Each hexane soluble fraction and each toluene soluble fraction were centrifuged twice to enhance the removal of possible colloidal suspensions of catalyst species. The catalytic species, Mo and Ni, were detected by graphite furnace atomic absorption spectrometry (for Ni) and inductively coupled argon plasma (for other trace metals) at concentrations of less than 1 to 20 ppm in the oil fractions, but at concentrations of several thousand ppm in the asphaltene fractions (see [illegible] I.B.1.12). Because the production of preasphaltenes from the pretreated Maya was alway[illegible]ble, the major fraction containing catalyst species was the asphaltene fraction. This result suggested that the test of the effect of hydrogenated Maya on thermal coal upgrading might be conducted only with the oil fraction from the pretreated Maya that was then compared in activity to the oil fraction of untreated Maya.

Structures of in situ Generated Molybdenum and Vanadium Sulfides. Catalytic species of Mo sulfide and V sulfide were produced in situ in the model hydrogenation reactions in the presence of excess sulfur for the analysis of the structural composition of metal sulfides by using X-ray diffraction. Mo and V sulfides were generated in situ from MoNaph and vanadium(III) acetylacetonate and vanadyl(IV) acetylacetonate with excess sulfur. Three Mo sulfide samples were prepared in situ from a model hydrogenation reaction at 380 °C with

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

Effect of Sulfur Amount on the Activity of Vanadium Catalyst. In spite of the appreciable activity of V species for upgrading of oil and coal reported in some patents,[3,4,5,6,7] in situ generated V catalytic species were proven in this work to be far less active for producing oil and asphaltenes from coprocessing reactions than Mo and Ni species. In Table I.B.1.13, the activities of V species including VNaph and a commercial powdered V_2S_3 catalyst are shown. In previous work on this subtask, V catalysts were shown to be far less active for coprocessing than either Mo or Ni catalysts, regardless of the type or amount of V catalyst.

The commercial powdered V_2S_3 catalyst showed higher activity for oil production and coal conversion compared to VNaph. But, when compared to the activity observed with Ni and Mo catalysts studied earlier, the activity of V_2S_3 for coal conversion and upgrading was still far lower.

The fact that the amount of sulfur may influence the activity of VNaph for coprocessing was based on information from a patent, which proposed an activity dependence of V on the H_2S partial pressure in oil hydrocracking processes.[8] About 0.59 g sulfur was added in a thermal coprocessing reaction and a catalytic coprocessing reaction with VNaph. This amount of S could theoretically produce about 12 to 15% H_2S in the gas phase. In the thermal reaction, this high

sulfur content increased coal conversion from 37% without sulfur to 56% with 0.584 g sulfur, but did not increase oil and asphaltene production at all. In the catalytic coprocessing reaction with VNaph, a high sulfur content (0.589 g sulfur, which was about 22 times the stoichiometric amount of sulfur required to produce V_2S_3) increased coal conversion to 66% as compared to 51% coal conversion with a much lower sulfur amount of 0.027 g sulfur. However, oil and asphaltene production was increased by only 2%. When compared to Ni and Mo catalysts, the activity of the V catalyst for coal coprocessing was still low, even under a high H_2S atmosphere. These results also suggested that V sulfide may not be an active coprocessing catalyst.

Size Exclusion Chromatographic Analysis of Coprocessing Products. Size exclusion chromatography was used to observe size changes in the products of coprocessing reactions with Maya residuum and Illinois No. 7 coal under different reaction conditions. Molecular size distributions in the oil, asphaltene, and preasphaltene fractions from each coprocessing reaction were compared with each other and also with those obtained under different reaction conditions. A properly selected UV wavelength for the detector produced a proportional response for the different compounds during quantitative analysis. A fixed wavelength of 254 nm, commonly used in asphalt and coal studies, was used. To reduce the possible self-assembling effect of the molecules, which may occur at low temperature in the carrier solvent (THF), the size exclusion chromotography column was operated at 50 °C, which is lower than the boiling point of THF. The intensity curve (corresponding to the UV absorbance) of the eluting fraction was smoothed to reduce noise. The starting and ending times of elution, the maximum eluting position, and the shape of broadness of the size distribution for each sample were compared.

First, the column was calibrated and its resolution was determined by analyzing the position and the shape of peaks from polystyrene standard samples of different molecular weights,

and from aromatic chemicals, such as naphthalene, anthracene, and pyrene (Table I.B.1.14). As shown in Figure I.B.1.1, the column separated different size molecules.

Second, the molecular size distributions of the oil, asphaltene, and preasphaltene fractions of each coprocessing reaction were determined. Figure I.B.1.2 shows an example of the molecular size distribution in three different fractions from the Illinois No. 6 coal-Maya residuum coprocessing reaction with NiNaph. The maximum peak elution times for the extracted fractions were in the order, preasphaltenes < asphaltenes < oil. In addition, compared to the oil and the asphaltenes peak, the preasphaltenes peak showed a steep ascending slope, possibly indicating that the preasphaltenes contained a greater portion of large size molecules than the other fractions.

The molecular size distribution of each fraction produced under different conditions was compared (Figure I.B.1.3, I.B.1.4, and I.B.1.5). Compared to the oil and asphaltene fractions of the original coal-Maya coprocessing reaction, the same fractions from thermal and catalytic coprocessing products showed broader molecular size distributions. These broad distributions, both in the large molecular size range and in the small molecular size range, indicated that the coprocessing reactions produced smaller sized products by hydrocracking, and perhaps, some larger sized products by recombination of several molecules. Regardless of the different reaction conditions, each fraction of oil, asphaltenes and preasphaltenes for the thermal and catalytic reactions showed a similar molecular size distribution. Preasphaltenes possessed more large molecules, and hence, showed earlier elution of the maximum peak position than asphaltenes. Asphaltenes possessed more large molecules than oil. The oil fractions showed a more symmetrically shaped distribution than the asphaltene and preasphaltene fractions.

To compare quantitatively the molecular size distribution of each product, the size exclusion chromotography curve was sliced into several regions as shown in Figure I.B.1.6, and

the area of each slice was calculated. The area of each slice is not directly proportional to the amount of compounds eluting in a region because of differences in UV response to different compounds. For example, alkanes show nearly negligible response regardless of their molecular size; however, aromatic compounds show high intensity responses even though they are small in size or few in number. Because aromatic compounds are the major components in coal-residuum coprocessing, the area of each slice was assumed to be proportional to the concentration of the components in that area and was used directly for comparison of molecular size distributions.

Two sets of experiments were compared separately because an appreciable change of the size exclusion chromotography operating pressure was found in two experimental sets conducted at different times. The increase of the operating pressure by about 200 psi may have occurred because of a gradual column plugging (mainly in the 50 Å pore size column) by large molecules in the samples. The initial elution time, the peak width, and the area of each slice were compared for each case (Tables I.B.1.15 and I.B.1.16). In the comparison of oil fractions, the VNaph catalyst was the most active for producing more small molecular components and fewer large molecular components for the different reactions shown. In the asphaltene fraction, the fractions produced by Ni and V catalysts contained more small molecular components than did the other cases. However, overall differences in size distributions of all three fractions obtained from different coprocessing reactions were not observed. In general, the asphaltene fractions of all coprocessing reactions showed the most appreciable change in peak shape, peak width and area distribution from those of the reactant (original). These differences indicated that the coprocessing reactions produced a broad range of small and large size toluene-soluble aromatic compounds from coal.

The difference in each molecular-size distribution was interpreted using the terms defined in Figure I.B.1.7. The area ratio of A_S/A_L (A_S: an area for the components smaller than the polystyrene of molecular weight 800; A_L: an area for the components larger than the polystyrene 800) indicated the relative amount of small components produced. The ratio of peak widths, D_s/D_l (D_s: a peak width between a point on the descending curve and the mean retention time, at the maximum peak position, D_l: a peak width between the mean retention time and a point on the ascending curve) represented both the relative amount of small components to large components produced and the peak shape. Compared to the reactant, the oil fraction from coprocessing reactions produced appreciable amounts of small components with the possible exception of MoNaph (Tables I.B.1.17 and I.B.1.18). When the asphaltene fractions are compared, Ni and V catalysts produced appreciable amounts of small components smaller than the polystyrene 800. In the preasphaltene comparison, most coprocessing reactions produced less A_S/A_L than the reactant, indicating that coprocessing converted coal to small size molecules which were soluble in THF, but were larger than the polystyrene 800 in size.

X-Ray Diffraction of In Situ Generated Molybdenum Sulfide. The sample (1) of in situ generated Mo sulfide, which was recovered from the reaction at 380 °C for 30 min using a copper sealant for the tubular microreactor, showed an X-ray powder diffraction pattern with several broad peaks and many sharp peaks. By matching the line positions with X-ray powder diffraction files,[9,10] the major sharp peaks appeared to represent an impurity, $CuSO_4.5H_2O$, which was produced in situ from the copper sealant for the tubular microreactor and the added sulfur. After the subtraction of impurity peaks, only broad peaks remained for the X-ray pattern shown in Table I.B.1.19.

Sample (2), which was prepared at a higher reaction temperature for a longer time without a copper sealant, also showed a very similar X-ray powder pattern to sample (1), but without the sharp peaks for $CuSO_4.5H_2O$. By comparing the X-ray diffraction pattern for sample (2) to the X-ray diffraction pattern of the commercial MoS_2, which was most likely MoS_2-2_1, and the X-ray powder diffraction file, the line positions of the broad peaks indicated that MoS_2-3R was the post plausible structure for the in situ generated Mo-sulfur compound.

Even though the X-ray powder diffraction patterns of the in situ generated Mo sulfide were not as sharp and conclusive as the commercial MoS_2, two different X-ray spectrometers produced the same diffraction patterns for the differently prepared Mo samples. The low intensity, broad XRD peaks observed for the in situ generated molybdenum species are thought to be caused by the presence of microcrystalline MoS_2 which had limited opportunity to grow larger because of the short, high temperature reaction conditions used. The low intensity of the peaks for the in situ generated species is also thought to be associated with the formation of microcrystalline MoS_2; microcrystals do not contain sufficient numbers of crystalline layers to produce diffraction patterns having intense peaks. The results may indicate that a microcrystalline form of MoS_2, having both a large unit surface and a high mobility resulting in high catalytic activity, is produced during the in situ reaction of MoNaph with excess sulfur.

CONCLUSIONS

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

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

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 prehydrotreated thermally and catalytically with naphthenates of Mo, Ni, and V. THF solubles of pretreated Maya were used in the thermal coprocessing reactions. The Maya residuum prehydrotreated with MoNaph and NiNaph converted more coal and upgraded more coal products to the lighter fractions than did Maya prehydrotreated with VNaph or without a catalyst. THF solubles of Maya prehydrotreated with naphthenates of Mo or Ni contained more oil than THF solubles of Maya prehydrotreated with VNaph 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 prehydrotreated with V or without a catalyst.

Mo and Ni (from MoNaph and NiNaph) even at low metal loading levels, such as 160 and 300 ppm, were quite active for producing oil and asphaltenes and for converting coal in coprocessing. They were nearly as active as those at concentrations of 3000 ppm and more active than the $NiMo/Al_2O_3$ commercial catalyst and V catalysts at 3000 ppm metal concentrations. The metal concentrations in the THF solubles of the Maya residuum pretreated with these metals were far higher than 200 ppm (more than 1000 ppm Mo and 650 ppm Ni). Therefore, the high activities observed for the pretreated Maya (THF-soluble fraction) for the subsequent thermal

coprocessing reactions were probably caused by the presence of these catalyst species remaining in the THF-soluble fractions.

The trace metal analysis of the fractionated pretreated Maya residuum showed that the oil fraction contained low concentrations of metals but that the asphaltene fraction contained high concentrations of metals. Therefore, the oil fraction of pretreated Maya could be used to test the effect of hydrogenated residuum on coal upgrading.

The activity of the V catalyst (from VNaph) was slightly increased by an increase in the amount of sulfur present, and V was more active only for IOM conversion to preasphaltenes than was the thermal reaction in which the same amount of sulfur was utilized. However, the activities of V catalysts were still far lower than the activities of the Ni and Mo catalysts.

A commercial V_2S_3 catalyst was more active for coal and residuum upgrading than were in situ generated V catalysts. However, the V_2S_3 catalyst was also less active for oil and asphaltene production than were NiMo, Ni, or Mo catalysts. Therefore, it was confirmed that the activities of V catalysts for coprocessing were far lower than Mo and Ni catalysts, regardless of the V species and the H_2S partial pressure. In fact, the activities of V catalysts were generally equal to or only slightly higher than the activities of thermal coprocessing reactions (without catalysts).

Even though the analysis of the coprocessing products using size exclusion chromotography showed some differences for different reaction conditions, the large differences expected for coprocessing reaction conditions which previously produced large differences in product quantity and quality were not observed using size exclusion chromotography to date. The size exclusion chromotography analysis showed consistent differences in the molecular size distributions for oil, asphaltene and preasphaltene fractions regardless of the reaction condition.

Because the same quantities of different components show different UV responses, the absolute amount of components for a specific molecular size produced from coprocessing reactions could not be determined exactly. In order to understand the activity and selectivity of different catalysts for coprocessing, further refinement of the size exclusion chromotography technique and the development and application of new analytical methods, which can measure the amount of heteroatoms, aromatic components, and upgraded coal molecules of a specific size or weight, is required.

The Mo species generated in situ under different reaction conditions showed the same X-ray powder diffraction patterns. Even though the diffraction peaks were broad, the peak positions and the ratios of their intensities showed that MoS_2-3R was a plausible structure for the in situ generated Mo sulfide. The broad peaks in the X-ray diffraction suggested that the in situ generated Mo sulfide consisted of very small crystals which were not well-grown during the reaction period and smaller than the optimal crystal size for X-ray diffraction analysis. This hypothesis is consistent with former results for the in situ generated Mo sulfide, which had a larger unit surface area and a higher catalytic activity for hydrogenation of model compounds than the MoS_2 prepared by precipitation methods.[11,12]

NOMENCLATURE

IOM	=	insoluble organic matter	THF	=	tetrahydrofuran
MoNaph	=	molybdenum naphthenate	VNaph	=	vanadium naphthenate
NiNaph	=	nickel naphthenate			

REFERENCES

1. Curtis, C. W.; Tsai, K. J.; Guin, J. A. *Fuel Proc. Tech.*, *16*, 71 (1987).

2. Curtis, C. W.; Cassell, F. N. *Energy and Fuels*, *2*, 1 (1988).

3. Gleim, W.K.T., et al. U.S. Patent 3,161,585 (1965).

4. Gleim, W.K.T., et al. U.S. Patent 3,252,895 (1966).

5. Herbstman S. U.S. Patent 4,125,455 (1978).

6. Aldridge, C.L., et al. U.S. Patent 4,298,454 (1981).

7. Gatsis, J.G. U.S. Patent 4,394,248 (1983).

8. Gatsis, J.G. U.S. Patent 3,915,842 (1975).

9. Berry, L.G. et al. "Powder Diffraction File Search Manual, Hanawalt Method, Inorganic Volume;" Joint Committee on Powder Diffraction Standards: Philadelphia (1967a).

10. Berry, L.G. et al. "Powder Diffraction File, Inorganic Volume;" Joint Committee on Powder Diffraction Standards: Philadelphia (1967).

11. Pellegrino, J.L. Master's Thesis, Auburn University, AL (1987).

12. Curtis, C. W.; Pellegrino, J.L. *Energy Fuels*, *3*, 160-168 (1989).

Table 1.B.1.1. Characterization of Maya and Khafji Residuum and Illinois No. 6 Coal

	Maya	Khafji	Illinois No. 6 Coal	
			Amoco	Auburn
Moisture (wt%)	0.0	0.0	7.5	6.3
Ash (wt%)	0.0	0.0	8.27	9.8
C (wt%)	83.7	83.8	68.67	
H (wt%)	9.76	10.2	4.49	
S (wt%)	5.4	5.4	0.94	
N (wt%)	ND[1]	ND	1.61	
O (wt%)	ND	ND	8.14	
Ni (ppm)	118	52	9,100	
V (ppm)	680	170	43,000	
Fe (ppm)	ND	ND	40,000	
Co (ppm)	ND	ND	3,600	

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

Table 1.B.1.2. Fractionated Maya and Illinois No. 6 Coal

(a) Maya[1]					
	Extracted Products (wt%)				
Sample No.	Oil	Asp	Preasp	IOM	Recovery (%)
1.	68.7	30.9	0.0	0.4	104.8
2.	68.7	31.2	0.0	0.1	104.0
Average	68.7±0.0	31.1±0.2	0.0±0.0	0.2±0.2	
(b) Mixture of Maya and Illinois No. 6 Coal[2]					
	Extracted Products (wt%)*				
Sample No.	Oil	Asp	Preasp	IOM	Recovery (%)[4]
3.	46.7	23.5	1.7	28.1	101.8
4.	46.0	23.9	1.5	28.6	101.2
Average	46.4±0.3	23.7±0.2	1.6±0.1	28.3±0.2	
(c) Calculated Fractions in Illinois No. 6 Coal[3]					
	Extracted Products (wt%)*				
Sample No.	Oil	Asp	Preasp	IOM	Recovery (%)[4]
3.	0.0	7.2	5.2	87.6	104.3
4.	0.0	6.3	4.8	88.9	103.7
Average	0.0	6.8±0.5	5.0±0.2	88.2±0.7	

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

Table 1.B.1.3. Extracted Fractions of Illinois No. 6 Coal[1]

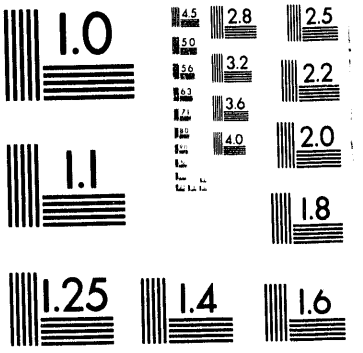
Extraction System	Extracted Products from Coal (wt%)*			
	Oil	Asp	Preasp	IOM
Coal[2]	0.0±0.0	0.1±0.05	6.7±0.5	93.2±0.6
Coal-Khafji Mixture[3]	2.3±1.1	3.9±0.8	6.3±0.1	87.5±0.5
Coal-Maya Mixture	0.0±0.0	4.3±0.4	5.1±0.3	90.5±0.6

[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.
*Asp = asphaltenes; Preasp = preasphaltenes

Table 1.B.1.4. Hydrogenation of Illinois No. 6 Coal in Hexadecane[1]

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

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


1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
6.3
3.6
4.0
2.0
1.1
1.8
1.25
1.4
1.6

2 of 3

Table 1.B.1.5. Coprocessing of Maya and Illinois No. 6 Coal

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

[1]No extra sulfur.
[2]Additional sulfur as much as required to produce metal sulfide: S = 0.19 g for MoS_2, S = 0.10 g for Ni_3S_2, and S = 0.027g for V_2S_3.
Asp = asphaltenes; Preasp = preasphaltenes; IOM = insoluble organic matter

Table 1.B.1.6. 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 using overall products obtained from a mixture of coal and pretreated Maya. Asp = aphaltenes, Preasp = preasphaltenes, IOM = insoluble organic matter.
[2]Toluene solubles (oil and asphaltenes).
[3]No additional sulfur.
[4]Additional sulfur as much as required to produce metal sulfide in situ in the pretreatment of Maya residua (12 g): S=0.024 g for MoS_2, and S = 0.034 g for V_2S_3.

Table 1.B.1.7. 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).
[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).
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 in situ in the pretreatment of Maya residuum (12 g); S=0.024 g for MoS_2, S=0.013 g for Ni_3S_2, and S=0.034 g for V_2S_3.

Table I.B.1.8. Thermal Reactions of Maya Pretreated with a $NiMo/Al_2O_3$ Catalyst

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

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

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

3 NC = not calculated.

Table I.B.1.9. Metal Concentrations in Catalytically Pretreated Maya[1]

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

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

Table I.B.1.10. Effect of Catalyst Loading Amount on Coprocessing of Khafji and Illinois No. 6 Coal

Reaction Condition (ppm)	S (g)	H_2 Used (%)	Product Distribution (wt%)					Coal Conversion (%)
			Gas	Oil	Asp	Preasp	IOM	
MoNaph[a]								
3000	0.057x3	25	2.3±0.7	61.8±1.2	22.3±1.9	9.6±0.6	4.0±2.0	86.4±6.7
1500	0.028x3	26	2.3±0.1	61.8±0.5	22.6±0.3	9.3±1.1	4.0±1.9	86.4±6.4
900	0.017	25	1.8	60.1	19.6	13.6	4.9	83.8
300 to ~350	0.018	20	2.0±0.4	59.7±0.1	17.7±0.1	15.8±0.2	4.8±0.4	84.2±6.2
180	0.019	14	2.1	55.8	18.2	16.8	7.1	75.8
160	0.019	14	2.1	58.7	18.2	14.3	6.7	78.1
NiOct[b]								
3000	0.031x3	12	1.9±0.0	61.6±0.3	18.4±0.3	11.6±0.4	6.5±0.1	78.0±0.4
1500	0.015x3	17	2.3±0.2	59.7±0.2	19.0±0.3	15.1±0.2	3.9±0.6	87.2±1.9
1500	0	23	2.6	59.1	18.8	16.4	3.1	89.8
800	0.009	19	1.6	58.6	19.5	15.4	4.9	83.7
NiMo/Alumina								
3000	0	18	2.6±0.2	58.3±0.3	17.4±0.2	10.2±0.3	11.5±0.2	61.9±0.6
1500	0	16	2.6±0.2	56.2±0.2	16.7±0.1	11.9±0.3	12.6±0.4	58.3±0.8

[a]MoNaph = Mo naphthenate
[b]NiNaph = Ni naphthenate

Table I.B.1.11. Effect of Catalyst Loading Amount on Coprocessing of Maya and Illinois No. 6 Coal

Reaction Condition (ppm)	S (g)	H_2 Used (%)	Product Distribution (wt%)					Coal Conversion (%)
			Gas	Oil	Asp	Preasp	IOM	
Reactants		0	0	46.4±0.3	23.7±0.2	1.6±0.1	28.3±0.2	
Thermal	0	9	2.4±0.1	49.9±0.6	18.7±0.4	9.9±0.2	19.1±0.1	37.4±0.2
MoNaph[a]								
3000	0.019	20	2.2±0.2	56.7±0.1	23.7±0.1	7.0±0.1	10.4±0.1	66.9±0.1
340	0.022	20	3.5	55.5	21.4	16.9	2.7	
220	0.004	17	1.9	54.9	20.1	16.0	7.1	91.7
160	0.020	19	2.8	54.1	20.7	18.1	4.3	77.0
								86.7
NiNaph[b]								
3000	0.010	21	2.6±0.1	51.1±1.7	23.1±1.4	17.8±1.0	5.3±1.2	82.8±4.1
340	0.018	17	2.7	54.4	20.4	18.3	4.2	
220	0.018	23	3.0	53.1	20.1	17.7	6.1	86.8
160	0.003	16	2.1	53.0	19.7	11.9	13.3	80.4
								56.2

[a]MoNaph = Mo naphthenate
[b]NiNaph = Ni naphthenate

Table I.B.1.12. Metal Contents in Catalytically Pretreated Maya[1]

Metal (ppm)	Original Maya		Pretreated Maya					
			with MoNaph[4]			with NiNaph[5]		with NiMo[6]
	Oil	Asp	Oil-T	Oil-B	Asp-T	Oil-T	Asp-T	THF-solubles
Mo	-0.2	12.0	0.4	0.7	1900.7	2.1	6.4	8.2
Ni	170	98	5	5	90	19	3550	26
Ca	47.2	15.4	57.9	53.7	25.6	65.8	12.5	60.9
K	-5.9	-3.0	-10.6	-4.5	0.7	1.2	7.1	-7.6
Mg	5.3	2.2	0.5	1.3	5.5	1.7	5.2	0.3
P	-8.9	2.4	-6.0	-4.3	18.5	-2.1	9.2	-4.2
Cu	-0.2	3.9	0.2	0.2	31.6	1.0	50.8	8.8
Fe	0.9	116.0	-2.6	-0.3	234.5	4.8	142.0	16.8
Mn	-0.4	0.0	0.3	0.0	1.3	0.4	0.8	0.0
Zn	-0.1	2.5	0.7	0.5	2.6	-0.1	16.5	0.0
Al	-145.0	21.8	-27.4	-40.8	57.5	-49.8	23.7	-148.0
Ba	0.1	0.0	0.1	0.2	0.1	0.0	0.1	-0.1
Co	-0.2	0.0	-0.3	0.0	1.2	0.0	10.2	-0.1
Cr	2.8	57.5	-0.7	0.2	87.1	1.0	56.1	7.6
Pb	-1.3	-0.7	-1.6	-0.5	6.2	-0.3	8.8	-1.3
Si	-6.0	3.2	-2.4	-1.2	8.7	-1.3	5.6	-6.9

[1]Negative values were obtained by the subtraction of reference from samples.
[2]Asp: asphaltenes; Oil-T: oil from top portion; Oil-B: oil from bottom portion; Asp-T: asphaltenes from top portion
[3]The metal content was measured based on the amount of each fraction, such as oil and asphaltenes, not on the amount of whole products. The numbers can be compared with those in THF-solubles reported last quarter only when being recalculated using a same weight basis.
[4]MoNaph = Mo naphthenate
[5]NiNaph = Ni naphthenate
[6]NiMo = NiMo/Alumina

Table I.B.1.13. Coprocessing of Maya and Illinois No. 6 Coal with V Catalyst

Reaction Condition	S (g)	H_2 Used (%)	Product Distribution (wt%)					Coal Conversion (%)
			Gas	Oil	Asp	Preasp	IOM	
Reactants		0	0	46.4±0.3	23.7±0.2	1.6±0.1	28.3±0.2	
Thermal	0	9	2.4±0.1	49.9±0.6	18.7±0.4	9.9±0.2	19.1±0.1	37.4±0.2
Thermal	0.584x22	0	0.1	48.4	18.9	18.6	14.0	55.7
VNaph[a] 3000 ppm	0.027	12	4.0±0.1	45.6±0.3	21.5±0.6	13.4±0.4	15.5±0.3	50.7±1.4
VNaph 3000 ppm	0.589x22	0	2.0	46.5	22.9	17.8	10.8	65.5
VNaph 470 ppm	0.020	0	2.2	49.2	17.7	12.8	18.1	42.1
V_2S_3 3000 ppm V	0	5	2.0±0.1	51.0±0.1	17.9±0.1	14.8±0.8	14.3±0.9	53.1±2.8
V_2S_3 3000 ppm V	0.028	11	2.0	52.4	17.9	16.2	11.5	62.4
$NiMo/Al_2O_3$ 3000 ppm Ni+Mo	0	19	2.3±0.2	52.2±3.2	24.3±2.2	11.0±0.5	10.2±1.2	67.7±3.5

[a]VNaph = Vanadium naphthenate

Table I.B.1.14. Retention Time and Peak Width of Reference Samples in Size Exclusion Chromatography (SEC)[a]

Polystyrene or Aromatics	Molecular Weight (Mw)	Molecular Weight Distribution (Mw/Mn)	Approx. Mean Retention Time, sec.	Approx. Initial Elution Time, sec.	Approx. Peak Width[b], sec.
Polystyrene (PS)					
PS-A	111,000	≤ 1.00	1220	1175	164
PS-B	33,000	≤ 0.92	1253	1199	178
PS-C	20,800	≤ 1.03	1276	1224	178
PS-D	4,000	≤ 1.29	1409	1343	242
PS-E	2,100	≤ 1.08	1442	1356	254
PS-F	1,574	≤ 1.06	1530	1430	265
PS-G	1,152	≤ 1.07	1569	1473	277
PS-H	800	≤ 1.20	1671	1578	288
PS-I	568	≤ 1.13	1717	1570	471
Pyrene	202	-	2378	2330	220
Anthracene	178	-	2312	2240	455
Naphthalene	128	-	2366	2314	202

[a] Samples were dissolved in tetrahydrofuran at levels of 0.1 wt% of polystyrene and 0.2 wt% of aromatics. Each sample was analyzed under the following HP-GPC condition: Styragel size exclusion columns in series (500-100-100-50 Å), 50°C column temperature, 1 ml/min flow rate of a carrier (Tetrahydrofuran), and UV detection with a fixed wave length at 254 nm.

[b] Peak width between the points where the intensities of UV absorption at the ascending and descending curves were 20% of the intensity at the maximum peak position (mean retention time).

Table I.B.1.15. Comparison of Molecular Size Distribution of Coprocessing Products - Set A

Reaction Condition and Product	Initial Elution Time[b] (min)	Peak Width[b] (min)	Molecular Size Distribution (area %)			
			Slice 1-3	Slice 4-6	Slice 7-9	Slice 10-12
Oil						
Reactant	22.0	14.5	17.4	56.2	23.8	2.6
Thermal	23.2	16.8	6.3	45.7	32.9	15.1
MoNaph	22.7	17.1	11.2	48.2	28.7	11.9
NiNaph	22.6	18.0	8.8	44.2	31.8	15.2
VNaph	22.9	17.8	6.3	41.3	34.5	17.9
$NiMo/Al_2O_3$	22.9	17.6	7.1	44.1	33.5	15.3
Asphaltenes						
Reactant	20.6	13.6	53.1	36.5	10.4	0.0
Thermal	21.8	15.4	31.1	43.6	21.5	3.8
MoNaph	21.8	15.5	30.6	44.4	21.0	4.0
NiNaph	21.5	18.3	19.2	42.4	29.5	8.9
VNaph	21.4	18.1	21.5	43.0	27.5	8.0
$NiMo/Al_2O_3$	21.4	17.7	22.8	43.5	26.6	7.1
Preasphaltenes						
Thermal	20.6	22.6	21.9	31.0	23.3	23.8
MoNaph	20.9	20.3	31.6	35.9	19.4	13.1
NiNaph	21.1	17.4	33.0	41.4	19.6	6.0
VNaph	20.6	20.3	28.4	38.4	22.8	10.4
$NiMo/Al_2O_3$	20.9	18.7	28.5	40.9	22.3	8.3

[a] Reactant (mixture of Maya and Illinois No. 6 Coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph, and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni, and V).

[b] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10% of the intensity at the maximum peak position (mean retention time). Initial elution time at the point where the UV intensity was 10% of that at the mean retention time.

Table I.B.1.16. Comparison of Molecular Size Distribution of Coprocessing Products - Set B

Reaction Condition and Product	Initial Elution Time[b] (min)	Peak Width[b] (min)	Molecular Size Distribution (area %)			
			Slice 1-3	Slice 4-6	Slice 7-9	Slice 10-12
Oil						
Reactant	22.1	14.4	16.5	57.3	23.9	2.3
Thermal	23.0	18.2	6.1	42.3	33.1	18.5
MoNaph	22.6	18.2	8.0	42.4	33.0	16.6
NiNaph	22.7	17.8	8.6	44.4	31.9	15.1
VNaph	23.2	17.7	4.8	40.2	35.7	19.3
$NiMo/Al_2O_3$	22.8	17.5	7.1	43.4	33.7	15.8
Asphaltenes						
Reactant	20.5	13.6	50.8	28.0	11.2	0.0
Thermal	20.8	18.8	29.4	41.2	22.3	7.1
MoNaph	21.4	18.5	24.9	44.8	22.6	7.7
NiNaph	21.3	18.7	20.9	42.5	27.8	8.8
VNaph	21.5	17.8	21.4	43.1	27.3	8.2
$NiMo/Al_2O_3$	21.6	18.4	18.7	43.4	28.6	9.3
Preasphaltenes						
Thermal	20.2	19.5	35.3	32.8	21.1	10.8
MoNaph	20.5	18.1	33.5	40.3	18.8	7.4
NiNaph	20.5	18.4	35.2	39.8	19.1	5.9
VNaph	20.7	19.0	30.6	38.1	22.6	8.6
$NiMo/Al_2O_3$	20.6	17.8	34.6	40.5	19.2	5.7

[a] Reactant (mixture of Maya and Illinois No. 6 Coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph, and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni, and V).

[b] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10% of the intensity at the maximum peak position (mean retention time). Initial elution time at the point where the UV intensity was 10% of that at the mean retention time.

Table I.B.1.17. Comparison of Size Exclusion Chromatographic Analysis of Coprocessing Products - Set A

Reaction Condition and Product Fractions[a]	Mean Retention Time (min)	Area Ratio of A_S/A_L [b]	20% Cut[c]			66.7% Cut[c]		
			Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l [d]	Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l [d]
Oil								
Reactant	27.4	0.97	22.5	11.8	1.42	24.4	5.8	0.89
Thermal	28.2	2.26	23.6	15.5	2.42	25.4	6.8	1.43
MoNaph	27.0	1.58	23.1	15.3	2.93	24.7	6.2	1.71
NiNaph	27.9	2.05	23.1	16.0	2.30	25.1	7.3	1.54
VNaph	28.5	2.62	23.5	15.9	2.19	25.5	8.0	1.68
$NiMo/Al_2O_3$	28.2	2.24	23.4	15.6	2.25	25.4	7.2	1.54
Asphaltenes								
Reactant	23.1	0.27	20.9	10.1	3.65	21.7	3.9	1.73
Thermal	24.0	0.70	22.0	12.9	5.40	22.8	4.9	2.97
MoNaph	24.1	0.71	22.0	12.5	5.22	22.9	4.7	3.21
NiNaph	27.5	1.32	21.8	15.7	1.76	23.1	9.5	1.17
VNaph	26.0	1.14	21.8	15.3	2.65	23.0	9.0	1.98
$NiMo/Al_2O_3$	25.9	1.07	21.7	15.1	2.55	22.8	9.2	1.86
Preasphaltenes								
Thermal	23.8	1.32	21.1	19.6	6.17	22.2	10.5	5.48
MoNaph	23.5	0.82	21.0	16.7	5.62	22.3	5.5	3.33
NiNaph	24.1	0.68	21.4	13.5	3.97	22.5	5.7	2.49
VNaph	23.6	0.93	21.0	16.8	5.54	22.2	8.1	4.99
$NiMo/Al_2O_3$	24.0	0.86	21.2	15.7	4.61	22.4	7.5	3.75

[a] Reactant (mixture of Maya and Illinois No. 6 Coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni, and V).

[b] Ratio of the area for small size components eluted before 1670 seconds (A_S) to that for large size components eluted after 1670 seconds (A_L). The areas were counted between 10% cut points[c] and 1670 seconds.

[c] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10, 20 or 66.7% of the intensity at the maximum peak position (mean retention time).

[d] Ratio of the molecular size distribution for small size components (D_s) eluted before the mean retention time (MRT) to that for large size components (D_l) eluted after MRT.

Table I.B.1.18. Comparison of Size Exclusion Chromatographic Analysis of Coprocessing Products - Set B

Reaction Condition and Product Fractions[a]	Mean Retention Time (min)	Area Ratio of A_S/A_L[b]	20% Cut[c]			66.7% Cut[c]		
			Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]	Initial Elution Time (min)	Peak Width (min)	Width Ratio of D_s/D_l[d]
Oil								
Reactant	27.2	0.98	22.6	11.6	1.56	24.5	5.7	1.10
Thermal	28.1	2.54	23.5	16.6	2.60	25.5	7.3	1.79
MoNaph	28.2	2.03	23.2	16.0	2.20	25.0	7.2	1.29
NiNaph	27.7	2.01	23.2	15.8	2.50	25.0	7.3	1.71
VNaph	29.2	2.95	23.8	15.8	1.91	25.8	8.1	1.34
$NiMo/Al_2O_3$	28.4	2.28	23.4	15.7	2.13	25.3	7.7	1.48
Asphaltenes								
Reactant	23.1	0.30	20.9	10.7	3.86	21.6	4.4	2.09
Thermal	25.0	0.83	21.0	15.2	2.85	22.2	8.2	1.91
MoNaph	24.7	0.91	21.7	13.9	3.69	22.9	7.4	3.10
NiNaph	27.8	1.21	21.7	15.5	1.56	23.0	9.3	0.92
VNaph	25.8	1.13	21.8	15.2	2.84	23.0	8.7	2.18
$NiMo/Al_2O_3$	27.5	1.30	22.0	15.4	1.80	23.3	8.9	1.13
Preasphaltenes								
Thermal	23.0	0.80	20.5	17.3	5.79	21.5	6.2	3.02
MoNaph	23.7	0.68	21.0	15.6	4.85	22.4	5.9	3.49
NiNaph	23.6	0.65	20.8	14.6	4.14	21.9	6.6	2.88
VNaph	23.7	0.85	21.0	15.9	4.75	22.1	7.5	3.59
$NiMo/Al_2O_3$	23.7	0.65	21.0	13.9	4.34	22.1	6.4	3.03

[a] Reactant (mixture of Maya and Illinois No. 6 Coal), Thermal (products from thermal coprocessing), MoNaph, NiNaph and VNaph (products from catalytic coprocessing with naphthenate of Mo, Ni, and V).

[b] Ratio of the area for small size components eluted before 1670 seconds (A_S) to that for large size components eluted after 1670 seconds (A_L). The areas were counted between 10% cut points[c] and 1670 seconds.

[c] Peak width between the points where the intensities of UV absorption at both the ascending and descending curves were 10, 20 or 66.7% of the intensity at the maximum peak position (mean retention time).

[d] Ratio of the molecular size distribution for small size components (D_s) eluted before the mean retention time (MRT) to that for large size components (D_l) eluted after MRT.

Table I.B.1.19. X-Ray Powder Diffraction Data for Molybdenum Sulfide and Copper Sulfate

Mo Sulfide Sample		Molybdenite $2H_1$				Molybdenite 3R		$CuSO_4 5H_2O$[e]	
D(Å)	I/Io[b]	D(Å)	I/Io[c]	D(Å)	I/Io[d]	D(Å)	I/Io[e]	D(Å)	I/Io[b]
7.69	23	6.145	100	6.146	100	6.145	100	10.4	5
6.80	20	2.742	6	3.072	2	2.712	23	5.73	35
6.55	20*	2.676	32	2.742	8	2.628	21	5.68	20
6.32	20	2.504	12	2.676	43	2.356	27	5.48	55
5.71	39	2.279	43	2.504	16	2.200	27	5.21	9
5.48	45	2.046	14	2.279	61	2.048	4	5.15	25
5.21	33	1.830	16	2.048	6	1.899	14	4.84	10
4.72	100	1.641	2	2.046	17	1.764	8	4.73	100
4.65	31	1.583	10	1.830	26	1.583	10	4.66	20
3.99	58	1.536	4	1.641	3	1.523	8	4.28	13
3.70	56	1.533	8	1.583	17	1.533	6	4.00	11
3.54	25	1.479	3	1.536	5	1.530	2	3.99	60
3.46	32			1.533	11	1.430		3.71	85
3.30	42			1.479	6			3.54	20
3.25	31							3.45	17
3.04	24							3.83	34
2.83	34							3.30	60
2.75	60							3.26	20
2.73	45							3.18	17
2.71	35							3.06	15
2.70	44							3.05	30
2.68	38*							2.90	11
2.66	66							2.82	40
2.64	32							2.79	20
2.63	33							2.75	50
2.61	30							2.72	15
2.59	45							2.66	40
2.56	33								
2.55	30								
2.42	22								

[a] Mo sample was generated in situ from a hydrogenation reaction of Indole with Mo naphthenate and excess sulfur (with a Cu sealant).

[b] Relative intensity

[c] Calculated pattern using a peak height (1,2)

[d] Calculated pattern using an integrated area (1,2)

[e] X-ray pattern data (1,2)
Maximum peak position of major broad peaks: d = 6.6, 2.67, 2.3, 2.025, 1.567

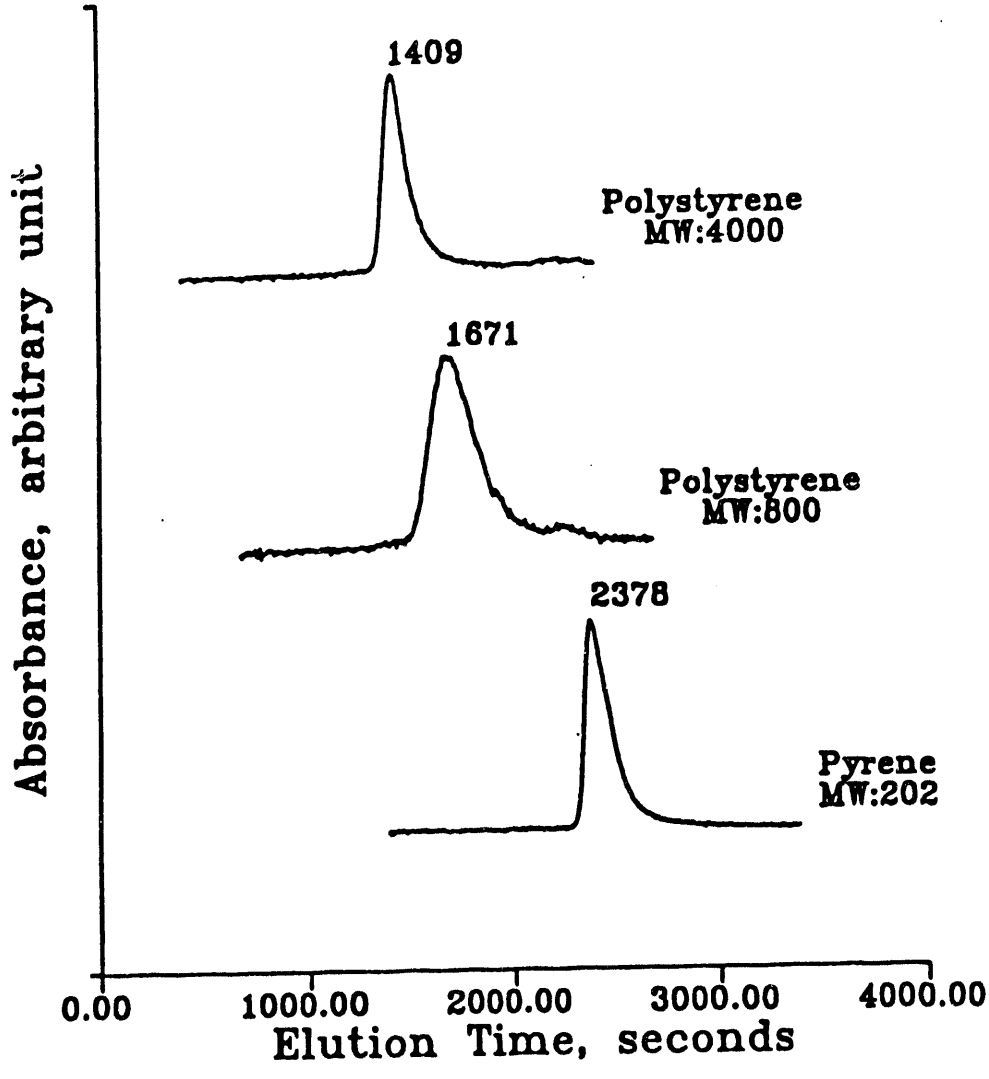


Figure I.B.1.1. **Size Exclusion Chromatogram of Different Molecular Weight Compounds**

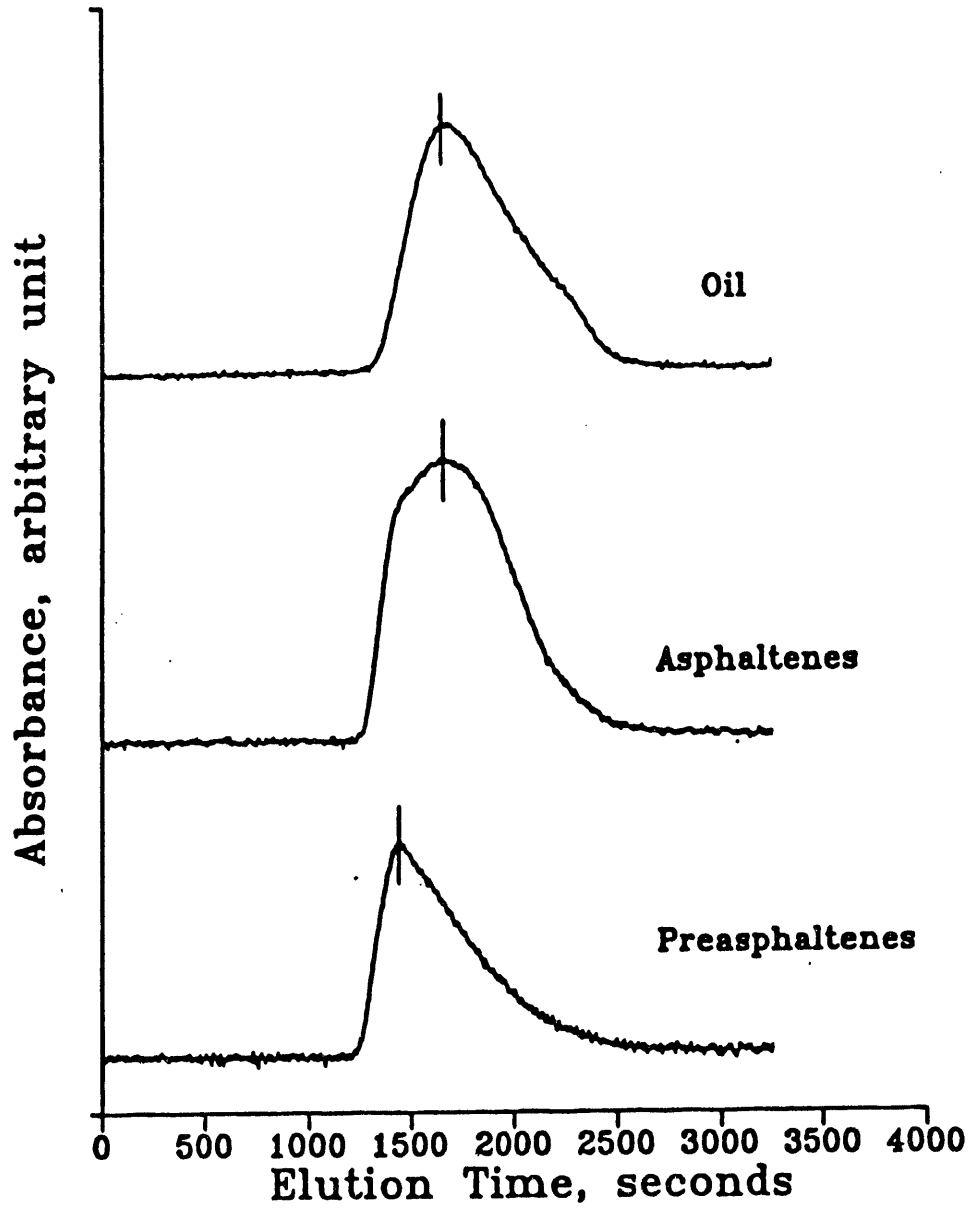


Figure I.B.1.2. Molecular Size Distribution of Oil, Asphaltene, and Preasphaltene Fractions from Coal-Maya Coprocessing Reactions with Nickel Naphthenate

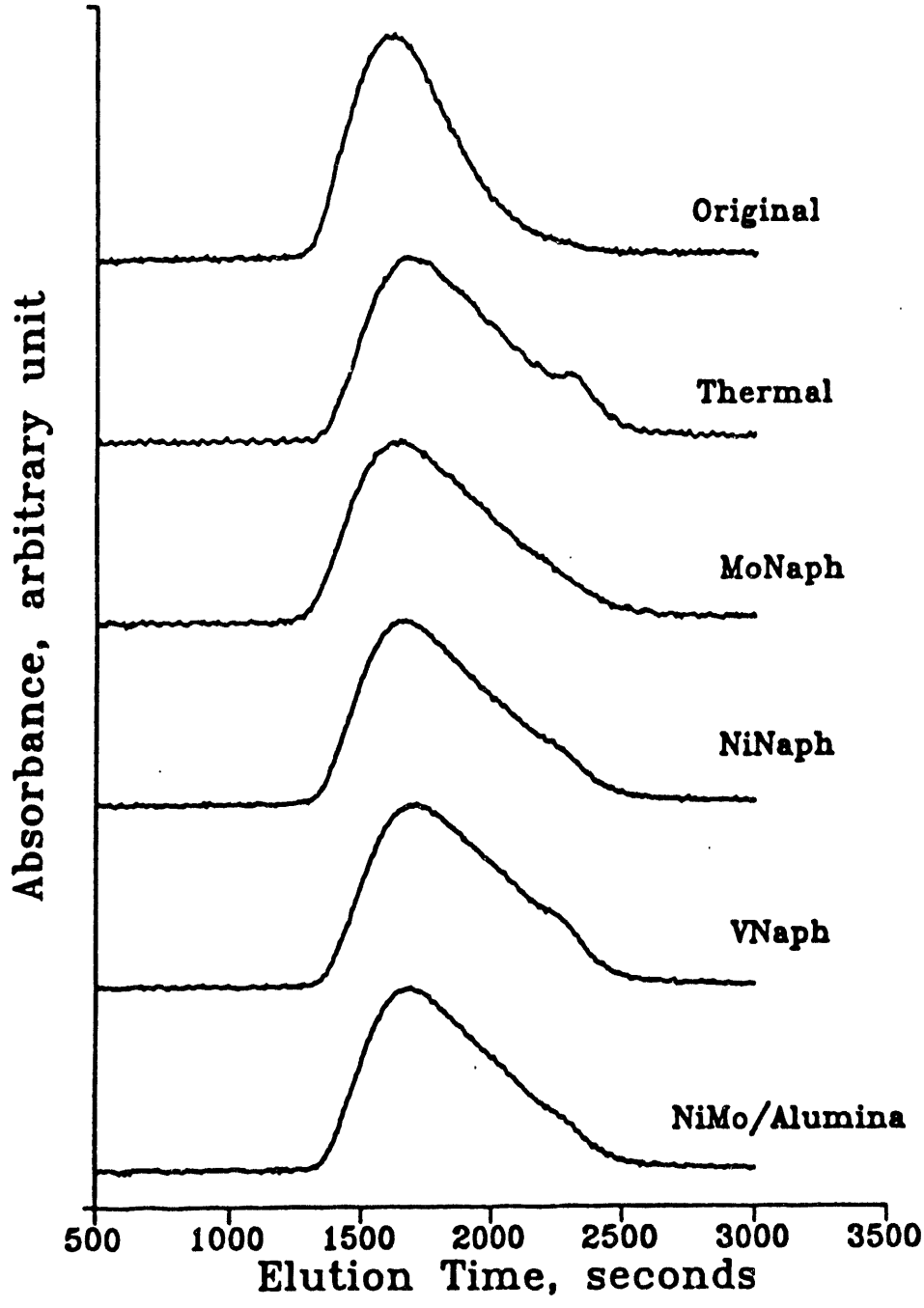


Figure I.B.1.3. Comparison of Molecular Size Distributions of Oil Fractions from Different Coprocessing Reactions

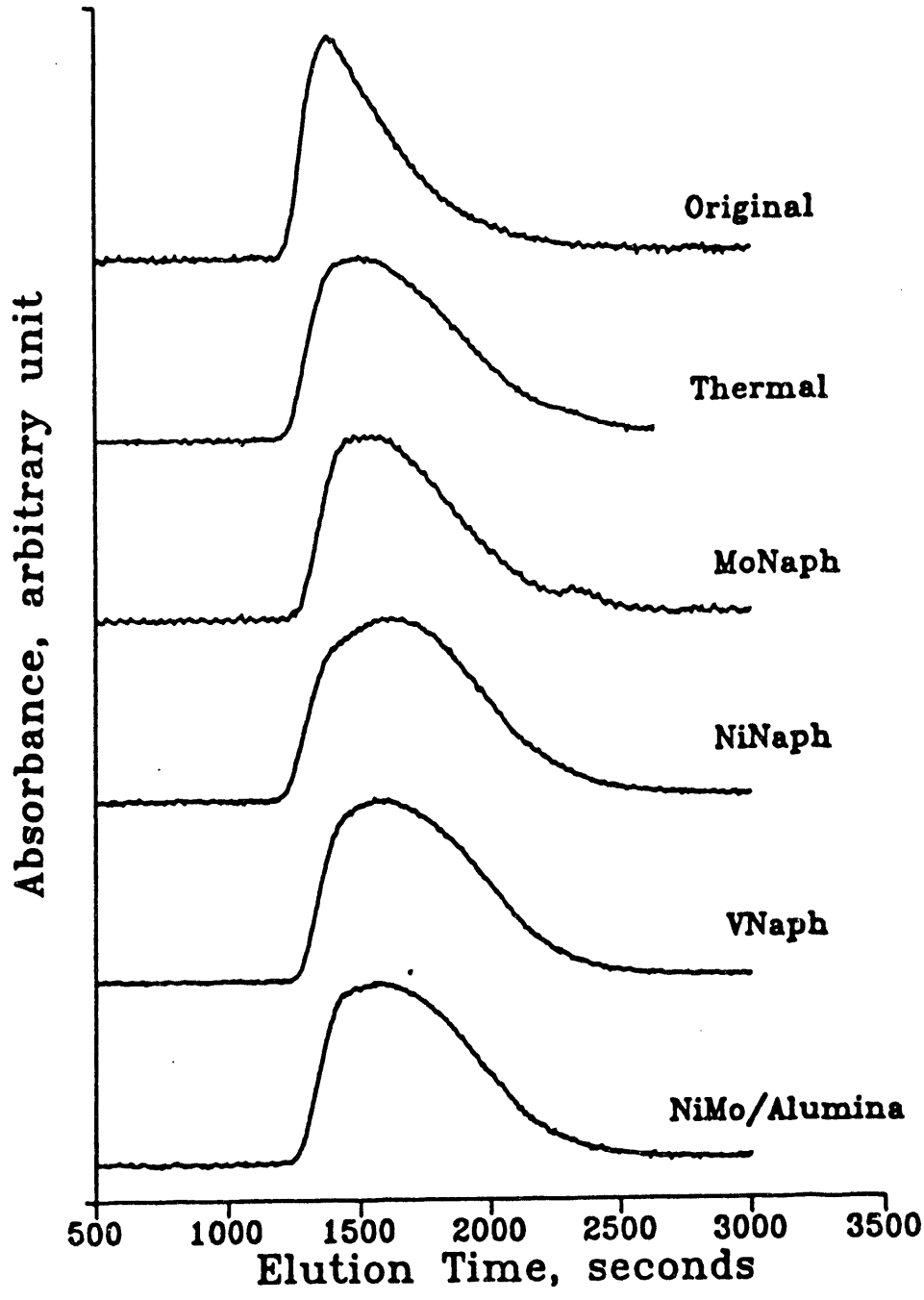


Figure I.B.1.4. Comparison of Molecular Size Distributions of Asphaltene Fractions from Different Coprocessing Reactions

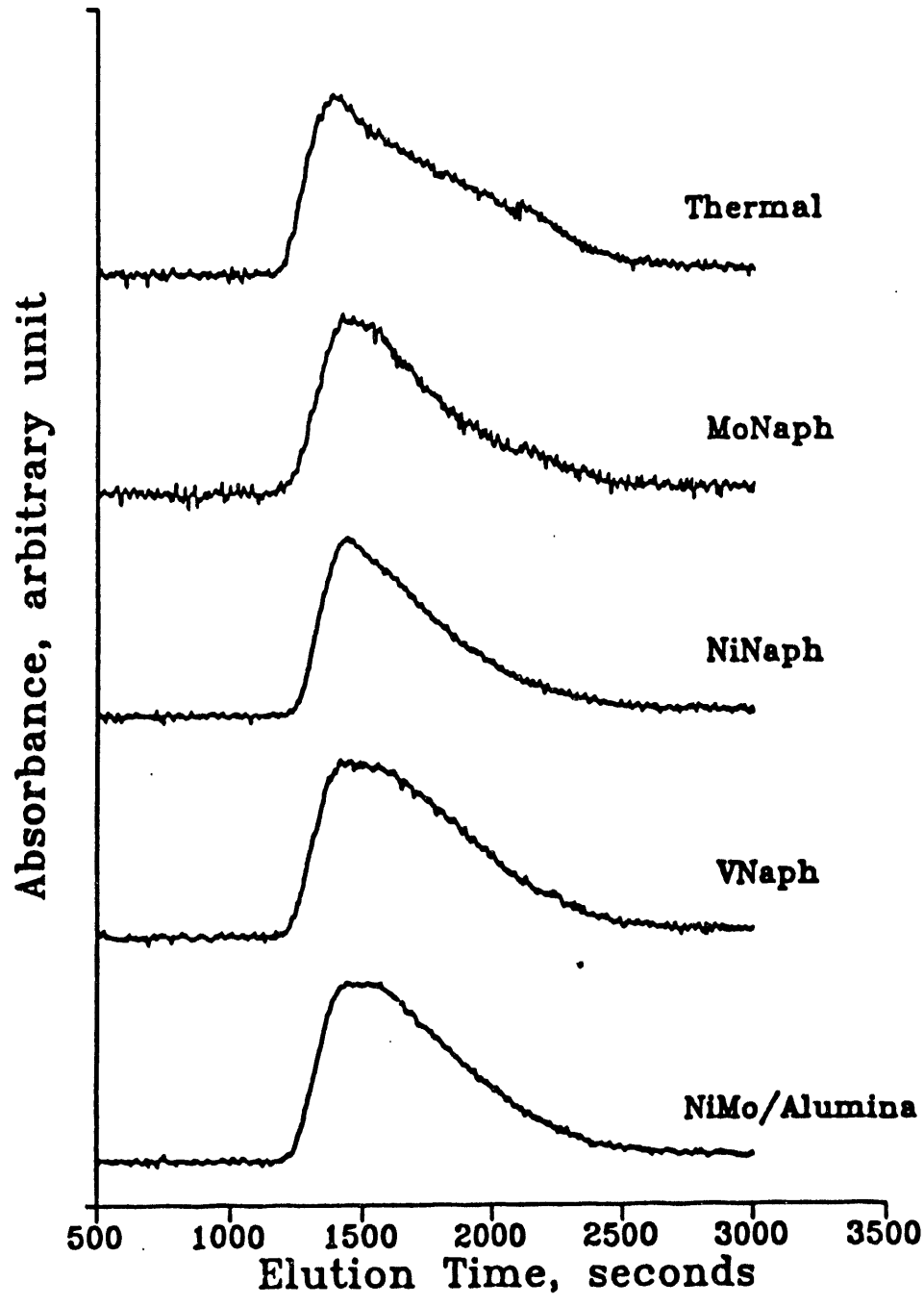


Figure I.B.1.5. Comparison of Molecular Size Distributions of Preasphaltene Fractions from Different Coprocessing Reactions

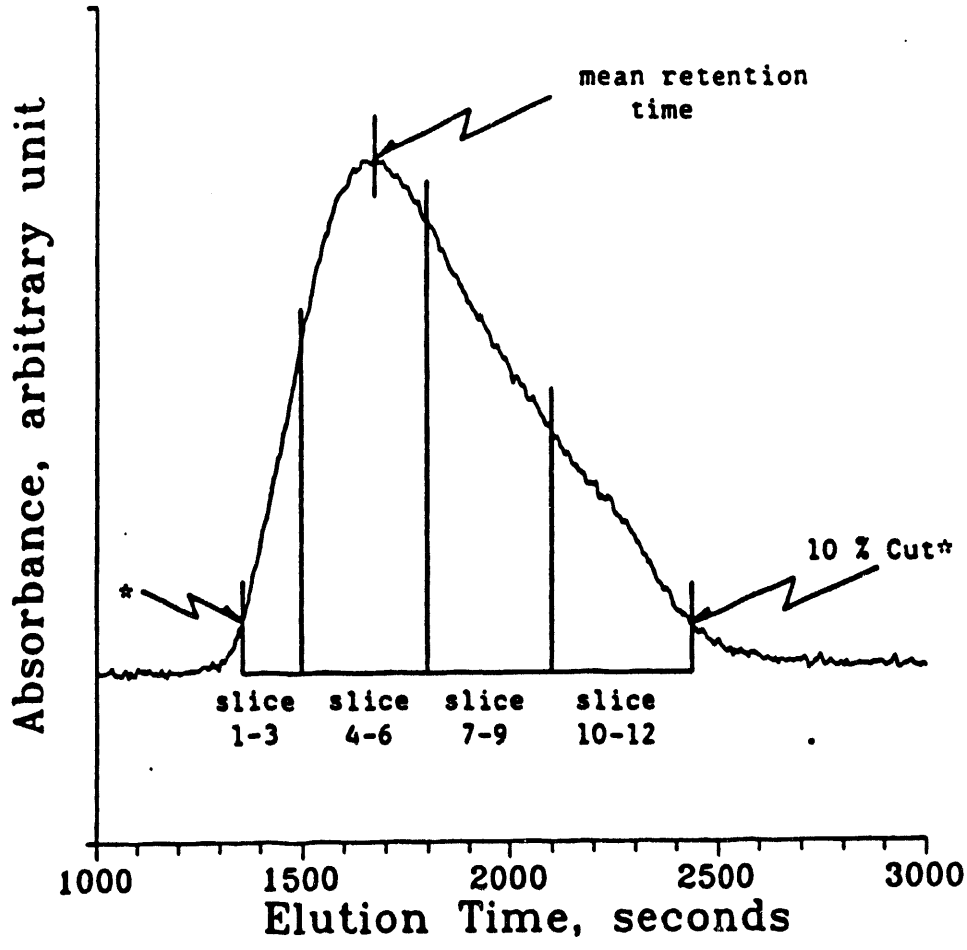


Figure I.B.1.6. SEC Curve Slicing for Quantitative Analysis Example

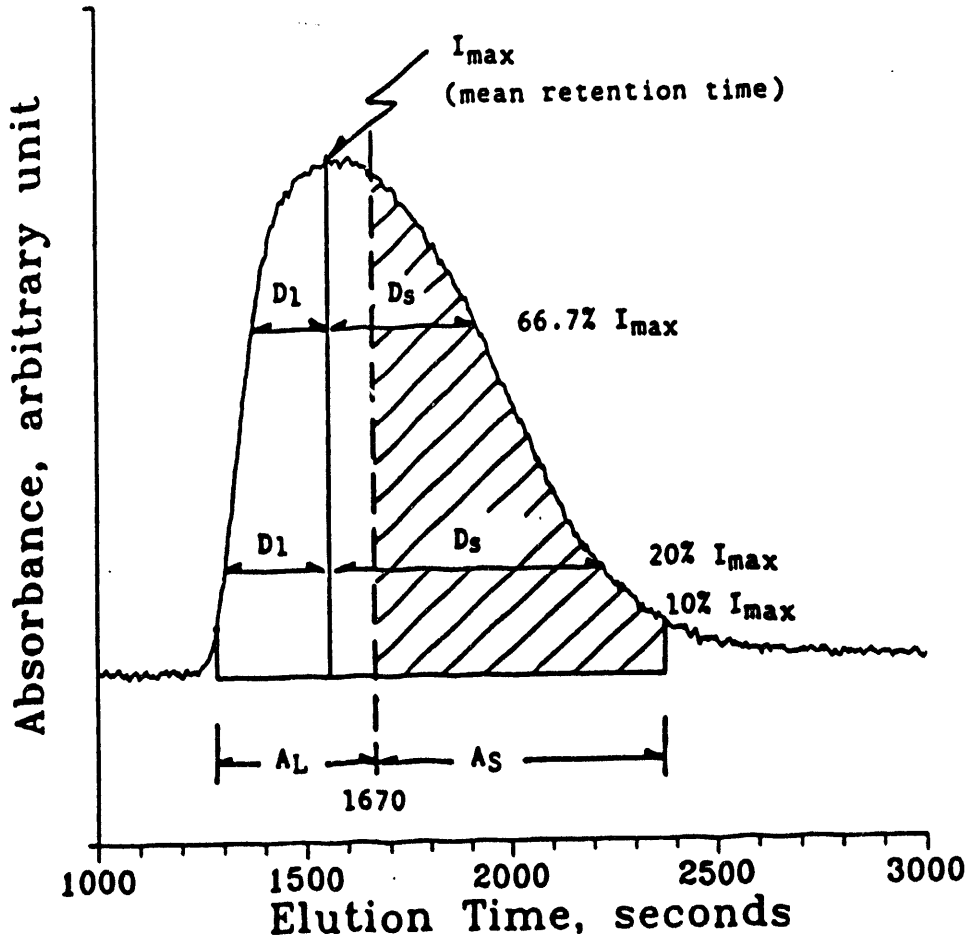


Figure I.B.1.7. Terms for Size Exclusion Chromatography Analysis

SUBTASK I.B.2.

EVALUATION OF ENHANCED FACTORS PREVALENT IN PRETREATED RESIDS

INTRODUCTION

The purpose of this subtask was to chemically evaluate and characterize the hydrotreated residua and residuum fractions produced in Subtask I.B.1. The ultimate goal was to determine the chemical factors that make particular hydrotreated residua more effectual as coprocessing solvents than others. In order to determine chemical factors that make certain hydrotreated residua more effectual as coprocessing solvents, analysis by Fourier transform infrared (FTIR) spectrometry and proton nuclear magnetic resonance (^{1}H-NMR) spectrometry was performed in order to examine and compare untreated residua with residua hydrotreated prior to coprocessing.

Quantitative analysis by FTIR spectrometry was conducted by using a Nicolet 5SXC FTIR spectrometer for the examination and comparison of untreated residua with residua hydropretreated prior to coprocessing in order to determine chemical factors that make certain hydropretreated residua more effectual as coprocessing solvents. Additional work was conducted on the reactions of aromatic compounds such as those present in coal and hydroaromatic compounds such as those present in residua to investigate hydrogen transfer from hydrogen donor hydroaromatic compounds to hydrogen acceptor aromatic compounds.

EXPERIMENTAL

FTIR Analysis of Untreated and Hydropretreated Maya Resid. In the FTIR spectra of all samples, there are two aromatic regions: 3,993 cm^{-1} to 2,995 cm^{-1} (Ar1) and 920 cm^{-1} to 628 cm^{-1} (Ar2). For quantitative comparisons of all spectra, two kinds of peak area ratios were

calculated using the data obtained from the Nicolet 5SXC FTIR spectrometer. They are (1) the 3,093 cm^{-1} to 2,995 cm^{-1} (Ar1) to the 2,995 cm^{-1} to 2,770 cm^{-1} aliphatic region (A1) and (2) the 920 cm^{-1} to 628 cm^{-1} (Ar2) to the 2,995 cm^{-1} (A1) peak area ratios. The peak area ratios of FTIR spectra of untreated Maya residuum and pretreated Maya residuum were compared and related to their efficiencies in coprocessing. The GC conditions for the analysis of all products are shown in Table I.B.2.1.

Determination of Response Factors. In order to utilize the internal standard method in GC analysis, it was necessary to determine the response factors between the analyzed compounds and the internal standard, biphenyl.

RESULTS AND DISCUSSION

Table I.B.2.2 shows the FTIR peak area ratios for 3,093 cm^{-1} - 2,995 cm^{-1} (AR1) to 2,995 cm^{-1} - 2,770 cm^{-1} (A1) and 920 cm^{-1} - 628 cm^{-1} (Ar2) to A1 for catalytically nickel naphthenate (NiNaph), molybdenum naphthenate (MoNaph), and vanadium naphthenate (VNaph) pretreated Maya asphaltene fractions. The aromatic character for both ratios give the same catalytic order: NiNaph < MoNaph < VNaph < thermal (no catalyst).

Table I.B.2.3 and Table I.B.2.4 show the ratios of Ar1 to A1 and Ar2 to A1 for the asphaltene fraction products from the catalytic coprocessing reactions with untreated residuum and for the asphaltene fraction products from thermal coprocessing reactions with catalytically pretreated Maya residuum. The aromatic characters of these products have the same catalytic order as hydropretreated Maya before coprocessing. The order is NiNaph < MoNaph < VNaph < thermal. These data indicate that the products from the reaction with pretreated Maya residuum have lower aromatic characters than the products with reactions with untreated Maya residuum.

The pretreated Maya residuum when reacted with coal resulted in higher coal conversion than did the untreated Maya residuum.

Table I.B.2.5 shows the FTIR peak area ratios for the untreated Maya residua THF solubles and prehydrotreated Maya residuum THF solubles. A lower aromatic character was observed for the THF solubles from catalytically pretreated Maya. The aromatic character ranked according to the order of MoNaph < NiNaph ≤ thermal (no catalyst). The highest aromatic character was observed for the original untreated Maya residuum. The activity of the catalysts for coal conversion with untreated and pretreated Maya residuum was NiNaph ≥ MoNaph > VNaph > thermal (Table I.B.2.6). The aromatic character found in products from catalytic coprocessing and in catalytically pretreated Maya residua using these same catalysts agree well with the reactivity of these catalysts in coal conversion with Maya residuum. It was hypothesized that catalytic pretreatment of Maya residuum prior to coprocessing leads to the formation of hydroaromatic compounds, hence, resulting in lower aromatic character than the aromatic compounds originally present in the residuum.

CONCLUSIONS

The coprocessing products formed from reactions with prehydrotreated Maya residuum had lower aromatic character and gave higher coal conversions than the coprocessing products formed from reactions with untreated Maya residuum. An inverse relation existed between aromatic character and coal conversion in catalytic order. For aromatic character, the catalytic order was NiNaph < MoNaph < VNaph ≤ thermal, while for coal conversion, the catalytic order was NiNaph > MoNaph > VNaph ≥ thermal.

NOMENCLATURE

IOM	=	insoluble organic matter	THF	=	tetrahydrofuran
MoNaph	=	molybdenum naphthenate	VNaph	=	vanadium naphthenate
NiNaph	=	nickel naphthenate			

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

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

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

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

MoNaph = molybdenum naphthenate; NiNaph = nickel naphthenate

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

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

MoNaph = molybdenum naphthenate; NiNaph = nickel naphthenate; VNaph = vanadium naphthenate

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

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

MoNaph = molybdenum naphthenate; NiNaph = nickel naphthenate; VNaph = vanadium naphthenate

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

Pretreating Catalysts	Areas		Ratio
	Ar1	A1	Ar1/A1
MoNaph	0.081	126.74	0.0006
NiNaph	0.3683	204.95	0.0018
VNaph	0.2246	119.0	0.0019
Untreated	0.2609	130.51	0.0020

MoNaph = molybdenum naphthenate; NiNaph = nickel naphthenate; VNaph = vanadium naphthenate

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

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

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

MoNaph = molybdenum naphthenate; NiNaph = nickel naphthenate; VNaph = vanadium naphthenate

TASK II

DEVELOPMENT OF POTENT NONAROMATIC HYDROAROMATIC DONORS FOR COPROCESSING

SUBTASK II.A.

SYNTHESIS OF NONAROMATIC HYDROAROMATICS

INTRODUCTION

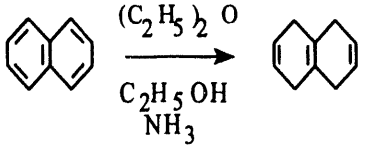
The coprocessing of coal with petroleum resid is advantageous because it allows the simultaneous upgrading of two very heavy hydrocarbon feedstocks to a material that is more readily converted to transportation fuels. In coprocessing, the resid serves as a diluent solvent and a transporting medium that may also participate somewhat in the liquefaction of coal. In conventional direct liquefaction processing, the solvent medium, which is coal derived, frequently contains hydroaromatic species that possess the ability to transfer hydrogen directly from the solvent to the coal. The quantity of such hydroaromatic species is relatively much less in resids than in coal-derived liquids. Resids typically do not show innately strong solvating power for coal.[1,2]

The purpose of this research was to determine if the addition of hydroaromaticity to resids in coal-resid coprocessing systems would enhance the solvating power of the resid solvent in terms of the amount of coal converted to tetrahydrofuran solubles. To accomplish this purpose, two approaches were taken. First, five different resids were reacted with Pittsburgh No. 8 bituminous coal in the presence and the absence of hydrogen donors. These hydrogen donors included conventional hydroaromatics such as tetralin, dihydroanthracene, and octahydroanthracene as would be found in coal-derived process solvents. Cyclic olefins, compounds that are hydroaromatic without an aromatic ring and which have been shown to be highly reactive under liquefaction conditions,[3-6] were also tested as hydrogen donors. This research is described in Subtask II.C. The two cyclic olefins used were 1,4,5,8-tetrahydronaphthalene, known as isotetralin, and hexahydroanthracene. The presence of hydroaromaticity in the coprocessing

systems substantially enhanced coal conversion. The second approach used was to induce hydroaromaticity in the resids themselves by subjecting them to Birch reduction. Birch reduction is a method employed to synthesize cyclic olefins such as 1,4,5,8-tetahydronaphthalene from aromatics such as naphthalene.

Other researchers have subjected resids to Birch reductions.[7,8,9] Mochida[9] used Ashland petroleum pitch which had been hydrogenated by Birch reduction to increase the hydrogen donating ability of the resid. The hydrogenated pitch showed excellent cocarbonizing activity with the coals. Three of the resids used in the coprocessing reactions in this study were subjected to Birch reduction and then used as solvents in coprocessing reactions. The reduction of these resids, like the addition of hydrogen donors, enhanced the conversion of coal to tetrahydrofuran solubles. The enrichment of the resid with inherent hydrogen donating ability shifted the resid from being primarily a dissolution medium to being a reactive medium.

The research discussed in this subtask is how to synthesize nonaromatic hydroaromatics from aromatics, such as 1,4,5,8-tetrahydronaphthalene (isotetralin) from naphthalene.



Synthesis of 1,4,5,8-Tetrahydronaphthalene (Isotetralin) by Birch Reduction of Naphthalene. The Birch reduction of naphthalene to form isotetralin using the procedure published by Vogel et al.[10] was modified in our laboratory. A 12-L, three-necked, round-bottomed flask was held firmly in a dry ice-acetone bath assembly and fitted with (1) a modified long stem (100 mm) 24/40 standard taper straight vacuum adapter connected to a 24/40 standard taper dewar-type dry ice-acetone condenser connected with teflon tubing on a Schwartz drying

tube (potassium hydroxide) connected with teflon tubing to a corrosive gas regulator connected to a tank of ammonia (Air Products, anhydrous grade, 99.99%, liquid phase), (2) a 34/45 standard taper tube-sealed stirrer connected with a flexible coupler to a heavy duty variable-speed motor, and (3) a 24/40 standard taper tubing adapter connected with Tygon tubing to a trap/cylindrical drying tube (potassium hydroxide [Fisher, CERTIFIED ACS grade])/trap/mineral oil bubbler assembly. The bath assembly and the condenser were charged with a dry ice-acetone (Fisher, OPTIMA) slurry, and 3 L of ammonia was condensed over a period of approximately 6 hr. The vacuum adapter/condenser/Schwartz drying tube/regulator/ammonia tank assembly was removed, and with vigorous stirring, 192.3 g of sodium metal (3- to 8-mm spheres [Aldrich]) was added in small portions over 1 hr using a 24/40 standard tape powder funnel fitted with a spring-loaded plunger and cover assembly developed in our laboratory. The powder funnel assembly was removed, and the 12-L flask was then fitted with a 24/40 standard taper 500 ml dropping funnel, through which a solution of 192.3 g (1.5 mol) of naphthalene (Fisher, CERTIFIED) in a mixture of 750 ml of ethyl ether (Fisher, anhydrous, REAGENT ACS) and 600 ml of ethanol (Fisher, CERTIFIED, HPLC grade) was added drop-wise to the blue sodium ammonia solution (if the solution changed to white during the addition, sufficient sodium was added to maintain the blue color) over a period of approximately 3 hr. After the addition was completed, the dropping funnel was removed and the reaction mixture was stirred under a N atmosphere at -78 C for another 6 hr. The dry ice-acetone slurry was then removed from the bath assembly and the ammonia was allowed to evaporate under a N_2 atmosphere over a period of approximately 2 days. The remaining white solid was processed with ice cooling and under a N atmosphere by slow addition of first 120 ml of methanol (Fisher, OPTIMA), using the dropping funnel, to destroy any unreacted sodium and then 4-5 L of ice water (distilled) to dissolve the salts. Next, 1 L of ethyl

ether was added for extraction of the reaction mixture. The ethyl ether phase was evaporated at room temperature under reduced pressure to give a coarse, white solid which was transferred to a medium porosity sintered glass funnel and washed thoroughly with distilled water. The product was recrystallized from methanol (approximately 1.6 L) using a heated funnel, followed by drying of the crystals under reduced pressure for the minimum time necessary, because of the relatively high vapor pressure of isotetralin, to give 148-158 g (75-80% yield) of isotetralin.

REFERENCES

1. Curtis, C.W.; Hwang, J.S. *Fuel Proc. Tech., 30*, 47-67 (1992).
2. Curtis, C.W.; Tsai, K.J.; Guin, J.A. *Fuel Proc. Tech., 16,* 71-87 (1987).
3. Curtis, C.W.; Guin, J.A.; Kwon, K.C. *Fuel,* 63:1404-1409 (1984).
4. Bedell, M.W.; Curtis, C.W. *Energy and Fuels, 5*, 469-476 (1991).
5. Bedell, M.W.; Curtis, C.W.; Hool, J.L., *Energy and Fuels*, *7*, 200-207 (1993a).
6. Bedell, M.W.; Curtis, C.W.; Hool, J.L., in press, *Fuel Proc. Tech.* (1993b).
7. Branthaver, J.F.; Sugihara, J.M. *Amer. Chem. Soc. Div. Petrol. Chem. Preprints*, 11(23), B-105 - B-107 (1966).
8. Mochida, I.; Tomari, Y.; Maeda, K.; Takeshita, K. *Fuel, 54*, 265-268 (1975).
9. Mochida, I.; Moriguchi, Y.; Korai, Y.; Fujitsu, H.; Takeshita, K. *Fuel, 60,* 746-747 (1980).
10. Vogel E.; Klu, W.; Breuer, A. *Organic Synthesis, 55,* 86-91 (1976).

SUBTASK II.B.

BIRCH REDUCTION OF RESIDS

Reduction of Maya, Deasphalted Resid Rock, and South Louisiana Petroleum Residua. The reduction of petroleum residuum paralleled that described for naphthalene given in Subtask II.A with the following exceptions. Petroleum residuum was found to be only slightly soluble in ethyl ether; therefore, tetrahydrofuran (Fisher, HPLC grade), a cyclic ether, was utilized as the solvent throughout. A solution of 1 L tetrahydrofuran, 400 ml ethanol, and 60 g resid was added dropwise to 128 g of sodium dissolved in 2 L of ammonia. After the reaction was completed and the ammonia was evaporated, a combination of 80 ml of methanol followed by 3 L of ice water (distilled) was added to the reaction mixture to react with any excess sodium. Since tetrahydrofuran is not as volatile as ethyl ether, it was not necessary to add additional tetrahydrofuran for purposes of extraction. The tetrahydrofuran phase was separated from the aqueous phase, distilled water was added, and the mixture was distilled (using glass beads as boiling chips) to just past 78 °C (the boiling point of ethanol) to remove the methanol, tetrahydrofuran, and ethanol. The Birch-reduced resid was then washed thoroughly with distilled water and dried at room temperature under reduced pressure.

Analysis of the Reduced Resids. The solvent fractionation of parent and reduced resids employed hexane, toluene, and tetrahydrofuran as fractionating solvents. The resids were first dissolved in hexane and then extracted, followed by toluene and then by tetrahydrofuran. The hexane solubles were termed oils; the hexane insolubles, toluene solubles, asphaltenes; the toluene insolubles, tetrahydrofuran solubles, preasphaltenes; and the tetrahydrofuran insolubles, insoluble organic matter. The solvent fractions obtained from the resids are given in Table II.B.1. Carbon,

hydrogen, and nitrogen analyses of the parent and reduced resids are given in Table II.B.2; these analyses were performed by Galbraith Laboratories.

Fourier transform infrared spectrometry (FTIR) was performed on the parent and the Birch reduced deasphalted resids. Samples were prepared by dissolving equal weights (0.1078 g) of each resid into 20 ml of spectrophometric grade carbon tetrachloride. The CCl spectrum was software-subtracted from each residuum spectrum. The average absorbance of the base line in the region of the spectral peaks was subtracted from the absorbance of each spectral peak to obtain the net absorborance for each peak.

Size exclusion chromatography was performed on the untreated and reduced resids using a Waters high-pressure liquid chromatograph equipped with four columns in series, two ultrastyragel columns (Waters) of 500 and 100 A and two 5 μ—phenogel columns (Phenomenex) of 100 and 50 A; tetrahydrofuran was used as the solvent; and ultraviolet detection at 254 nm was employed.

Analysis of the Birch Reduced Resids. Deasphalted resids parent and reduced resids were analyzed by FTIR and the differences in their spectra were compared. Absorbance ratios were calculated from the background-subtracted base line-corrected FTIR spectra of the asymmetric methyl (CH_3) and methylene (CH_2) C-H stretching vibrations at 2957 cm^{-1} and 2928 cm^{-1}, respectively, and the symmetric CH_3 and CH_2 C-H stretching vibrations at 2871 cm^{-1} and 2856 cm^{-1}, respectively, for the parent and Birch-reduced deasphalted resids. The asymmetric CH_3:CH_2 absorbance ratios for the parent and reduced deasphalted resids were 0.54 and 0.65, respectively; the symmetric CH_3:CH_2 absorbance ratios were 0.71 for the parent deasphalted resid and 0.81 for the reduced deasphalted resid. The increases in the absorbance ratios for the Birch-reduced deasphalted resid as compared to the parent resid reflected an increase of the CH_3 character of the

reduced resid. An increase in CH_3 character for the reduced deasphalted resid was expected because the Birch-reduction chemically reduced the resid, adding hydrogen to the system. The validity of the FTIR data was tested by computing the ratio of the absorbances of the asymmetric CH_3 and symmetric CH_3 stretching vibrations, and that of the asymmetric CH_2 and the symmetric CH_2 stretching vibrations for the parent and reduced deasphalted resids. The asymmetric/symmetric CH_3 ratios and CH_2 ratios were the same for both the parent and reduced resids at 1.6 and 2.0, respectively.

Gel permeation chromatography was performed to evaluate the effect of Birch reduction on the size distribution of the reduced and parent resids. Comparisons of the molecular size distributions of the parent and reduced resids are presented in Figure II.B.1. For each set of parent and reduced resids, the reduced resid gave a molecular size distribution that is shifted toward larger molecular size. In the case of Maya resid, the parent resid began eluting at 650 sec while initial elution time of the reduced resid was 610 sec. (The chromatograms before 600 sec were flat with no features from the resids visible.) The entire chromatogram of the reduced resid was shifted toward shorter elution times, indicating that the reduced sample contained molecules of larger size than did the parent. The product distributions of Maya parent and reduced resids obtained through solvent fractionation indicated that less soluble products, preasphaltenes and asphaltenes, were formed during the reduction process. This decrease in resid solubility was also observed in the Li-ethylenediamine reduction of Boscan asphaltene fractions.[1]

The gel permeation chromatography chromatograms of the other two parent and reduced resid pairs also gave shifts to high molecular sizes for the reduced resids. The shift in molecular size for the reduced deasphalted resid was rather substantial which agreed with the decrease in the oil fraction and increase in the asphaltenes observed in product distribution. The shift to larger

molecular size was much less for south Louisiana reduced resid compared to the parent south Louisiana resid. These chromatograms agreed with the product distributions that showed little difference in the solubility fractions of the south Louisiana resid parent and reduced resids.

The elemental analysis consisting of carbon, hydrogen, and nitrogen analysis of the resids is given in Table II.B.2. This analysis showed an increase in the hydrogen content of the reduced resids compared to each of their corresponding parent resids. The carbon content was also substantially lower indicating a change in the chemistry of the resid.

REFERENCE

1. Branthaver, J.F., Personal communication, 1992.

Table II.B.1. Product Distribution of Parent and Reduced Resids

Resid	Product Distribution, wt%			
	Oil	Asphaltenes	Preasphaltenes	IOM
ANS[b,e]	82.6(0.1)	17.4(0.1)	0.0	0.0
Maya[b]	80.5(1.1)	19.5(1.1)	0.0	0.0
Reduced Maya[a,c]	35.1	31.2	20.1	13.6
DAU[b,e]	75.6(1.6)	24.4(1.6)	0.0	0.0
Reduced DAU[c]	68.4	31.6	0.0	0.0
SLA[b,e]	93.2(0.5)	6.8(0.5)	0.0	0.0
Reduced SLA[c]	93.8	6.2(0.1)	0.0	0.0
Yates[b,e]	87.6(0.1)	12.4(0.1)	0.0	0.0

[a]Product fractionations with reduced resids were performed only once because of limited amount of materials.
[b][Bedell, 1991]
[c][Wang, 1992]
[e]ANS = Alaska North Slope resid; SLA = south Louisiana resid;
DAU = resid from deasphalting unit; Yates = Yates resid

Table II.B.2. Carbon, Hydrogen, and Nitrogen Analysis of Parent and Reduced Resids

Resid	Carbon, %	Hydrogen, %	Nitrogen, %
Maya	84.3	9.6	0.8
Reduced Maya	75.8	10.0	<0.5
DAU[a]	85.3	9.0	0.8
Reduced DAU	82.0	9.7	0.5
SLA	87.2	11.3	0.5
Reduced SLA	75.0	11.5	0.6

[a] DAU = deasphalted resid; SLA = south Louisiana resid

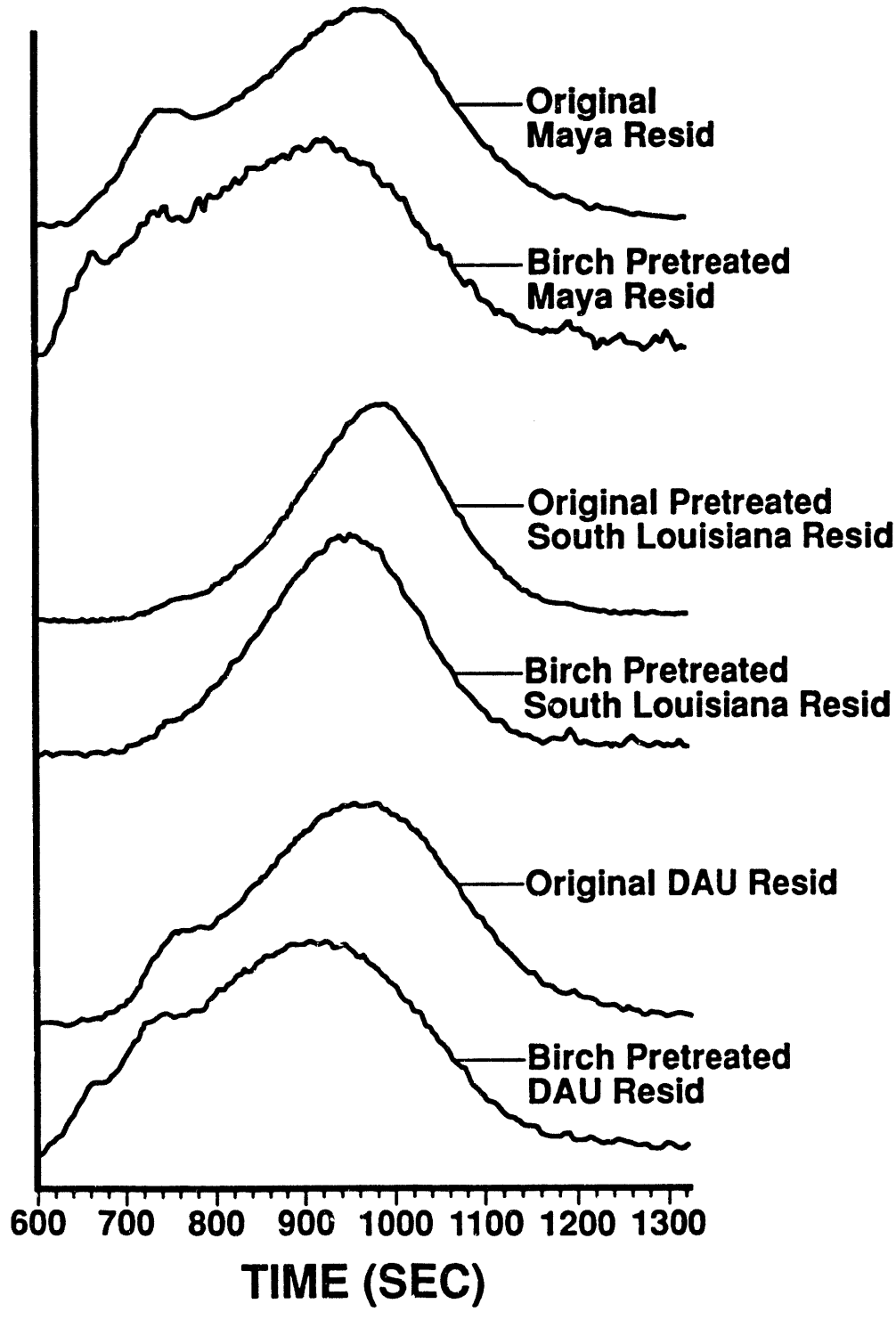


Figure II.B.1. GPC of Original and Birch Pretreated Resids.

SUBTASK II.C.

COPROCESSING OF PITTSBURGH NO. 8 COAL WITH REDUCED RESID

Coprocessing Reactions of Pittsburgh No. 8 with Various Resids Donor and Hydrogen

Coprocessing reactions were performed with Pittsburgh No. 8 coal and five different resids to evaluate the effect of the resid on the conversion of coal to tetrahydrofuran solubles. Once the reactions established the degree to which the various resids liquefied coal, hydrogen donor species comprised of either cyclic olefins or hydroaromatic compounds were added to the reaction system and the amount of coal conversion to tetrahydrofuran solubles were determined. The resids tested were selected from five different petroleum sources and presented a range of hexane soluble materials from a low of 75.6% for deasphalted resid to a high of 93.2% for south Louisiana resid. The parent resids were reacted alone at coprocessing conditions to determine if any tetrahydrofuran insoluble materials were produced. After reaction, all of the parent resids remained totally tetrahydrofuran soluble contributing no solids to the reaction.

EXPERIMENTAL

Materials. The chemicals used in this study were obtained from the following manufacturers and used as received: 1,4,5,8-tetrahydronaphthalene or isotetralin from Wiley Organics Inc. and from the synthesis described herein which yielded a product of 97.2% purity, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydroanthracene from Aldrich Chemical Co.; Pittsburgh No. 8 and Upper Freeport coals from the Argonne Premium Coal Sample Program, Western Kentucky No. 9 from the PSU/DOE sample program, Maya vacuum resid from Amoco Oil Co., Alaskan North Slope resid, Yates resid, deasphalted resid from a blend of resids that had been treated in a deasphalting unit and south Louisiana resid

from Exxon Oil Co., and reduced resids, Maya, deasphalted resid and south Louisiana resid, prepared as described herein. The characteristics of the coals are given in Table II.C.1 and properties of resids are given in Table II.C.2.

Procedure. The reactions performed included the coprocessing reactions of the three resids and three reduced resids with Pittsburgh No. 8 coal and the three untreated resids with hydrogen donors added at 0.5 wt% donable hydrogen. The parent Maya and reduced Maya resids were also reacted with two other coals, Western Kentucky and Upper Freeport. For this study, the following reaction conditions were employed: 30 min reaction time, 1,250 psig hydrogen at ambient temperature, 380 °C reaction temperature, 2.0 g coal, 4.0 g parent resid or reduced resid, and 700 cpm vertical agitation rate using stainless steel tubular reactors of approximately 50 cm^3 volume. When a hydrogen donor was added, 4.0 g of total solvent mixture was charged which included a hydrogen donor at 0.5 wt% donable hydrogen with the balance being resid. In these coprocessing reactions, the amount of hydrogen available from molecular hydrogen was 0.35 g and the amount of hydrogen available from the added donor species was 0.03 g, if all of the hydrogen were released from the donor under these reaction conditions. However, as has been shown previously,[1-3] not all of the hydrogen are released from the hydrogen donor species under these conditions.

The hydrogen donor compounds and their products from the coal liquefaction and coprocessing reactions were analyzed by gas chromatography using a Varian 3400 GC equipped with an Al-clad HT-5 capillary column from SGE and flame ionization detection. The internal standard method was used for quantitation with biphenyl as the internal standard. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectral analysis using a VG70 EHF mass spectrometer.

For this work, coal conversion was defined as

$$\text{conversion} = \{1 - [\text{IOM/coal charge}_{(maf)}]\} \times 100$$

where IOM is the insoluble organic matter remaining after the reaction and maf means moisture and ash free. The moisture and ash contents of Pittsburgh No. 8 coal were 4.5$\pm$0.6% and 10.2$\pm$0.14%, respectively, and were provided by the supplier.

RESULTS AND DISCUSSION

The reactions of the five different resids both in the presence and absence of added hydrogen donor resulted in different amounts of coal conversion as presented in Table II.C.3. The coal conversion to tetrahydrofuran solubles without hydrogen donor ranged from 25.0% for Yates to 39.6% for deasphalted resid. Hence, the chemistry of the resids affected the liquefaction of the coal and the solubility of the products. The general trend observed was that as the hexane soluble fraction of the resids decreased, the amount of coal conversion obtained increased. Deasphalted resid which contained the least amount of hexane-soluble materials produced the highest amount of coal conversion; likewise, Yates and south Louisiana resids which contained the highest amount of hexane solubles produced the lowest coal conversion. The correlation between hexane-soluble content and the amount of coal conversion achieved generally held true for those systems with added hydrogen donors as well. The reactions containing the hydrogen donors, isotetralin, hexahydroanthracene, and dihydroanthracene, reacted with 1.2 g resid, showed increased coal conversion with resids of lower hexane-soluble content. The reaction involving dihydroanthracene with 3.0 g of resid also showed an increased coal conversion with resids having less hexane solubles except for a reversal in the hexane solubles of Alaskan North Slope and Maya resid.

These reaction systems were conducted on the basis of each reaction having equivalent moles of donable hydrogen. Hence, lesser amounts of hydrogen donor were required for those systems having more hydrogen to donate and greater amounts were required for those donors that had fewer donable hydrogen. Hence, dihydroanthracene had only two hydrogen to donate and required more hydrogen donor to make its full complement of hydrogen. In order to maintain the 4 g of solvent charge, the reactions with dihydroanthracene were performed then with 1.2 g of resid while the other reaction systems contained three or more grams of resid; hence, dihydroanthracene replaced a substantial portion of the resid as solvent. The reaction of dihydroanthracene with 1.2 g of resid yielded high levels of coal conversion with all the resids. These high levels of conversion were most likely influenced by a strong solvating effect of dihydroanthracene because of its inherent aromaticity and compatibility with coal. Therefore, a second set of reactions was performed with dihydroanthracene in which an equivalent amount of donable hydrogen from dihydroanthracene was introduced as in the experiments with 1.2 g of resid, but the resid was charged at 3.0 g in order to mitigate the solvating effect of dihydroanthracene.

In the coprocessing reactions that contained 3.0 g of resid or more, the reactive hydrogen donors, i.e., dihydroanthracene, hexahydroanthracene, and isotetralin, increased the coal conversion obtained substantially above that of the resid alone. The amount of increase ranged from 23.1% with Maya resid to 28% with Yates resid while the amount with the other three resids had intermediate increases.

Products from the Hydrogen Donors. The reaction products produced from the hydrogen donors during the coprocessing reactions were analyzed and are shown in Table II.C.4. Different levels of reactivity of the donors were observed. Octahydroanthracene which yielded

only a small increase in coal conversion did not react much yielding at most ~26% conversion to dihydroanthracene as the major product and anthracene as the minor product. By contrast, hexahydroanthracene whose addition improved coal conversion rather substantially compared to octahydroanthracene completely converted in all of the resids. The primary reaction product from hexahydroanthracene was dihydroanthracene although significant amounts of octahydroanthracene and anthracene were also formed. The reactions of dihydroanthracene in the presence of both 1.2 and 3.0 g resid produced nearly equivalent amounts of octahydroanthracene and anthracene while nearly one-third of the dihydroanthracene remained unreacted. The two-ring cyclic olefin, isotetralin, reacted similarly to the three-ring hexahydroanthracene while tetralin reacted similarly to octahydroanthracene. Isotetralin completely converted forming both tetralin and naphthalene while tetralin remained virtually unreacted.

The reactivity of the hydrogen donors tracked the reactivity of the coprocessing systems where the more reactive donors produced increased coal conversions. In the most reactive systems involving deasphalted resid, the product slates of the different hydrogen donors shifted slightly toward the more fully dehydrogenated products. For example, more dihydroanthracene and less octahydroanthracene were recovered from reactions with hexahydroanthracene and deasphalted resid than with the other resids. Hence, more hydrogen was transferred and more coal conversion was obtained.

Coprocessing with Reduced Resids

The addition of hydrogen donors, particularly highly reactive donors like cyclic olefins and dihydroanthracene, enhanced the conversion of coal to tetrahydrofuran solubles in each of resids tested. The next step to be tested was whether hydrogen donability could be generated within the

resid itself. Since the synthesis of the reactive cyclic olefins from aromatics can be successfully performed by the Birch reduction, a modified version of the Birch reduction procedure as described in the Subtask II.B was performed on the resids. The reduced resids were then used in the coprocessing reactions.

Coprocessing with Reduced Resids. Each of the reduced resids was reacted with Pittsburgh No. 8 coal at the same conditions as used for the coprocessing reactions with added hydrogen donors. The reduced Maya resid was also reacted with Western Kentucky No. 9 and Upper Freeport coals. The coal conversions achieved in these reactions as well as comparisons to the coal conversions obtained with the parent resid and the resid with added isotetralin are presented in Table II.C.5.

A substantial increase in coal conversion to tetrahydrofuran solubles was observed in the reaction with Pittsburgh No. 8 coal containing reduced Maya resid where coal conversion reached 43.3% compared to the parent Maya at 20.1%. The amount of coal conversion achieved with the reduced resid was comparable to that obtained with the added isotetralin at 41.5%. Increase in coal conversion obtained with reduced resid demonstrated that the hydrogen incorporated into the resid by the Birch reduction was readily available to the coal during coprocessing. The similarity in the coal conversions achieved with the reduced resid and with isotetralin added to the parent resid suggested similar levels of readily donable hydrogen being present in the system. In the isotetralin system, 80.2% of the donable hydrogen was donated which corresponds to about 0.4 wt% hydrogen or 0.024 g of hydrogen donated. Although only a portion of the donable hydrogen from isotetralin was probably accepted by coal, this amount of donated hydrogen gives an upper limit to the amount of readily donable hydrogen likely to be present in the resid, if a one-to-one correlation between donable hydrogen and coal conversion to tetrahydrofuran solubles is assumed.

Additional reactions were performed with the reduced Maya crude and Western Kentucky No. 9 and Upper Freeport coals. Western Kentucky No. 9 is a reactive, high volatile bituminous coal like Pittsburgh No. 8 coal, while Upper Freeport is a much less reactive, medium volatile B bituminous coal.[3] The reaction of the reduced Maya resid with Western Kentucky coal produced 43.7% conversion to tetrahydrofuran solubles which was slightly higher than the conversion obtained with Maya plus added isotetralin and approximately 20% more than that obtained with the parent resid. The Upper Freeport coal showed much less reactivity than either Western Kentucky No. 9 or Pittsburgh No. 8 coal with any of the resid solvent systems. However, the reduced Maya resid produced a small increase in coal conversion compared to the parent resid that was equivalent to that obtained with the parent resid plus isotetralin as solvent.

Two very different resids in terms of hexane-soluble content, deasphalted resid and south Louisiana resid, were also reduced with the modified Birch procedure. These reduced resids were also reacted with Pittsburgh No. 8 coal. Both reduced resids produced increases in coal conversion compared to those obtained with their respective parent resids. The coal conversions obtained with the reduced resids produced similar yields as the parent resids with added isotetralin. In the deasphalted resid reaction with isotetralin, 71.8% of the donable hydrogen from isotetralin was donated which corresponds to 0.36 wt% or 0.022 g of hydrogen. In the south Louisiana resid reaction with isotetralin, 72.2% of the donable hydrogen was donated which corresponds to 0.36 wt% or 0.022 g. Again, it is highly likely that only a portion of the donated hydrogen from isotetralin was accepted by the coals, but these levels of hydrogen donation give an upper limit to the amount of donable hydrogen that was incorporated into the resids during the Birch reduction. As with the reduced Maya resid, the modified Birch reduction incorporated hydrogen into the resids that was donable to the liquefying coal.

An important feature in the efficacy of the reduced resid was the reactivity of coal itself. Regardless of the quality of the dissolution medium the coal must be able to accept hydrogen that the solvent contains. Reactive coals such as Pittsburgh No. 8 or Western Kentucky No. 9 could accept hydrogen from reduced resids or from added donors[3] while the less reactive Upper Freeport could not accept much hydrogen from either a reduced resid or from added hydrogen donors during the reaction time allowed.[3]

CONCLUSIONS

Reduction of resids by the modified Birch method increased the amount of coal conversion obtained during coprocessing. This reduction shifted the role of the resid solvent from that of a diluent solvent to that of hydrogen donor solvent that actively promoted coal conversion. This same effect was observed when model hydrogen donors were added to five different resids. The presence of hydrogen donors in the resid, either as inherent species or as added species, definitely improved the ability of coprocessing systems to convert coal and achieve a higher quality product.

REFERENCES

1. Bedell, M.W., Ph.D. Dissertation, Auburn University (1991).
2. Wang, S.L. Master's Thesis, Auburn University (1992).
3. Bedell, M.W.; Curtis, C.W.; Hool, J.L. in press *Fuel Proc. Tech.* (1993b).

Table II.C.1. Proximate Analysis of the Coals[a]

Coal	Moisture %	Ash %	Volatile Matter %	Sulfur %	Btu	Rank
Kentucky No. 9	7.12	10.97	35.77	4.50	11936	HVB[b]
Upper Freeport	1.13	13.03	27.14	2.29	13315	MVB
Pittsburgh No. 8	1.65	9.10	37.20	2.15	13404	HVB

[a] All values are weight percents for the as-received coals.
[b] HVB = high volatile bituminous; MVB = medium volatile bituminous

Table II.C.2. Properties of the Resids Used in This Study

Properties	Maya	DAU[d]	ANS	Yates	SLA
Source of Residuum	Mexico	Blend	Alaska	Texas	Louisiana
Specific Gravity, g/cc	1.1	NA[b]	1.0174	0.9980	0.9848
API Gravity	NA	NA	7.6	10.3	12.2
Ramsbottom Carbon, wt%	26.4	NA	NA	NA	NA
Conradson Carbon, wt%	NA	NA	21.8	15.7	13.2
C, wt%	83.7	NA	NA	NA	NA
H, wt%	9.8	NA	NA	NA	NA
S, wt%	5.4	NA	2.38	2.84	1.89
N, wt%	ND[a]	NA	0.64	0.45	0.32
Ni, ppm	118	NA	51.4	19.1	19.6
V, ppm	680	NA	11.3	47.2	47.5
Hexane, Solubles, wt%	80.5(1.0)[c]	75.6(1.6)	87.6(0.1)	82.6(1.0)	93.2(0.5)
Hexane Insolubles, wt%	19.5(1.0)	24.4(1.6)	12.4(0.1)	17.4(1.0)	6.8(0.5)
Toluene Insolubles, wt%	0	0	0	0	0

[a]Not detected
[b]Not availabl.
[c]Numbers in parentheses indicate standard deviations
[d]DAU = deasphalted resid; ANS = Alaskan North Slope resid; SLA = south Louisiana resid

Table II.C.3. Coal Conversion Obtained from Coprocessing Reactions with Pittsburgh No. 8 Coal with Different Resids and Hydrogen Donors[a]

Hydrogen Donors	Coal Conversion (%) with				
	Maya	DAU	ANS	Yates	SLA
DHA[b] (1.2)	62.9(0.2)[c]	65.6(2.1)	62.3(0.9)	62.7(0.4)	55.3(2.0)
DHA (3.0)	55.3(1.3)	66.5(0.4)	58.8(1.0)	53.0(0.1)	50.4(1.0)
HHA	55.0(1.1)	55.1(1.5)	51.4(3.0)	48.8(1.6)	40.2(1.5)
OHA	43.3(0.8)	47.6(0.1)	39.5(0.6)	39.6(2.4)	33.8(0.1)
ISO	41.5(0.6)	45.6(0.5)	40.4(2.6)	37.6(0.9)	33.8(3.7)
TET	32.3(1.6)	41.4(0.1)	28.0(0.5)	24.9(0.5)	30.1(1.5)
NONE	32.2(1.5)	39.6(1.9)	35.1(1.9)	25.0(1.0)	25.1(3.2)

[a]Reaction Conditions: Pittsburgh No. 8 coal, 1,250 psi hydrogen at ambient, 380 °C, 30 min
[b]DHA = dihydroanthracene; TET = tetralin; HHA = hexahydroanthracene;
DAU = resid from deasphalting unit; OHA = octahydroanthracene; ANS = Alaskan north slope
ISO = isotetralin; SLA = south Louisiana
[c]All coal conversions are in weight percent; the numbers in parentheses are the standard deviations for that point.

Table II.C.4. Analysis of the Reaction Products from Model Donors in Reactions with Pittsburgh No. 8 Coal with Various Resids[a]

Compound/Conditions	OHA[b] Wt%	DHA Wt%	ANT Wt%
DHA (1.2)	37.1(0.8)[c]		
Maya	31.3(1.3)	29.4(0.2)	33.5(0.7)
DAU	33.2(7.2)	31.3(0.1)	37.4(1.4)
ANS	35.6(0.4)	28.4(0.2)	38.4(7.5)
Yates	37.2(0.8)	28.6(1.2)	35.8(1.4)
SLA		27.4(0.8)	35.4(1.6)
DHA (3.0)	35.8(2.8)		
Maya	33.6(0.7)	27.1(0.5)	37.1(3.2)
DAU	43.9(0.6)	28.3(0.5)	38.1(1.2)
ANS	35.6(1.2)	23.0(0.3)	33.1(0.4)
Yates	39.9(1.0)	27.7(0.3)	36.7(1.0)
SLA		23.8(0.3)	36.3(1.2)
HHA	30.6(1.0)		
Maya	26.6(0.6)	52.0(1.0)	17.4(1.7)
DAU	31.0(0.9)	56.9(0.4)	16.5(0.2)
ANS	28.2(1.8)	52.8(0.5)	16.2(0.2)
Yates	28.6(0.6)	54.4(0.6)	17.4(1.2)
SLA		54.2(0.3)	17.2(0.3)
OHA	73.6(1.0)		
Maya	77.7(1.6)	24.7(0.6)	1.7(0.4)
DAU	85.9(0.8)	21.4(1.4)	0.9(0.5)
ANS	85.1(0.6)	14.1(0.8)	0.0
Yates	82.5(0.1)	14.9(0.6)	0.0
SLA		16.8(0.1)	0.7(0.1)
Compound/Conditions	**TET[b] Wt%**	**NAP Wt%**	
ISO			
Maya	19.8(1.2)[c]	80.2(1.2)	
DAU	28.2(0.9)	71.8(0.9)	
ANS	24.8(2.1)	75.2(2.1)	
Yates	25.5(1.2)	74.5(1.2)	
SLA	27.8(0.3)	72.2(0.3)	
TET			
Maya	78.7(1.6)	21.3(1.6)	
DAU	90.4(1.4)	9.6(1.4)	
ANS	79.6(0.8)	20.4(0.8)	
Yates	88.5(0.3)	11.5(0.3)	
SLA	83.5(3.4)	16.5(3.4)	

[a]Reaction Conditions: Pittsburgh No. 8 coal, 1,250 psi hydrogen at ambient, 380 °C, 30 min.
[b]OHA = octahydroanthracene; DAU = deasphalting unit; DHA = dihydroanthracene; ANS = Alaskan north slope; SLA = south Louisiana; ANT = anthracene; HHA = hexahydroanthracene; TET = tetralin; ISO = isotetralin; NAP = naphthalene
[c]Numbers in parentheses indicaestandard deviations.

Table II.C.5. Effect of Birch Reduction Pretreatmen of Resids on Coal Conversion During Coprocessing

Reaction	Coal Conversion, %		
	Pittsburgh No. 8	Western Kentucky No. 9	Upper Freeport
MAYA			
Reduced Resid	43.3(2.6)[b]	43.7(2.9)	16.9(0.8)
Original Resid	20.1(3.3)	24.3(3.3)	14.0(1.6)
Original Resid + Isotetralin	41.5(0.6)	44.8(0.3)	16.5(3.4)
DAU			
Reduced Resid	47.0(1.9)		
Original Resid	39.6(1.9)		
Original Resid +Isotetralin	45.6(0.5)		
SLA			
Reduced Resid	31.4(1.7)		
Original Resid	25.1(3.2)		
Original Resid + Isotetralin	33.8(3.7)		

[a]Reaction Conditions: Pittsburgh No. 8 coal, 1,250 psi hydrogen at ambient, 380 °C, 30 min.
[b]Numbers in parentheses indicate standard deviations.

SUBTASK II.D.1

CHEMISTRY AND REACTIVITY OF NONAROMATIC HYDROAROMATIC DONORS

INTRODUCTION

In both thermal and catalytic coal liquefaction reactions, hydrogen transfer reactions are important avenues by which hydrogen is transferred to coal and substantially increases the amount of coal conversion and upgrading.[1-4] Hydrogen donors typically used are hydroaromatic and phenolic compounds.[5-14] A new set of hydrogen donor compounds has been discovered that is much more effective than conventional hydroaromatics in transferring hydrogen to coal.[6] These donors are cyclic olefins, i.e., hydroaromatic species that do not contain aromatic rings. An example is isotetralin, 1,4,5,8-tetrahydronaphthalene. Cyclic olefins can be synthesized from aromatic species by using the Birch reduction[15] in which the aromatic species is treated with an alkali metal, usually sodium, and alcohols in liquid ammonia to produce partially saturated species. Other metals can be used such as lithium in the Benkeser[16] reduction to achieve the same end products. Electrocatalytic reductions[17] using water as the solvents and the supporting electrolyte, tetrabutylammonium hydroxide, can also produce cyclic olefins.

The efficiency of isotetralin for converting coal to tetrahydroanthracene solubles has been shown to be much higher than its conventional hydroaromatic analogue, tetralin.[6] In reactions with Western Kentucky No. 9/14 coal, isotetralin converted 80.6% of the coal to tetrahydrofuran solubles compared to only 58% for tetralin. This dramatic increase in coal conversion with isotetralin led to the current investigation of cyclic olefins as hydrogen donors for coal liquefaction.

The objective of this research is to test cyclic olefins as donors for coprocessing. 1,4,5,8,9,10-Hexahydroanthracene and 1,4,5,8-tetrahydronaphthalene, isotetralin, are the cyclic

olefins under study. The first step in fulfilling this objective was to investigate the chemistry of these compounds under liquefaction conditions. Both the thermal and catalytic reactivity of the cyclic olefins at elevated temperatures under hydrogen and nitrogen atmospheres has been determined and compared to the reactivity of their respective hydroaromatic analogues, dihydroanthracene, octahydroanthracene, and tetralin. The catalysts used were presulfided, pulverized $NiMo/Al_2O_3$ and Mo/Al_2O_3. Reaction pathways for both cyclic olefins have been proposed.

EXPERIMENTAL

Reaction Procedures. The reactivity of the cyclic olefins was tested in stainless steel tubing bomb reactors with volumes of 20 cm^3 under the following conditions: 380 °C, horizontal agitation at 425 cpm, 1,250 psig nitrogen or hydrogen pressure at ambient temperature, reaction times ranging from 2 min to 1 hr, 2.0 g hexadecane as the diluent solvent, reaction mixtures containing 3 wt% hydrogen donor which translates into 0.033 to 0.179 wt% donable hydrogen from the model donors and, for catalytic reactions, a total active metal loading of 3,000 ppm. Donable hydrogen is defined as the number of hydrogen atoms lost from a given compound to form its respective aromatic compound. For example, hexahydroanthracene ($C_{14}H_{16}$) loses six hydrogen atoms to form anthracene ($C_{14}H_{10}$). Therefore, hexahydroanthracene contains six donable hydrogen atoms. Two catalysts were used, Shell 324, $NiMo/Al_2O_3$, and Amocat 1B, Mo/Al_2O_3, to evaluate the catalytic reactivity of the hydrogen donors at liquefaction conditions. Each catalyst was presulfided in a heated flowing stream of 10% H_2S in hydrogen for approximately 5 hr, pulverized, and sized between 100 and 200 mesh before being used. The catalyst was stored in a desiccator.

The reactions of both cyclic olefins and three conventional hydroaromatic donor compounds with Western Kentucky No. 9 coal were also performed. For this study the following reaction conditions were employed: 30 min reaction time, 1,250 psig N_2 atmosphere at ambient temperature, 380 or 410°C reaction temperature, 2.0 g coal, 4.0 g total solvent mixture including 0.1-0.5 wt% donable hydrogen of the model compound with the balance being fluorene as the diluent solvent, and 700 cpm vertical agitation rate using stainless steel tubing bomb reactors of approximately 50 cm^3 volume. The reaction temperatures were limited to 380 and 410 °C because of the high reactivity of the cyclic olefins. At higher temperatures these cyclic olefins react so quickly that their effect on liquefaction is difficult to observe.

The chemicals used were obtained from the following manufacturers and used as received: tetralin, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydroanthracene, fluorene and hexadecane from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene from Wiley Organics Inc.; 1,4-dihydronaphthalene (90% purity) and 1,2-dihydronaphthalene from CTC Organics; Western Kentucky No. 9 coal from the PSU/DOE sample bank. Because of the limited availability and cost of 1,2-dihydronaphthalene only a limited number of experiments were performed with it.

The products from the model reactivity studies, were analyzed by gas chromatography using a Varian 3400 GC equipped with a HT-5 column from SGE and FID detection. The internal standard method was used for quantitation with biphenyl as the internal standard. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectral analysis using a VG 70EHF mass spectrometer.

RESULTS AND DISCUSSION

Model Reactivity Studies

Two model reactivity studies involving cyclic olefins were performed. The first examined the thermal and catalytic reactivity of isotetralin at liquefaction temperatures and then compared its reactivity to that of tetralin. Possible reaction mechanisms are proposed based on the products obtained in high temperature reactions from isotetralin, tetralin, 1,4-dihydronaphthalene, and 1,2-dihydronaphthalene. The second involved the reactivity of hexahydroanthracene under thermal and catalytic liquefaction conditions. This reactivity was then compared to that of octahydroanthracene and dihydroanthracene, and a reaction mechanism was proposed. In the tables describing these reactions the data are given in pairs where the first is the weight percent recovered and the second, in parentheses, is the standard deviation for that data point.

Isotetralin and Tetralin Reactivity

Isotetralin Reactivity. Isotetralin was highly reactive under thermal reaction conditions in both nitrogen and hydrogen atmospheres. All of the isotetralin readily converted at reaction times of 30 min in nitrogen and 15, 30, and 60 min in hydrogen as shown in Table II.D.1.1. The product slate for the thermal reactions, regardless of atmosphere consisted of (1,2-dihydronaphthalene), (1,4-dihydronaphthalene), tetralin, and naphthalene. However, at shorter reaction times in both nitrogen and hydrogen, not all of the isotetralin reacted. After 2 min of reaction at 380 °C in nitrogen, more than 46% of the isotetralin remained with the major product being 1,4-dihydronaphthalene present at ~48%. Small amounts of naphthalene and tetralin were also observed. After 30 min of reaction in nitrogen atmosphere at 380 °C, the predominant product was naphthalene, with the other major product being 1,4-dihydronaphthalene, and minor amounts of both 1,2-dihydronaphthalene and tetralin being formed.

The same products were observed in a hydrogen atmosphere; however, the product slate was time dependent. At short reaction time (2 min), more than 50% of the isotetralin did not react with the major product being 1,4-dihydronaphthalene at ~39%. With increasing reaction times from 15 to 60 min, the amount of naphthalene produced doubled from 30.5 to 61.1% while the amount of 1,2-dihydronaphthalene and 1,4-dihydronaphthalene decreased from a combined total of more than 50 to ~13%. The 1,2-dihydronaphthalene to 1,4-dihydronaphthalene isomer ratio varied widely with varying reaction times from the 1,4-dihydronaphthalene isomer being predominant at 2 min to the two isomers being nearly equivalent at 15 min to the 1,2-dihydronaphthalene isomer being predominant at 60 min. At 60 min, the amount of 1,4-dihydronaphthalene produced was unexpectedly small; perhaps 1,4-dihydronaphthalene was hydrogenated to tetralin which would account for the increased amount of tetralin produced at this reaction time.

Isotetralin was highly reactive under catalytic reaction conditions when either presulfided $NiMo/Al_2O_3$ or Mo/Al_2O_3 was used. These catalysts were chosen because of their different hydrogenation activities, with $NiMo/Al_2O_3$ usually being more active. Isotetralin was only observed at less than 1% in the reaction products after 2 min of reaction with Mo/Al_2O_3. None of the other catalytic reactions at 380 °C had any isotetralin remaining in the products. In the presence of $NiMo/Al_2O_3$ and a hydrogen atmosphere, isotetralin produced tetralin and decalin as the major products; naphthalene was only observed at short (2 min) reaction time as shown in Table II.D.1.2. With increasing reaction times, less tetralin was produced and more decalin was formed. Decalin constituted 90% of the product at 60 min. With $NiMo/Al_2O_3$, the tran to cis isomer ratio was approximately 3:1 and was independent of reaction time within experimental error.

With Mo/Al_2O_3, the predominant product formed was tetralin at a level of 76 to 79% for the four reaction times 2, 15, 30, and 60 min. Cis- and trans-decalin (c- and t-decalin) as well as naphthalene was also formed, yielding approximately 20% decalin and 1% naphthalene at reaction times greater than 15 min. The intermediate octahydronaphthalene was observed at the 2 min reaction time. The t- to c-decalin isomer ratio was approximately 2.5:1 and was constant for reaction times ranging from 15 min to 1 hr. The product slate from isotetralin with Mo/Al_2O_3 was nearly independent of time; i.e., all the products were formed within the first 15 min and did not change with reaction times up to 60 min.

The isomeric analogue of isotetralin, tetralin, reacted only slightly after 30 min of thermal reaction in nitrogen producing ~1% naphthalene and achieved less than 4% conversion in a hydrogen atmosphere, forming 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and naphthalene (Table II.D.1.1) in contrast to isotetralin which completely reacted. After 30 min reaction with $NiMo/Al_2O_3$ in hydrogen, only ~75% of tetralin converted whereas isotetralin completely reacted (Table II.D.1.2). The products formed from tetralin were t- and c-decalin, while those from isotetralin were tetralin as well as t- and c-decalin. The amount of tetralin present in the products was actually higher for isotetralin than for tetralin. The t- to c-decalin isomer ratio was the same for both compounds, (3:1), within experimental error. Neither isotetralin nor tetralin formed naphthalene as a product.

With Mo/Al_2O_3 after 15 min of reaction, only 5% of the tetralin reacted and naphthalene and decalin were formed as products; again by contrast, isotetralin completely reacted forming 75 to 80% tetralin, 1% naphthalene, and the remaining decalin (Table II.D.1.2). The t- to c-decalin isomer ratio in the Mo/Al_2O_3 reactions was the same within experimental error for both isotetralin and tetralin reactants (2.5:1).

Proposed Reaction Pathway for Isotetralin. A possible reaction pathway for isotetralin is proposed in Figure II.D.1. This pathway is based on the experimental reaction products obtained from the thermal and catalytic reactions presented in Tables II.D.1.1-II.D.1.4.

Additional experiments were performed at both 380 and 225 °C to help elucidate the reaction pathway (Tables II.D.1.3 and II.D.1.4). The reactions involved quick heat-up and quench in which the reactors were heated to reaction temperature and then quickly cooled. The reaction time was ~2 min. These short-time reactions of isotetralin at 380 °C in a hydrogen atmosphere yielded tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, naphthalene, and isotetralin as reaction products (Table II.D.1.3). The primary components in the products were unreacted isotetralin at ~52% and 1,4-dihydronaphthalene at ~39%. The same products were observed with a N_2 atmosphere except that 1,2-dihydronaphthalene was not detected. Hence, in the short-time reaction at 380 °C not all of the isotetralin reacted.

Short-time thermal reactions of the reaction product 1,4-dihydronaphthalene in hydrogen and nitrogen left nearly 75% of the 1,4-dihydronaphthalene unreacted while nearly equivalent amounts, 10 to 13%, each of naphthalene and 1,2-dihydronaphthalene were formed (Table II.D.1.3). 1,4-Dihydronaphthalene, was also reacted for 30 min at 380 °C in both hydrogen and nitrogen (Table II.D.1.1); the products tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and naphthalene were formed in hydrogen yielding naphthalene at ~45% and tetralin at ~42% as the primary products. In nitrogen, no 1,2-dihydronaphthalene was formed; naphthalene at ~60% was the primary product while ~28% of the 1,4-dihydronaphthalene remained unreacted. Short-time thermal reactions of tetralin were not performed since only ~4% of the tetralin reacted at 380 °C after 30 min.

Short-time reactions of isotetralin, tetralin, 1,2-dihydronaphthalene and 1,4-dihydronaphthalene were also performed catalytically using $NiMo/Al_2O_3$ and Mo/Al_2O_3 to gain further information on the reaction pathway. At 380 °C with $NiMo/Al_2O_3$ isotetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene were each converted and none of the compounds was observed in any of the reaction systems; the products observed were t-decalin, c-decalin, octahydronaphthalene, tetralin, and naphthalene (Table II.D.1.4). The major product was tetralin at ~77%. A trace amount of octahydronaphthalene, an intermediate between tetralin and the decalins, was observed. Short-time reactions performed at 225 °C with $NiMo/Al_2O_3$ gave 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, tetralin, c-decalin, and t-decalin as products. Neither naphthalene nor octahydronaphthalene was detected.

Short-time reactions with isotetralin were also performed with Mo/Al_2O_3 at 225 and 380°C. Reactions at 225 °C gave products of t-decalin, c-decalin, tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and isotetralin. The primary product was tetralin at ~45% with ~24% isotetralin remaining. A substantial amount (12%) of octahydronaphthalene and a small amount (~2%) of naphthalene were formed at 380 °C but were not observed at 225 °C. Thus, a short reaction time and a mild hydrogenation catalyst were required to observe any unreacted isotetralin in catalytic reactions.

Short-time experiments at 380 °C using 1,4-dihydronaphthalene as the starting reactant with $NiMo/Al_2O_3$ and Mo/Al_2O_3 produced tetralin as the major product at 94 and 89%, respectively. Naphthalene and t-decalin were the only other products observed. A different set of products was obtained at 225 °C with both catalysts: Tetralin, 1,2-dihydronaphthalene, 1,4-dihydronaphthalene, and naphthalene. Tetralin at ~64% was the major product in the $NiMo/Al_2O_3$ reactions, while only 1% 1,4-dihydronaphthalene remained unreacted. By contrast,

the reaction with Mo/Al_2O_3 produced ~19% 1,2-dihydronaphthalene as the primary product while 61% of the 1,4-dihydronaphthalene remained unreacted. Short-time reactions of 1,2-dihydronaphthalene at 380 °C with both $NiMo/Al_2O_3$ and Mo/Al_2O_3 produced more than 90% tetralin; the only other product was naphthalene. At 225 °C, the 1,2-dihydronaphthalene produced tetralin as the primary product and a small amount of 1,4-dihydronaphthalene with $NiMo/Al_2O_3$. Less reactivity with the same products was observed with Mo/Al_2O_3. When tetralin was the reactant, no reaction occurred in 2 min except for the $NiMo/Al_2O_3$ system at 380 °C where ~3% t-decalin was formed as shown in Table II.D.1.4.

The proposed reaction pathway for isotetralin presented in Figure II.D.1.1 is formulated on the basis of the reaction products observed from isotetralin from both thermal and catalytic reactions and from the reaction products produced from subsequent reactions involving the reaction products from isotetralin as reactants. All of the data presented in Tables II.D.1.1 through II.D.1.4 have been incorporated with the pathway. Isotetralin reacted following pathways that either (1) isomerized to form tetralin as indicated by the large amounts of tetralin produced during catalytic short-time reactions, (2) dehydrogenated to form 1,4-dihydronaphthalene or 1,2-dihydronaphthalene as indicated by the thermal reactions, or (3) hydrogenated to form more highly hydrogenated species of naphthalene such as octahydronaphthalene and subsequently t- or c-decalin. The first two pathways, isomerization or dehydrogenation, could result subsequently in hydrogenation through more fully hydrogenated naphthalenes such as octahydronaphthalene to t- and c-decalin or dehydrogenation to naphthalene, respectively.

Hexahydroanthracene and Its Hydroaromatic Analogues Reactivity

Hexahydroanthracene Reactivity. The thermal and catalytic reactivity of 1,4,5,8,9,10-hexahydroanthracene was also examined. Thermal reactions of hexahydroanthracene, under both

nitrogen and hydrogen atmospheres, yielded several different isomers of dihydroanthracene as the predominant product with 9,10-dihydroanthracene being the major isomer observed. The amount of dihydroanthracene produced ranged from ~68 to ~83% depending upon the specific reaction times employed as shown in Table II.D.1.5. Lesser products included tetrahydroanthracene and anthracene.

Short-time reactions of ~2 min in both hydrogen and nitrogen resulted in a substantial amount of hexahydroanthracene remaining unreacted, 47% for nitrogen and ~61% for hydrogen. After 30 min of reaction in a N_2 atmosphere, a trace amount of hexahydroanthracene was observed. In a hydrogen atmosphere, 10% hexahydroanthracene remained after 15 min, but with increasing reaction times, the amount of hexahydroanthracene present decreased to less than 2% at both 30 and 60 min. After 60 min of reaction in hydrogen, dihydroanthracene formation decreased to 68% from a high of 83% at 30 min, while anthracene and tetrahydroanthracene formation increased. Anthracene production increased from ~2% at 15 min to levels of 7 and ~5% at 30 and 60 min, respectively, while tetrahydroanthracene doubled to ~20% when the time was increased from 30 to 60 min. A small amount of octahydroanthracene was formed after a 60 min reaction in hydrogen.

As was observed with the isotetralin catalytic reactions, $NiMo/Al_2O_3$ was a more active hydrogenation catalyst than Mo/Al_2O_3 in the hexahydroanthracene reaction system. The reaction products using $NiMo/Al_2O_3$ were more saturated than those from the Mo/Al_2O_3 reaction as can be observed from the reaction products given in Table II.D.1.6. The predominant products from hexahydroanthracene hydrogenation with $NiMo/Al_2O_3$ were isomers of fully saturated anthracene, perhydroanthracene; the other major products were isomers of octahydroanthracene with a minor amount of tetrahydroanthracene isomers observed. Increasing reaction times favored the

formation of the fully saturated product perhydroanthracene yielding nearly 88% perhydroanthracene after 60 min of reaction, while the amount of octahydroanthracene produced decreased from nearly 50% after 15 min to 12.2% after 60 min. No hexahydroanthracene was observed in any of the reactions with $NiMo/Al_2O_3$. Likewise, complete conversion of hexahydroanthracene was observed with Mo/Al_2O_3; however, the predominant product was octahydroanthracene formed at a level of 71 to 84% for the four reaction times. Other products present in lesser amounts were perhydroanthracene and tetrahydroanthracene. Increasing reaction times increased the amount of perhydroanthracene formed from 9% at 15 min to ~13% after 60 min of reaction. Increased reaction time resulted in a decrease of tetrahydroanthracene formed from ~24% at 2 min to ~3% at 60 min.

Comparison of the Reactivity of Hexahydroanthracene to its Hydroaromatic Analogues. A comparison of the products from the thermal reactions of hexahydroanthracene, octahydroanthracene, and dihydroanthracene after 30 min of reaction is given in Table II.D.1.5. In a N_2 atmosphere, hexahydroanthracene completely reacted with dihydroanthracene as the predominant product and minor products of tetrahydroanthracene and anthracene. In contrast, octahydroanthracene did not react and dihydroanthracene converted only 5%, with anthracene as the only product. In a hydrogen atmosphere after a 30 min reaction more than 98% of hexahydroanthracene was converted, with the predominant product again being dihydroanthracene. By comparison octahydroanthracene did not react and only 8% of dihydroanthracene converted to tetrahydroanthracene and anthracene. Hexahydroanthracene was much more reactive than either octahydroanthracene or dihydroanthracene at 380°C under both hydrogen and nitrogen atmospheres.

The catalytic reactivity of hexahydroanthracene with both $NiMo/Al_2O_3$ and Mo/Al_2O_3 is compared to that of dihydroanthracene and octahydroanthracene in Table II.D.1.6. The catalytic reactions of dihydroanthracene, octahydroanthracene, and hexahydroanthracene with $NiMo/Al_2O_3$ in a hydrogen atmosphere produced hydrogenated anthracene as the predominant products. All three reactants formed perhydroanthracene, octahydroanthracene, and tetrahydroanthracene during a 30 min reaction. Dihydroanthracene and hexahydroanthracene were completely converted to more hydrogenated products, whereas 68% of octahydroanthracene converted. With the Mo/Al_2O_3 catalyst, hexahydroanthracene completely reacted, while ~8% of the dihydroanthracene, and ~98% of the octahydroanthracene remained unreacted. Under catalytic conditions, hexahydroanthracene showed higher reactivity and conversion than either of the conventional hydrogen donor compounds, dihydroanthracene or octahydroanthracene. Complete conversion of hexahydroanthracene was observed in all reactions except the thermal reaction with hydrogen.

Proposed Reaction Pathway for Hexahydroanthracene. The thermal reaction pathway for hexahydroanthracene proposed in Figure II.D.1.2 is based upon the observed reaction products formed from reactions involving hexahydroanthracene and its reaction products, dihydroanthracene and octahydroanthracene, under nitrogen and hydrogen atmospheres. Short-time (2 min) experiments were performed at 380 and 225 °C under thermal and catalytic conditions (Tables II.D.1.7 and II.D.1.8, respectively) to further elucidate the reaction pathway. At 2 min reaction time, the products observed from thermal reactions were dihydroanthracene and tetrahydroanthracene while anthracene was not observed at either temperature or atmosphere. Substantial amounts of hexahydroanthracene remained at both conditions with the most dehydrogenation occurring at 380 °C in nitrogen. At short-time conditions, dihydroanthracene converted

~0.5% to anthracene at 380 °C in nitrogen and less than 2% to anthracene in hydrogen or in either atmosphere at 225 °C. Octahydroanthracene did not react at short-time conditions.

Catalytic reactions of hexahydroanthracene at short-time resulted in octahydroanthracene as the primary product (Table II.D.1.8). Hexahydroanthracene completely reacted except in the 225 °C reaction with Mo/Al_2O_3 where nearly 50% hexahydroanthracene remained. A small amount of dehydrogenation products, tetrahydroanthracene and dihydroanthracene, were observed. At 380 °C, 13% of dihydroanthracene converted to form equal amounts of perhydroanthracene and tetrahydroanthracene with $NiMo/Al_2O_3$ while more than 25% converted with Mo/Al_2O_3 to form tetrahydroanthracene. No dihydroanthracene reacted catalytically at 225°C. Octahydroanthracene reacted at 380 °C with $NiMo/Al_2O_3$ to form 17% perhydroanthracene; octahydroanthracene did not hydrogenate at any of the other short-time reaction conditions.

The reaction pathway proposed for the dehydrogenation and hydrogenation of hexahydroanthracene is presented in Figure II.D.1.2. The first step in the dehydrogenation of hexahydroanthracene appeared from the reaction products to be the loss of a pair of hydrogens to form several isomers of tetrahydroanthracene. Although the direct dehydrogenation of hexahydroanthracene to dihydroanthracene can not be ruled out, in all of the thermal reactions with either nitrogen or hydrogen, tetrahydroanthracene appeared as an intermediate. Also, in the hydrogenation of dihydroanthracene, tetrahydroanthracene always appeared as an intermediate. Therefore, the products suggested that the dehydrogenation pathway passed through tetrahydroanthracene to several isomers of dihydroanthracene with the predominant product being 9,10-dihydroanthracene. Further loss of a pair of hydrogens resulted in the final dehydrogenation product, anthracene. After 60 min of thermal reaction, a small amount of octahydroanthracene was formed although none was observed at shorter reaction times.

Hexahydroanthracene also hydrogenated to form more fully saturated anthracenes; however, in the process some tetrahydroanthracene, a dehydrogenation product, was always formed. Hexahydroanthracene was catalytically hydrogenated to several isomers of octahydroanthracene. Octahydroanthracene was then further hydrogenated to the fully saturated PHA which was the final step in the hydrogenation process.

CONCLUSIONS

The results from this study point to the primary conclusion that cyclic olefins are highly reactive hydrogen donor species. Isotetralin reacted more than tetralin under all of the reaction conditions. The primary dehydrogenation pathway of isotetralin was dehydrogenating to 1,4-dihydronaphthalene and then forming naphthalene. The last step, 1,4-dihydronaphthalene to naphthalene, was reversible but the first step was not. By contrast, the primary dehydrogenation pathway for tetralin was tetralin forming 1,2-dihydronaphthalene and then forming naphthalene and all of the steps were reversible. The reactions with hexahydroanthracene showed that hexahydroanthracene was more reactive than either octahydroanthracene or dihydroanthracene. The primary reaction pathway proceeded by hexahydroanthracene dehydrogenating to tetrahydroanthracene which then formed dihydroanthracene and finally anthracene.

REFERENCES

1. Hessley, R.; Reasoner, J.; Riley, J. *Coal Science*; John Wiley and Sons, New York, NY (1986).

2. Maekawa, Y.; Nakata, Y.; Veda, S.; Yoshida, T.; Yoshida, Y. *ACS Symposium Series*, *139*, 315 (1980).

3. Schlosberg, R.H. *Chemistry of Coal Conversion*; Plenum Press, New York, NY (1985).

4. McMillen, D.; Malhotra, R.; Hum, G.; Chang, S. *Energy and Fuels, 1*, 193 (1987).

5. Bedell, M.W.; Curtis, C.W. *ACS Fuel Div. Preprints*; *2*, 577, (1990).

6. Curtis, C.W.; Guin, J.; Kwon, K. *Fuel*; *63*, 1404 (1984).

7. Neavel, R.C. *Fuel*; *63*, 237 (1984).

8. Utz, B.R.; Appell, H.R.; Blaustein, B.D. *Fuel; 55*, 1085 (1976).

9. Kitaoka, Y.; Mikio, U.; Ito, H.; Mikami, K. *Fuel; 61*, 919 (1982).

10. Bockrath, B.C. *Coal Science*; *2*, 65 (1982).

11. Franz, J.A.; Camaioni, D.M. *Prep. Paper, ACS Div. Fuel Chem.*; 26(1):105 (1981).

12. Ratto, J.; Henedy, C.; Skowronski, R. *ACS Symposium Series*; *139*, 347 (1980).

13. Virk, P.; Bass, D.; Eppig, C.; Ekpenyong, D. *ACS Symposium Series*; *139*, 330 (1980).

14. Derbyshire, F.J., Whitehurst, D. *Fuel; 60*, 655 (1981).

15. Kaiser, E. *Synthesis;* 391 (1972).

16. Mejer, S.; Porycki, J.; Jablonski, C. *Rocz. Chem.*; *51*, 1755 (1977).

17. Kariv-Miller, E.; Pacut, R. *Tetrahedron; 42*, 2185 (1986).

Table II.D.1.1. Thermal Reactivity of Isotetralin, Tetralin and 1,4-Dihydronaphthalene

			Product Distribution, wt%				
Donor	Conditions[a]	Time (min)	NAP	1,2-DHN	1,4-DHN	TET	ISO
ISO	N_2	2	3.6(0.1)	0.0	48.4(0.3)	1.6(0.1)	46.4(0.3)
	N_2	30	55.1(1.5)	4.6(0.5)	36.7(1.0)	3.6(0.4)	0.0
	H_2	2	2.2(0.2)	3.1(.07)	39.1(1.8)	3.3(1.5)	52.3(2.9)
	H_2	15	30.5(0.5)	23.8(4.6)	27.9(12.3)	17.8(6.0)	0.0
	H_2	30	52.6(2.3)	10.0(2.6)	26.8(3.7)	10.6(1.2)	0.0
	H_2	60	61.1(2.1)	11.5(1.7)	1.1(0.3)	26.3(3.5)	0.0
TET	N_2	30	0.8(0.2)	0.0	0.0	99.2(3.8)	0.0
	H_2	30	0.7(0.1)	1.0(0.1)	2.1(0.3)	96.2(2.3)	0.0
1,4-DHN	N_2	30	60.2(1.7)	0.0	28.5(1.6)	11.3(0.8)	0.0
	H_2	30	44.9(0.3)	11.5(0.3)	1.7(0.5)	41.9(0.6)	0.0

[a] Reaction conditions: 380 °C, 425 cpm, 1,250 psig N_2 or H_2 charge at ambient temperature.

[b] Abbreviations: NAP = naphthalene; 1,2,-DHN = 1,2-dihydronaphthalene; 1,4-DHN = 1,4-dihydronaphthalene; TET = tetralin; and ISO = isotetralin

Table II.D.1.2. Catalytic Reactivity of Isotetralin, Tetralin and 1,4-Dihydronaphthalene

			Product Distribution					
Donor	Conditions[a]	Time (min)	NAP[c]	TET	ISO	OHN	c-DEC	t-DEC
ISO	NiMo	2	1.1(0.3)	77.6(0.6)	0.0	1.3(0.3)	5.1(0.3)	15.0(0.8)
	NiMo	15	0.0	43.0(1.2)	0.0	0.0	14.4(0.4)	42.6(1.3)
	NiMo	30	0.0	36.6(9.8)	0.0	0.0	15.4(2.7)	48.0(7.8)
	NiMo	60	0.0	8.5(4.3)	0.0	0.0	21.8(0.2)	69.6(0.4)
	Mo	2	1.7(0.04)	77.9(0.2)	0.6(0.1)	12.8(1.9)	1.8(0.3)	5.2(1.9)
	Mo	15	1.1(0.1)	79.7(3.3)	0.0	0.0	5.4(0.7)	13.8(3.3)
	Mo	30[b]	1.0(0.1)	77.6(2.0)	0.0	0.0	6.0(0.6)	15.4(0.9)
	Mo	30[b]	1.2(0.2)	76.0(0.9)	0.0	0.0	5.9(0.5)	16.9(0.5)
	Mo	60	0.8(0.0)	75.8(1.2)	0.0	0.0	6.5(0.1)	16.9(1.1)
TET	NiMo	30	0.0	24.5(3.5)	0.0	0.0	19.1(0.5)	56.4(1.5)
	Mo	30	0.7(0.5)	94.9(1.5)	0.0	0.0	1.3(0.2)	3.1(0.6)
1,4-DHN	NiMo	30	0.0	51.7(3.7)	0.0	0.0	12.4(1.1)	35.9(2.7)
	Mo	30	4.7(1.7)	95.8(1.7)	0.0	0.0	0.0	0.0

[a] Reaction conditions: 380 °C, 425 cpm, 1,250 psig H_2 charge at ambient temperature, 3,000 ppm active metal loading.
[b] Reactions were performed 4 months apart.
[c] Abbreviations: NAP = naphthalene, TET = tetralin, ISO = isotetralin, OHN = octahydronaphthalene, c-DEC = cis-decalin, t-DEC = trans-decalin

Table II.D.1.3. Thermal Reactivity of Isotetralin and 1,4-Dihydronaphthalene at Short Reaction Time

			Reaction Products, wt%				
Donor	Conditions[a]	Time (min)	NAP[b]	1,2-DHN	1,4-DHN	TET	ISO
ISO	N_2, 380°C	2	3.6(0.1)	0.0	48.4(0.3)	1.6(0.1)	46.4(0.3)
	H_2, 380°C	2	2.2(0.2)	3.1(0.7)	39.1(1.8)	3.3(1.5)	52.3(2.9)
	N_2, 225°C	2	0.0	0.0	2.8(0.3)	0.0	97.2(0.3)
	H_2, 225°C	2	0.0	0.0	1.7(0.3)	0.0	98.3(0.3)
1,4-DHN	N_2, 380°C	2	13.3(0.4)	11.3(0.2)	75.4(0.2)	0.0	0.0
	H_2, 380°C	2	13.0(0.2)	12.8(0.9)	74.2(1.1)	0.0	0.0
	N_2, 225°C	2	10.7(1.7)	10.9(0.3)	78.4(1.5)	0.0	0.0
	H_2, 225°C	2	9.2(0.3)	11.0(0.2)	79.8(0.3)	0.0	0.0

[a] Reaction conditions: agitation at 425 cpm, 1,250 psig H_2 or N_2 charge at ambient temperature.
[b] Abbreviations: NAP = naphthalene; 1,2-DHN = 1,2-dihydronaphthalene; 1,4-DHN = 1,4-dihydronaphthalene; TET = tetralin; ISO = isotetralin

Table II.D.1.4. Catalytic Reactivity of Isotetralin, Tetralin, 1,4-Dihydronaphthalene, and 1,2-Dihydronaphthalene at Short Reaction Time

			Reaction Products, wt%							
Donor	Conditions[a]	Time (min)	NAP[b]	1,2-DHN	1,4-DHN	TET	ISO	OHN	c-DEC	t-DEC
ISO	380°C, NiMo	2	1.1(0.3)	0.0	0.0	77.5(0.6)	0.0	1.3(0.3)	5.1(0.3)	15.0(0.8)
	380°C, Mo	2	1.7(0.04)	0.0	0.0	77.9(0.2)	0.6(0.1)	12.8(1.9)	1.8(0.3)	5.2(1.3)
	225°C, NiMo	2	0.0	0.9(1.0)	4.4(0.4)	79.9(1.0)	0.0	11.3(0.4)	0.0	3.5(0.0)
	225°C, Mo	2	0.0	8.1(0.1)	11.2(0.3)	44.9(1.6)	23.9(2.1)	9.4(0.4)	0.0	2.5(0.3)
TET	380°C, NiMo	2	0.0	0.0	0.0	96.8(1.1)	0.0	0.0	trace	3.2(1.1)
	380°C, Mo	2	trace	0.0	0.0	100.0	0.0	0.0	0.0	0.0
	225°C, NiMo	2	trace	0.0	0.0	100.0	0.0	0.0	0.0	0.0
	225°C, Mo	2	trace	0.0	0.0	100.0	0.0	0.0	0.0	0.0
1,4-DHN	380°C, NiMo	2	3.7(0.2)	0.0	0.0	94.9(0.2)	0.0	0.0	trace	3.2(1.1)
	380°C, Mo	2	11.0(0.2)	0.0	0.0	89.0(0.2)	0.0	0.0	0.0	trace
	225°C, NiMo	2	15.3(0.1)	19.8(2.8)	1.0(1.1)	63.9(4.0)	0.0	0.0	0.0	0.0
	225°C, Mo	2	11.4(0.1)	18.8(0.9)	60.8(0.4)	9.0(0.3)	0.0	0.0	0.0	0.0
1,2-DHN	380°C, NiMo	2	9.1(4.7)	0.0	0.0	90.9(4.7)	0.0	0.0	0.0	0.0
	380°C, Mo	2	6.8(3.5)	0.0	0.0	93.2(3.5)	0.0	0.0	0.0	0.0
	225°C, NiMo	2	0.0	17.3(8.5)	3.1(0.5)	79.6(8.0)	0.0	0.0	0.0	0.0
	225°C, Mo	2	trace	44.7(0.4)	trace	55.3(0.4)	0.0	0.0	0.0	0.0

[a] Reaction conditions: 425 cpm, 1,250 psig H_2 charge at ambient temperature
[b] Abbreviations: NAP = naphthalene; 1,2-DHN = 1,2-dihydronaphthalene; 1,4-DHN = 1,4-dihydronapthalene; TET = tetralin; ISO = isotetralin; OHN = octahydronaphtha; c-DEC = cis-decalin; t-DEC = trans-decalin

Table II.D.1.5. Thermal Reactivity of Hexahydroanthracene, Dihydroanthracene, and Octahydroanthracene

			Product Distribution, wt%				
Donor	**Conditions[a]**	**Time (min)**	**ANT[b]**	**DHA**	**THA**	**HHA**	**OHA**
HHA	N_2	2	0.0	40.8(3.3)	12.2(1.0)	47.0(4.3)	0.0
	N_2	30	15.0 (2.7)	71.5(10.0)	13.5(2.9)	trace	0.0
	H_2	2	0.0	29.3(0.5)	9.8(0.4)	60.9(0.7)	0.0
	H_2	15	2.1(0.2)	78.1(8.1)	9.8(5.1)	10.0(5.3)	0.0
	H_2	30	7.0(0.8)	83.1(4.4)	8.6(1.8)	1.3(0.4)	0.0
	H_2	60	5.1(0.9)	68.5(3.9)	20.2(3.7)	1.7(0.4)	4.5(1.3)
DHA	N_2	30	5.0(0.6)	95.0(3.7)	0.0	0.0	0.0
	H_2	30	5.7(0.5)	92.1(2.1)	2.2(0.8)	0.0	0.0
OHA	N_2	30	0.0	0.0	trace	0.0	100.0
	H_2	30	0.0	0.0	0.0	0.0	100.0

[a] Reaction conditions: 380°C, 425 cpm, 1,250 psig H_2 or N_2 charged at ambient temperature.
[b] Abbreviations: ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene.

Table II.D.1.6. Cataiytic Reactivity of Hexahydroanthracene, Dihydroanthracene and Octahydroanthracene

			Product Distribution, wt%			
Donor	Conditions[a]	Time (min)	PHA[b]	OHA	THA	DHA
HHA	NiMo	2	7.8(0.6)	84.7(0.3)	7.5(0.8)	0.0
	NiMo	15	48.7(9.9)	49.6(5.3)	1.7(0.5)	0.0
	NiMo	30	54.8(8.5)	43.5(10.5)	1.7(0.3)	0.0
	NiMo	60	87.8(4.4)	12.2(2.1)	trace	0.0
	Mo	2	4.5(0.3)	71.4(0.6)	24.1(0.3)	0.0
	Mo	15	9.0(0.2)	79.1(7.5)	11.9(0.9)	0.0
	Mo	30	7.0(0.5)	80.4(5.9)	12.6(0.9)	0.0
	Mo	60	13.3(0.4)	84.1(3.3)	2.6(0.2)	0.0
DHA	NiMo	30	64.0(2.2)	35.1(5.0)	0.9(0.1)	0.0
	Mo	30	0.0	70.8(2.0)	21.1(1.0)	8.1(1.1)
OHA	NiMo	30	67.9(4.9)	32.1(3.7)	0.0	0.0
	Mo	30	0.0	97.8(4.2)	2.2(0.1)	0.0

[a] Reaction conditions: 380 °C, 425 cpm, 1,250 psig H_2 charged at ambient temperature.
[b] Abbreviations: PHA = perhydroanthracene; OHA = octahydroanthracene; THA = tetrahydroanthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene.

Table II.D.1.7. Thermal Reactivity of Hexahydroanthracene, Dihydroanthracene and Octahydroanthracene at Short Reaction Time

Product Distribution, wt%							
Donor	**Conditions[a]**	**Time (min)**	**ANT[b]**	**DHA**	**THA**	**HHA**	**OHA**
HHA	N_2, 380°C	2	0.0	0.8(3.3)	12.2(2.0)	47.0(4.3)	0.0
	H_2, 380°C	2	0.0	29.3(0.5)	9.8(0.4)	60.9(0.7)	0.0
	N_2, 225°C	2	0.0	1.9(0.4)	0.8(0.1)	97.3(0.3)	0.0
	H_2, 225°C	2	0.0	1.2(0.4)	0.5(0.2)	98.3(0.2)	0.0
DHA	N_2, 380°C	2	0.4	99.6(0.3)	0.0	0.0	0.0
	H_2, 380°C	2	1.4(1.6)	98.6(1.6)	0.0	0.0	0.0
	N_2, 225°C	2	1.1(0.1)	98.9(0.1)	0.0	0.0	0.0
	H_2, 225°C	2	1.7(0.2)	98.3(0.2)	0.0	0.0	0.0
OHA	N_2, 380°C	2	0.0	0.0	0.0	0.0	100.0
	H_2, 380°C	2	0.0	0.0	0.0	0.0	100.0
	N_2, 225°C	2	0.0	0.0	0.0	0.0	100.0
	H_2, 225°C	2	0.0	0.0	0.0	0.0	100.0

[a] Reaction conditions: 425 cpm, 1,250 psig N_2 or H_2 charge at ambient temperature.
[b] Abbreviations: ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene.

Table II.D.1.8. Catalytic Reactivity of Hexahydroanthracene, Dihydroanthracene and Octahydroanthracene at Short Reaction Time

			Product Distribution, wt%					
Donor	Conditions[a]	Time (min)	PHA[b]	OHA	HHA	THA	DHA	ANT
HHA	380°C, NiMo	2	7.8(0.6)	84.7(0.3)	0.0	7.5(0.8)	0.0	0.0
	380°C, Mo	2	4.5(0.3)	71.4(0.2)	0.0	24.1(0.3)	0.0	0.0
	225°C, NiMo	2	2.2(0.2)	74.0(4.1)	0.0	23.8(4.0)	0.0	0.0
	225°C, Mo	2	2.3(0.2)	42.8(3.3)	49.2(4.4)	3.8(0.9)	1.9(0.1)	0.0
DHA	380°C, NiMo	2	6.9(0.8)	0.0	0.0	6.3(1.2)	86.8(0.4)	0.0
	380°C, Mo	2	0.0	0.0	0.0	22.7(1.0)	74.8(1.0)	2.5(0.2)
	225°C, NiMo	2	0.0	0.0	0.0	trace	100.0	0.0
	225°C, Mo	2	0.0	0.0	0.0	trace	100.0	0.0
OHA	380°C, NiMo	2	17.2(3.2)	82.8(3.2)	trace	0.0	0.0	0.0
	380°C, Mo	2	0.0	100.0	0.0	0.0	0.0	0.0
	225°C, NiMo	2	0.0	100.0	0.0	0.0	0.0	0.0
	225°C, Mo	2	0.0	100.0	0.0	0.0	0.0	0.0

[a] Reaction Conditions: 425 cpm, 1,250 psig H_2 charge at ambient temperatue.
[b] Abbreviations: PHA = perhydroanthracene; OHA = octahydroanthracene; HHA = hexahydroanthracene; THA = tetrahydroanthracene; DHA = dihydroanthracene; ANT = anthracene

Figure 11.D.1.1. REACTION PATHWAY FOR ISOTETRALIN.

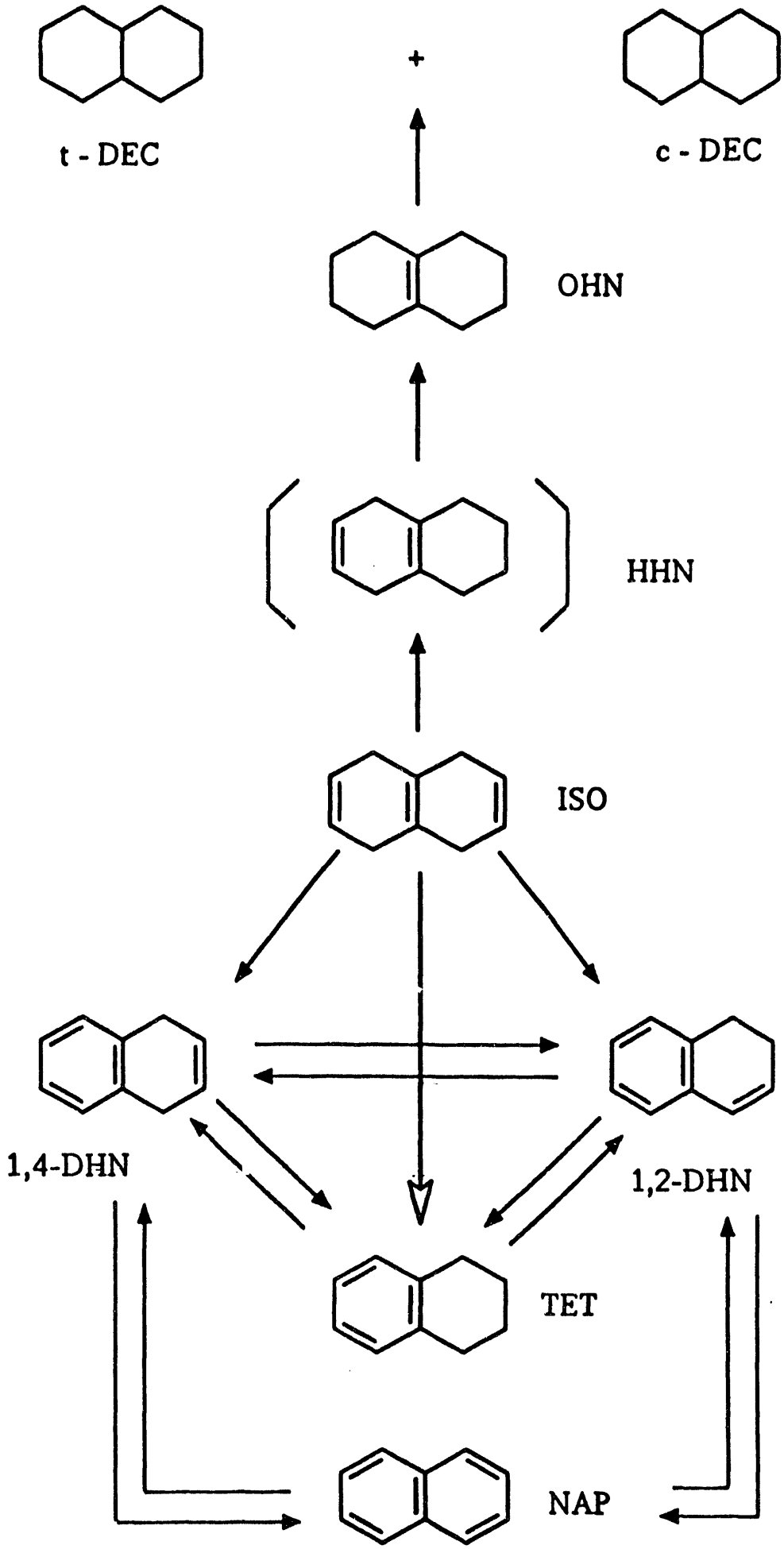
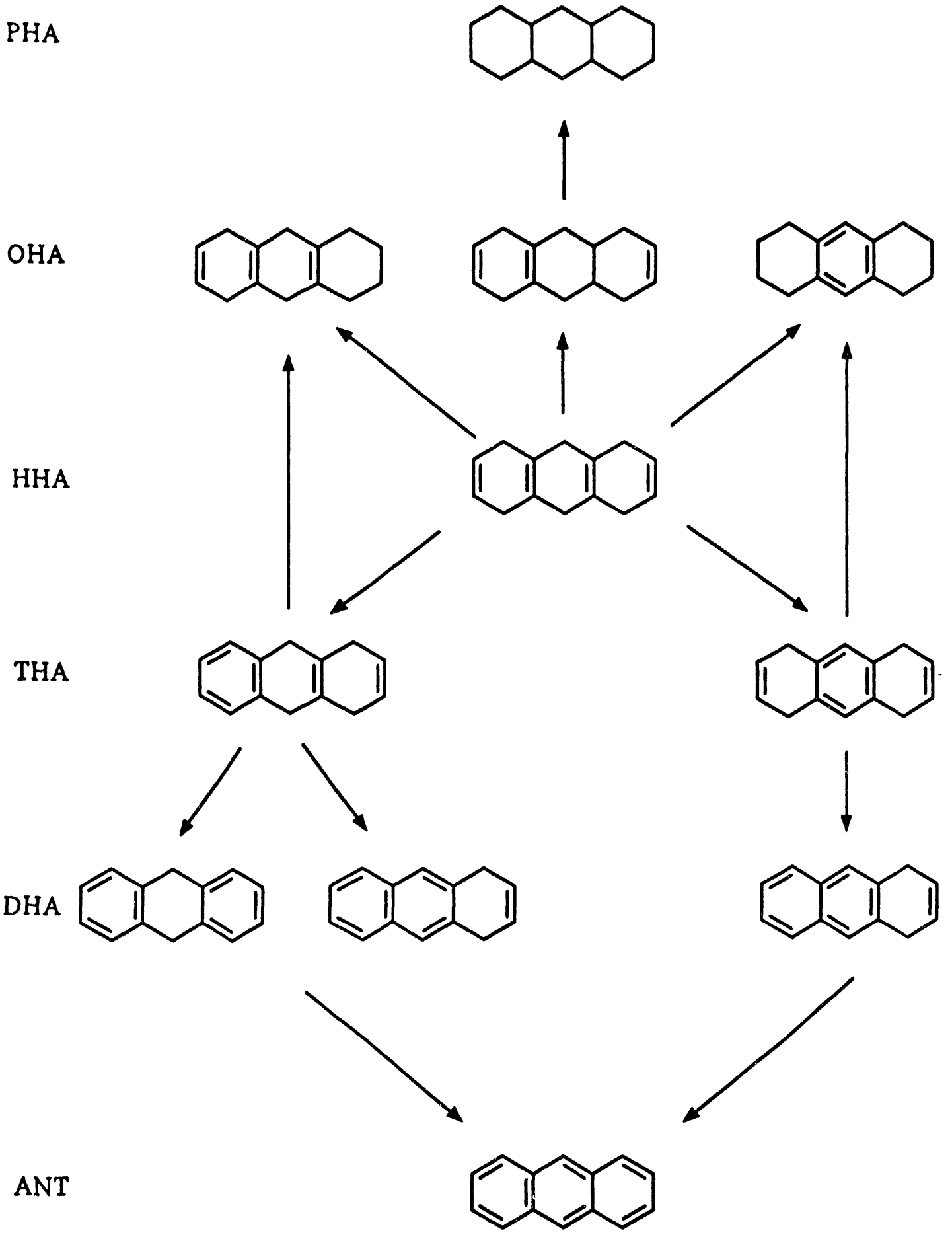


Figure II.D.1.2. REACTION PATHWAY FOR HEXAHYDROANTHRACENE.



SUBTASK II.D.2.a

CHEMISTRY AND REACTIVITY OF NONAROMATIC HYDROAROMATIC DONOR ENRICHED PETROLEUM SOLVENTS

INTRODUCTION

The current emphasis in coal liquefaction is two-stage processing. The first stage is sometimes a high-temperature, high-severity thermal break-up of the coal macromolecule. This stage is followed by catalytic upgrading of the thermal reaction products. One of the keys to making coal liquefaction an economically feasible process is the control of hydrogen utilization. Effective and efficient hydrogen utilization can increase the amount of coal conversion and produce upgrading of the coal liquids to a more valuable product slate. Hydrogen donor reactions are considered to be an important mechanism by which hydrogen is transferred from solvent to coal during liquefaction.[1-3] These reactions are considered to be important in liquefying coals thermally[4] as well as in some catalytic systems.[5] The types of compounds that have typically been considered to be hydrogen donors are hydroaromatic species and phenols.[6-13] A set of reactions employing a series of hydrogen donors[4] has shown that cyclic olefins, i.e., hydroaromatic compounds without the aromatic rings, are effective donors for coal liquefaction. Subsequent research by Bedell and Curtis[13] has shown that cyclic olefins are highly reactive at liquefaction conditions forming other partially saturated aromatics and aromatics as products. Cyclic olefins serve as active donors for liquefying coal at temperatures of 380 and 410 °C under an inert atmosphere.

This investigation evaluates the efficacy of hydrogen donation from cyclic olefins and compares the amount of coal conversion and the types of coprocessing products achieved with those of their conventional hydroaromatic analogues. The cyclic olefins used in this study were

isotetralin (ISO) and 1,4,5,8,9,10-hexahydroanthracene (HHA); their hydroaromatic analogues, tetralin (TET), dihydroanthracene (DHA) and octahydroanthracene (OHA), were also used. The reaction of Western Kentucky No. 9 coal with these hydrogen donors was performed at conditions that included N_2 and hydrogen atmospheres with diluent solvents of fluorene, hexadecane, and Maya resid in thermal and catalytic reactions. Two different presulfided catalysts, Mo/Al_2O_3 and $NiMo/Al_2O_3$, were employed. In the reactions with nitrogen, the only source of hydrogen was from the hydrogen donor; in the hydrogen atmosphere, the hydrogen available from molecular hydrogen was 10 times more than that from the hydrogen donor, if all the donable hydrogen were released as molecular hydrogen.

EXPERIMENTAL

The reactions of the cyclic olefins, ISO and HHA, and three conventional hydroaromatic donor compounds, TET, DHA and OHA, with Western Kentucky No. 9 coal were performed. The following reaction conditions were employed: 30 min reaction time, 1,250 psig N_2 or H_2 atmosphere at ambient temperature, 380 or 410 °C reaction temperature, 2.0 g coal, 4.0 g total solvent mixture including different levels of donable hydrogen ranging from 0.1 to 0.5 wt%, with the balance being fluorene, hexadecane, or Maya resid as the diluent solvent, and 700 cpm vertical agitation rate using stainless steel tubular reactors of approximately 50 cm^3 volume. The reaction temperatures were limited to 380 and 410 °C because of the high reactivity of the cyclic olefins. In the reactions with hydrogen, the amount of hydrogen available from molecular hydrogen was 0.35 g and the amount of hydrogen available from the added donor when added at 0.5 wt% was 0.03 g if all of the hydrogen were released from the hydrogen donor. If the hydrogen was released from the hydrogen donor as molecular hydrogen, the effect would be increasing the initial hydrogen pressure from 1,250 psig to 1,366 psig. Since the amount of

molecular hydrogen present initially was already in excess, this small amount of additional hydrogen would have little effect on the coal conversion obtained in the reaction. In the reactions with nitrogen, the 0.03 g of possible molecular hydrogen from the donors would correspond to an initial hydrogen pressure of 108 psig at ambient. The amount of coal conversion to tetrahydrofuran (THF) solubles was determined in at least duplicate reactions.

The chemicals were obtained from the following manufacturers and used as received: tetralin, 1,4,5,8,9,10-hexahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydroanthracene, fluorene and hexadecane from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene from Wiley Organics Inc.; Western Kentucky No. 9 coal from the PSU/DOE sample bank; and Maya vacuum resid from Amoco Oil Co. For the catalytic reactions with hexadecane and the coprocessing reactions with Maya resid, two commercial hydrogenation catalysts were used, Mo/Al_2O_3 (Amocat 1B) and $NiMo/Al_2O_3$ (Shell 324). Each catalyst was presulfided in a temperature programmed flowing stream of 10% H_2S in hydrogen for approximately 5 hr at temperatures ranging from 200 to 470 °C, which was increased in a step-wise fashion. The presulfided catalysts were cooled in a N_2 atmosphere and stored in a desiccator. The catalysts were pulverized and sized between 100 and 200 mesh before being used.

The hydrogen donor compounds and their products from the coal liquefaction and coprocessing reactions were analyzed by gas chromatography using a Varian 3400 GC equipped with a HT-5 column from SGE and FID detection. The internal standard method was used for quantitation with biphenyl as the internal standard. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectral analysis using a VG70 EHF mass spectrometer. For this work coal conversion is defined as conversion = {1-[IOM (maf)/coal charge (maf)]} x 100 where IOM is the insoluble organic matter remaining after the reaction and

maf is defined as moisture and ash free. The moisture content of Western Kentucky No. 9 coal was experimentally determined to be 4.5 $\pm$ 0.6% and the ash content, 10.16 $\pm$ 0.14%.

The THF soluble fraction of the reaction products was analyzed by liquid chromatography. This technique, a modification of the procedure that was developed by Boduszynski et al.,[15,16] consisted of eluting a series of solvents, hexane, toluene, chloroform, chloroform/ methanol mixture in a 4 to 1 volumetric ratio, and THF through two 80 ml chromatography columns. The first column consisted of basic alumina, which yielded the actual compound class separation. The four compound classes obtained consisted of (1) hydrocarbons, (2) nitrogen heterocycles, (3) hydroxyl aromatics, and (4) polyfunctional compounds.

RESULTS AND DISCUSSION

Reactions of Hydrogen Donors with Western Kentucky No. 9 Coal

A series of reactions using ISO and HHA and their hydroaromatic analogues, TET, OHA, and DHA, with Western Kentucky No. 9 coal was performed to determine the effectiveness of hydrogen donation from cyclic olefins in comparison to their analogues. These reactions used either fluorene or hexadecane as the diluent solvent and were reacted at a variety of conditions. The two model solvents were chosen because of their relative inertness under the reaction conditions employed and to minimize interferences in the GC analysis of the products. Hexadecane, a straight chain aliphatic solvent, represented an inert solvent with low coal solvating ability, while fluorene, an aromatic species, represented a coal-derived solvent, having greater coal solvating ability.

The reactions were analyzed by first determining the amount of coal conversion achieved under the various reaction conditions. The soluble products were analyzed in two ways. First, the reaction products from the model donors were determined by gas chromatography in order

to determine the degree of reactivity and type of reaction products achieved. Second, the THF soluble fraction of the liquefied coal was fractionated into compound classes to evaluate the effect of the different donors and reaction conditions on the product achieved.

Reactions with Fluorene as the Diluent Solvent. A series of thermal reactions was conducted in a N_2 atmosphere with fluorene as the diluent solvent. Reactions were performed with the five donor species at an equivalent loading of 0.5 wt% donable hydrogen as well as with HHA, DHA, and OHA at three different levels of donable hydrogen, 0.5, 0.2, 0.1 wt%. The amount of coal conversion to THF solubles obtained in duplicate or more reactions and the standard deviation for each of the reactions is presented in Table II.D.2.a.1. At the 0.5 wt% level of donable hydrogen, HHA and ISO yielded more coal conversion than did any of their respective hydroaromatic analogues. Hexahydroanthracene produced an increase in coal conversion of ~12% more than its nearest analogue, DHA, and 13% more than OHA. (Note: all percentages are given in weight percent.) Isotetralin yielded ~14% [illegible] version than TET. At lower donable hydrogen levels, HHA consistently converted more coal than did either DHA or OHA, albeit, in decreasing differential amounts as the level of donable hydrogen decreased. This differential decrease implied that a deficiency of hydrogen occurred at these lower levels of donable hydrogen. This decreased conversion suggested that the free radicals from coal were being formed at a faster rate than could be capped by the limited amount of available donable hydrogen. However, the very reactive HHA produced greater coal conversion than its analogues, even in this hydrogen deficient regime. The cyclic olefin HHA also produced greater conversion, 78.2%, than OHA, 75.5%, and DHA, 76.6%, at 2.5 times lower level of donable hydrogen, i.e., 0.2 wt% versus 0.5 wt% for OHA and DHA. A similar decrease in efficiency at lower hydrogen donor levels was observed with a series of twenty-three donors reported previously.[4]

Reactions of Western Kentucky No. 9 coal were performed in N_2 and H_2 atmospheres, both thermally and catalytically with the addition of hydrogen donors at a constant level of 0.5 wt% donable hydrogen. The amount of coal conversion achieved with fluorene as a diluent solvent and under a number of different experimental conditions is described in Table II.D.2.a.2. The thermal reactions with Western Kentucky No. 9 coal under nitrogen at both 380 and 410 °C showed differences in the amount of coal conversion achieved with the different types of added donor species. However, a greater difference was observed between HHA and ISO and their respective analogues at 380 °C than at 410 °C. Previous reactivity studies[13] of these hydrogen donors in the presence of coal showed that the donors converted more quickly to their respective reaction products at 410 °C than they did at 380 °C. The cyclic olefins rapidly produced dehydrogenated products, principally aromatic species, e.g., anthracene for HHA and naphthalene for TET, that did not serve as donors to coal.[13]

Substantial coal conversion occurred in these reactions at 410 °C under nitrogen regardless of the type of donor added because the solvent fluorene had a substantial soivating power at this condition. Even without a donor present, fluorene yielded 57.4% coal conversion. Fluorene itself, however, did not serve as a hydrogen donor to this system. This conclusion was reached by performing an experiment in which fluorene was added to a Western Kentucky No. 9 coal reaction system at a level of 0.5 wt% donable hydrogen. Two donable hydrogens per fluorene molecule were assumed and hexadecane was used as the diluent solvent. Less than 29% coal conversion was observed with fluorene under either a N_2 or a hydrogen atmosphere. By comparison, ISO, added at this same level using hexadecane as a solvent in a hydrogen atmosphere, yielded 49.7% coal conversion. Only 27% coal conversion was obtained in the reaction of coal and hexadecane under hydrogen. Hence, fluorene served as a good physical solvating

agent for Western Kentucky No. 9 coal under the conditions employed, but did not act as a hydrogen donor.

In order to investigate the effect of atmosphere on the coal conversions obtained in the liquefaction reactions, hydrogen was also used in the reaction of the five donors with Western Kentucky No. 9 coal in fluorene. No substantial difference in coal conversion was observed either with or without the addition of model donors. Consistent coal conversions were obtained at ~77%. Since these reactions were performed in hydrogen, the high conversion of the coal probably resulted from either the solvating or hydrogen shuttling properties of fluorene. In either case, the effect of the added hydrogen donors was masked by the diluent solvent in a hydrogen atmosphere. In order to more fully investigate the effect of the hydrogen donor species in a thermal reaction system under hydrogen, the reactions were repeated using a more inert diluent solvent, hexadecane.

Reactions with Hexadecane as the Diluent Solvent. In reactions with Western Kentucky No. 9 coal and fluorene under a N_2 atmosphere, a coal conversion of 57% was observed just from the solvent fluorene alone, Table II.D.2.a.1, indicating a substantial solvating power of fluorene under the reaction conditions employed. In contrast, the corresponding reactions in hexadecane produced only ~27% coal conversion to THF solubles, indicating that hexadecane itself had little reactivity, did not readily donate hydrogen, and did not provide a good solvating medium for the Western Kentucky No. 9 coal. Coal conversions obtained thermally in a hydrogen atmosphere with hexadecane as the diluent solvent showed substantial coal conversions that were dependent upon the model hydrogen donor species present in the system, Table II.D.2.a.2. Isotretralin, a cyclic olefin, produced a coal conversion of nearly 50%, which was almost 20% greater than its conventional donor analogue, TET. Hexahydroanthracene produced 65% coal conversion, which

was 18% greater than its analogue OHA. Dihydroanthracene also had a high reactivity yielding approximately 3% more coal conversion than the cyclic olefin HHA. Dihydroanthracene in a hydrogen atmosphere was as an effective hydrogen donor compound as HHA, although it was less effective in a N_2 atmosphere. In reactions in the absence of coal, the rate of dehydrogenation of DHA was much less than that of HHA, e.g., DHA was less than 8% converted in a hydrogen atmosphere with a 60 min reaction time while HHA was more than 98% converted.[13] Yet, in the presence of coal, DHA donated its hydrogen as illustrated by the relatively high degree of conversion obtained, 68%. It appears that DHA was unreactive and an ineffectual hydrogen donor species when reacted by itself, but in the presence of an acceptor, DHA was a very reactive species.

Catalytic reactions were performed to evaluate the effect of commercial hydrogenation catalysts, Mo/Al_2O_3 and $NiMo/Al_2O_3$, on the conversion of coal and the reaction products obtained from the hydrogen donors. Presulfided Mo/Al_2O_3 decreased the amount of coal conversion obtained with the two cyclic olefins, ISO and HHA, when compared to that obtained with the thermal reaction systems. The reduction in coal conversion with HHA was rather substantial, being more than 10%. Coal conversion in the presence of Mo/Al_2O_3 with OHA increased, while DHA remained essentially the same and TET decreased. Reactions were performed in a hydrogen atmosphere with $NiMo/Al_2O_3$ to explore the effect of a more active hydrogenation catalyst on the ultimate coal conversion in the presence of the added hydrogen donors. When compared to the corresponding thermal reaction, the presence of $NiMo/Al_2O_3$ decreased coal conversion in the reactions containing ISO and HHA; ISO decreased substantially more than HHA. A small increase in conversion occurred in the reactions containing DHA and OHA. Dihydroanthracene and HHA produced greater coal conversion with $NiMo/Al_2O_3$ than with Mo/Al_2O_3.

Octahydroanthracene produced nearly equivalent conversion with the two catalysts, while ISO and TET produced more conversion with Mo/Al_2O_3.

The lower conversion obtained with the cyclic olefins in the catalytic reactions compared to the thermal most likely occurred because the more active catalytic systems enhanced the rate of dehydrogenation of the cyclic olefins causing them to release their donable hydrogen at a rate faster than the acceptor sites of the dissolving coal matrix could utilize this hydrogen. Model compound reactions[13] under equivalent conditions suggested that the cyclic olefins were partially dehydrogenated in the initial stages of the reaction, even in the catalytic systems under hydrogen. In the process of losing their initial hydrogen rapidly, ISO and HHA were converted to hydrogen donor species as 1,2-dihydronaphthalene and 1,4-dihydronaphthalene or tetrahydroanthracene and DHA, respectively. Then in the catalytic systems these dehydrogenation products were rehydrogenated to TET or OHA and perhydroanthracene (PHA), respectively. These hydro-aromatic donor species have been shown to be much less reactive than the cyclic olefins[13] and, therefore, would produce correspondingly less overall coal conversion for a given reaction time than if the cyclic olefins were able to retain their full activity, thereby, making the reactivity of the highly reactive donor system similar to that of the conventional donors.

Coprocessing Reactions of Hydrogen Donors with Western Kentucky No. 9 coal and Maya Resid. The effect of using resid as a solvent on coal conversion with the added cyclic olefins was investigated by using Maya resid as the diluent solvent and performing corresponding reactions as those with either fluorene or hexadecane. Similar effects of the hydrogen donors were observed as occurred in the hexadecane reaction systems. For the reactions at 380 °C under nitrogen, Table II.D.2.a.2, ISO produced ~ 12% more coal conversion that TET; HHA produced ~ 12% more coal conversion than OHA and ~ 10% less conversion that DHA.

Dihydroanthracene was relatively more active at 0.5 wt% donable hydrogen level than was HHA. As was previously mentioned, the experiments were configured to maintain a constant level of potentially donable hydrogen (0.5 wt%), as well as to hold the total mass of the reaction mixture constant. All of the reactions with added hydrogen donors except those with DHA, contained approximately the same quantity of resid, 3.0 to 3.5 g, while the reactions with DHA had ~1.2 g resid present. Since the higher observed coal conversion with DHA when compared to HHA most probably resulted from a solvent effect caused by DHA being the predominant solvent species rather than the resid, reactions were repeated with 3.0 g resid present while maintaining the same amount of donable hydrogen. When the two reactions involving DHA were compared, the higher resid content (3 g) resulted in lower conversion, 56%, compared to 66% when the lower amount of resid, 1.2 g, was present. Hence, the poorer solvating properties of the resid compared to DHA affected the reaction by inhibiting the amount of coal conversion obtained. Because of this solvent effect, the subsequent coprocessing studies all included two sets of DHA reactions, one at lower resid loading and one at the higher in order to compare the hydrogen donability of the cyclic olefins and hydroaromatic donors on a more equivalent basis.

In a N_2 atmosphere, increasing the reaction temperature from 380 to 410 °C, coal conversion decreased slightly for the cyclic olefins, ISO and HHA, while increasing for their hydroaromatic analogues, TET, OHA, and DHA. However, the ranking of coal conversion with model donors remained the same. In a hydrogen atmosphere at 380 °C, coal conversion increased for all of the reactions when compared to that obtained under nitrogen. The conversion obtained for the two cyclic olefins, ISO and HHA, increased approximately 16% each in a hydrogen atmosphere. This dramatic increase in coal conversion with the cyclic olefins suggested that the hydrogen atmosphere shifted the equilibrium toward the cyclic olefin, slowing the rate of the

reaction, and thereby, allowing the cyclic olefins to remain in the reaction system for a longer length of time. This longer lifetime, in turn, allowed the reactive cyclic olefins to release their hydrogen at a slower rate that more closely matched the acceptance rates of the liquefying coal, resulting in higher coal conversion.

Catalytic coprocessing reactions employing presulfided $NiMo/Al_2O_3$ and Mo/Al_2O_3 were also performed. In both catalytic reaction systems, ISO produced more coal conversion than TET; HHA yielded greater coal conversion than OHA, but substantially less conversion than either of the DHA reactions. When comparing the coal conversion obtained in the reactions with Mo/Al_2O_3 to that in the thermal reactions, there was an increase in coal conversion in the reactions with OHA, TET, and no added hydrogen donor compound in the catalyst system, little change in conversion with the reactions of ISO and DHA (with 3.0 g resid), and a decrease in conversion for those reactions with HHA and DHA (with 1.2 g resid). For the reactions with $NiMo/Al_2O_3$, an increase in coal conversion over the thermal reactions occurred in those reactions with DHA (3.0 g resid), OHA, TET, and with no added donor. A decrease in coal conversions was obtained with ISO and HHA, while no change was observed in the coal conversion with DHA and 1.2 g resid. The effect of the two catalysts on coal conversion varied with the type of donor present. Coal conversion was less with Mo/Al_2O_3 when compared to $NiMo/ Al_2O_3$, while coal conversion for the reactions with TET was lower than that obtained with only resid present.

Reactions involving HHA and OHA with $NiMo/Al_2O_3$ were performed at two different catalyst metal loadings, 3,000 ppm and 12,000 ppm (Table II.D.2.a.2) to determine the effect of a four-fold increase in active metals on coal conversion. No substantial differences in the coal conversion were obtained at the two loading levels. This similarity in conversion indicated that at a loading of 3,000 ppm, reactivity was not limited by the amount of catalyst that was present.

Analysis of Products From the Model Hydrogen Donors

The THF soluble fraction was further analyzed by GC to determine the effect of the coal reaction on the reactions occurring with the added hydrogen donors. Table II.D.2.a.3 presents the product distributions for the reactions at three levels of donable hydrogen. The distributions of the products from the donor species in reactions with the two different diluent solvents for each of the six different reaction conditions are presented in Table II.D.2.a.4. By having the product distributions, the net amount of hydrogen lost though dehydrogenation or donation in each reaction system can be calculated.

Reactions with Fluorene as the Diluent Solvent. A substantial difference in the reactivity of the cyclic olefins, ISO and HHA, and the hydroaromatic donors, TET, OHA, and DHA, was observed for the reactions with fluorene as the diluent solvent. The cyclic olefins completely converted to form predominantly naphthalene and anthracene, respectively, whereas all the hydroaromatic donors only partially converted to form their respective aromatic, naphthalene and anthracene. In comparing the two studies with different atmospheres at 380 °C, the reactions in a N_2 atmosphere produced more aromatic products than those obtained in a H_2 atmosphere except for the TET reaction. At 410 °C, under nitrogen, substantially more aromatic species were produced from each donor, regardless of donor type, than at 380 °C. Under a hydrogen atmosphere both HHA and DHA were partially hydrogenated to produce substantial amounts of OHA, 40.5% and 63.8%, respectively. However, in hydrogen the added donor OHA remained virtually unreacted. For the reactions with DHA, HHA and OHA, as the level of donable hydrogen decreased from 0.5 wt% to 0.1 wt%, the reaction product slate shifted toward more fully dehydrogenated species.

Reactions with Hexadecane as the Diluent Solvent. HHA reacted completely and DHA converted more than 75% in the thermal reactions with hexadecane under hydrogen. Reactions with OHA, which produced about half the coal conversion as reactions with the other two donors, was only about ~15% converted. Isotetralin in hydrogen reacted completely while TET converted less than 20%.

Analyzing the reaction products from the added donors in catalytic reactions, as given in Table II.D.2.a.4, showed that the products were shifted toward the more hydrogenated species with $NiMo/Al_2O_3$ but not with Mo/Al_2O_3 as compared to the thermal reactions. Less anthracene and DHA were produced in the $NiMo/Al_2O_3$ reactions with HHA and OHA as initial donors compared to those produced in the thermal reactions. By contrast, more OHA was produced catalytically from both DHA and HHA than thermally. Isotetralin was completely converted in both catalytic reaction systems, while TET showed little reactivity. Since in the catalytic environment, catalytic rehydrogenation of the aromatic formed from the cyclic olefin to a hydroaromatic can occur, ISO probably dehydrogenated to naphthalene, which in turn was partially hydrogenated to TET. When TET was the added donor, it was only slightly dehydrogenated in the reactions performed, and the dehydronaphthalene or naphthalene that was formed might have been rehydrogenated to TET. Since only the net change in TET to naphthalene can be determined, it is possible that the cycle of dehydrogenation and rehydrogenation was repeated many times. If this was occurring, coal conversion would be expected to be higher because of the net amount of hydrogen being donated. However, for the reactions with TET, coal conversion remained low. Therefore, it is unlikely that the dehydrogenation and rehydrogenation cycle occurred to any great extent.

For the thermal reactions under hydrogen with hexadecane as the dilute solvent, the net hydrogen released from HHA was nearly twice that which was released from OHA, while DHA incorporated molecular hydrogen from the gas phase or from the coal matrix itself [9,16] because of its production of OHA. As would be expected by the greater amount of hydrogen released from HHA when compared to OHA, HHA produced a higher degree of coal conversion. However, DHA produced the most coal conversion, yet had a net incorporation of hydrogen. The amount of hydrogen released from ISO was more than four times that released from TET. The amount of hydrogen released from ISO corresponded to the higher coal conversion obtained with ISO, while lower coal conversion and low hydrogen donation was observed with TET.

Reactions with Maya Resid as the Diluent Solvent. In reactions with Maya resid, at 380°C under nitrogen, OHA and HHA dehydrogenated forming DHA and anthracene, while DHA dehydrogenated forming anthracene as shown in Table II.D.2.a.5. Both DHA and HHA produced more than 15% OHA, which was a much poorer donor than either reactant. In the HHA reaction system, DHA may have been formed initially and then hydrogenated to OHA. TET, when added to the coprocessing reaction system, showed little reactivity, with only 25% naphthalene being produced. Isotetralin completely converted to yield ~15% TET and 85% naphthalene. All of the model donors in a N_2 atmosphere dehydrogenated more at 410 °C than at 380 °C. For the reactions at 380 °C in a hydrogen atmosphere, the product slate was shifted from the dehydrogenated products toward more partially hydrogenated species.

In both catalytic systems, OHA was unreactive, with less than 10% reacting to form DHA. Dihydroanthracene added to the Maya resid and Western Kentucky No. 9 coal reaction system yielded similar product slates, regardless of the reaction conditions. The primary reaction product was OHA at ~75% with less than 10% ANT being formed. For the reactions involving HHA

with Mo/Al_2O_3, the primary reaction product was DHA at 75%; also formed were 8% anthracene and 18% OHA. With $NiMo/Al_2O_3$, HHA formed approximately equal amounts of OHA and DHA, but no anthracene. With both catalysts, ISO completely converted to TET and naphthalene, while TET either did not react or dehydrogenated to form naphthalene and then underwent rehydrogenation to TET.

Liquid Chromatographic Analysis of the Soluble Coal Products

Analysis of the coal liquefaction products into compound classes by liquid chromatography was performed as reported in Table II.D.2.a.6. The primary result that was observed in all the reactions was as coal conversion increased, and by definition, IOM decreased, the amount of hydrocarbons from coal liquefied to THF solubles increased. A possible explanation for this phenomenon is that since coal is primarily composed of hydrocarbons, as the coal matrix liquefied more coal conversion was obtained resulting in more hydrocarbons being converted to THF solubles. The reactions involving cyclic olefins solubilized more hydroxyl aromatic com-pounds than those with the hydroaromatic donors. It may be that the hydroxyl aromatics are linked to more labile bonds in the coal matrix. If these are the bonds that were broken initially, the reactive cyclic olefins may be able to cap the free radicals formed by the coal products from the scission of these bonds, thus promoting more soluble products. Szladow[17] and Bailey et al.,[18] both state that oxygen functionalities, including hydroxyl oxygen, play an important role in the liquefaction of coal and Szladow[17] reports hydroxyl aromatic species "has a significant effect on the benzene solubility of early liquefaction products."

While there are no clear trends immediately discernable with the nitrogen heterocycles and polyfunctional compounds, significant differences existed among individual reactions. In all the reactions, both thermal and catalytic, less than 2% nitrogen heterocycles were observed in the

THF soluble fraction produced from the coal in reactions with fluorene and hexadecane, and less than 5% in reactions with the Maya resid (Table II.D.2.a.7). More polyfunctional com-pounds were solubilized as coal conversion was increased for many of the reactions; however, there were exceptions to this trend. The relation between coal conversion obtained with the different hydrogen donor compounds and the fractions removed from the coal may lend insight into the nature of the dissolution of the coal matrix into smaller macromolecules that would be more suitable for further downstream processing by tailoring the reaction system to extract preferentially specific molecular structures.

Liquid chromatography analysis of the reactions with Maya resid with OHA and HHA in the presence of 12,000 ppm catalyst, as well as 3,000 ppm, are also presented in Table II.D.2.a.7. Both sets of reactions at the higher catalyst loading solubilized more hydrocarbons, while the overall coal conversion remained essentially constant. The amount of nitrogen heterocycles obtained was much less in the reactions with 12,000 ppm catalyst compared to 3,000 ppm. The amount of hydroxyl aromatics and polyfunctional compounds produced also decreased. It appears that the additional catalyst, while not affecting the overall coal conversion, increased the amount of heteroatom removal from the soluble fraction of the coal derived liquids while increasing the amount of hydrocarbons produced. Therefore, an increase in catalyst loading was beneficial for the upgrading during coal liquefaction by facilitating the removal of more heteroatomic species from the coal matrix.

SUMMARY

The purpose of the study undertaken was to investigate the hydrogen donating ability of cyclic olefins and their effect on coal conversion. The cyclic olefins are highly effective and

efficient hydrogen donor species. Under all the reaction conditions studied the cyclic olefin ISO produced greater coal conversion than its analogue TET; HHA always produced greater coal conversion than its analogue OHA, and produced conversions equivalent to or slightly less than DHA.

For all of the reactions studied, the cyclic olefins were completely converted, while the conventional hydrogen donor compounds remained at least partially unconverted. Coal conversion obtained with the cyclic olefins was greatest when the reaction severity was lower (i.e., thermal and 380° C). The longer the cyclic olefins were present in the reaction system, the greater was the coal conversion. Hence, cyclic olefins as donors are best suited for lower severity coal liquefaction conditions. When the reaction severity was increased (i.e., catalytic or 410 °C), coal conversion with the conventional donor compounds OHA, DHA, or TET, was enhanced. The increased reaction severity was required to force these less reactive compounds to release their donable hydrogen to the coal macromolecules. The matching of the kinetics of hydrogen release and hydrogen acceptance appears to be critical for achieving the best conditions for hydrogen donation and the resulting increased coal conversion.

NOMENCLATURE

DHA	= dihydroanthracene	TET	= tetralin
HHA	= hexahydroanthracene	THA	= tetrahydroanthracene
ISO	= isotetralin	THF	= tetrahydrofuran
OHA	= octahydroanthracene		

REFERENCES

1. Hessley, R., Reasoner, J., Riley, J. *Coal Science,* John Wiley and Sons, New York, NY, 1986.

2. Schlosberg, R.H. *Chemistry of Coal Conversion*, Plenum Press, New York, NY, 1985.

3. McMillen, D., Malhotra, R., Hum, G., Chang, S. *Energy and Fuels, 1*, 193-198, 1987.

4. Curtis, C. W., Guin, J., Kwon, K. *Fuel, 63,* 1404-1409, 1984.

5. Neavel, R.C. *Fuel*, 55(3):237-242, 1976.

6. Utz, B.R., Appell, H.R., Blaustein, B.D. *Fuel*, 65(8):1085-1089, 1986.

7. Kitaoka, Y., Mikio, U., Ito, H., Mikami, K. *Fuel*, *61*, 919-924, 1982.

8. Bockrath, B. *Coal Science, Vol. 2*, Academic Press, New York, NY, 1982.

9. Franz, J.A., Camaioni, D.M. *Prep. Paper. ACS Div. Fuel Chem.*, *26*(1):105-113, 1981.

10. Ratto, J., Heredy, C., Skowronski, R. *ACS Symposium Series*, *139*, 347-370, 1980.

11. Virk, P., Bass, D., Eppig, C., Ekpenyong, D. *ACS Symposium Series*, *139,* 329-343, 1980.

12. Derbyshire, F. J., Whitehurst, D. *Fuel*, *60*, 655-662, 1981.

13. Bedell, M., Curtis, C. *Energy and Fuels*, *5,* 469-476, 1991.

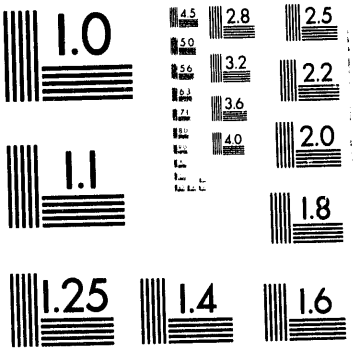
14. Boduszynski, M., Hurtubise, R. *Anal. Chem.*, *54*, 372-375, 1982.

15. Boduszynski, M., Hurtubise, R. *Anal. Chem.*, *54*, 375-381, 1982.

16. Skowronski, R., Ratto, J., Goldberg, I., Heredy, L. *Fuel*, *63,* 440-448, 1984.

17. Szladow, A., Dissertation, Pennsylvania State University, September Material Science Engineering, 117, 1979.

18. Bailey, N.T., Ikejiani, O., Lawson, G., Monsef-Mirtai, P. *Fuel*, *71*, 45-52, 1992.


1.0
4.5
2.8
2.5
5.0
3.2
2.2
5.6
3.6
2.0
4.0
1.1
1.8
1.25
1.4
1.6

3 of 3

Table II.D.2.a.1. Conversion with Western Kentucky No. 9 Coal at Three Levels of Donable Hydrogen[a]

Compound	Wt Donable Hydrogen, %	Coal Conversion, %
Octahydroanthracene	0.5 0.2 0.1	75.5(0.7)[b] 70.2(2.6) 60.3(0.7)
Hexahydroanthracene	0.5 0.2 0.1	88.6(0.04) 78.2(0.5) 64.2(2.5)
Dihydroanthracene	0.5 0.2 0.1	76.6(0.8) 73.8(1.1) 62.5(1.2)
Isotetralin	0.5	81.0(0.8)
Tetralin	0.5	66.8(0.9)
None	0.0	57.4(2.3)

[a]Reaction Conditions: Western Kentucky No. 9 coal, nitrogen at 1250 psi at ambient, fluorene, 30 min, 380 °C.

[b]The first number in the Coal Conversion column is the % coal conversion to THF solubles; the number in the parenthesis is the standard deviation for that point.

Table II.D.2.a.2. Conversion of Western Kentucky No. 9 Coal at Different Reaction Conditions[a]

Reaction Conditions	Coal Conversions with Added Donors, %						
	DHA	HHA	OHA	ISO	TET	NONE	
FL[b], N_2, 380°C	76.6(0.8)[c]	88.6(0.04)	75.5(0.7)	81.1(0.9)	66.8(0.9)	57.4(2.3)	
FL, N_2, 410°C	80.9(0.5)	84.3(1.1)	80.8(0.6)	78.1(0.6)	70.1(0.2)	66.5(0.5)	
FL, H_2, 380°C	76.6(1.0)	76.7(0.1)	77.6(0.8)	76.3(0.8)	79.0(0.3)	78.8(3.4)	
HEX, H_2, 380°C	68.3(1.0)	65.0(3.3)	37.2(0.4)	49.7(1.0)	29.8(0.2)	27.1(1.8)	
Mo/$A1_2O_3$, HEX, H_2, 380°C	66.9(0.7)	52.2(2.6)	40.6(1.4)	46.5(0.5)	24.2(2.1)	19.7(1.2)	
NiMo/$A1_2O_3$, HEX, H_2, 380°C	71.6(2.1)	58.9(2.9)	39.8(2.4)	28.6(0.3)	20.8(0.2)	25.6(2.0)	
Reaction Conditions	**DHA**	**DHA**	**HHA**	**OHA**	**ISO**	**TET**	**NONE**
g Resid → Present	**1.2**	**3**	**3.1**	**3.3**	**3.5**	**3.5**	**4**
Maya, N_2, 380°C	66.2(3.7)	56.4(2.1)	50.2(0.9)	38.2(3.6)	28.1(2.5)	16.5(1.4)	15.3(1.2)
Maya, N_2, 410°C	68.3(2.4)	67.3(1.3)	46.2(0.8)	41.5(1.7)	25.9(0.6)	21.1(1.1)	15.6(1.3)
Maya, H_2, 380°C	73.6(0.7)	65.0(1.6)	65.9(0.7)	45.4(1.0)	44.8(0.3)	31.7(2.6)	24.3(3.3)
Mo/$A1_2O_3$, Maya, H_2, 380°C	70.8(0.3)	64.8(1.4)	54.0(2.8)	52.1(2.9)	47.4(3.3)	37.6(1.1)	39.4(1.8)
NiMo/$A1_2O_3$, Maya, H_2, 380°C 12,000 ppm	73.2(0.1)	69.0(0.6)	58.3(3.3) 58.7(0.2)	51.7(4.1) 55.8(2.0)	42.6(1.5)	37.4(1.1)	31.9(3.3)

[a]Reaction Conditions: Western Kentucky No. 9 Coal, 1250 psi H_2 or N_2 at ambient, 30 min.
[b]FL = fluorene, DHA = dihydroanthracene, OHA = octahydroanthracene, TET = tetralin, HEX = hexadecane, HHA = hexahydroanthracene, ISO = isotetralin
[c]The numbers in parentheses are the standard deviations for each system.

Table II.D.2.a.3. Analysis of Model Donor Products from Reactions with Western Kentucky No. 9 Coal at Varying Levels of Donable Hydrogen[a]

Compound/ Conditions	DH Wt%	Reaction Products (wt%)			Net H Difference[c] (grams)
		OHA[b]	DHA	ANT	
OHA	0.5	51.4(0.6)	42.2(0.4)	6.4(0.3)	0.01138
	0.2	23.1(0.4)	51.3(0.6)	25.6(0.5)	0.00762
	0.1	trace	42.2(2.2)	57.8(2.2)	0.00534
HHA	0.5	18.5(0.5)	45.2(0.2)	36.3(0.6)	0.01824
	0.2	11.9(0.5)	20.6(0.7)	67.5(1.2)	0.00937
	0.1	9.3(0.8)	8.9(0.8)	81.8(1.1)	0.00512
DHA	0.5	18.1(0.6)	21.5(0.3)	60.4(0.8)	0.00265
	0.2	12.2(0.7)	10.4(0.6)	77.4(1.2)	0.00524
	0.1	8.6(0.5)	4.8(0.7)	86.6(0.5)	0.00383
Model Compound	**DH Wt%**	**TET**	**NAP**		**Net H Donated**
ISO	0.5	14.4(0.7)	85.6(0.7)		0.01294
TET	0.5	68.5(0.6)	31.5(0.6)		0.00462

[a]Reaction Conditions: Western Kentucky No. 9 coal, nitrogen, fluorene, 30 min reaction time, 380 °C.

[b]OHA = octahydroanthracene; ISO = isotetralin; DHA = dihydroanthracene; TET =tetralin ANT = anthracene; DH = donable hydrogen; HHA = hexahydroanthracene

[c]Net H difference is the difference between the total amount of hydrogen released and the amount of hydrogen required to form other species of the same ring series.

Table II.D.2.a.4. Analysis of Model Donor Products from Reactions with Western Kentucky No. 9 Coal at 0.5 Wt% Donable Hydrogen at Different Reaction Conditions[a]

Compound/Conditions	Reaction Products, Wt%			Net H Difference (grams)
	OHA[b]	DHA	ANT	
OHA				
FL, N_2, 380°C	51.2(0.6)	42.4(0.4)	6.4(0.3)	0.01138
FL, N_2, 410°C	19.3(1.2)	44.0(0.9)	36.7(1.4)	0.02076
FL, H_2, 380°C	89.7(0.3)	10.3(0.3)	0.0	0.00246
HEX, H_2, 380°C	85.4(0.1)	14.6(0.1)	0.0	0.00324
Mo/Al_2O_3, HEX, H_2, 380°C	6.9(0.4)	85.3(0.7)	7.8(0.4)	0.02125
NiMo/Al_2O_3, HEX, H_2, 380°C	89.3(0.2)	10.7(0.2)	0.0	0.00237
HHA				
FL, N_2, 380°C	18.5(0.5)	45.2(0.2)	36.3(0.6)	0.01824
FL, N_2, 410°C	14.3(1.1)	24.2(2.5)	61.5(3.5)	0.02203
FL, H_2, 380°C	40.6(8.7)	47.1(2.7)	12.3(6.3)	0.00921
HEX, H_2, 380°C	47.5(0.3)	45.7(0.1)	6.8(0.3)	0.00659
Mo/Al_2O_3, HEX, H_2, 380°C	19.1(2.5)	34.9(1.8)	46.0(0.9)	0.02465
NiMo/Al_2O_3, HEX, H_2, 380°C	56.3(0.8)	43.7(0.8)	0.0	0.00392
DHA				
FL, N_2, 380°C	18.1(0.6)	21.5(0.2)	60.4(0.8)	0.00265
FL, N_2, 410°C	14.5(0.9)	15.3(0.4)	70.2(1.0)	0.00879
FL, H_2, 380°C	63.8(0.9)	25.1(0.7)	11.1(0.3)	-0.05314
HEX, H_2, 380°C	59.9(2.3)	24.6(2.4)	14.5(1.5)	-0.04970
Mo/Al_2O_3, HEX, H_2, 380°C	77.1(0.5)	16.8(0.3)	6.1(0.2)	-0.00766
NiMo/Al_2O_3, HEX, H_2, 380°C	71.0(0.7)	22.4(0.5)	6.6(0.2)	-0.06097

Compound/Conditions	Reaction Products, Wt%			Net H Difference (grams)
	TET	NAP		
ISO				
FL, N_2, 380°C	14.4(0.7)	85.6(0.7)		0.01294
FL, N_2, 410°C	4.9(0.5)	95.1(0.5)		0.01439
FL, H_2, 380°C	96.1(0.3)	3.9(0.3)		0.00060
HEX, H_2, 380°C	17.8(1.3)	82.2(1.3)		0.01248
Mo/Al_2O_3, HEX, H_2, 380°C	100.0	0.0		0.0
NiMo/Al_2O_3, HEX, H_2, 380°C	84.8(0.4)	15.2(0.4)		0.00230
TET				
FL, N_2, 380°C	68.5(0.6)	31.5(0.6)		0.00462
FL, N_2, 410°C	36.6(0.6)	63.4(0.6)		0.00958
FL, H_2, 380°C	21.1(1.1)	78.9(1.1)		0.01200
HEX, H_2, 380°C	79.8(0.7)	20.2(0.7)		0.00298
Mo/Al_2O_3, HEX, H_2, 380°C	100.0	0.0		0.0
NiMo/Al_2O_3, HEX, H_2, 380°C	100.0	0.0		0.0

[a]Reaction Conditions: Western Kentucky No. 9 coal, 1250 psi N_2 or H_2 at ambient, 30 min reaction time.

[b]OHA = octahydroanthracene; HHA = hexahydroanthracene; DHA = dihydroanthracene; FL = fluorene; ANT = anthracene; HEX = hexadecane

Table II.D.2.a.5. Analysis of Model Donor Products from Reactions with Western Kentucky No. 9 Coal and Maya Resid at 0.5 Wt% Donable Hydrogen at Different Reaction Conditions

Reaction/Conditions	Reaction Products, Wt%			Net H Difference (grams)
	OHA[a]	DHA	ANT	
OHA				
Maya, N_2, 380°C	52.7(0.4)	39.0(0.6)	8.3(0.8)	0.01121
Maya, N_2, 410°C	39.7(1.3)	35.4(0.8)	24.9(0.6)	
Maya, H_2, 380°C	77.0(4.3)	23.0(4.3)	0.0	0.00511
Mo/Al_2O_3, Maya, H_2, 380°C	89.4(0.3)	10.6(0.3)	0.0	0.00235
NiMo/Al_2O_3, Maya, H_2, 380°C	89.2(0.7)	10.8(0.7)	0.0	0.00244
HHA				
Maya, N_2, 380°C	17.4(0.6)	39.9(1.2)	42.7(1.3)	0.01924
Maya, N_2, 410°C	15.3(0.4)	27.7(0.8)	57.0(1.1)	
Maya, H_2, 380°C	40.2(1.6)	47.8(0.3)	12.0(1.6)	0.00928
Mo/Al_2O_3, Maya, H_2, 380°C	17.6(0.3)	74.8(0.8)	7.6(1.0)	0.01551
NiMo/Al_2O_3, Maya, H_2, 380°C	47.9(1.4)	52.1(1.4)	0.0	0.00577
DHA (3g resid)				
Maya, N_2, 380°C	17.2(1.1)	17.8(0.4)	65.0(1.3)	0.00486
Maya, N_2, 410°C	14.9(0.8)	8.7(1.2)	76.4(2.3)	
Maya, H_2, 380°C	49.8(4.2)	24.9(0.7)	25.3(3.5)	-0.03373
Mo/Al_2O_3, Maya, H_2, 380°C	72.2(0.2)	20.2(0.1)	7.6(1.0)	-0.06122
NiMo/Al_2O_3, Maya, H_2, 380°C	70.9(0.3)	21.0(0.2)	8.1(0.3)	-0.05597
DHA (1.2g resid)				
Maya, N_2, 380°C	15.6(0.8)	18.7(0.5)	65.7(1.2)	0.00650
Maya, N_2, 410°C	16.2(1.6)	9.9(0.5)	73.9(1.2)	
Maya, H_2, 380°C	51.9(2.3)	26.5(0.2)	21.6(2.4)	-0.03942
Mo/Al_2O_3, Maya, H_2, 380°C	74.4(0.5)	19.7(0.3)	5.9(0.2)	-0.06434
NiMo/Al_2O_3, Maya, H_2, 380°C	68.1(0.3)	26.1(0.4)	5.8(0.2)	-0.05860

Reaction/Conditions	Reaction Products, Wt%			Net H Difference (grams)
	TET	NAP		
ISO				
Maya, N_2, 380°C	14.9(0.3)	85.1(0.3)		0.01285
Maya, N_2, 410°C	5.0(0.4)	95.0(0.4)		
Maya, H_2, 380°C	21.0(0.7)	79.0(0.7)		0.01195
Mo/Al_2O_3, Maya, H_2, 380°C	40.2(0.5)	59.8(0.5)		0.00906
NiMo/Al_2O_3, Maya, H_2, 380°C	68.0(0.8)	32.0(0.9)		0.00484
TET				
Maya, N_2, 380°C	74.6(0.5)	25.4(0.5)		0.00371
Maya, N_2, 410°C	60.2(1.3)	39.8(1.3)		
Maya, H_2, 380°C	90.9(0.4)	9.1(0.4)		0.00135
Mo/Al_2O_3, Maya, H_2, 380°C	100.0	trace		0.0
NiMo/Al_2O_3, Maya, H_2, 380°C	100.0	trace		0.0

[a]OHA = octahydroanthracene, ANT = anthracene, TET = tetralin, DHA = dihydroanthracene, HHA = hexahydroanthracene, ISO = isotetralin, NAP = naphthalene

Table II.D.2.a.6. Compound Class Analysis for Reactions with Western Kentucky No. 9 Coal at Varying Levels of Donable Hydrogen

		THF Soluble Fractions, Wt%				
FL, N_2, 380°C	**DH, Wt%**	**HC**	**NHC**	**HAR**	**PFC**	**IOM**
NONE	0.0	54.8(0.2)	0.0	2.6(0.2)	0.0	42.6(2.3)
TET[a]	0.5	62.3(0.8)	trace	1.8(1.2)	2.7(1.5)	33.2(0.9)
ISO	0.5	68.8(1.4)	0.5(0.7)	7.6(0.7)	4.2(1.1)	18.9(0.9)
OHA	0.5	60.5(1.8)	trace	3.6(1.1)	11.4(0.7)	24.5(0.7)
	0.2	60.3(1.7)	1.4(0.1)	6.2(1.2)	2.3(0.3)	29.8(2.7)
	0.1	52.7(0.4)	1.7(0.5)	4.3(0.1)	1.6(0.1)	39.7(0.7)
HHA	0.5	65.0(2.6)	1.6(1.4)	8.2(1.6)	13.8(2.1)	11.4(0.04)
	0.2	67.4(2.1)	1.2(1.1)	6.6(1.3)	3.0(0.3)	21.8(0.5)
	0.1	57.3(1.3)	0.5(0.4)	5.0(0.3)	1.4(0.9)	35.8(2.5)
DHA	0.5	70.0(0.5)	0.4(0.5)	3.5(0.1)	2.7(0.1)	23.4(0.8)
	0.2	59.0(3.0)	1.2(1.1)	7.3(2.2)	6.3(3.2)	26.2(1.1)
	0.1	51.4(2.5)	1.4(1.3)	6.2(2.6)	3.5(0.5)	37.5(1.2)
FL, N_2, 410°C		**HC**	**NHC**	**HAR**	**PFC**	**IOM**
NONE	0.0	55.6(0.9)	0.4(0.1)	8.8(0.6)	1.6(0.2)	33.6(0.3)
TET	0.5	61.7(0.3)	1.4(1.9)	5.9(1.0)	1.1(1.2)	29.9(0.2)
ISO	0.5	68.7(2.7)	1.0(1.1)	6.5(0.8)	1.9(1.6)	21.9(0.6)
OHA	0.5	68.6(1.2)	0.9(1.1)	9.0(0.1)	2.3(0.1)	19.3(0.6)
HHA	0.5	70.4(3.3)	1.2(1.0)	10.8(1.5)	1.8(1.5)	15.8(1.1)
DHA	0.5	66.8(2.4)	1.8(1.2)	10.1(0.6)	2.2(0.6)	19.1(0.5)
HEX, H_2, 380°C		**HC**	**NHC**	**HAR**	**PFC**	**IOM**
NONE	0.0	20.9(0.6)	2.6(0.1)	2.3(0.2)	1.3(0.7)	72.9(1.8)
TET	0.5	23.6(0.8)	0.9(0.4)	3.3(0.3)	2.0(0.1)	70.2(0.2)
ISO	0.5	40.0(1.3)	1.0(0.5)	6.7(2.8)	2.0(1.0)	50.3(1.0)
OHA	0.5	31.8(1.5)	0.4(0.2)	4.7(1.6)	0.3(0.1)	62.8(0.4)
HHA	0.5	53.6(1.4)	1.3(1.9)	8.9(1.5)	1.2(1.0)	35.0(3.3)
DHA	0.5	49.7(0.7)	3.1(1.7)	7.7(2.3)	7.8(1.5)	31.7(1.0)

Table II.D.2.a.6. Compound Class Analysis for Reactions with Western Kentucky No. 9 Coal at Varying Levels of Donable Hydrogen (Cont'd)

Mo/Al_2O_3, HEX, H_2, 380°C	DH, Wt%	THF Soluble Fractions, Wt%				IOM
		HC	NHC	HAR	PFC	
NONE	0.0	17.8(0.8)	0.3(0.2)	1.5(0.6)	0.1(0.1)	80.3(1.2)
TET	0.5	20.7(0.6)	0.8(0.2)	2.6(0.7)	0.1(0.1)	75.8(2.1)
ISO	0.5	32.9(4.6)	1.9(1.2)	9.3(3.4)	2.4(1.3)	53.5(0.5)
OHA	0.5	35.2(1.0)	0.9(0.5)	4.3(0.4)	0.2(0.1)	59.4(1.4)
HHA	0.5	40.1(1.3)	1.4(0.5)	8.8(0.1)	1.9(0.9)	47.8(2.6)
DHA	0.5	53.3(1.5)	2.2(1.8)	9.7(1.0)	1.7(1.3)	33.1(0.7)
$NiMo/Al_2O_3$, HEX, H_2, 380°C		HC	NHC	HAR	PFC	IOM
NONE	0.0	22.8(0.2)	0.8(0.3)	1.6(0.2)	0.4(0.2)	74.4(2.0)
TET	0.5	18.6(0.6)	0.4(0.2)	1.6(0.6)	0.2(0.1)	79.2(0.2)
ISO	0.5	27.5(0.2)	0.0	1.1(0.2)	0.0	71.4(0.3)
OHA	0.5	32.9(1.1)	1.5(0.1)	4.8(1.1)	0.6(0.1)	60.2(2.4)
HHA	0.5	51.6(1.0)	0.4(0.8)	6.2(0.4)	0.7(0.9)	41.1(2.9)
DHA	0.5	57.5(2.1)	0.6(0.9)	9.0(3.2)	4.5(1.4)	28.4(2.1)

[a]TET = tetralin, ISO = isotetralin, HHA = hexahydroanthracene, OHA = octahydroanthracene, DHA = dihydroanthracene, HC = hydrocarbons, NHC = nitrogen heterocycles, HAR = hydroxyl aromatics, PFC = polyfunctional compounds, IOM = insoluble organic matter

Table II.D.2.a.7. Compound Class Analysis for Reactions of Western Kentucky No. 9 Coal with Maya Resid

	THF Soluble Fractions, Wt%				
N_2, 380°C	**HC**	**NHC**	**HAR**	**PFC**	**IOM, Wt%**
NONE	12.3(0.2)	1.7(0.1)	1.2(0.2)	0.1(0.02)	84.7(1.2)
TET[a]	14.2(0.5)	0.7(0.2)	0.4(0.2)	1.2(0.1)	83.5(1.4)
ISO	23.4(0.3)	0.5(0.2)	3.4(0.3)	0.9(0.4)	71.8(2.5)
OHA	32.0(1.3)	1.0(0.2)	2.7(1.5)	2.5(0.1)	61.8(3.6)
HHA	36.7(1.4)	4.9(1.0)	7.4(0.8)	1.2(0.4)	49.8(0.9)
DHA (3.0)[b]	45.8(1.4)	1.6(0.04)	4.5(1.8)	4.5(0.6)	43.6(2.1)
DHA (1.2)[c]	58.8(2.2)	1.8(1.2)	1.1(0.4)	4.5(1.4)	33.8(3.7)
N_2, 410°C	**HC**	**NHC**	**HAR**	**PFC**	**IOM, Wt%**
NONE	13.4(0.5)	1.1(0.3)	1.1(0.4)	0.0	84.4(1.3)
TET	16.6(1.0)	1.4(0.3)	1.1(0.3)	2.0(0.7)	78.9(1.1)
ISO	17.6(2.2)	1.4(0.3)	4.7(0.6)	2.2(0.3)	74.1(0.6)
OHA	31.7(0.3)	1.6(0.4)	3.2(0.7)	5.0(1.1)	58.5(1.7)
HHA	34.4(0.9)	1.6(0.6)	8.3(1.1)	1.9(0.4)	53.8(0.8)
DHA (3.0)	53.9(1.7)	0.9(0.6)	6.5(1.3)	6.0(0.4)	32.7(1.3)
DHA (1.2)	55.7(0.6)	1.1(0.5)	4.7(0.7)	6.8(0.8)	31.7(2.4)
H_2, 380°C	**HC**	**NHC**	**HAR**	**PFC**	**IOM, Wt%**
NONE	21.3(0.6)	1.2(0.5)	1.0(1.0)	0.8(0.1)	75.7(3.3)
TET	21.5(0.3)	4.5(1.3)	3.3(1.1)	2.4(0.02)	68.3(2.6)
ISO	37.2(0.5)	3.3(0.3)	3.1(0.1)	1.2(0.2)	55.2(0.3)
OHA	34.2(0.6)	2.7(0.3)	6.0(0.04)	2.5(0.3)	54.6(1.0)
HHA	49.8(0.6)	2.8(1.4)	6.1(0.3)	7.2(0.3)	34.1(0.7)
DHA (3.0)	60.0(0.7)	3.3(0.9)	2.7(0.2)	3.0(0.05)	35.0(1.6)
DHA (1.2)	69.3(1.9)	0.7(0.0)	2.4(1.8)	1.2(0.1)	26.4(0.7)

Table II.D.2.a.7. Compound Class Analysis for Reactions of Western Kentucky No. 9 Coal with Maya Resid (Cont'd)

Mo/Al_2O_3, H_2, 380°C	THF Soluble Fractions, Wt%				IOM, Wt%
	HC	NHC	HAR	PFC	
NONE	32.6(1.2)	1.3(1.3)	3.8(1.5)	1.7(1.0)	60.6(1.8)
TET	30.4(1.6)	2.9(0.7)	1.8(1.1)	2.5(0.3)	62.4(1.1)
ISO	36.1(1.5)	3.1(0.2)	4.4(0.8)	3.8(2.5)	52.6(3.3)
OHA	46.7(2.3)	1.2(0.04)	1.7(1.0)	2.4(1.4)	47.9(2.9)
HHA	45.5(0.2)	1.6(0.5)	6.0(0.6)	0.9(0.3)	46.0(2.8)
DHA (3.0)	59.1(2.4)	0.8(0.4)	1.9(0.05)	3.0(2.1)	35.2(1.4)
DHA (1.2)	65.5(1.7)	1.0(1.0)	2.9(0.3)	1.4(0.4)	29.2(0.3)
$NiMo/Al_2O_3$, H_2, 380°C	**HC**	**NHC**	**HAR**	**PFC**	**IOM, Wt%**
NONE	24.7(1.1)	2.5(0.1)	2.2(0.3)	2.5(0.4)	68.1(3.3)
TET	30.3(1.9)	3.0(0.2)	1.9(0.5)	2.2(0.1)	62.6(1.1)
ISO	33.0(0.8)	1.4(0.3)	5.3(0.8)	2.9(0.2)	57.4(1.5)
OHA	30.3(1.3)	12.2(0.4)	4.9(1.7)	4.3(0.0)	48.3(4.1)
HHA	36.1(1.4)	11.3(0.9)	5.5(0.3)	5.4(0.2)	41.7(3.3)
DHA (3.0)	51.9(1.6)	10.2(0.6)	4.0(1.2)	2.9(0.9)	31.0(0.6)
DHA (1.2)	52.1(0.4)	7.0(0.8)	4.8(0.7)	9.3(0.6)	26.8(0.1)
OHA 12000 ppm	47.4(1.5)	2.0(0.7)	3.6(0.1)	2.8(0.7)	44.2(2.0)
DHA 12000 ppm	52.2(0.5)	3.0(1.5)	2.6(1.1)	0.9(0.8)	41.3(0.2)

[a] TET = tetralin, ISO = isotetralin, HHA = hexahydroanthracene, OHA = octahydroanthracene, DHA = dihydroanthracene, HC = hydrocarbons, NHC = nitrogen heterocycles, HAR = hydroxyl aromatics, PFC = polyfunctional compounds, IOM = insoluble organic matter

[b] 3 grams of resid are present.

[c] 1.2 grams of resid are present.

SUBTASK II.D.2.b

REACTIVITY OF ARGONNE COAL IN THE PRESENCE HYDROAROMATIC DONOR ENRICHED PETROLEUM SOLVENTS

INTRODUCTION

Cyclic olefins are highly reactive hydrogen donors that readily donate their hydrogen to coal at liquefaction temperatures in atmospheres of either hydrogen or nitrogen.[1] These compounds are hydroaromatic in character but do not contain aromatic rings. Typical examples of cyclic olefins are 1,4,5,8-tetrahydronaphthalene, commonly known as isotetralin (ISO), and 1,4,5,8,9,10-hexahydroanthracene (HHA). The reactivity of cyclic olefins and the reaction products that they produce at liquefaction conditions have been examined.[1] These compounds have been shown to serve as effective hydrogen donors to Western Kentucky No. 9 coal at both 380 and 410 °C.[1,2] Current investigation involved reacting these cyclic olefins and their hydroaromatic analogues with eight different coals from the Argonne Premium Coal Sample Bank.

Coals from the Argonne Premium Coal Sample Bank have been tested for their reactivity under a number of conditions.[3-6] Baldwin and coworkers[7] have evaluated the liquefaction reactivities of four Argonne coals, ranging from subbituminous to low volatile bituminous, in four solvents, naphthalene, phenanthrene, tetralin, and 1-methylnaphthalene. Wyodak subbituminous coal was most reactive kinetically, regardless of the solvent, while Illinois No. 6 high volatile bituminous coal showed the most reactivity in terms of ultimate conversion to toluene solubles. Cyclic olefins when compared to hydroaromatic donors have been shown to be more effective donors for the conversion of Western Kentucky No. 9/14[8] and Western Kentucky No. 9 coal.[1]

The objective of this investigation was to establish the universality of the ability of cyclic olefins to donate hydrogen to coals of different rank. A series of reactions was performed in

which cyclic olefins were reacted with eight coals from the Argonne Premium Coal Sample Bank. These coals varied in rank from lignite to low volatile bituminous coal. The efficacy of the hydrogen donation from the cyclic olefins to the different coals was compared to that obtained from hydroaromatic analogues of the cyclic olefins. Two sets of reactions were performed. The first set used hexadecane as a solvent to evaluate the hydrogen donability in an inert, nonparticipating solvent. The second set of reactions used Maya resid as the solvent to evaluate the efficacy of the different hydrogen donors in a coprocessing system. The efficacy of hydrogen donation by the cyclic olefins and the hydroaromatic donors was measured by determining coal conversion to tetrahydrofuran (THF) solubles of the different Argonne coals. The extent of hydrogen donation was monitored by evaluating the reaction products produced from the donors.

EXPERIMENTAL

Reactions of cyclic olefins, ISO and HHA, and three conventional hydroaromatic donor compounds, tetralin, dihydroanthracene (DHA), and octahydroanthracene (OHA), with coals of different rank from the Argonne Premium Coal Sample Bank and a Western Kentucky No. 9 coal from the PSU/DOE Coal Sample Bank were performed. The proximate analysis and rank of coals used in the reactions are presented in Table II.D.2.b.1. The reactions were performed in stainless steel tubular reactors of approximately 50 cm^3. Reaction conditions employed were: 30 min reaction time, 1,250 psig N_2 atmosphere at ambient temperature, 380°C reaction temperature, 2.0 g coal, and 4.0 g total solvent mixture including 0.1-0.5 wt% of the model donors so that the amount of donable hydrogen remained constant at 0.5 wt% with the balance being hexadecane as the diluent solvent. The reactor was agitated at 700 cpm in a vertical orientation. For the coprocessing reactions Maya vacuum resid, whose properties are described in Table II.D.2.b.2, was used as the solvent. All other reaction conditions remained the same.

The chemicals used were obtained from the following manufacturers and used as received: tetralin, HHA, OHA, DHA, and hexadecane from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene or ISO from Wiley Organics Inc.; Illinois No. 6, Upper Freeport, Pocahontas No. 3, Pittsburgh No. 8, Lewiston-Stockton, Blind Canyon, Wyodak-Anderson, and Beulah-Zap coals from the Argonne Premium Coal Sample Bank, Western Kentucky No. 9 coal from the PSU/DOE sample bank; Maya vacuum resid from Amoco Oil Co.

The hydrogen donor compounds and their reaction products were analyzed by gas chromatography using a Varian 3400 GC equipped with a HT-5 column from SGE and FID detection. The internal standard method was used for quantitation with biphenyl as the internal standard. Peaks were identified by comparing retention time with authentic compounds and by GC mass spectral analysis using a VG 70EHF mass spectrometer. For this work, coal conversion is defined as conversion = {1 - [IOM (maf) / coal charge (maf)]} x 100 where IOM is the insoluble organic matter remaining after the reaction and maf is defined as moisture and ash free. The moisture and ash contents for the Argonne coals were provided by the supplier and are listed in Table II.D.2.b.1. The moisture and ash content of Western Kentucky No. 9 coal was experimentally determined to be 4.5 $\pm$ 0.6% and 10.16 $\pm$ 0.14%, respectively.

RESULTS AND DISCUSSION

Reaction of Hydrogen Donors With Argonne Coals

Eight coals from the Argonne Premium Coal Sample Bank and Western Kentucky Coal from the PSU/DOE sample bank were reacted with a series of hydrogen donor compounds which were composed of cyclic olefins and hydroaromatic donors. The reactions of these donors with the Western Kentucky have been reported previously[1] but are given here as a reference point.

These hydrogen donors were composed of two- and three-ring species; hydrogen donability should be compared within the two- or three-ring systems because of the higher inherent reactivity of the three-ring compounds in the dissolution of coal.[8] Liquefaction reactions without a hydrogen donor were also performed to provide a base line level of reactivity for these coals of widely different rank at these reaction conditions. Two measures of reactivity were evaluated. First, the amount of coal conversion to THF solubles was determined for each reaction set; and, second, the reaction products from the added hydrogen donor compounds were determined by gas chromatography.

Two different sets of reactions were performed. The first used hexadecane as the solvent while the second used Maya resid. The two sets of reactions are presented sequentially with the results from the reactions in hexadecane being first and those in Maya being resid second. In these reactions, the amount of hydrogen available to the coal from the 1,250 psig molecular hydrogen charged was 0.35 g. If all of the hydrogen were released from the hydrogen donor under these reaction conditions, then 0.03 g of hydrogen would be released from the donor which would be only ~8% of the total hydrogen available to the coal. However, neither the cyclic olefins nor the hydroaromatic species used in this research released their hydrogen completely at these reaction conditions[1] as can be seen from the product distributions of the hydrogen donors obtained in this work.

Reactions Using Hexadecane as Solvent. Coal conversions obtained from reactions of the eight Argonne coals and Western Kentucky No. 9 with added hydrogen donors in hexadecane are presented in Table II.D.2.b.3. The percent coal conversion given in the table as well as in the discussion of this table are in terms of weight percent. Each reaction was at the least duplicated with the numbers in parentheses indicating standard deviations.

The base-line reactions performed without the addition of hydrogen donor clearly demonstrated striking differences in the inherent reactivity of the coals themselves. Reactions in hydrogen without an added hydrogen donor ranked the reactivity of the coals, based on averages, for conversion to THF solubles as Illinois No. 6 > Western Kentucky No. 9 > Pittsburgh No. 8 > Blind Canyon > Wyodak-Anderson and Upper Freeport > Beulah-Zap and Lewiston-Stockton >> Pocahontas No. 3. The amount of coal conversion ranged from ~56% for Illinois No. 6 coal to zero for Pocahontas No. 3 coal under the conditions of this study. The high volatile bituminous coals, Western Kentucky No. 9, Illinois No. 6, Pittsburgh No. 8, and Blind Canyon, were most reactive with the exception of Lewiston-Stockton which was also a high volatile bituminous coal. The ranking of the reactivity of the coals became less distinct when the different hydrogen donors were added to the reaction system.

The coals were also ranked based on a computed signal-to-noise ratio which simultaneously measures average and variability of coal conversion. The signal-to-noise formula used is shown below for the "Larger The Better" case (i.e., larger coal conversion (%) is better). Larger signal-to-noise values correspond to larger averages and/or smaller variation measures, both of which are desirable characteristics.

$$S/N = -10 \log_{10} \left[\frac{1}{\bar{y}^2} \left[1 + \frac{3\ \sigma_n^2}{\bar{y}^2} \right] \right]$$

where $\bar{y}$ = average

σ_n^2 = sample variance based on values

The rankings were identical to those obtained based just on averages, with Illinois No. 6 having the largest S/N = 34.92. Table II.D.2.b.4 shows S/N values for all coals.

For all the added donors, the coals, Illinois No. 6, Western Kentucky No. 9, and Pittsburgh No. 8, were the most reactive yielding high conversion. By contrast, Pocahontas No. 3 was completely unreactive at liquefaction conditions used, regardless of the donor present. The reactivity order of the moderately reactive coals that included Upper Freeport, Beulah-Zap, Lewiston-Stockton, and Wyodak-Anderson, varied depending upon the model hydrogen donor that was present.

The addition of hydrogen donors to the different coal systems increased the amount of coal conversion obtained compared to no donor addition as was previously observed with Western Kentucky No. 9 coal. The coals varied in response to the type of hydrogen donor present. The added cyclic olefins, ISO and HHA, and the hydroaromatic donor, DHA, achieved the highest coal conversions of the Argonne Premium Coals. The hydroaromatic donors, OHA and tetralin, resulted in much less coal conversion than either their three- or two-ring analogues, respectively. The donor DHA always resulted in the highest coal conversion based on averages and S/N values. Hexahydroanthracene, with all coals but one, ranked second in coal conversion. Thereafter, rankings of the hydrogen donors for coal conversion varied.

Previous work has shown that cyclic olefins are very reactive at 380 °C; they convert readily and release their hydrogen very quickly.[1,9] The lower coal conversions from the coals of lower reactivity reacted in conjunction with the cyclic olefins may have been caused by the cyclic olefins releasing their hydrogen too quickly to the liquefying coal system; the dissolving molecules could not accept the hydrogen quickly enough to assimilate the hydrogen as it was released. The hydroaromatic donor, DHA, by contrast, has been shown to release its hydrogen more slowly[1,9] thereby allowing these coals to accept the hydrogen. The behaviors described serve to explain the coal conversions observed with coals of different reactivity. The coals of lower reactivity, Upper

Freeport, Lewiston-Stockton, and Blind Canyon, yielded higher coal conversions with DHA than with the cyclic olefins. By contrast, the coals of higher reactivity were better able to assimilate the quickly released hydrogen from the cyclic olefins yielding higher coal conversions.

Illinois No. 6 coal was extremely reactive and produced more than 55% coal conversion to THF solubles without added donor. This amount was more than twice that obtained with Western Kentucky No. 9, the second most reactive coal. Because of its high inherent reactivity, only 14% more coal conversion was obtained with Illinois No. 6 coal with the added donor DHA and only 12% more with HHA than with no added donor. These amounts were the smallest differential from no donor present to added donor. Hence, the addition of a hydrogen donor to an inherently reactive coal like Illinois No. 6 only contributed a smaller portion to the overall coal conversion obtained under the reaction conditions employed.

The other reactive coals, Western Kentucky No. 9 and Pittsburgh No. 8, had much lower inherent reactivities than did Illinois No. 6; however, both coals contained a substantial capacity to accept hydrogen from added hydrogen donors that resulted in enhanced coal conversion. Examining the reactions with Pittsburgh No. 8 given in Table 3 illustrates this point. The reaction of Pittsburgh No. 8 with DHA yielded 36.3% more coal conversion than the reaction with no donor. The reaction with HHA added resulted in 51.8% coal conversion, which was ~5% less than DHA, 13% more than OHA and 31.7% more than no donor added.

The effect of two-ring hydrogen donors on coal conversion to THF solubles was usually less than the three-ring system, although for some coals, addition of ISO was as effective or more effective than the addition of OHA. Addition of ISO promoted coal conversion in all the liquefaction systems except Pocahontas. Isotetralin was more reactive and a more effective hydrogen

donor than tetralin. Tetralin only slightly promoted coal conversion in the reactive coal systems, while it showed little effect in the less reactive coal systems.

The coals of moderate reactivity, Lewiston-Stockton, Wyodak-Anderson, and Beulah-Zap, responded more favorably to DHA than to HHA. The addition of DHA resulted in 36% more conversion of Lewiston-Stockton coal, in nearly 48% more conversion of Blind Canyon, and ~28% more conversion with Beulah-Zap than when the coals were reacted without a hydrogen donor present. The cyclic olefin HHA, though effective in increasing coal conversion for these coals compared to the no donor reaction, was substantially less effective than DHA; however, HHA was more effective in converting coal than OHA. The difference between the conversions obtained from HHA and OHA was dependent upon the coal used. These results again point to the specificity of interaction between the coal and hydrogen donor present.

The low rank coals, Wyodak-Anderson and Beulah-Zap, had a much higher as-received moisture content than did the bituminous coals. These low rank coals had moisture contents in the range of 30% while the bituminous coals were in the 1 to 8% range. In order to perform the reactions with the low rank coals on the same moisture level basis as the bituminous coals, the low rank coals were dried to the same moisture level as the bituminous coals prior to the reactions with added hydrogen donors. To evaluate the effect of drying the coals as well as to compare the conversions obtained with the dried coals, a pair of reactions was repeated for both Wyodak-Anderson and Beulah-Zap with the as-received coals. The reactions for Wyodak-Anderson coal were performed with ISO and tetralin, while those for Beulah-Zap used HHA and DHA. No statistically meaningful differences were obtained in the coals conversions with the dried and as-received coals for all four sets of reactions. Therefore, under these reaction conditions, the additional moisture had no effect on the coal conversions obtained; however, the high water

content would affect the amount of energy (and cost) to heat the as-received coals to reaction temperature.

Supplementary to the previous analyses, an attempt was made to functionally relate, for each donor, the coal conversion to the proximate analysis variables (moisture, etc.) given in Table II.b.2.6.1 (Note: Btu was divided by 1,000.). For each donor, a multiple linear regression equation was fitted. If a fitted equation provided an adequate description of the relationship between coal conversion and the proximate analysis variables, then the equation could possibly be used to predict coal conversion for other coals if their proximate analysis variable values were known. The fitted equation terms and the associated coefficient of determination, R^2, for each equation are shown in Table II.D.2.b.5. When the R^2 values are used as a basis, all equations can be considered as "good," with the DHA equation excelling. Across the five donors, equation terms for each proximate analysis variable differ, suggesting that the contribution of a proximate analysis variable is donor sensitive. Since there were only nine coals that provided data for the fitted equations, thereby limiting the degree of freedom for any error analysis,[8] future research might examine additional coals for purposes of refining and re-enforcing the validity of the empirical equations shown here.

Reaction Products from Model Donors. The product distributions from the cyclic olefin and hydroaromatic donors added to the nine different coal reaction systems were analyzed. The products obtained during the reaction as well as net amount of hydrogen donated are presented in Table II.D.2.b.6.

The two most reactive three-ring donors were HHA and DHA while OHA showed little reactivity. Hexahydroanthracene completely converted in all of the reactions performed, producing the products of OHA, DHA, and anthracene. The primary hydrogenated product formed

in all of the coal systems except for Upper Freeport was DHA. The amount of DHA formed ranged from a high of 81.1% in the Illinois No. 6 reaction to a low of 38.0% in the Beulah-Zap reaction. The amount of anthracene was quite similar for six of the coals, ranging from 6.8% for Kentucky No. 9 to 13.3% for Lewiston-Stockton; however, substantially more anthracene was formed in the reactions containing the low rank coals, Wyodak and Beulah-Zap, and HVB coal of low reactivity, Blind Canyon.

Dihydroanthracene also showed substantial reactivity, although not all of the DHA was converted to form reaction products of OHA and anthracene. Both the amount of anthracene and the amount of OHA formed were higher from DHA than from HHA for each corresponding coal except for Lewiston-Stockton. The amount of anthracene formed for Wyodak, Beulah-Zap, and Blind Canyon was quite high, ranging from 56 to 51.3 to 44.3%, respectively.

Octahydroanthracene was the least reactive three-ring donor and gave the least conversion to DHA and anthracene. In fact, in four of the nine coal reactions, no anthracene was formed. The most products of both DHA and anthracene were again formed in the three coals mentioned previously with the other donors, Blind Canyon, Wyodak, and Beulah-Zap.

The two-ring hydrogen donors showed quite different reactivities. Isotetralin completely converted to naphthalene (NAP) and tetralin in all of the coal reactions performed. Naphthalene was the primary reaction product formed which ranged from 84.6% produced in the Beulah-Zap reaction to 67.3% formed in the Pocahontas No. 3 reaction system. Tetralin only formed one product, NAP. The amount of NAP produced ranged from none in both the Upper Freeport and Lewis-Stockton coals to ~25% in the Beulah-Zap reaction.

Net Hydrogen Difference. For both the two- and three-ring systems, the cyclic olefins completely converted in the liquefaction reactions when hexadecane was used as the solvent. Cyclic olefins were much more reactive and yielded the most H_2 for each respective coal.

The net hydrogen difference produced from the model donors was calculated based upon the product slate. This amount was determined as the difference in the total amount of hydrogen released and the amount of hydrogen required to form other species of the same ring series. For example, when HHA reacted, hydrogen was released when DHA and anthracene were formed, but hydrogen was consumed when OHA was produced. The amount of net hydrogen released to the system was dependent upon the amount of HHA converted and the relative amounts of each product produced. The results of these calculations for the reactions in hexadecane are presented in Table II.D.2.b.6. The following results were observed in the reactions of the hydrogen donors with the coals regardless of the coal: (1) ISO released more hydrogen than did tetralin or OHA and (2) HHA released more hydrogen than OHA. Dihydroanthracene reacted differently from the other donors. Dihydroanthracene incorporated hydrogen from the liquefaction system into the model donor products. This net uptake of hydrogen occurred when OHA was formed in larger amounts and using more hydrogen than DHA released. The net hydrogen difference observed with the DHA system then was a negative number as indicated by Table II.D.2.b.6.

Reactions Using Maya Resid as Solvent. Coprocessing reactions were performed with the Argonne coals and Western Kentucky No. 9 coal using Maya resid as the solvent. The reactions were performed in the same manner as was done previously. The coals were liquefied in Maya resid without any added donor; the coal conversion was obtained is presented in Table II.D.2.b.7 under the column of no donor added. The coal conversions presented in the table are in terms of weight percent. The coals showed different levels of reactivity in the Maya resid just

as they did in the hexadecane. Because of the low reactivity exhibited by Pocahontas No. 3 in the hexadecane reactions and by the test case performed here with the added donor HHA, Pocahontas No. 3 coal was not used in these experiments. The reactivity of the coals with no donor added ranked, based on averages and S/N values, as Illinois No. 6 > > Pittsburgh No. 8 > Western Kentucky No. 9 and Blind Canyon > Upper Freeport ≅ Beulah-Zap > Lewiston-Stockton ≅ Wyodak-Anderson > > Pocahontas No. 3. Higher coal conversion was obtained with hexadecane as the solvent for Western Kentucky No. 9, Illinois No. 6 and Wyodak-Anderson coals, while all other coals showed higher conversions in Maya resid.

The additions of added donors to the coprocessing system increased the amount of coal conversion achieved. The amount of the improvement varied with the type of donor and the reactivity of the coal. As with the reactions in hexadecane, the amount of hydrogen donor was kept constant and, hence, the reaction with DHA had only 1.2 g of resid present which was about one-third that present in the other reactions. These reactions with 1.2 g resid and 2.76 g DHA always produced the highest coal conversion regardless of the coal present. The preponderance of DHA in the coprocessing system was sufficient to change the solvent character compared to the other added donor systems. Therefore, the DHA reaction system was changed to increase the amount of resid to 3.0 g which was similar to that present in the other reactions and to leave the amount of DHA present at 2.76 g which provided the same amount of donable hydrogen to the system as the other added donors. This change caused the amount of coal conversion to decrease. Hence, the presence of resid in the system acted as an inhibitor to coal conversion for the same amount of donable hydrogen. The resid itself may have utilized some of the hydrogen transferred from the hydrogen donor.[10]

When donors were compared with a loading level of 3.0 g of resid or above, the two donors, DHA and HHA, promoted nearly equivalent amounts of coal conversion, particularly for the highly reactive coals like Kentucky No. 9, Illinois No. 6, Pittsburgh No. 8, and Blind Canyon. In some cases, HHA yielded more coal conversion than DHA while in others the reverse was true. For some of the less reactive coals like Upper-Freeport and Wyodak-Anderson, DHA and HHA promoted nearly equivalent coal conversions. But for others, like Lewiston-Stockton and Beulah-Zap, DHA was much more effective for converting coal than HHA. Pocahontas No. 3 showed no reactivity with HHA.

The two-ring donors, ISO and tetralin, exhibited similar behavior in Maya resid as they did in hexadecane. Isotetralin always promoted more coal conversion than tetralin and for some coals promoted as much or more than did the three-ring OHA. In some cases, tetralin had a positive effect on coal conversion compared to the no-donor case while in others it did not. More reactive coals tended to respond more favorably to the presence of tetralin than did the less reactive coals.

Reaction Products from Model Donors. The THF soluble fractions of the coprocessing reactions with Maya resid were analyzed to determine the reaction products achieved by the model donors. The analysis of the reaction products is presented in Table II.D.2.b.8.

Of the three-ring donors, HHA was the most reactive and completely converted in all of the coal systems to form DHA, OHA, and anthracene. The amounts of these products varied considerably from coal to coal. 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, anthracene was the primary reaction product. The reaction with Illinois No. 6 showed the most unusual distribution with

73.5% OHA and 26.5% DHA and no anthracene being formed. This distribution resulted in a negative net hydrogen difference from the donors. All of the remaining coal reactions with HHA showed positive and fairly high net hydrogen differences.

The reaction products were similar for the two sets of DHA reactions with the Argonne coals and Western Kentucky coal. Between 12 to 30% DHA was not converted depending upon the coal type. For Western Kentucky No. 9, Illinois No. 6, and Upper Freeport coals, OHA was the primary reaction product, while for Blind Canyon, Wyodak-Anderson, and Beulah-Zap the primary reaction product was anthracene. Pittsburgh No. 8 and Lewiston-Stockton produced nearly equivalent amounts of DHA and anthracene. The net hydrogen difference with DHA was negative except for the reaction with Pittsburgh No. 8 coal.

Octahydroanthracene showed more reactivity for most of the coals in the Maya resid systems than in the hexadecane solvent. The primary product was DHA and the secondary product was anthracene. The net hydrogen difference was positive but an order of magnitude less than HHA.

The two-ring systems, ISO and tetralin, showed similar reactivities as in the hexadecane solvent. Isotetralin completely converted forming NAP as the primary product and tetralin as the secondary product. For most of the coals, tetralin converted more to NAP in Maya resid than it did in hexadecane. The net amount of hydrogen transferred for ISO was considerably larger than for tetralin as was the coal conversion.

CONCLUSIONS

The universality of cyclic olefins for donating hydrogen to coals of varying ranks was established. The three-ring cyclic olefin, HHA, and the hydroaromatic, DHA, were both highly

effective for converting coal to THF solubles with DHA being slightly more reactive in most systems. By contrast, the hydrogen-rich three-ring donor, OHA, was not an effective donor, showing little reactivity and the least conversion of coal of the three-ring systems. The cyclic olefin, ISO, was more reactive and donated much more hydrogen than tetralin. Hence, ISO was a more effective hydrogen donor for converting coals to THF solubles than tetralin and, in some reactions, more effective than OHA.

Reactivity rankings of coals under various test conditions were made on the basis of comparison of averages and on the basis of comparison of signal-to-noise ratios. In most cases, the rankings were the same (most rankings shown in the paper pertain to averages). Western Kentucky No. 9 and Illinois No. 6 generally ranked higher than the other coals. Throughout, however, there was a high level of specificity of interactions between the coals tested and the hydrogen donor and test conditions present.

These reactions clearly showed that in order to achieve coal conversion in a thermal reaction that not only does an effective donor need to be present but the coal must be reactive and able to accept hydrogen. Matching the reaction rates of the reacting coal and the hydrogen donation is essential for maximizing coal conversion. The nondonor solvent present in the system had a limited effect on the efficacy of the donor in the reacting system and ultimately on the conversion of coal.

NOMENCLATURE

DHA	= dihydroanthracene	NAP	= naphthalene
HHA	= hexahydroanthracene	OHA	= octahydroanthracene
ISO	= isotetralin	THF	= tetrahydrofuran

REFERENCES

1. Bedell, M.W.; Curtis, C.W. "The Chemistry and Reactivity of Cyclic Olefins as Donors in Coal Liquefaction," *Energy and Fuels,* 5:469, 1991.

2. Bedell, M.W.; Curtis, C.W. "Comparison of Hydrogen Transfer from Cyclic Olefins and Hydroaromatics Under Thermal and Catalytic Conditions," *Energy and Fuels*, 7:200-207, 1993.

3. Shin, S.C.; Baldwin, R.M.; Miller, R.M.; "Correlation of Bituminous Coal Hydroliquefaction Activation Energy with Fundamental Coal Properties," *Energy and Fuels*, 3(2):194-199, 1989.

4. Wiser, W.H.; Shabtai, J.; Yang, Q.; Yang, Z.; "High Conversion in Coal Liquefaction with Low HC Gas Production," *ASC Fuel Chem. Div. Preprints,* 37(1):456-463, 1992.

5. Winans, R.E.; Hayatsu, R.; Squires, T.G.; Carrado, K.A.; Batto, R.E.; "Use of Model Componds in Coal Structure and Reactivity Studies," *ACS Fuel Chem. Div. Preprints,* 35(2):423-429, 1990.

6. Baldwin, R.M.; Kannar, D.R.; Nguanprasert, O.; Miller, R.L.; "Liquefaction Reactivity Enhancement of Coal by Mild Alkylation and Solvent Swelling Techniques," *Fuel*, 70:429-433, 1991.

7. Baldwin, R.M.; Shin, S.C.; Miller, R.L.; "Liquefaction Reactivity Measurements on Argonne Premium Coal Samples," *ACS Fuel Chem. Div. Preprints,* 32(4):352-358, 1987.

8. Curtis, C.W.; Guin, J.A.; Kwon, K.C. "Coal Solvolysis Using Hydrogen Donor Solvents," *Fuel*, 63:1404-1409, 1984.

9. Bedell, M.W.; Curtis, C.W.; "Mechanisms of Hydrogen Donation from Cyclic Olefins to Pittsburgh No. 8 Coal," *ACS Fuel Chem. Div. Preprints,* 37:968-975, 1992.

10. Owens, R.M.; Curtis, C.W.; "Hydrogen Transfer from Naphthenes to Coal During Coprocessing," *ACS Fuel Chem. Div. Preprints, 36*, 884-891, 1991.

Table II.D.2.b.1. Proximate Analysis of the Argonne Premium Sample Coals[a]

Coal	Moisture %	Ash %	Volatile Matter %	Sulfur %	Btu	Rank
Kentucky No. 9	7.12	10.97	35.77	4.50	11936	HVB
Illinois No. 6	7.97	14.25	36.86	4.45	10999	HVB
Upper Freeport	1.13	13.03	27.14	2.29	13315	MVB
Pocahontas No. 3	0.65	4.74	18.48	0.66	14926	LVB
Pittsburgh No. 8	1.65	9.10	37.20	2.15	13404	HVB
Lewiston Stockton	2.42	19.36	29.44	0.69	11524	HVB
Blind Canyon	4.63	4.49	43.72	0.59	13280	HVB
Wyodak-Anderson	28.09	6.31	32.17	0.45	8426	Sub B
Beulah Zap	32.24	6.59	30.45	0.54	7454	LIG

[a] All values are weight percents for the as-received coals.
[b] HVB = high volatile bituminous; MVB = medium volatile bituminous; LVB = low volatile bituminous; Sub B = subituminous; LIG = lignite

Table II.D.2.b.2. Properties of Maya Resid

Source of Residuum	Mexico
Specific Gravity, g/cm^3	1.0535
Ramsbottom Carbon, wt%	26.38
C, wt%	83.7
H, wt%	9.76
S, wt%	5.4
N, wt%	ND[a]
Ni, ppm	118
V, ppm	680
Hexane Soluble, wt%	71.8
Hexane Insoluble, wt%	28.2
Toluene Insoluble, wt%	0

[a] ND = not determined.

Table II.D.2.b.3. Coal Conversion for Reactions of Argonne Coals with Hydrogen Donors in Hexadecane[a]

Coal Reacted	Coal Conversion (%) with					
	DHA[d]	HHA	OHA	ISO	TET	No Donor Added
Kentucky No. 9	68.3(1.0)[c]	65.0(3.3)	49.7(1.0)	37.2(0.4)	29.8(0.2)	25.6(1.8)
Illinois No. 6	69.6(2.0)	67.7(0.2)	66.1(2.8)	65.5(1.6)	62.1(2.0)	55.7(0.1)
Upper Freeport	47.1(2.0)	15.8(1.2)	13.0(1.7)	20.9(2.5)	8.3(0.7)	11.4(0.5)
Pocahontas No. 3	4.5(0.1)	-4.4(0.1)	-6.1(2.0)	-6.7(1.5)	-3.1(1.0)	-5.7(1.7)
Pittsburgh No. 8	56.4(0.1)	51.8(0.6)	38.8(1.0)	42.3(5.3)	30.5(3.8)	20.1(3.3)
Lewiston Stockton	41.7(1.9)	25.2(2.1)	19.6(1.2)	20.9(1.1)	9.1(2.6)	6.0(3.1)
Blind Canyon	64.8(3.9)	41.6(1.6)	27.9(0.7)	25.3(0.2)	15.2(2.0)	17.4(0.4)
Wyodak-Anderson (dried)[b] (as received)	50.6(0.6)	40.5(1.3)	21.4(1.2)	21.1(2.9) 22.3(1.8)	14.9(1.5) 15.5(0.2)	11.7(1.5)
Beulah Zap (dried)[b] (as received)	35.6(3.0) 34.8(1.9)	20.8(3.0) 21.4(3.2)	13.3(1.0)	13.8(0.1)	5.0(2.5)	8.1(2.1)

[a] Reaction Conditions: hexadecane as solvent, 1,250 psi hydrogen at ambient, 30 min reaction time, 380 °C
[b] Dried to approximately 4% moisture content
[c] Numbers in parentheses indicate standard deviations.
[d] DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene; ISO = isotetralin; TET = tetralin

Table II.D.2.b.4. S/N Values for Coal Conversion (%).

Coal	Donor					
	DHA[b]	HHA	OHA	ISO	TET	NONE
Kentucky No. 9	36.69	36.22	33.92	31.41	29.48	28.10
Illinois No. 6	36.84	36.61	36.38	36.32	35.85	34.92
Upper Freeport	33.44	23.90	22.06	26.22	18.29	21.11
Pocahontas No. 3	13.06	12.87[a]	14.49[a]	15.92[a]	8.65[a]	14.09[a]
Pittsburgh No. 8	35.03	34.28	31.77	32.33	29.49	25.73
Lewiston Stockton	32.38	27.94	25.80	26.37	18.23	13.01
Blind Canyon	36.18	32.36	28.90	14.48	23.42	24.80
Wyodak-Anderson	34.08	32.14	26.57	26.25	23.33	21.15
Beulah-Zap	30.94	26.10	22.40	22.80	11.55	17.37

[a] Uses + averages (not - averages).
[b] DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene
ISO = isotetralin; TET = tetralin

Table II.D.2.b.5. Multiple Regression Equations.

Donor	Constant	Moisture Content	Ash	Volatile Matter	Sulfur	BTU	R^2
DHA[a]	-658.087	8.118	7.509	3.580	3.493	37.025	0.98
HHA	272.673	-3.817	-3.180	1.410	7.957	-19.571	0.92
OHA	584.113	-7.882	-6.210	0.241	8.624	-37.956	0.96
ISO	28.180	-0.153	3.088	6.564	-116.334	-0.290	0.94
TET	498.825	-7.100	-5.965	0.665	6.126	-32.788	0.86

[a] DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene;
ISO = isotetralin; TET = tetralin

Table II.D.2.b.6. Analysis of the Products from the Hydrogen Donors in Reactions with Argonne Coals in Hexadecane

Compound/ Coal Reacted	OHA[a] Wt%	DHA Wt%	ANT Wt%	NET H Difference, g
OHA				
Kentucky No. 9	85.4(0.1)[b]	14.6(0.1)	0.0	0.00324
Illinois No. 6	77.4(0.7)	13.1(0.9)	9.5(0.2)	0.00575
Upper Freeport	96.1(0.7)	3.9(0.7)	0.0	0.00086
Pocahontas No. 3	94.8(1.6)	4.5(1.1)	0.7(0.5)	0.00121
Pittsburgh No. 8	90.4(0.6)	9.6(0.6)	0.0	0.00213
Lewiston Stockton	86.6(0.3)	13.4(0.3)	0.0	0.00287
Blind Canyon	76.0(0.8)	22.0(0.7)	2.0(0.1)	0.00548
Wyodak-Anderson	62.0(0.9)	32.2(0.6)	5.8(0.4)	0.00888
Beulah-Zap	67.9(0.3)	27.9(0.2)	4.2(0.1)	0.00748
HHA				
Kentucky No. 9	47.5(0.3)	45.7(0.1)	6.8(0.3)	0.00659
Illinois No. 6	11.6(1.8)	81.1(1.5)	7.3(0.6)	0.01726
Upper Freeport	52.1(0.3)	39.9(0.3)	8.0(0.4)	0.00531
Pocahontas No. 3	15.8(0.6)	74.1(0.5)	10.1(0.3)	0.01631
Pittsburgh No. 8	43.1(1.0)	44.8(0.6)	12.1(0.5)	0.00843
Lewiston Stockton	38.9(0.9)	47.8(0.3)	13.3(0.6)	0.01568
Blind Canyon	19.1(0.1)	50.8(0.6)	30.1(0.7)	0.01739
Wyodak-Anderson	18.2(0.2)	39.0(1.4)	42.8(1.6)	0.01896
Beulah-Zap	18.6(1.4)	38.0(1.1)	43.4(2.5)	0.01891
DHA				
Kentucky No. 9	60.9(2.3)	24.6(2.4)	14.5(1.5)	-0.04970
Illinois No. 6	45.6(2.6)	32.8(0.3)	21.6(0.6)	-0.03378
Upper Freeport	56.0(0.5)	23.6(0.1)	20.4(0.5)	-0.05444
Pocahontas No. 3	60.8(1.4)	18.4(0.6)	20.8(1.1)	-0.04746
Pittsburgh No. 8	44.2(0.6)	26.4(0.1)	29.4(0.6)	-0.03013
Lewiston Stockton	35.3(0.9)	29.5(0.6)	35.2(1.4)	-0.02044
Blind Canyon	34.8(0.3)	20.9(0.1)	44.3(0.3)	-0.01718
Wyodak-Anderson	28.6(1.1)	15.4(0.4)	56.0(1.5)	-0.00806
Beulah-Zap	35.2(3.9)	13.5(0.6)	51.3(4.5)	-0.01537

[a] OHA = octahydroanthracene; ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene
[b] Numbers in parentheses indicate standard deviations.

Table II.D.2.b.6. Analysis of the Products from the Hydrogen Donors in Reactions with Argonne Coals in Hexadecane (Cont'd)

Compound/ Coal Reacted	TET Wt%	NAP Wt%	NET H Difference, g
ISO[a]			
Kentucky No. 9	17.8(1.3)[b]	82.2(1.3)	0.01248
Illinois No. 6	23.5(0.6)	76.5(0.6)	0.01157
Upper Freeport	21.8(1.1)	78.2(1.1)	0.00296
Pocahontas No. 3	32.7(6.3)	67.3(6.3)	0.01018
Pittsburgh No. 8	20.5(0.7)	79.5(0.7)	0.01202
Lewiston Stockton	30.3(1.7)	69.7(1.7)	0.01054
Blind Canyon	20.5(1.4)	79.5(1.4)	0.01202
Wyodak-Anderson	18.6(0.1)	81.4(0.1)	0.01231
Beulah-Zap	15.4(0.6)	84.6(0.6)	0.01279
TET			
Kentucky No. 9	79.8(0.7)	20.2(0.7)	0.00298
Illinois No. 6	94.0(1.5)	6.0(1.5)	0.00091
Upper Freeport	100.0	0.0	0.0
Pocahontas No. 3	97.4(0.5)	2.6(0.5)	0.00087
Pittsburgh No. 8	88.2(0.5)	11.8(0.5)	0.00178
Lewiston-Stockton	100.0	trace	0.0
Blind Canyon	85.7(0.6)	14.3(0.6)	0.00216
Wyodak-Anderson	86.7(1.2)	13.3(1.2)	0.00201
Beulah-Zap	74.5(5.0)	25.5(5.0)	0.00386

[a] ISO = isotetralin; TET = tetralin; NAP = naphthalene
[b] Numbers in parentheses indicate standard deviations

Table II.D.2.b.7. Coal Conversion for Reactions of Argonne Coals with Hydrogen Donors in Maya Resid[a]

g Resid → Present	Coal Conversion (%) with						
	1.2	3.0	3.1	3.3	3.5	3.5	4.0
Coal Reacted	DHA[e]	DHA	HHA	OHA	ISO	TET	No Donor Added
Kentucky No. 9	73.6(0.7)[c]	65.0(1.6)	65.9(0.7)	45.4(1.0)	44.8(0.3)	31.7(2.6)	24.3(3.3)
Illinois No. 6	71.8(0.3)	56.6(0.3)	62.7(1.7)	52.4(0.4)	58.9(2.4)	55.5(0.5)	51.3(2.4)
Upper Freeport	48.3(0.5)	36.4(2.1)	35.3(0.1)	23.7(2.9)	16.5(3.4)	9.6(0.2)	14.0(1.6)
Pocahontas No. 3	NP[d]	NP	-2.1(0.4)	NP	NP	NP	NP
Pittsburgh No. 8	62.9(0.2)	55.3(1.3)	55.0(1.1)	43.3(0.8)	41.5(0.6)	32.3(1.6)	32.3(1.5)
Lewiston Stockton	38.0(4.2)	36.0(0.4)	25.3(0.4)	19.8(1.0)	20.6(1.5)	9.8(1.2)	10.0(0.2)
Blind Canyon	66.5(3.8)	59.8(1.9)	53.3(1.2)	39.1(2.8)	35.4(0.1)	16.4(1.2)	24.1(3.2)
Wyodak-Anderson[b]	53.8(2.0)	39.6(1.1)	37.9(1.8)	20.3(2.7)	18.1(3.0)	13.5(1.5)	8.7(1.7)
Beulah Zap[b]	44.0(0.8)	29.0(0.3)	20.5(1.3)	15.2(1.5)	15.4(1.3)	5.5(1.0)	11.1(1.4)

[a] Reaction Conditions: Maya resid as solvent, 1250 psi, hydrogen at ambient, 30 min reaction time, 380 °C.
[b] Dried to approximately 4% moisture content.
[c] Numbers in parentheses indicate standard deviations.
[d] NP = not performed
[e] DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene; ISO = isotetralin; TET = tetralin

Table II.D.2.b.8. Analysis of the Products from the Hydrogen Donors in Reactions with Argonne Coals in Maya Resid

Compound/ Coal Reacted	OHA[a] Wt%	DHA Wt%	ANT Wt%	NET H Difference, g
OHA				
Kentucky No. 9	77.0(4.3)[b]	23.0(4.3)	0.0	0.00511
Illinois No. 6	36.3(0.6)	47.9(0.4)	15.8(0.9)	0.01535
Upper Freeport	88.5(0.1)	11.5(0.1)	0.0	0.00255
Pocahontas No. 3	N/A	N/A	N/A	N/A
Pittsburgh No. 8	73.6(1.0)	24.7(0.6)	1.7(0.4)	0.00225
Lewiston Stockton	75.5(2.0)	24.5(2.0)	0.0	0.00544
Blind Canyon	59.9(0.1)	35.4(0.1)	4.7(0.1)	0.00926
Wyodak-Anderson	68.7(2.2)	25.5(1.2)	5.8(1.3)	0.00739
Beulah Zap	53.8(2.0)	32.6(0.4)	13.6(1.1)	0.01126
HHA				
Kentucky No. 9	40.2(1.6)	47.8(0.3)	12.0(1.6)	0.00928
Illinois No. 6	73.5(0.5)	26.5(0.5)	0.0	-0.00180
Upper Freeport	37.8(0.5)	48.1(0.2)	14.1(0.4)	0.01021
Pocahontas No. 3	18.2(0.3)	51.7(1.1)	30.1(0.8)	0.01765
Pittsburgh No. 8	30.6(1.0)	52.0(1.0)	17.4(1.7)	0.01268
Lewiston Stockton	31.4(1.3)	39.8(0.2)	28.8(1.2)	0.01362
Blind Canyon	18.1(0.4)	49.4(0.1)	32.5(0.3)	0.01806
Wyodak-Anderson	19.3(1.2)	35.7(1.1)	45.0(2.4)	0.01886
Beulah Zap	15.7(2.0)	40.3(1.1)	44.0(1.3)	0.01983
DHA (3.0 g resid)				
Kentucky No. 9	49.8(4.2)	24.9(0.7)	25.3(3.5)	-0.03373
Illinois No. 6	57.2(1.7)	12.5(0.0)	30.3(1.7)	-0.04139
Upper Freeport	49.8(1.9)	24.0(0.3)	26.2(1.6)	-0.03543
Pocahontas No. 3	N/A	N/A	N/A	N/A
Pittsburgh No. 8	35.8(2.8)	27.1(0.5)	37.1(3.2)	-0.02030
Lewiston Stockton	34.3(2.5)	27.7(0.6)	38.0(3.1)	0.01869
Blind Canyon	27.5(0.2)	21.5(0.1)	51.0(0.3)	-0.00863
Wyodak-Anderson	28.6(0.4)	15.9(0.2)	55.5(1.1)	-0.00822
Beulah Zap	28.3(0.7)	15.7(0.7)	56.0(2.1)	-0.00837
DHA (1.2 g resid)				
Kentucky No. 9	51.9(2.3)	26.5(0.2)	21.6(2.4)	-0.03942
Illinois No. 6	47.1(2.3)	23.1(0.4)	29.8(2.6)	-0.03258
Upper Freeport	46.0(0.4)	24.9(0.1)	29.1(0.5)	-0.03182
Pocahontas No. 3	N/A	N/A	N/A	N/A
Pittsburgh No. 8	37.1(0.8)	29.4(0.2)	33.5(0.7)	-0.02268
Lewiston Stockton	31.9(1.0)	29.8(0.5)	38.3(1.3)	-0.01646
Blind Canyon	26.4(0.4)	24.7(0.3)	48.9(0.2)	-0.00831
Wyodak-Anderson	24.9(1.4)	20.2(0.7)	54.9(0.8)	-0.00512
Beulah Zap	33.3(1.3)	17.6(0.4)	49.1(1.2)	-0.01437

[a] OHA = octahydroanthracene; ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene
[b] Numbers in parentheses indicate standard deviations.

Table II.D.2.b.8. Analysis of the Products from the Hydrogen Donors in Reactions with Argonne Coals in Maya Resid (Cont'd)

Compound/ Coal Reacted	TET Wt%	NAP Wt%	NET H Difference, g
ISO[a]			
Kentucky No. 9	21.0(0.7)[b]	79.0(0.7)	0.01195
Illinois No. 6	22.0(0.5)	78.0(0.5)	0.01179
Upper Freeport	21.9(1.1)	78.1(1.1)	0.01181
Pocahontas No. 3	N/A	N/A	N/A
Pittsburgh No. 8	19.8(1.2)	80.2(1.2)	0.01213
Lewiston-Stockton	25.5(1.0)	74.5(1.0)	0.00778
Blind Canyon	16.8(0.6)	83.2(0.6)	0.01258
Wyodak-Anderson	22.7(1.1)	77.3(1.1)	0.01169
Beulah-Zap	7.4(0.6)	92.6(0.6)	0.01400
TET			
Kentucky No. 9	90.9(0.4)	9.1(0.4)	0.00135
Illinois No. 6	79.7(0.8)	20.3(0.8)	0.00307
Upper Freeport	84.2(4.6)	15.8(4.6)	0.00239
Pocahontas No. 3	N/A	N/A	N/A
Pittsburgh No. 8	78.7(1.6)	21.3(1.6)	0.00322
Lewiston-Stockton	83.7(0.8)	16.3(0.8)	0.00246
Blind Canyon	100.0	0.0	0.0
Wyodak-Anderson	75.3(1.0)	24.7(1.0)	0.00373
Beulah-Zap	68.7(1.1)	31.3(1.1)	0.00473

[a] ISO = isotetralin; TET = tetralin
[b] Numbers in parentheses indicate standard deviations.

SUBTASK II.E

KINETICS AND REACTIVITY OF CYCLIC OLEFINS

INTRODUCTION

The objective of the research performed in Task II.E was to determine the kinetic and thermodynamic properties of the cyclic olefins as donors for coprocessing. The cyclic olefins used in this study were 1,4,5,8,9,10-hexahydroanthracene (HHA) and 1,4,5,8-tetrahydronaphthalene, isotetralin (ISO). The first step in fulfilling the objective was to investigate the chemistry of these compounds under coprocessing conditions. Both the thermal and catalytic reactivity of the cyclic olefins at elevated temperatures under hydrogen and nitrogen atmospheres was determined and compared to the reactivity of their respective hydroaromatic analogues, dihydroanthracene (DHA), octahydroanthracene (OHA), and tetralin (TET). The catalysts used were presulfided, pulverized $NiMo/Al_2O_3$ and Mo/Al_2O_3. The experimental reactivity and product slates were determined for each of the model compounds. Then for both thermal and catalytic reactions pseudo-first order reaction rate constants, Arrhenius parameters, and Gibbs free energy values were determined.

EXPERIMENTAL PROCEDURE

Reaction Procedures. The reactivity of the cyclic olefins and their conventional hydroaromatic analogues was tested in stainless steel tubular microreactors having volumes of $\sim 20\ cm^3$. The reaction conditions used were reaction temperatures ranging from 100 to 475 °C, horizontal agitation at 425 cpm, nitrogen or hydrogen pressures of 1250 psig introduced at ambient temperature, and reaction times ranging from 2 min to 1 hr. The reaction system consisted of 2.0 g hexadecane as the diluent solvent; 3 wt% hydrogen donor was added to the

diluent solvent; and a total active metal loading of 3000 ppm was charged in each reaction. Two supported catalysts were used, Shell 324 $NiMo/Al_2O_3$, a commercial hydrotreating catalyst, and Amocat 1B, Mo/Al_2O_3, to evaluate the catalytic reactivity of the different hydrogen donors at liquefaction conditions. Each catalyst was presulfided in a heated flowing stream of 10% H_2S in hydrogen for approximately 5 hr, pulverized and sized to between 100 and 200 mesh before being used. After pulverization, the catalysts were stored in a desiccator.

The chemicals used in the kinetics experiments were obtained from the following manufacturers and used as received: TET, 1,4,5,8,9,10-HHA, 1,2,3,4,5,6,7,8-OHA, 9,10-DHA, hexadecane from Aldrich Chemical Co.; 1,4,5,8-tetrahydronaphthalene from Wiley Organics Inc.

The products from the model reactivity studies were analyzed by gas chromatography using a Varian 3400 GC equipped with a HT-5 column obtained from SGE and FID detection. The internal standard method was used for quantitation, with biphenyl as the internal standard. The peaks were identified by comparing retention times with authentic compounds and by GC mass spectral analysis using a VG 70EHF mass spectrometer.

BACKGROUND AND THEORY

For the thermal dehydrogenation reactions of the cyclic olefins and their conventional hydrogen donor compounds, it was assumed that the reaction kinetics could be approximated by a pseudo-first order rate expression. The overall reaction was expressed as A → products, where A was either ISO, TET, DHA, HHA, or OHA. On the basis of the first order kinetics and defining C as the concentration of the reactant A, the rate law was expressed as

$$\text{rate} = -dC/dt = kC \qquad (1)$$

separation of variables and integration of equation (1) yielded

$$\int_{C_0}^{C} dC/C = -k\int_0^t dt \tag{2}$$

where C_o is the initial concentration of reactant A, k is the apparent rate constant, t is the time of the reaction and C is the concentration of reactant A at time t. It, therefore, follows that

$$\ln C_o/C = kt \tag{3}$$

The weight percent of the reactant was determined at discrete reaction times ranging from 2 min to 120 min, as required in the experimental reactions. The selection of the time and temperature range for a given reactant was dependent upon the reactivity of that given reactant. The weight percent remaining of reactant A at time t was defined as λ and was proportional to the concentration of the reactant. Assumming that λ varied in a linear fashion with the extent of reaction, the concentration A can be defined as

$$C(t) = p\ (\lambda - \lambda_\infty) \tag{4}$$

where λ_∞ is the value of the weight percent of A at the end of the reaction, e.g., as $t \to \infty$, $\lambda = 0$ and p is a proportionality constant. When the additional boundary condition, $t = 0$, $\lambda = 100$, is used, i.e. no reaction has initially occurred, then

$$C_0 = p\ (\lambda_0 - \lambda_\infty)\ . \tag{5}$$

Substitution of equations (4) and (5) into equation (3) yields

$$\ln \{(\lambda_0 - \lambda_\infty) / (\lambda - \lambda_\infty)\} = kt\ ; \tag{6}$$

however, $\lambda_0 = 100$, and $\lambda_\infty = 0$, therefore, equation (6) becomes

$$\ln (\lambda_0 / \lambda) = kt \qquad \text{or} \qquad \ln (100 / \lambda) = kt \tag{7}$$

which upon rearrangement becomes

$$\lambda = 100\, e^{-kt} \tag{8}$$

and the linear form of equation (8) becomes

$$\lambda = -kt + \ln(100) \tag{9}$$

Therefore, a plot of ln λ versus t should yield a straight line. The slope of the line obtained is the apparent rate constant, k, for the reaction at a given temperature. From the experimental results obtained from the different hydrogen donors, the ln λ versus t data was analyzed using linear regression to obtain the best fit and a subsequent value for k. The apparent rate constant was determined at three different temperatures for each of the five hydrogen donors.

After the apparent rate constants were determined at three different temperatures for each donor, the effect of temperature on the rate constants was investigated by using the Arrhenius equation

$$\ln k = \ln k_0 - E_a / RT \tag{10}$$

where E_a is the activation energy, k_0 is the frequency factor, T is the temperature in Kelvin, and R is the universal gas constant. The magnitude of the activation energy is an indication of the temperature sensitivity of a given reaction. The frequency factor accounts for other factors that influence the rate of reaction such as frequency of collisions and geometric constraints. Reactions

with large values of E_a are sensitive to temperature, while those reactions with small values of E_a are relatively unaffected by changes in temperature. Using equation (10), E_a and k_0 can be determined for each of the model compounds studied.

The thermodynamic formulation of the activated complex theory was used to develop an equation relating the entopic and enthalpic contribution of the reaction to the Arrhenius parameters, E_a and k_0. The following equations were obtained for a gas phase, uni-molecular reaction of the form A → products:

$$E_a = \Delta H + RT \tag{11}$$

and

$$k_0 = \{(e\ k_b\ T)/h\}\ e^{(\Delta S/R)} \tag{12}$$

where k_b is Boltzman's constant, h is Planck's constant, ΔS is the change in entropy and e = 2.718. The Gibbs free energy of formation as a function of temperature can be obtained from equation (13)

$$\Delta G = \Delta H - T\ \Delta S \tag{13}$$

In order to use equation (13), equations (11) and (12) must be rearranged to obtain $\Delta H = f(E_a,T)$ and $\Delta S = f(k_0,T)$. These relations become

$$\Delta H = E_a - RT \tag{14}$$

and

$$\Delta S = R\ \ln\ (k_0/T) + R\beta \tag{15}$$

where β is a constant and is equal to ln $\{h / (e\ k_b)\}$. Substitution of equations (14) and (15) into equation (13) yields

$$\Delta G = E_a - RT(1+\beta) - RT \ln(k_0/T) \tag{16}$$

which gives $\Delta G = f(E_a, K_0, T)$. A relationship for the Gibbs free energy as a function of temperature can be developed for a given compound, with the corresponding values of E_a and k_0. The value calculated for ΔG can be used to form a basis for comparing reactions of the different hydrogen donors. The more negative the value for ΔG is for a reaction, the more spontaneous the reaction proceeds, and, hence, the more reactive is the hydrogen donor.

Thermal Reaction Product Slates

The cyclic olefins and their conventional hydrogen donor compounds were thermally reacted as individual compounds at various reaction times at three different temperatures. The number of different reaction times varied but up to seven reaction times, including $\lambda=0$ at $t=0$, were used in fitting the first order reaction kinetics under both N_2 and H_2 atmospheres with a given compound at a single temperature. The results from the thermal reactivity using ISO, TET, HHA, OHA, and DHA are presented in Tables II.E.1 through II.E.5.

The predominant reaction product from ISO was 1,4-octahydronaphthalene at reaction temperatures of 225 °C and 300 °C (Table II.E.1); minor amounts of 1,2-dihydronaphthalene (1,2-DHN) and naphthalene were also formed at 300 °C. A more varied product slate was obtained from ISO at 380 °C. After 10 min of reaction time, 1,4-DHN and naphthalene were the predominant reaction products, with lesser amounts of TET and 1,2-DHN being formed. After reaction times of 30 or 60 min, naphthalene was the predominant reaction product. For the

reactions with TET at 380 °C (Table II.E.2), TET did not convert substantially and the product slate consisted of small amounts of naphthalene, 1,2-DHN, 1,4-DHN, and t-decalin. In the reactions of TET at 425 °C and at 450 °C, more conversion of TET occurred, particularly at longer reaction times; 1,2-DHN and 1,4-DHN were the primary reaction products. A minor amount of naphthalene was also formed except at 60 min in N_2 at 450 °C, where naphthalene became the predominant product.

The thermal reactions of the three-ring hydrogen donor compounds, OHA, DHA, and HHA, are presented in Tables II.E.3-II.E.5. The primary reaction products formed from OHA at 425 °C were DHA, tetrahydroanthracene (THA), and anthracene (Table II.E.3). Then when the reaction temperature was raised to 450 °C, the predominant reaction product from OHA became THA, with lesser amounts of DHA and anthracene also being formed. At a reaction temperature of 475 °C, DHA and THA were the primary reaction products from OHA. The reaction of DHA at 380 °C yielded only THA and anthracene as reaction products in both H_2 and N_2 atmospheres (Table II.E.4). At a reaction temperature of 425 °C, anthracene was the only reaction product formed, except at a reaction time of 60 min under hydrogen where 3.2% THA was formed. At 450 °C under hydrogen, anthracene was the primary reaction product from DHA, with a minor amount of THA also being produced. As shown in Table II.E.5, the cyclic olefin, HHA, did not show much conversion but did convert to small amounts of THA and DHA at 225 °C. At 300 °C, somewhat more conversion of HHA occurred yielding DHA as the primary reaction product, although some THA was still formed. At 380 °C, DHA was the primary reaction product from HHA, with a lesser amount of THA and anthracene also being formed.

The reaction data given in Tables II.E.1-II.E.5 clearly show that two cyclic olefins, ISO and HHA, were much more reactive than their conventional hydrogen donor analogues, TET,

OHA, and DHA. The cyclic olefins were reactive at much lower temperatures, 225 °C and 300 °C, while their conventional donor analogues required reaction temperatures of up to 475 °C in order to show any appreciable reactivity. The cyclic olefins were essentially totally converted in 15 min at 380 °C, e.g., ISO was 100% converted under hydrogen and 98.4% converted under nitrogen, and HHA was 90% converted under hydrogen and 98% converted under nitrogen. By contrast, the conventional hydrogen donors, TET and OHA did not convert under either nitrogen or hydrogen at 15 min at 380 °C, while DHA yielded only 2.1% conversion under hydrogen and 3.0% under nitrogen at 380 °C in 15 min. The cyclic olefins not only required lower reaction temperatures for conversion than did the conventional donors, but also shorter reaction times at a given temperature to be very reactive.

Kinetic Analysis and Arrhenius Plots for the Thermal Reaction of the Compounds Under Nitrogen and Hydrogen

The apparent rate constants k and linear regression correlation coefficients were determined for each given model compound in reactions under nitrogen and hydrogen at each reaction temperature by using equation (9) and the data presented in Tables II.E.1-II.E.5. The apparent rate constants and correlation coefficients are summarized in Table II.E.6. The fit of the data to pseudo-first order reaction kinetics was excellent for all of the compounds under both atmospheres. The correlation coefficients were greater than 0.93 for all the reactions, and frequently greater than 0.96. For all of the compounds studied, under both atmospheres, the rate constant increased with increased temperature. As the reaction temperature increased, the reactivity of the model compounds for dehydrogenation also increased.

For the reactions at 380 °C under nitrogen, the rate constant for ISO was 366 times greater than that of TET; for the reactions under hydrogen, the rate constant for ISO was 228 times

greater than that of TET. For the reactions involving the three-ring compounds at 380 °C under N_2, the rate constant for HHA was 144 times greater than that for DHA, while under hydrogen it was 100 times greater. Octahydroanthracene was completely unreactive at 380 °C under both nitrogen and hydrogen at reaction times up to 90 min; therefore, no rate constant could be determined for OHA at 380 °C. At 380 °C under N_2, the apparent rate constant for ISO was slightly greater than that which was obtained for HHA, 0.27 versus 0.24; while in a hydrogen atmosphere the rate constant for ISO was nearly 2.5 times greater than that of HHA, 0.34 versus 0.14.

Arrhenius plots were developed for the five model compounds under both nitrogen and hydrogen by using the apparent rate constant data given in Table II.E.6 and equation (10). From the linear regression of these data, values for the activation energy, E_a, and frequency factor, k_0, were determined. These values are summarized in the last column of Table 6. The fit of all the data to the Arrhenius plots was excellent, as evidenced by the linear regression correlation coeffcients being 0.95 or greater.

For the model compounds reacted under nitrogen, the activation energy and frequency factors yielded the ranking of OHA and TET > DHA > ISO > HHA. For the model compounds reacted under hydrogen, the activation energy and frequency factors gave the ranking of OHA > TET > ISO > HHA > DHA.

Determination of Gibbs Free Energy for the Thermal Reactions

The Gibbs free energy of reaction was plotted as a function temperature by using Arrhenius parameters and the thermodynamic formulation of the activated complex theory, according to equation (16). The Gibbs free energy (ΔG) of reaction is plotted over a temperature

range of 127 °C to 577 °C in Figure II.E.1 for the reactions of the five model compounds in a N_2 atmosphere. One of the most striking features of this plot was that the two cyclic olefins, ISO and HHA, had much lower values for ΔG than their conventional hydrogen donor analogues over the temperature range, except at very high temperatures (T > 475 °C). At these very high temperatures, the values for all the compounds were similar. This plot and associated theory are useful tools to explain the observed experimental reactivity ranking of the model hydrogen donor compounds. At any given temperature, the reactions having the most negative ΔG values proceed most spontaneously. For example, at a reaction temperature of 380 °C under nitrogen, ISO and HHA were very reactive compared to TET, DHA, and OHA. Isotetralin and HHA had much lower values of ΔG than those for their hydrogen donor analogues (Figure II.E.1). The experimental reactivity ranking for the hydroaromatic donors at 380 °C was DHA > TET > OHA, which was also predicted from the ΔG values given in Figure II.E.1. Figure II.E.1 also predicts that OHA should always be the least reactive compound, which was observed experimentally.

The Gibbs free energy of reaction is presented versus temperature for the reaction of the five model compounds in a hydrogen atmosphere in Figure II.E.2. The cyclic olefins, ISO and HHA, had much lower values for ΔG than their hydroaromatic analogues and, therefore, are predicted to be more reactive compounds. This result was the same as that obtained in the N_2 atmosphere. The reactivity of the cyclic olefins was supported by the experimental results obtained in a hydrogen atmosphere. At 380 °C, the reactivity of the conventional donors should rank as TET > DHA > OHA, based upon the values of the Gibbs free energy in hydrogen. This order of reactivity was also observed experimentally.

Another important feature of Figure II.E.2 is the relatively flat slope of DHA which suggested that at higher temperatures in a hydrogen atmosphere, DHA should be much less

reactive than either OHA or TET. This prediction was supported experimentally. Examination of reactions performed in hydrogen at 60 min at 450 °C reveals that ~80% of TET was converted, ~57% of OHA was converted while less than 30% of DHA was converted.

The activated complex theory provides a useful tool for modeling the expeimental reaction system of cyclic olefins and hydroaromatic donor. Agreement was found among the thermal reactivity and experimental behavior of the donors and the predictions from the Gibbs free energy of reaction as well as pseudo-first order reaction kinetics. These agreements were obtained under both N_2 and H_2 atmospheres.

Catalytic Reaction Product Slates

Catalytic reactions of the cyclic olefins and their hydrogen donor analogues were performed with a commercial $NiMo/Al_2O_3$ catalysts (Shell 324) and a Mo/Al_2O_3 catalyst (Amocat 1b) at various reaction times and three different temperatures. Tables II.E.7-II.E.11 present the product distributions obtained from the different donors that were obtained in these catalytic reactions. There were up to five reaction times, including $\lambda = 0$ at $t = 0$, used to fit the experimental data to the pseudo-first order kinetics model.

Reactions with ISO and Mo/Al_2O_3 catalyst were performed at three temperatures 225, 175, and 125 °C (Table II.E.7). At 225 °C, the primary reaction products from ISO were TET and OHN, with lesser amounts of 1,4- and 1,2-DHN being formed. At 175 °C less hydro-genation occurred giving the primary reaction products of 1,4-DHN and TET. At 125 °C even less hydrogenation occurred with 1,4-DHN as the predominant reaction product with a minor amount of TET and 1,2-DHN also formed. Reactions with ISO at 175, 140, and 100 °C with the $NiMo/Al_2O_3$ catalyst, presented also in Table II.E.7, gave similar results as the Mo/Al_2O_3

reactions except that the more active $NiMo/Al_2O_3$ yielded the hydrogenated products at lower temperature. At 175 °C, 1,4-DHN, TET, and octahydronaphthalene were the primary reaction products, with a small amount of 1,2-DHN also being produced. The same products were obtained in the reactions at 140 °C, but with TET being the major product at 15 and 30 min. At 100 °C, 1,4-DHN was the only product formed. Higher reaction temperatures of 380, 425, and 450 °C were required to obtain reactivity with TET and Mo/Al_2O_3 as presented in Table II.E.8. The products produced were 1,2-DHN, t-decalin and a small amount of naphthalene. The same products were formed in the reactions of TET with the $NiMo/Al_2O_3$ catalyst; however, slightly more hydrogenation was observed with the production of c-decalin, at 380, 425, and 450 °C (Table II.E.8).

Octahydroanthracene, THA, and ANT were the only reaction products of DHA at reaction temperatures of 380, 350, and 300 °C (Table II.E.9). An additional hydrogenation product of perhydroanthracene was produced from DHA in reactions with the $NiMo/Al_2O_3$ catalyst at the same reaction temperatures. Reactions with OHA and the Mo/Al_2O_3 catalyst were performed at 450, 425, and 380 °C as presented in Table II.E.10, yielding the primary reaction product of PHA at 450 °C, with lesser amounts of THA also being formed. At lower reaction temperatures, nearly equivalent amounts of perhydroanthracene and THA were produced. By contrast, perhydroanthracene was the primary reaction product from OHA in reactions with the $NiMo/Al_2O_3$ catalyst at reaction temperatures of 380, 425, and 450 °C as shown in Table II.E.10. Tetrahydroanthracene, DHA, and anthracene were also produced in lesser amounts. The cyclic olefin, HHA, was primarily converted to OHA in reactions with the Mo/Al_2O_3 catalyst; at reaction temperatures of 225 and 175 °C (Table II.E.11); lesser amounts of THA and perhydroanthracene were also produced. At 125 °C, nearly equivalent amounts of OHA and

THA were produced. Reactions were also performed with HHA and $NiMo/Al_2O_3$ at 175, 140, and 100 °C. OHA was the primary reaction product, with lesser amounts of THA and DHA also being formed.

In examining the data given in Table II.E.7 through II.E.11, the cyclic olefins are much more reactive catalytically than their hydroaromatic analogues since both ISO and HHA required lower temperatures to convert and form hydrogenated products compared to the hydroaromatic species. Temperatures of less than 225 °C were required for the cyclic olefins compared to temperatures of 450 °C for the hydroaromatic species. The cyclic olefins also needed much shorter reaction times to be converted to hydrogenation products. This high degree of reactivity of the cyclic olefins was also observed in the thermal reaction systems as discussed previously.

Kinetic Analysis and Arrhenius Plots for the Catalytic Reaction of the Compounds Under Nitrogen and Hydrogen

The apparent rate constant k and linear regression correlation coefficients were determined for the reactions of the model compounds at each reaction temperature in the reactions using $NiMo/Al_2O_3$ and Mo/Al_2O_3 catalysts. The results obtained by application of equation (9) and the data presented in Tables II.E.7 through II.E.11 are summarized in Table II.E.12. The fit of the experimental data to the pseudo-first order reaction kinetic model as indicated by correlation coefficient was good for the reactions with both $NiMo/Al_2O_3$ and Mo/Al_2O_3 catalysts. The straight line correlation coefficients were 0.92 or greater and were usually greater than 0.95. The rate constants increased with an increase in reaction temperature for all of the compounds studied in the presence of either catalyst. Hence, higher reaction temperature increased the rate of reaction for all model compounds.

At reaction temperatures greater than ~225 °C, the cyclic olefins reacted so rapidly with the catalysts that no kinetic data could be obtained. By contrast, the hydroaromatic donors were unreactive at these lower temperatures. Because there was no common reaction temperature at which both the cyclic olefins and the hydroaromatic donors were reactive, no direct comparison of rate constants among these different types of donors can be made.

However, the rate constants between the two cyclic olefins and among the hydroaromatic donors can be compared. Comparison of the reactions of HHA and ISO with Mo/Al_2O_3 at 225 °C shows that the rate constant for ISO was 2 times that for HHA, while at 125 °C the rate constant for HHA was 1.9 times that of ISO. The reactions of HHA and ISO with $NiMo/Al_2O_3$ yielded a rate constant for HHA at 175 °C and 100 °C that was greater than for ISO, but at 140 °C the rate constant for ISO was larger.

The three hydroaromatic donors had a common reaction temperature of 380 °C with both catalysts. With Mo/Al_2O_3 as the catalyst, the rate constant for DHA was 35.9 times greater than that obtained for TET, and 27.1 times greater than that of OHA. With the $NiMo/Al_2O_3$ catalyst, rate constants for TET and OHA were nearly equivalent and were 10 times less than DHA.

Arrhenius plots were developed for the five model donors reacted with both $NiMo/Al_2O_3$ and Mo/Al_2O_3 by using the apparent rate constants and equation (10). Linear regression of this data gave values for E_a and k_o which are summarized in the last column of Table II.E.12. The fit of the Arrhenius plots to the experimental data was usually good as indicated by the correlation coefficients being 0.97 or greater. However, three exceptions were noted; the reactions of DHA and OHA with the $NiMo/Al_2O_3$ catalyst and the reaction of HHA with the Mo/Al_2O_3 catalyst. The coefficients for these reactions ranged from ~0.85 to ~0.90. The poor fit of the Arrhenius plots to these reactions was believed to be caused by experimental fluctuations, rather than a

change in the effect of temperature on the activation energy. The Gibbs free energy for the catalytic reactions was plotted, the best fit to the experimental data was obtained and the corresponding values for E_a and k_o were determined.

The reactions of the model donors with the Mo/Al_2O_3 catalyst yielded activation energies that gave the following ranking: TET > DHA > OHA > ISO > HHA. The activation energies obtained from reactions with $NiMo/Al_2O_3$ showed the following ranking: DHA > HHA > ISO > TET > OHA.

Determination of Gibbs Free Energy for the Catalytic Reactions

Plots of the Gibbs free energy versus temperature were developed by using the Arrhenius parameters for each model donor in the catalytic reaction system and equation (16). Figures II.E.3 and II.E.4 present the results that were obtained for the reactions with the Mo/Al_2O_3 and $NiMo/Al_2O_3$ catalysts, respectively. The Gibbs free energy plots of the cyclic olefins with Mo/Al_2O_3 had much lower (more negative) values for ΔG than did the hydroaromatic donors. The more negative ΔG values imply that the reactions with cyclic olefins should be more spontaneous than those with the hydroaromatic donor. The cyclic olefins should then give up their hydrogen more readily than the hydroaromatic donor. Experimentally, the cyclic olefins were considerably more reactive than their hydroaromatic donors.

The Gibbs free energies obtained from reaction temperatures of 125, 175, and 225°C suggest that the release of hydrogen from ISO should be favored compared to HHA because ISO had lower values for ΔG than those for HHA. When experimental results from Table II.E.7, for ISO, and Table II.E.11, for HHA, are compared, ISO converted more than did HHA at any given reaction time.

At 380 °C, a common reaction temperature for the hydroaromatic donors, the reactivity ranking indicated by the magnitude of the Gibbs free energy was that DHA should be more reactive than either OHA or TET. Octahydroanthracene and TET should also have nearly equivalent levels of reactivity. The experimental results given in Tables II.E.9, II.E.10, and II.E.8 showed that DHA converted 93.7% in 60 min, while OHA converted 9.5% and TET converted 7.2%, respectively. The experimental results are in excellent agreement with those predicted by the relative values of the Gibbs free energy.

Similar results were obtained with $NiMo/Al_2O_3$ as were obtained with Mo/Al_2O_3. The cyclic olefins, ISO and HHA, had much lower values for the Gibbs free energy than did TET, OHA and DHA. Hence, the cyclic olefins required much lower reaction temperatures and shorter reaction times for conversion compared to the hydroaromatic donors.

The Gibbs free energy plots given in Figure II.E.4 suggest that ISO and HHA should have very similar reactivities because of the overlap of their respective times. This prediction was substantiated by the results for the conversion of ISO and HHA at 175 °C. With a reaction time of 2 min 47.5% of ISO converted, while 44.2% of HHA converted; with a reaction of 5 min 81% of ISO converted, while 77.6% of HHA converted; and with a reaction time of 7 min 91.6% of ISO converted, while 95.2% of HHA converted. The experimental reactivity of ISO and HHA were nearly equivalent, as was predicted by the Gibbs free energy values.

At 380 °C, which was a common reaction temperature for OHA, DHA, and TET, the prediction from Figure II.E.4 is that DHA should be much more reactive than either TET or OHA. TET and OHA should have very similar reactivities. In a 2 min reaction, 13.2% of DHA converted; by contrast, 3.2% of TET and 17.2% of OHA converted. The prediction by the Gibbs free energy correctly described the experimental results for DHA and TET, yet underestimated

the reactivity of OHA. However, for the reactions of OHA and DHA, as was previously discussed, the experimental deviations were higher as indicated by low correlation coefficients for the Arrhenius plots. The correlation coefficients were only 0.85 for DHA and 0.88 for OHA. The variability of the experimental results for the reactions may limit the accuracy of the Gibbs free energy plots based upon the calculated values for E_a and k_o. However, regardless of the slight variations in the ranking of the conventional donor compounds reactivity, the trend that the cyclic olefins were much more reactive than OHA, DHA, or TET was substantiated by their much lower values for the Gibbs free energy of reaction. The magnitudes of the differences between the cyclic olefins and their analogues are great enough to be outside the influence of experimental variations.

SUMMARY

Experimental reactions were performed with cyclic olefins and hydroaromatic donors under thermal and catalytic reaction conditions. The experimental data obtained for both the thermal and catalytic reactions were adequately modeled by pseudo-first order reaction kinetics. For all of the thermal reactions, as the reaction temperature increased, the rate constants also increased. The thermal rate constants for the cyclic olefins were much greater than those for the hydroaromatic analogues. Plots of the Gibbs free energy versus temperature were developed by using the thermodynamic formulation of the activated complex theory, which relates the activation energy and frequency factors to ΔG. The ΔG values for both cyclic olefins were lower than those for the hydroaromatic analogues. Since the more negative ΔG values indicate a more spontaneous reaction, the cyclic olefins should be more reactive which was verified experimentally. The kinetic rate constants and Gibbs free energy values obtained showed that

under catalytic reaction conditions the cyclic olefins were considerably more reactive than their hydroaromatic analogues.

NOMENCLATURE

DHA	=	dihydroanthracene	OHA	=	octahydroanthracene
DHN	=	dihydronaphthalene	TET	=	tetralin
HHA	=	hexahydroanthracene	THA	=	tetrahydroanthracene
ISO	=	isotetralin			

Table II.E.1. Thermal Reaction Products from Isotetralin

Reaction Conditions	Weight Percent Recovered				
	NAP[a]	1,2-DHN	1,4-DHN	TET	ISO
225°C					
Hydrogen:					
2 min	0.0	0.0	1.7(0.3)[b]	0.0	98.3(0.3)
30 min	0.0	0.0	2.4(0.1)	0.0	97.6(0.1)
60 min	0.0	0.0	3.5(0.2)	0.0	96.5(0.2)
90 min	0.0	0.0	4.3(0.1)	0.0	95.7(0.1)
Nitrogen:					
2 min	0.0	0.0	2.8(0.3)	0.0	97.2(0.3)
30 min	0.0	0.0	3.9(0.1)	0.0	96.1(0.1)
60 min	0.0	0.0	4.1(0.8)	0.0	95.9(0.8)
90 min	0.0	0.0	6.4(3.8)	0.0	93.6(3.8)
120 min	0.0	0.0	7.8(1.4)	0.0	92.2(1.4)
300°C					
Hydrogen:					
2 min	0.7(0.04)	0.7(0.05)	11.9(0.2)	0.0	86.7(0.2)
15 min	0.0	trace	15.6(0.5)	0.0	84.4(0.5)
30 min	0.0	1.0(0.1)	15.6(0.5)	0.0	83.4(0.5)
60 min	0.0	6.1(2.1)	25.8(3.7)	5.7(2.1)	62.4(9.0)
90 min	0.0	10.6(0.7)	27.9(0.5)	8.8(1.0)	52.7(2.2)
Nitrogen:					
2 min	0.6(0.04)	0.6(0.04)	11.0(0.3)	0.0	87.8(0.3)
15 min	0.0	0.0	12.4(3.7)	0.0	87.6(3.7)
30 min	0.0	0.0	15.4(0.8)	0.0	84.6(0.8)
60 min	0.0	0.0	23.1(0.8)	0.0	76.9(0.8)
90 min	0.0	0.0	30.9(0.5)	0.0	69.1(0.5)
380°C					
Hydrogen:					
2 min	2.2(0.2)	3.1(0.7)	39.1(1.8)	3.3(1.5)	52.4(2.9)
5 min	7.3(1.0)	9.4(4.2)	56.8(4.8)	8.5(3.2)	18.0(3.6)
10 min	30.4(0.4)	15.2(1.1)	35.2(0.4)	15.9(1.8)	3.3(0.6)
15 min	30.5(0.5)	23.8(4.6)	27.9(12.3)	17.8(6.0)	0.0
30 min	52.6(2.3)	10.0(2.6)	26.8(3.7)	10.6(1.2)	0.0
60 min	61.1(2.1)	11.5(1.7)	1.1(0.3)	26.3(3.5)	0.0
Nitrogen:					
2 min	3.6(0.1)	0.0	48.4(0.3)	1.6(0.1)	46.4(0.3)
5 min	5.6(0.4)	0.9(0.3)	67.7(0.9)	0.3(0.2)	25.5(0.9)
10 min	17.4(0.5)	2.3(0.3)	73.2(2.0)	1.2(0.4)	5.9(2.0)
15 min	23.4(0.4)	2.5(0.6)	70.3(0.7)	2.2(0.3)	1.6(0.2)
30 min	55.1(1.5)	4.6(0.5)	36.7(1.0)	3.6(0.4)	0.0
60 min	78.2(0.6)	4.8(0.2)	13.8(0.6)	3.2(0.3)	0.0

[a] Numbers in parentheses indicate standard deviations.
[b] NAP = naphthalene; DHN = dihydronaphthalene; TET = tetralin; ISO = isotetralin.

Table II.E.2. Thermal Reaction Products from Tetralin

Reaction Conditions	Weight Percent Recovered				
	NAP[b]	1,2-DHN	1,4-DHN	t-DEC	TET
380°C					
Hydrogen:					
15 min	0.0	0.0	0.0	0.0	100.0
30 min	0.7(0.1)[a]	1.0(0.1)	2.1(0.3)	0.0	96.2(2.3)
60 min	trace	0.0	trace	5.3(0.9)	94.7(0.9)
90 min	0.0	0.0	7.3(0.1)	6.3(0.1)	86.4(0.4)
Nitrogen:					
15 min	0.0	0.0	0.0	0.0	100.0
30 min	0.8(0.2)	0.0	0.0	0.0	99.2(3.8)
60 min	0.6(0.1)	1.6(0.3)	2.0(0.6)	0.0	96.8(0.9)
90 min	1.0(0.03)	2.3(0.2)	3.1(0.4)	0.0	93.6(0.5)
425°C					
Hydrogen:					
2 min	0.0	4.8(0.3)	6.2(0.4)	0.0	89.0(0.6)
15 min	0.0	3.5(0.2)	8.6(0.1)	0.0	87.9(0.3)
30 min	0.9(0.1)	12.3(0.1)	32.0(1.0)	0.0	54.8(1.0)
60 min	1.9(0.2)	6.1(0.2)	61.7(5.4)	0.0	30.3(5.2)
Nitrogen:					
2 min	1.3(0.1)	4.6(0.4)	7.9(1.6)	0.0	86.2(1.7)
15 min	1.2(0.02)	12.5(0.6)	6.3(0.6)	0.0	80.0(1.2)
30 min	1.9(0.1)	8.6(0.3)	33.9(1.5)	0.0	55.6(1.7)
60 min	1.8(0.1)	8.5(1.2)	52.1(3.0)	0.0	37.6(2.0)
450°C					
Hydrogen:					
2 min	0.0	10.9(0.6)	11.8(1.5)	0.0	77.3(1.7)
15 min	1.2(0.1)	12.0(0.1)	53.9(0.5)	0.0	32.9(0.4)
30 min	2.2(0.3)	8.4(0.8)	63.9(0.3)	0.0	25.5(0.7)
60 min	5.0(0.5)	5.4(0.4)	68.0(1.4)	0.0	21.6(1.3)
90 min	8.3(0.3)	8.7(0.1)	74.8(1.0)	0.0	8.2(0.5)
Nitrogen:					
2 min	trace	10.4(0.6)	5.0(0.3)	0.0	84.6(0.3)
15 min	2.0(1.3)	23.8(1.5)	18.6(3.7)	0.0	55.6(4.4)
30 min	10.0(3.4)	22.4(5.4)	35.7(3.9)	0.0	31.9(1.7)
60 min	55.4(3.4)	5.7(0.6)	28.5(1.9)	0.0	10.4(1.2)

[a] Numbers in parentheses indicate standard deviations.
[b] NAP = naphthalene; DHN = dinhydronaphthalene; t-DEC = trans-decalin; TET = tetralin.

Table II.E.3. Thermal Reaction Products from Octahydroanthracene

Reaction Conditions	Weight Percent Recovered			
	ANT[b]	DHA	THA	OHA
425°C				
Hydrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	0.0	0.0	trace	100.0
30 min	trace	1.6(0.2)	2.5(0.4)	96.0(0.6)
60 min	7.1(1.0)[a]	5.4(0.3)	trace	87.5(1.3)
Nitrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	0.0	0.0	trace	100.0
30 min	1.4(0.1)	2.4(0.7)	2.1(0.4)	94.1(1.1)
60 min	2.0(0.4)	7.4(0.5)	5.1(1.0)	85.4(1.0)
450°C				
Hydrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	1.9(0.4)	1.5(0.4)	4.6(1.3)	91.1(1.8)
30 min	5.8(3.6)	12.2(3.2)	20.5(1.4)	61.5(5.8)
60 min	7.9(0.1)	17.4(0.1)	31.3(0.6)	43.4(0.8)
Nitrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	0.0	4.2(0.6)	0.0	95.8(0.6)
30 min	3.3(0.6)	14.7(1.2)	11.9(1.4)	70.1(2.7)
60 min	6.4(1.3)	12.4(2.3)	22.0(3.6)	59.2(2.6)
475°C				
Hydrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	1.7(0.4)	4.7(1.6)	12.8(3.6)	80.8(1.7)
30 min	5.2(1.2)	31.9(6.1)	23.0(7.8)	39.9(3.0)
60 min	18.3(0.9)	27.4(2.2)	39.9(1.1)	14.4(2.4)
Nitrogen:				
2 min	0.0	0.0	0.0	100.0
15 min	0.6(0.3)	8.0(1.4)	8.8(1.8)	82.6(0.9)
30 min	5.1(0.5)	32.8(1.0)	25.5(1.6)	36.6(2.2)
60 min	16.5(0.5)	36.4(1.2)	34.4(1.8)	12.7(3.0)

[a] Numbers in parentheses indicate standard deviations.
[b] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; OHA = octahydroanthracene

Table II.E.4. Thermal Reaction Products from Diydroanthracene

Reaction Conditions	Weight Percent Recovered		
	ANT[b]	THA	DHA
380°C			
Hydrogen:			
2 min	1.4(1.6)[a]	0.0	98.6(1.6)
15 min	2.1(0.1)	0.0	97.9(0.1)
30 min	5.7(0.5)	2.2(0.8)	92.1(2.1)
60 min	3.6(0.2)	4.2(0.2)	92.2(0.4)
90 min	5.1(0.1)	7.6(0.1)	87.3(0.2)
Nitrogen:			
2 min	0.4(0.3)	0.0	99.6(0.3)
15 min	3.0(0.3)	0.0	97.0(0.3)
30 min	5.0(0.6)	0.0	95.0(0.6)
60 min	9.6(0.9)	0.0	90.4(0.9)
425°C			
Hydrogen:			
2 min	2.9(0.6)	0.0	97.1(0.6)
15 min	7.5(0.3)	0.0	92.5(0.3)
30 min	8.8(1.1)	0.0	91.5(1.1)
60 min	11.1(1.2)	3.2(1.4)	85.7(0.4)
Nitrogen:			
2 min	11.6(0.3)	0.0	88.4(0.3)
15 min	30.1(1.5)	0.0	69.9(1.5)
30 min	35.8(0.9)	0.0	64.2(0.9)
60 min	60.3(5.3)	0.0	39.7(5.3)
450°C			
Hydrogen:			
2 min	4.4(0.3)	2.0(2.3)	93.6(2.4)
15 min	12.5(0.3)	2.5(0.5)	85.0(0.7)
30 min	12.7(0.1)	4.8(0.2)	82.5(0.3)
60 min	20.5(1.0)	8.3(0.5)	71.3(1.2)
Nitrogen:			
2 min	26.9(9.2)	0.0	73.1(9.2)
15 min	47.8(3.8)	0.0	52.2(3.8)
30 min	75.1(0.5)	0.0	24.9(0.5)
60 min	91.5(0.5)	1.9(0.4)	6.6(0.5)

[a] Numbers in parentheses indicate standard deviations.
[b] ANT = anthracene; THA = tetrahydroanthracene; DHA = dihydroanthracene

Table II.E.5. Thermal Reaction Products from Hexahydroanthracene

Reaction Conditions	Weight Percent Recovered				
	ANT[b]	DHA	THA	HHA	OHA
225°C					
Hydrogen:					
2 min	0.0	1.2(0.4)[a]	0.5(0.2)	98.3(0.2)	0.0
30 min	0.0	2.1(0.1)	1.2(0.2)	96.6(0.2)	0.0
60 min	0.0	2.1(0.5)	1.4(0.2)	96.5(0.6)	0.0
90 min	0.0	2.7(0.2)	1.6(0.1)	95.7(0.3)	0.0
120 min	0.0	3.2(0.3)	2.6(0.1)	94.2(0.3)	0.0
Nitrogen:					
2 min	0.0	1.9(0.4)	0.8(0.1)	97.3(0.3)	0.0
30 min	0.0	3.1(0.01)	2.1(0.1)	94.8(0.1)	0.0
60 min	0.0	5.8(0.6)	3.9(0.5)	90.3(1.1)	0.0
90 min	0.0	7.5(2.4)	5.2(1.2)	87.2(3.5)	0.0
300°C					
Hydrogen:					
2 min	0.0	4.5(0.3)	2.4(0.2)	93.1(0.4)	0.0
15 min	0.0	6.1(0.2)	2.3(0.2)	91.6(0.4)	0.0
30 min	0.0	14.4(0.3)	4.2(0.1)	81.4(0.2)	0.0
60 min	0.0	20.6(0.2)	13.0(0.3)	66.4(0.5)	0.0
Nitrogen:					
2 min	0.0	0.0	5.5(0.2)	94.5(0.2)	0.0
15 min	0.0	6.7(0.1)	2.2(0.1)	91.1(0.1)	0.0
30 min	0.0	16.0(3.1)	6.7(2.6)	77.3(5.7)	0.0
60 min	0.0	31.4(1.7)	9.9(1.3)	58.7(1.1)	0.0
380°C					
Hydrogen:					
2 min	0.0	29.3(0.5)	9.8(0.4)	60.9(0.7)	0.0
5 min	6.2(0.1)	51.2(0.5)	6.2(0.2)	36.4(0.2)	0.0
10 min	8.3(1.3)	60.8(5.9)	16.5(8.9)	14.4(1.7)	0.0
15 min	2.1(0.2)	78.0(8.1)	9.8(5.1)	10.0(5.3)	0.0
30 min	7.0(0.8)	83.1(4.4)	8.6(1.8)	1.3(0.4)	0.0
60 min	5.2(0.9)	68.5(3.9)	20.2(3.7)	1.7(0.4)	4.5(1.3)
Nitrogen:					
2 min	0.0	40.8(3.3)	12.2(1.0)	47.0(4.3)	0.0
5 min	0.0	76.0(3.6)	6.3(2.0)	17.7(1.5)	0.0
10 min	1.3(1.5)	83.4(1.8)	4.5(2.9)	10.8(2.6)	0.0
15 min	3.5(0.1)	85.1(0.2)	9.3(0.1)	2.0(0.1)	0.0
30 min	15.0(2.7)	71.5(10.)	13.5(2.9)	trace	0.0
60 min	11.2(0.6)	85.7(0.6)	3.1(0.03)	0.0	0.0

[a] Numbers in parentheses indicate standard deviations.
[b] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene

Table II.E.6. Apparent Rate Constants and Arrhenius Parameters for the Model Compound Reactivity Studies

Reaction Conditions	Apparent Rate Constant (k)	Correlation Coefficient for Rate Constant	Arrhenius Parameters
DHA[a]			
Nitrogen:			
380°C	0.00167	0.99861	Ea/R = 21,975
425°C	0.01426	0.98632	$k_o = 6.85 \times 10^{11}$
450°C	0.04372	0.99624	r = 0.9995
Hydrogen:			
380°C	0.00140	0.95254	Ea/R = 8,147
425°C	0.00233	0.96478	$k_o = 3.41 \times 10^{2}$
450°C	0.00505	0.96901	r = 0.95251
HHA			
Nitrogen:			
225°C	0.00142	0.98638	Ea/R = 10,623
300°C	0.00864	0.99179	$k_o = 1.92 \times 10^{6}$
380°C	0.24067	0.98263	r = 0.97395
Hydrogen:			
225°C	0.00040	0.93072	Ea/R = 12,238
300°C	0.00641	0.98657	$k_o = 1.64 \times 10^{7}$
380°C	0.14086	0.99267	r = 0.99592
OHA			
Nitrogen:			
425°C	0.00271	0.97051	Ea/R = 27,006
450°C	0.00944	0.96606	$k_o = 1.67 \times 10^{14}$
475°C	0.03606	0.98928	r = 0.99918
Hydrogen:			
425°C	0.00226	0.96235	Ea/R = 28,224
450°C	0.01468	0.98485	$k_o = 9.59 \times 10^{14}$
475°C	0.03335	0.99130	r = 0.97972
ISO			
Nitrogen:			
225°C	0.00055	0.93852	Ea/R = 12,780
300°C	0.00337	0.94919	$k_o = 4.76 \times 10^{7}$
380°C	0.27118	0.99846	r = 0.95691
Hydrogen:			
225°C	0.00041	0.93232	Ea/R = 13,990
300°C	0.00652	0.97460	$k_o = 4.90 \times 10^{8}$
380°C	0.34391	0.99992	r = 0.98695

Table II.E.6. Apparent Rate Constants and Arrhenius Parameters for the Model Compound Reactivity Studies

Reaction Conditions	Apparent Rate Constant (k)	Correlation Coefficient for Rate Constant	Arrhenius Parameters
TET			
Nitrogen:			
380°C	0.00074	0.96811	Ea/R = 27,027
425°C	0.01578	0.98755	$k_o = 7.69 \times 10^{14}$
450°C	0.03698	0.99932	r = 0.99233
Hydrogen:			
380°C	0.00151	0.94641	Ea/R = 19,712
425°C	0.01975	0.98308	$k_o = 2.27 \times 10^{10}$
450°C	0.02405	0.94310	r = 0.96353

[a] DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene; ISO = isotetralin; TET = tetralin.

Table II.E.7. Product Distributions from the Reaction of Isotetralin with Mo/Al_2O_3 and $NiMo/Al_2O_3$

Reaction Conditions	Weight Percent Recovered				
	OHN[b]	TET	1,2-DHN	1,4-DHN	ISO
Mo/Al_2O_3					
225°C:					
2 min	9.4(0.4)[a]	45.0(1.6)	8.1(0.1)	11.2(0.3)	23.9(2.1)
5 min	19.3(0.2)	64.2(0.1)	6.7(0.3)	4.0(1.4)	5.7(0.1)
10 min	22.7(0.1)	77.3(0.1)	0.0	0.0	0.0
15 min	20.9(0.5)	79.1(0.5)	0.0	0.0	0.0
175°C:					
2 min	0.0	3.4(0.2)	1.8(0.02)	14.6(0.8)	80.3(1.03)
15 min	0.7(0.8)	7.7(4.7)	5.7(3.8)	25.1(14.8)	60.8(6.2)
30 min	5.6(1.2)	33.3(1.4)	8.1(1.1)	29.3(3.5)	23.4(2.0)
125°C:					
2 min	0.0	0.0	0.0	6.7(0.9)	93.3(0.9)
15 min	0.0	0.0	0.9(0.1)	10.9(0.2)	88.3(0.2)
30 min	0.0	1.6(0.3)	1.5(0.1)	10.8(1.0)	86.0(1.5)
60 min	0.0	7.4(0.2)	7.0(0.4)	11.0(0.5)	74.6(1.1)
$NiMo/Al_2O_3$					
175°C:					
2 min	2.6(3.0)	12.3(5.6)	6.9(0.9)	25.7(10.1)	52.5(0.7)
5 min	25.7(1.1)	35.8(3.5)	5.2(0.4)	14.3(5.4)	19.0(0.5)
7 min	38.4(3.2)	42.7(4.9)	4.9(0.3)	5.6(1.5)	8.4(0.8)
15 min	40.0(4.3)	58.4(3.6)	0.0	0.0	0.0
140°C:					
2 min	0.0	4.7(0.02)	3.0(0.2)	12.0(0.1)	80.3(0.2)
15 min	4.8(1.1)	13.1(3.9)	8.4(1.0)	11.7(1.0)	62.1(5.1)
30 min	16.1(4.3)	38.6(2.8)	13.4(0.2)	8.1(2.5)	23.9(4.4)
100°C:					
2 min	0.0	0.0	0.0	1.9(1.0)	96.6(1.0)
15 min	0.0	0.0	0.0	9.0(0.8)	89.6(0.9)
30 min	0.0	0.0	0.0	20.3(0.2)	78.2(0.2)

[a] Numbers in parentheses indicate standard deviations.
[b] OHN = octahydronaphthalene; TET = tetralin; DHN = dihydronaphthalene; ISO = isotetralin.

Table II.E.8. Product Distributions from the Reaction of Tetralin with Mo/Al_2O_3 and $NiMo/Al_2O_3$

Reaction Conditions	Weight Percent Recovered				
	t-DEC[b]	c-DEC	1,2-DHN	NAP	TET
Mo/Al_2O_3					
450°C:					
15 min	28.4(0.1)[a]	0.0	29.0(0.5)	2.4(0.1)	40.3(0.2)
30 min	39.2(0.2)	0.0	40.9(0.4)	1.9(0.4)	18.0(1.0)
60 min	44.1(1.4)	0.0	42.8(1.5)	2.0(0.2)	11.1(0.4)
425°C:					
15 min	0.0	0.0	17.7(0.3)	2.2(0.2)	80.2(0.5)
30 min	0.8(0.2)	0.0	45.6(0.8)	3.0(0.1)	50.7(0.8)
60 min	35.7(0.6)	0.0	36.5(0.9)	1.6(0.3)	26.2(0.9)
380°C:					
2 min	0.0	0.0	0.0	trace	100.0
15 min	2.7(0.3)	0.0	0.0	0.0	97.3(0.3)
30 min	3.1(0.6)	1.3(0.2)	0.0	0.7(0.5)	94.9(1.5)
60 min	1.2(1.4)	0.0	6.0(0.2)	0.0	92.8(1.4)
$NiMo/Al_2O_3$					
450°C:					
15 min	30.2(0.2)	10.1(1.3)	26.5(1.9)	1.6(1.10	31.6(0.8)
30 min	44.4(1.3)	10.6(0.6)	25.9(0.3)	0.9(1.1)	18.2(1.1)
60 min	56.8(0.5)	12.2(1.4)	28.6(0.8)	1.4(0.4)	1.0(0.1)
425°C:					
15 min	24.0(0.8)	8.9(0.8)	24.5(0.7)	1.9(0.1)	40.7(1.5)
30 min	33.9(1.5)	9.1(0.7)	35.3(3.4)	1.2(0.4)	20.4(3.2)
60 min	43.6(1.0)	6.2(0.9)	43.9(1.1)	0.5(0.1)	5.8(0.7)
380°C:					
2 min	3.2(1.1)	trace	0.0	0.0	96.8(1.1)
15 min	33.0(1.6)	12.0(0.5)	0.0	0.0	55.0(2.1)
30 min	56.5(1.5)	19.0(0.5)	0.0	0.0	24.5(3.5)
60 min	57.4(1.2)	20.7(0.5)	0.0	0.0	21.9(1.4)

[a] Numbers in parentheses indicate standard deviations.
[b] t-DEC = trans-decalin; c-DEC = cis-decalin; DHN = dihydronaphthalene; NAP = naphthalene; TET = tetralin

Table II.E.9. Product Distributions from the Reaction of Dihydroanthracene with Mo/Al_2O_3 and $NiMo/Al_2O_3$

Reaction Conditions	Weight Percent Recovered				
	PHA[b]	OHA	THA	ANT	DHA
Mo/Al_2O_3					
380°C:					
2 min	0.0	0.0	22.7(1.0)	2.5(0.2)	74.8(1.0)
15 min	0.0	40.2(4.4)[a]	34.5(1.0)	1.1(0.2)	24.2(3.2)
30 min	0.0	70.8(2.0)	21.2(1.0)	0.0	8.0(1.1)
60 min	0.0	76.0(0.2)	17.7(0.1)	0.0	6.3(0.1)
350°C:					
15 min	0.0	0.0	7.6(1.8)	3.0(0.4)	89.4(1.8)
30 min	0.0	0.0	13.9(4.3)	3.1(0.2)	83.0(4.2)
60 min	0.0	10.6(6.9)	26.9(1.3)	2.2(0.2)	57.8(3.9)
300°C:					
15 min	0.0	0.0	2.3(0.1)	1.7(0.1)	96.0(0.2)
30 min	0.0	0.0	4.4(1.1)	1.6(0.4)	94.0(1.4)
60 min	0.0	0.0	8.1(0.8)	1.5(0.1)	90.4(0.7)
$NiMo/Al_2O_3$					
380°C:					
2 min	6.9(0.8)	0.0	6.3(1.2)	0.0	86.8(0.4)
5 min	12.7(0.8)	55.9(0.3)	8.8(0.6)	0.0	26.6(0.5)
15 min	17.5(0.5)	68.6(0.6)	12.9(0.3)	0.0	1.0(0.5)
30 min	64.0(2.2)	35.0(5.0)	1.0(0.1)	0.0	0.0
350°C:					
15 min	21.3(0.4)	7.4(0.1)	2.5(0.5)	0.0	68.8(1.8)
30 min	30.1(1.2)	6.0(0.4)	2.4(1.0)	0.0	61.6(4.2)
60 min	49.9(0.4)	3.8(0.1)	2.3(0.3)	0.0	44.0(3.9)
300°C:					
15 min	21.1(0.7)	10.1(0.3)	0.0	0.0	68.8(0.2)
30 min	24.8(0.7)	8.5(0.3)	0.0	0.0	66.7(1.4)
60 min	30.1(0.3)	7.5(0.1)	0.0	0.0	62.4(0.7)
90 min	34.6(0.5)	19.8(0.3)	0.0	0.0	45.6(0.9)

[a] Numbers in parentheses indicate standard deviations.
[b] PHA = perhydroanthracene; OHA = octahydroanthracene; THA = tetrahydroanthracene; ANT = anthracene; DHA = dihydroanthracene.

Table II.E.10. Product Distributions from the Reaction of Octahydroanthracene with Mo/Al_2O_3 and $NiMo/Al_2O_3$

Reaction Conditions	Weight Percent Recovered				
	PHA[b]	THA	DHA	ANT	OHA
Mo/Al_2O_3					
450°C:					
15 min	16.2(0.3)[a]	17.5(0.6)	0.0	0.0	66.3(0.8)
30 min	19.1(0.4)	18.9(1.1)	0.0	0.0	62.1(0.8)
60 min	13.6(4.6)	36.5(3.6)	0.0	11.8(1.6)	38.2(5.3)
425°C:					
15 min	8.3(0.6)	9.7(0.1)	0.0	0.0	82.0(0.7)
30 min	9.3(0.7)	18.1(2.7)	0.0	0.0	72.6(2.0)
60 min	22.9(0.9)	12.2(1.1)	0.0	0.0	65.0(1.8)
380°C:					
2 min	0.0	0.0	0.0	0.0	100.1
30 min	0.0	2.2(0.1)	0.0	0.0	97.8(0.1)
60 min	4.7(0.1)	2.6(0.1)	2.2(0.2)	0.0	90.5(0.2)
90 min	6.5(0.2)	4.9(0.5)	2.6(0.2)	0.0	86.0(0.8)
$NiMo/Al_2O_3$					
450°C:					
15 min	50.5(0.3)	9.4(0.1)	7.1(0.2)	3.5(0.2)	29.5(1.0)
30 min	63.3(1.9)	5.8(1.3)	7.0(0.5)	5.3(0.4)	18.6(1.3)
60 min	75.8(2.2)	3.8(0.7)	5.3(0.4)	7.3(2.2)	7.9(1.0)
425°C:					
15 min	42.2(1.2)	8.3(0.4)	4.0(0.2)	0.0	45.5(1.7)
30 min	66.8(0.3)	3.9(0.9)	3.4(0.5)	0.0	25.9(1.3)
60 min	78.6(3.1)	2.3(0.6)	2.6(0.6)	0.0	16.5(1.8)
380°C:					
2 min	17.2(3.2)	trace	0.0	0.0	82.8(3.2)
15 min	52.9(0.4)	0.0	0.0	0.0	47.1(0.4)
30 min	68.0(4.9)	0.0	0.0	0.0	32.0(3.7)
60 min	80.4(0.3)	0.0	0.0	0.0	19.6(0.3)

[a] Numbers in parentheses indicate standard deviations.
[b] PHA = perhydroanthracene; THA = tetrahydroanthracene; DHA = dihydroanthracene; ANT = anthracene; OHA = octahydroanthracene

Table II.E.11. Product Distributions from the Reaction of Hexahydroanthracene with Mo/Al_2O_3 and $NiMo/Al_2O_3$

Reaction Conditions	Weight Percent Recovered				
	PHA[b]	OHA	THA	DHA	HHA
Mo/Al_2O_3					
225°C:					
2 min	2.3(0.2)[a]	42.8(3.3)	3.8(0.9)	1.9(0.1)	49.2(4.4)
5 min	7.2(0.2)	47.7(3.8)	15.6(4.4)	0.0	29.5(1.0)
15 min	5.8(0.2)	78.7(1.3)	14.0(2.9)	0.0	1.5(1.8)
175°C:					
2 min	0.0	8.9(0.2)	5.9(0.2)	0.0	85.2(0.5)
15 min	0.0	10.2(0.3)	6.7(0.2)	0.0	83.1(0.5)
30 min	0.0	29.8(4.8)	8.1(0.7)	1.2(0.2)	60.9(4.5)
125°C:					
2 min	0.0	0.5(1.7)	2.0(1.1)	0.0	97.5(2.8)
15 min	0.0	2.0(1.4)	2.7(0.7)	0.0	95.2(2.0)
30 min	0.0	12.0(0.2)	4.7(0.3)	5.95(2.5)	77.4(2.1)
$NiMo/Al_2O_3$					
175°C:					
2 min	0.0	32.2(0.5)	10.0(0.3)	2.1(0.1)	55.8(0.8)
5 min	0.0	50.2(1.5)	26.4(0.5)	1.0(0.2)	22.4(2.1)
6 min	0.0	69.9(1.0)	25.3(0.8)	0.0	4.8(0.2)
140°C:					
2 min	0.0	14.8(1.3)	10.2(0.8)	1.7(0.4)	73.3(1.7)
15 min	0.0	23.2(5.4)	9.2(0.4)	1.5(0.1)	66.1(5.1)
30 min	0.0	38.9(2.9)	7.3(0.5)	1.2(0.1)	52.6(3.2)
60 min	0.0	55.7(1.4)	10.2(0.5)	5.4(0.3)	28.7(1.1)
100°C:					
2 min	0.0	8.3(0.6)	4.0(0.3)	1.3(0.1)	86.4(0.9)
15 min	0.0	13.9(0.6)	8.9(0.7)	1.3(0.3)	76.0(1.5)
30 min	0.0	17.8(0.1)	10.6(0.9)	1.6(0.04)	70.0(0.7)

[a] Numbers in parentheses indicate standard deviations.
[b] PHA = perhydroanthracene; THA = tetrahydroanthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene

Table II.E.12. Apparent Rate Constants and Arrhenius Parameters for the Model Compound Catalytic Reactivity Studies

Reaction Conditions	Apparent Rate Constant (k)	Correlation Coefficient for Rate Constant	Arrhenius Parameters
DHA			
Amocat 1B:			
380°C	0.04662	0.91585	Ea/R = 15,271
350°C	0.00913	0.98452	$k_o = 5.47 \times 10^8$
325°C	0.00162	0.98452	r = 0.98719
Shell 324:			
380°C	0.32024	0.99535	Ea/R = 16,005
350°C	0.01285	0.97363	$k_o = 6.31 \times 10^9$
300°C	0.00714	0.92195	r = 0.84895
HHA			
Amocat 1B:			
225°C	0.27672	0.99744	Ea/R = 6,827
175°C	0.01403	0.93771	$k_o = 1.48 \times 10^6$
125°C	0.00796	0.93897	r = 0.90529
Shell 324:			
175°C	0.41279	0.97223	Ea/R = 8,499
140°C	0.01865	0.97747	$k_o = 5.89 \times 10^7$
100°C	0.01036	0.92164	r = 0.97333
OHA			
Amocat 1B:			
450°C	0.01507	0.97803	Ea/R = 14,590
425°C	0.00687	0.95319	$k_o = 8.57 \times 10^6$
380°C	0.00172	0.98408	r = 0.99944
Shell 324:			
450°C	0.03969	0.96163	Ea/R = 2,510
425°C	0.02893	0.95466	$k_o = 1.18 \times 10^0$
380°C	0.02633	0.96853	r = 0.88137
ISO			
Amocat 1B:			
225°C	0.56506	0.99341	Ea/R = 9,516
175°C	0.04508	0.97607	$k_o = 1.20 \times 10^8$
125°C	0.00430	0.97135	r = 0.99635
Shell 324:			
175°C	0.35181	0.99877	Ea/R = 8,370
140°C	0.04430	0.97346	$k_o = 3.82 \times 10^7$
100°C	0.00783	0.99431	r = 0.98996

Table II.E.12. Apparent Rate Constants and Arrhenius Parameters for the Model Compound Catalytic Reactivity Studies (Continued)

Reaction Conditions	Apparent Rate Constant (k)	Correlation Coefficient for Rate Constant	Arrhenius Parameters
TET			
Amocat 1B:			
450°C	0.03575	0.95051	Ea/R = 23,311
425°C	0.02299	0.99546	k_0 = 4.78x10^{12}
380°C	0.00130	0.97524	r = 0.97774
Shell 324:			
450°C	0.07561	0.98836	Ea/R = 6,702
425°C	0.04664	0.99646	k_0 = 7.56x10^{2}
380°C	0.02716	0.92257	r = 0.98773

DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene; ISO = isotetralin; TET = tetralin

Figure II.E.1.

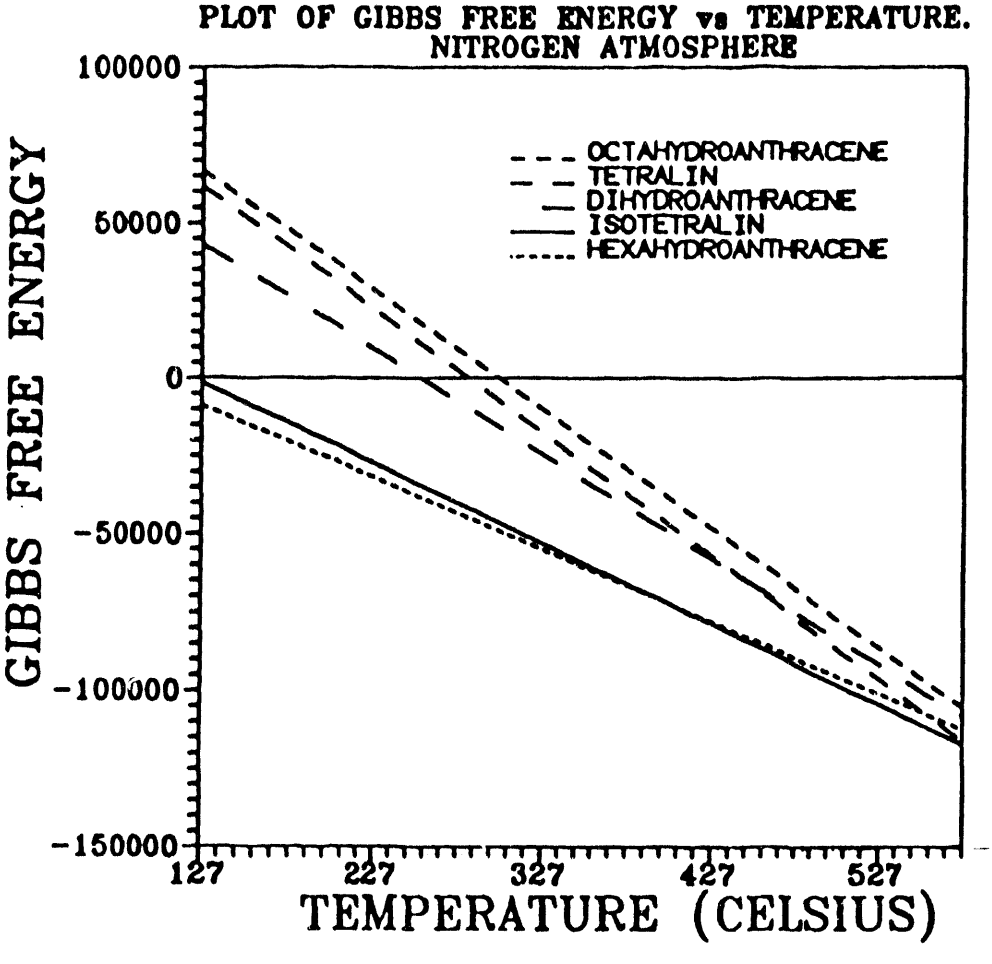

PLOT OF GIBBS FREE ENERGY vs TEMPERATURE.
NITROGEN ATMOSPHERE
OCTAHYDROANTHRACENE
TETRALIN
DIHYDROANTHRACENE
ISOTETRALIN
HEXAHYDROANTHRACENE
GIBBS FREE ENERGY
100000
50000
0
-50000
-100000
-150000
127
227
327
427
527
TEMPERATURE (CELSIUS)

Figure II.E.2.

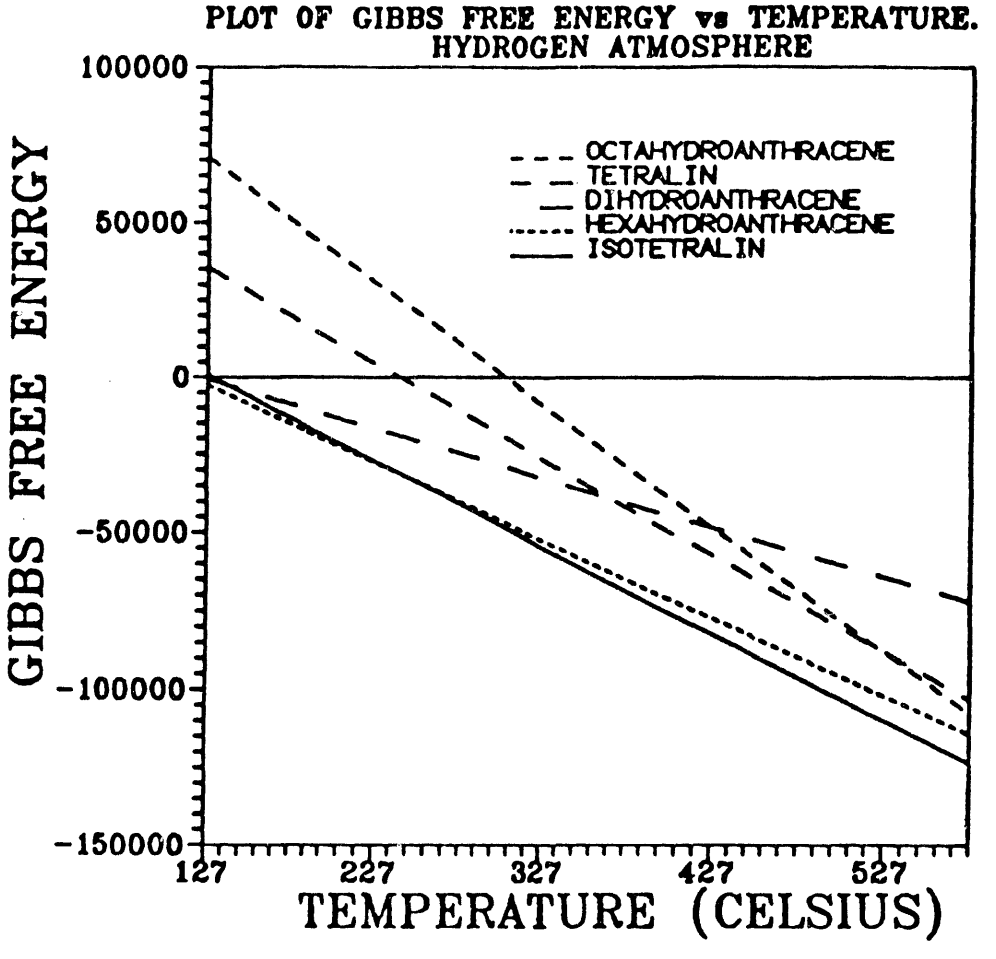

PLOT OF GIBBS FREE ENERGY vs TEMPERATURE.
HYDROGEN ATMOSPHERE
GIBBS FREE ENERGY
100000
50000
0
-50000
-100000
-150000
127
227
327
427
527
TEMPERATURE (CELSIUS)
OCTAHYDROANTHRACENE
TETRALIN
DIHYDROANTHRACENE
HEXAHYDROANTHRACENE
ISOTETRALIN

Figure II.E.3.

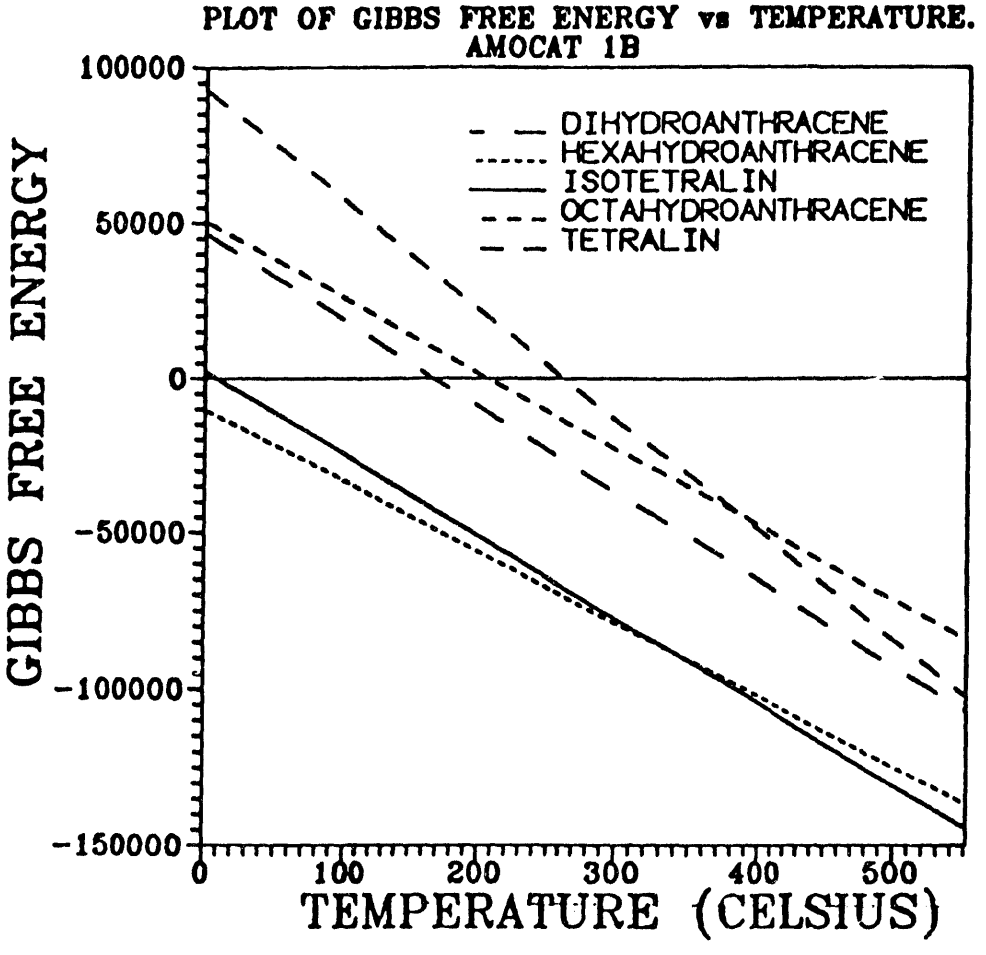
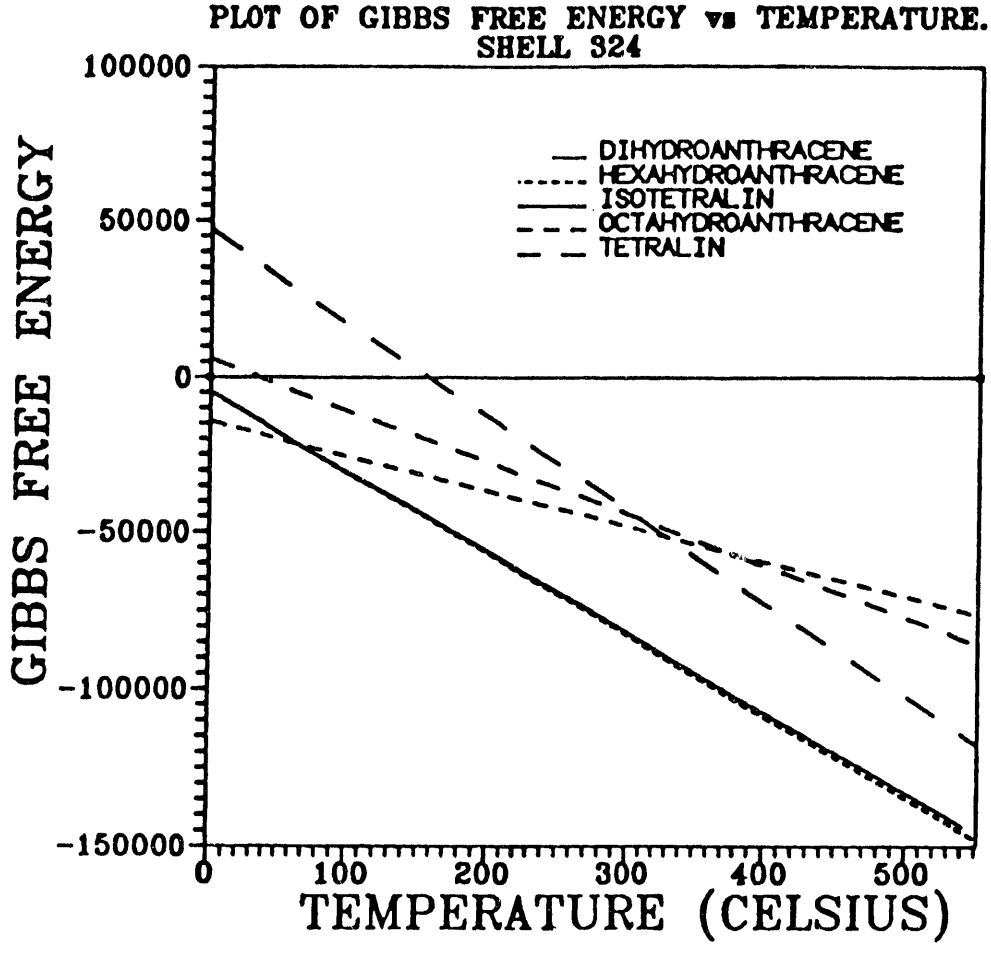

PLOT OF GIBBS FREE ENERGY vs TEMPERATURE.
AMOCAT 1B
DIHYDROANTHRACENE
HEXAHYDROANTHRACENE
ISOTETRALIN
OCTAHYDROANTHRACENE
TETRALIN
GIBBS FREE ENERGY
100000
50000
0
-50000
-100000
-150000
0
100
200
300
400
500
TEMPERATURE (CELSIUS)

Figure II.E.4.


PLOT OF GIBBS FREE ENERGY vs TEMPERATURE.
SHELL 324
GIBBS FREE ENERGY
100000
50000
0
-50000
-100000
-150000
0
100
200
300
400
500
TEMPERATURE (CELSIUS)
DIHYDROANTHRACENE
HEXAHYDROANTHRACENE
ISOTETRALIN
OCTAHYDROANTHRACENE
TETRALIN

APPENDIX A

ISOMERIZATION OF DECALIN BY SLURRY-PHASE CATALYSTS

Naphthalene and tetralin have been used extensively as model species to evaluate hydrogenation and hydrogen donation reactions that occur in coprocessing reactions.[1,2] Under the conditions of elevated temperature, 380 to 425 °C, and high hydrogen pressure, 2,500 to 3,000 psia, at reaction temperature, a selectivity preference for trans-decalin has been observed.[2-4] This brief study provides a systematic investigation of the isomerization of decalin under catalytic coprocessing conditions.

Several sets of reactions were performed using slurry phase catalysts composed of different acid salts of molybdenum, nickel, and vanadium as well as a supported presulfided $NiMo/Al_2O_3$ for comparison. The initial set of experiments used cis-decalin as the reactant; the amount of trans-decalin formed thermally and with various catalysts was determined. Secondly, a mixture of cis- and trans-decalin was used as the reactant in both thermal and catalytic reactions. The change in the trans to cis ratio was established. The last set of reactions involved determining the effect of catalyst type, sulfur amount introduced to the reaction and reaction temperature on the isomerization of decalin produced from the hydrogenation of naphthalene. A reaction pathway for the production of trans-decalin is postulated.

EXPERIMENTAL

Two reactants, cis-decalin (100% purity) and a mixture of trans- and cis-decalin, were reacted at 380°C for 30 min. thermally and catalytically with Mo, Ni, and V slurry-phase catalysts, and presulfided Shell 324 $NiMo/Al_2O_3$ supported catalyst and MoS_2 produced during a hydrogenation reaction of hexadecane with molybdenum naphthenate (MoNaph) and excess

sulfur at 380 °C for 30 min. The $NiMo/Al_2O_3$ was presulfided before use by heating the catalyst in a heated gas stream of 10 vol% H_2S in H_2. The presulfided catalyst was then pulverized to 150 mesh and stored in a vacuum desiccator.

Four grams of reactant were reacted in ~20 cm^3 stainless steel reactors. The reactants used for the isomerization reactions were cis-decalin for the first set and a mixture of trans- and cis-decalin for the second set. For most reactions, 1,250 psig hydrogen was introduced at ambient temperature. In some reactions, a N_2 atmosphere was also used; N_2 was introduced at 700 psig at ambient temperature. Catalyst loading of 1,500 ppm active metal was introduced into each reaction. Elemental sulfur was added to the reactions with MoNaph, vanadium acetylacetonate (VAcAc), and vanadylacetylacetonate (VOAcAc) at a 3:1 stoichiometric ratio of sulfur:metal. Sulfur was not added to catalytic reactions with nickel because it had been previously shown that the presence of sulfur poisons the activity of slurry-phase nickel catalysts for various model systems.[4]

Catalytic hydrogenation reactions of naphthalene were performed at 380 °C for 30 min in a hydrogen atmosphere. Hydrogen was introduced at 1,250 psig at ambient temperature. The slurry-phase catalysts, MoNaph, VOAcAc, and VAcAc were reacted with different levels of elemental sulfur. The slurry-phase nickel catalysts of nickel octoate (NiOct) and nickel acetylacetonate (NiAcAc) were used without sulfur while $NiMo/Al_2O_3$ was presulfided in a flowing stream of 10% H_2S in H_2 prior to use.

RESULTS AND DISCUSSION

Isomerization of Cis-Decalin. The isomerization of cis-decalin under thermal and catalytic conditions is presented in Table A.1. A small amount of isomerization, ~5%, occurred

under thermal conditions at 380 °C in a hydrogen atmosphere. The presence of the slurry-phase catalysts, VAcAc and MoNaph, both increased the amount of isomerization substantially. VAcAc produced 26% trans-decalin while MoNaph produced 17%. The supported $NiMo/Al_2O_3$ Shell 324 hydrogenation catalyst also promoted isomerization at 12%. However, neither the slurry phase nickel catalyst, NiOct, nor MoS_2 produced ex situ from MoNaph and excess sulfur promoted isomerization. In fact, both of these catalyst yielded less trans-decalin than did the thermal reaction. Isomerization decreased in a N_2 atmosphere compared to a hydrogen atmosphere. Less than 1% isomerization was observed with MoS_2 atmosphere.

Hence, cis-decalin was isomerized to trans-decalin to different extents depending upon the reaction conditions employed. The catalytic activity for isomerization of cis-decalin ranked in the order of VAcAc > MoNaph > $NiMo/Al_2O_3$ > > NiOct and MoS_2.

Isomerization of Trans- and Cis-Decalin. The next series of reactions was performed with an initial mixture of trans- and cis-decalin, which was 64% cis-decalin and 36% trans-decalin. The reactions were performed thermally and with a variety of catalysts. Most of the reactions were performed in a hydrogen atmosphere; however, several were performed in both H_2 and N_2 atmospheres as given in Table A.2. The amount of trans- and cis-decalin produced during the reaction was determined and the percent change in the trans to cis ratio was calculated. The percent change in trans to cis ratio is defined as the cis to trans ratio after reaction minus the cis to trans reactant ratio divided by the reactant ratio times 100%.

Thermal reactions were performed in the presence and absence of sulfur with the trans- and cis-decalin mixture. The thermal reaction without sulfur increased the amount of trans-decalin somewhat; a similar production of trans-decalin was observed thermally with cis-decalin as the reactant. However, when sulfur was added to the thermal reaction, a larger increase in the

production of trans-decalin occurred. The thermal reaction without sulfur in a N_2 atmosphere produced, as expected, less trans-decalin than in a hydrogen atmosphere.

When the trans- and cis-decalin reaction mixture was used as the reactant in catalytic reactions, similar activities and selectivities of the slurry-phase catalysts were observed as when cis-decalin was used as the reactant. The order of selectivity for isomerization of the different catalysts was again VAcAc > MoNaph > $NiMo/Al_2O_3$ > > MoS_2 and NiOct. VAcAc was the most active catalyst for isomerization yielding in the product mixture more trans-decalin than cis-decalin and a percent change of more than 100%. MoNaph was also active for isomerization by producing a percent change of 75%; $NiMo/Al_2O_3$ yielded a percent change of 51% which was less than that, 61%, of the thermal reaction with sulfur. Both NiOct and MoS_2 yielded almost no change in the trans to cis ratio from the original reactant.

A thermal reaction was performed in N_2 with the trans-cis reactant mixture as well as two catalysts, $NiMo/Al_2O_3$ and MoS_2. Neither catalyst showed much activity for isomerization in N_2; in fact, their trans to cis ratios were nearly identical to the thermal reaction without sulfur. Therefore, a hydrogen atmosphere was required for isomerization to occur.

Catalytic Hydrogenation of Naphthalene. The effect of different slurry phase catalysts, the amount of sulfur added to the reaction, and the reaction temperature was evaluated in terms of the trans- to cis-decalin ratio produced from naphthalene. The production of decalin from the naphthalene hydrogenation reaction was different from the other two reaction systems studied. When naphthalene is used as the reactant, then decalin must be produced via hydrogenation while in the first two reaction series decalin was present and only isomerization occurred. The catalyst utilized in the naphthalene hydrogenation must be sufficiently active under the reaction conditions to produce decalin. Without a catalyst, naphthalene hydrogenation occurred to a very limited

extent under these reaction conditions forming tetralin (1 to 2%), not decalin, as the reaction product.[2]

The trans to cis ratio of decalin produced from naphthalene under catalytic conditions is presented in Table A.3. At 380 °C, different catalysts showed different activity and selectivity for trans-decalin formation compared to the isomerization reactions of cis-decalin or the cis- and trans-decalin reaction. The selectivity of the catalysts for producing trans-decalin at 380°C ranked in the order of $NiMo/Al_2O_3$ > MoNaph > VAcAc, VOAcAc > NiOct, NiAcAc. Increases in the sulfur amount added to the reaction had little effect on the trans- to cis-decalin ratio. By contrast, increase in temperature from 380 to 400 and 425 °C increased the trans to cis ratio for the slurry-phase catalysts tested under these conditions, which included MoNaph, VOAcAc, VAcAc, and NiOct. In fact, at 425 °C, the trans to cis ratio was nearly equivalent for the four catalysts tested, indicating that the higher temperature governed the ratio more than did the type of catalyst.

SUMMARY

The isomerization of decalin at coal liquefaction conditions was affected substantially by different slurry-phase catalysts as well as the presence of sulfur. VAcAc was the most selective catalyst for isomerizing cis-decalin to trans-decalin followed by MoNaph. Both of these catalysts were reacted in the presence of excess decalin. Likewise, when the reactant was a combination of cis- and trans-decalin, the same two slurry phase catalysts were most active for isomerization to trans-decalin. However, when the starting material was naphthalene, the hydrogenation reaction to decalin must occur before the isomerization can occur. Hence, different catalysts were more active compared to when the reaction was isomerization.

REFERENCES

1. Curtis, C. W.; Chung, W. J. *Energy and Fuels*, *3*, 160, 1989.

2. Kim, H; Curtis, C. W. *Energy and Fuels*, *4*, 206, 1990a.

3. Kim, H; Curtis, C. W. *Energy and Fuels*, *4*, 214, 1990b.

4. Kim, H; Curtis, C. W. *Fuel Science and Technology International*, *9*, 229, 1991.

Table A.1. Thermal and Catalytic Isomerization of Cis-Decalin[a]

Reaction Condition	Decalin Distribution (%)[b]		trans- to cis-Decalin Ratio
	trans	cis	
Decalin as Reactant	0.0	100.0	0.0
H_2 Atmosphere[c]			
Thermal	4.6	95.4	0.05
VAcAc[d]	25.6	74.4	0.35
MoNaph	17.4	82.6	0.21
$NiMo/Al_2O_3$	12.0	88.0	0.14
NiOct	2.0	98.0	0.02
MoS_2[e]	3.2	96.8	0.03
N_2 Atmosphere[c]			
MoS_2	0.7	99.3	0.01

[a] Reactions were conducted at 380°C for 30 min with 4 g of reactant. Elemental sulfur was added in reactions with VAcAc (0.034 g) and MoNaph (0.024 g).

[b] Area ratio of GC peaks.

[c] H_2 (1,250 psig) and N_2 (700 psig) were charged at ambient temperature.

[d] VAcAc (vanadium acetylacetonate), MoNaph (molybdenum naphthenate), NiOct (nickel octoate).

[e] MoS_2 powder was produced from a hydrogenation reaction of hexadecane with MoNaph and excess sulfur at 380°C for 30 min.

Table A.2. Thermal and Catalytic Isomerization of Trans- and Cis-Decalin[a]

Reaction Condition	Decalin Distribution (%)[b]		trans- to cis-Decalin Ratio	% Change in trans- to cis-Ratio
	trans	cis		
Decalin as Reactant	36.2	63.8	0.57	0
H_2 Atmosphere[c]				
Thermal without S	39.9	60.1	0.66	15.8
Thermal with S	47.9	52.1	0.92	61.4
VAcAc[d]	54.1	45.9	1.18	107.0
MoNaph	49.9	50.1	1.00	75.4
$NiMo/Al_2O_3$	46.2	53.8	0.86	50.8
NiOct	36.6	63.4	0.58	1.8
MoS_2[e]	37.5	62.5	0.60	5.3
N_2 Atmosphere[c]				
Thermal without S	37.2	62.8	0.59	3.5
$NiMo/Al_2O_3$	37.6	62.4	0.60	5.3
MoS_2[e]	37.0	63.0	0.49	3.5

[a] Reactions were conducted at 380°C for 30 min with 4 g of reactant. Elemental sulfur was added in the thermal reaction (0.018 g) and the catalytic reactions with VAcAc (0.034 g) and MoNaph (0.024 g).

[b] Area ratio of GC peaks.

[c] H_2 (1,250 psig) and N_2 (700 psig) were charged at ambient temperature.

[d] VAcAc (vanadium acetylacetonate), MoNaph (molybdenum naphthenate), NiOct (nickel octoate).

[e] MoS_2 powder was produced from a hydrogenation reaction of hexadecane with MoNaph and excess sulfur at 380°C for 30 min.

Table A.3. Catalytic Hydrogenation of Naphthalene[a]

Reaction Condition	Sulfur[c] Added (g)	trans- to cis-Decalin Ratio[d]		
		Reaction Temperature		
		380°C	400°C	425°C
MoNaph[b]	0.024 0.048 0.072	1.4 1.4 1.4	1.6	2.0
VOAcAc	0.034 0.057	1.1 1.1	1.4	1.9
VAcAc	0.034 0.057 0.113	1.1 1.1 1.4	1.3	1.9
NiOct	0.0	0.4	0.6	1.9
NiAcAc	0.0	0.6	NP[e]	NP
$NiMo/Al_2O_3$	0.0	2.9	NP	NP

[a] Reactions were conducted at 380°C for 30 min with 4 g reactant.
[b] MoNaph (molybdenum naphthenate), VOAcAc (vanadylacetylacetonate), VAcAc (vanadium acetylacetonate), NiOct (nickel octoate), NiAcAc (nickel acetylacetonate).
[c] Sulfur added as elemental sulfur
[d] Area ratio of GC peaks.
[e] NP = not performed.

DATE FILMED

4 / 12 / 94

END