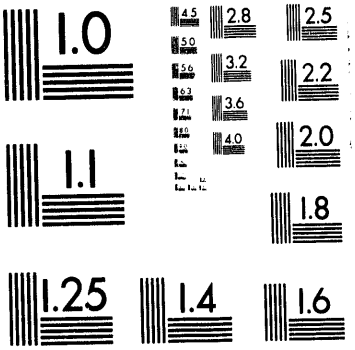
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DOE/PC/88801--T14

20/92

Coprocessing Through Fundamental and Mechanistic Studies in Hydrogen Transfer and Catalysis

Quarterly Report
for
Contract No. DE-AC22-88PC88801
to
Department of Energy

March 28, 1992 to June 30, 1992

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Acknowledgements

The experimental work of Shu-Li Wang is gratefully acknowledged as is the technical assistance of Frank Bowers and Joe Aderholdt.

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Introduction

Manuscript "An Investigation of Hydrogen Transfer from Naphthenes During Coprocessing"

Introduction

During the months of April and May, 1992, experimental work on Task I, "Elucidation of Hydrogen Transfer Reactions in Coprocessing" was completed. The research was reported in detail in the April and May status reports. A manuscript that fully describes that work is currently under preparation and will be included in the final report. The title of the manuscript is "An Investigation of Hydrogen Transfer in Coprocessing Using Model Donors and Reduced Resids." This manuscript covers work that was performed in both Task I and Task II of this contract.

During June 1992, a manuscript entitled "An Investigation of Hydrogen Transfer from Naphthenes During Coprocessing" was prepared. This manuscript fully describes the first part of the work that was performed on Task I in this project. The manuscript follows.

AN INVESTIGATION OF HYDROGEN TRANSFER FROM NAPHTHENES DURING COPROCESSING

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ABSTRACT

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 (PHP) with anthracene (ANT) resulted in the formation of pyrene (PYR) and dihydroanthracene. The weight percents of the products formed varied according to the initial ratio of ANT/PHP with a minimum appearing at a 2:1 weight ratio. Increased reaction times and high ANT/PHP ratios also yielded tetrahydroanthracene (THA). Reactions of Illinois No. 6 coal from the Argonne Premium Coal Sample Bank with PHP, ANT, and PYR resulted in higher coal conversion with PHP and lower with ANT and PYR. Reactions of PHP with resid resulted in less retrogressive reactions occurring in the resid than with either PYR or ANT. Apparent hydrogen transfer from coal or resid to ANT and PYR was observed. Combining PHP with ANT or PYR with coal, resid or coal plus resid yielded higher conversions and less retrogressive reactions. Hydrogen transfer occurred from PHP to ANT or PYR and to the coal and resid as evinced by the increased conversion.

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. (1984) 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. Reactions

were also performed with perhydroanthracene (PHA) synthesized in our laboratory and pyrene. 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 individually and with the coal and resid combinatorially. Hydrogen transfer from both the naphthene 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 pyrene and anthracene from Aldrich Chemical with a purity of 99% or higher and perhydropyrene also from Aldrich at a purity of 97%. Perhydroanthracene 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 perhydroanthracene by gas chromatography 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 1. The residuum used was Maya Resid from Amoco whose properties are shown in Table 2. The solvents used for the extraction analyses were toluene and tetrahydrofuran (THF) from Fisher Scientific.

Procedure. Model compound and coprocessing reactions were conducted in small tubular microreactors of ~20 cm^3 charged with nitrogen 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 gas chromatography. The gaseous products from the reaction were analyzed using a Varian 3700 gas chromatograph 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 naphthene, aromatic or both were reacted at the same conditions as the model reactions except the reactions were conducted for 60 min only. 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 (IOM) and ash-free.

Definitions for Model Systems. The following definitions of hydrogenation (HYD), dehydrogenation (DHYD) and hydrogen efficiency (HEFF) were employed for this work in order to compare readily the results of the different reaction conditions. Percent HYD 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 (THA). One hundred percent HYD is defined as ANT hydrogenating to a 100% yield of THA. One hundred percent DHYD is defined as PHP dehydrogenation to a 100% yield of PYR; thus, the percent DHYD is equal to the percent yield of PYR. HEFF 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 moles of hydrogen were donated; for every mole of dihydroanthracene (DHA) formed from ANT, 1 mole of hydrogen was accepted; and for every mole of THA formed from ANT, 2 moles 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 IOM 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 IOM divided by resid charged and multiplied by 100. Coal and resid conversion is defined as maf coal plus resid charged minus IOM divided by maf coal and resid charged and multiplied by 100. Liquid to solid ratio is defined as the amount of toluene (TOL) solubles divided by the amount of TOL insolubles present. Another term, degree of upgrading (DUP) to TOL solubles which describes the degree of upgrading or degrading of the system in terms of the amount of TOL solubles, was defined in order to provide a comparison among the different reactions with coal, resid, and coal plus resid. DUP is defined as the TOL solubles in the product minus the TOL 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 DUP 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 (Owens, 1991). The experiments performed evaluated the hydrogen transfer from naphthenic PHP to aromatics ANT or PYR and from naphthenic PHA 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 naphthene and aromatic with coal. The same set of reactions was performed with Maya Resid: naphthene with resid, aromatics with resid, and naphthene and aromatic with resid. The final set of reactions performed involved naphthene, aromatic, coal and resid. Baseline 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 PHA. When reacted individually in N_2 at 430°C, neither PHP, PYR, nor ANT reacted; however, PHA reacted, forming ~20% ANT under these conditions. For the PYR and PHP system, reactions were performed using only a 1:1 PYR to PHP weight ratio. Only PYR and PHP were detected in the products and no hydrogen was observed in the

product gases. Hence, no net change was observed in that reaction system. The reactions of PYR with PHA were quite limited, because of the small quantity of PHA that was synthesized. For the PYR and PHA system, reactions were conducted with PYR in excess using a 4:1 PYR to PHA ratio. Although the PYR and PHA reactions formed small amounts of ANT (less than 10%), the yield was less than with the PHA 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 PHA dehydrogenation.

The initial ANT and PHP reactions were performed with a 1:1 weight ratio of ANT to PHP in a nitrogen atmosphere. Reactivity was observed as the production of the partially saturated DHA 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 to PHP ranging from 0.14: ~ 10. The results from these reactions are presented in Tables 3 through 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 to 12 mole % DHA was formed at low weight ratios (0.14:0.5) of ANT to PHP but decreased by two-thirds at an ANT/PHP weight ratio of 2:1. The amount of DHA formed increased somewhat to 5 and 6 mole % at higher ANT/PHP weight ratios, but at weight ratios of 5.0 to 10.0 the product of THA was also observed. At longer reaction times of 90 and 180 min THA appeared at somewhat lower ANT to PHP weight ratios and more was formed. PYR 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 to PHP ratios at all three reaction times. At the higher ANT to PHP ratios, the hydrogen donor PHP was limited while ANT was available in excess.

The production of THA only occurred when higher concentrations of DHA were present. DHA has been shown to act both as a hydrogen donor and a hydrogen acceptor under liquefaction conditions (Bermejo et al., 1990; Bedell and Curtis, 1991). A likely mechanism for THA production was that DHA formed from ANT hydrogenation acted as a hydrogen acceptor and utilized hydrogen released from PHP to form THA.

The product distributions for ANT and PHP reactions as a function of reaction time are given in Table 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 DHA formed increased with reaction time. Only trace amounts of THA were formed before 120 min. At 120 min and at both weight ratios THA was formed, although more THA was formed at the higher weight ratio. These results correspond to those obtained in Tables 3-5. As the reaction time and weight ratio increased, more THA was produced in the reaction system.

Figures 1 and 2 present the % HYD of ANT and the % DHYD of PHP, respectively, as a function of the weight ratio of ANT to PHP for the 60, 90, and 180 min reactions. The HYD of ANT given in Figure 1 showed a dependence on the weight ratio of ANT to PHP. At low and high weight ratios, more HYD 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 THA occurred which manifested itself as an increase in the HYD of ANT. By contrast, the DHYD of PYR shown in Figure 2 appeared to increase linearly with increasing weight ratios of ANT to PHP. 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 7 usually ranged from low to high with a minimum being present at a 2:1 ANT to PHP ratio for the 60 min reaction. 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 moles of hydrogen for every mole of PYR formed and ANT accepts 1 mole of hydrogen for every mole of DHA formed, the most favorable condition for stoichiometric conversion would be an ANT/PYR weight ratio of 6.53:1. The observed high HEFF 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 HEFF, the hydrogen could not be detected.

These data indicate that hydrogen transfer occurred under these conditions, albeit only a small amount of the naphthene 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 of the reactions were performed thermally in an inert nitrogen 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 8 and 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 TOL 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 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 IOM present substantially, resulting in the very low coal conversion which was less than the 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 9).

Both the amount of THF soluble and TOL solubles produced during the reaction ranked the systems in the same order as the coal conversion (Table 8). The THF solubles were similar for the three systems, ranging from 14 to 17.5%, but the TOL 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 9) indicating that dehydrogenation of PHP occurred during the reaction. This PYR originated from the 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 9). Production of DHA and THA in the coal/ANT system indicated that hydrogen was transferred from coal to ANT, since the coal present was the only source of hydrogen.

The 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 TOL-soluble or THF-soluble yields. Lower coal conversion with ANT in the system may result from a lower solvating power for coal than pyrene 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% DHA and 24.7% THA. More than 15% PYR was formed from PHP during the reaction (Table 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 nitrogen atmosphere, the resid underwent substantial retrogressive reactions causing 20% of the resid to become THF insoluble (Table 8). The addition of PHP resulted in 97% of the resid remaining THF soluble which was much more than the resid reacted alone. Neither the addition of ANT nor PYR blocked the retrogressive reactions occurring in the nitrogen 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 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 DHA and THA 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, intemediate 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 nitrogen atmosphere and helped to inhibit retrogressive reactions. The amount of toluene and THF solubles produced during these reactions were quite similar (Table 8). In resid/ANT/PHP reaction more than 30% of ANT hydrogenated yielding 17.4% DHA and 16.1% THA as products (Table 9). More than 10% PYR was produced. The HEFF 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 8). The amount of TOL and THF solubles present in both quaternary reactions was quite similar. Substantial hydrogenation of ANT to DHA at 14.0% and THA at 21.5% occurred while 30% PYR was produced (Table 9). ANT 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 DUP, occurring in each system (Table 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 DUP 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 nitrogen atmosphere and when no other donor was present, both coal and

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

Acknowledgement

We gratefully acknowledge the support of the Department of Energy under Contract No. DE-AC22-88PC88801.

Nomenclature

ANT	=	anthracene	IOM	=	insoluble organic matter
DHA	=	dihydroanthracene	PHP	=	perhydropyrene
DHYD	=	dehydrogenation	PYR	=	pyrene
HEFF	=	hydrogen efficiency	THA	=	tetrahydroanthracene
HYD	=	hydrogenation	DUP	=	degree of upgrading to toluene solubles
PHA	=	perhydroanthracene			

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Table 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 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 detected.

Table 3. Product Distribution for 60 Minute Anthracene and Perhydropyrene Reactions

ANT/PHP Weight Ratio	Product Distribution (mole %)				
	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 4. Product Distribution for 90 Minute Anthracene and Perhydropyrene Reactions

ANT/ PHP Weight Ratio	Product Distribution (mole %)				
	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 5. Product Distribution for 180 Minute Anthracene and Perhydropyrene Reactions

ANT/PHP Weight Ratio	Product Distribution (mole %)				
	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 6. Product Distributions for Anthracene and Perhydropyrene Reactions at Different Reaction Times[a]

Reaction Time (min)	ANT/PHP Weight Ratio	Product Distribution (mole %)				
		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 minutes, N_2 atmosphere.

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

Table 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 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 minutes, N_2 atmosphere
[b] ANT = anthracene; PHP = perhydropyrene; PYR = pyrene
[c] Standard deviations

Table 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 minutes, 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.

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