

# HYDROGEN TRANSFER FROM NAPHTHENES TO COAL 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<sub>2</sub> atmosphere. The reaction of perhydropyrene (PHP) with anthracene (ANT) resulted in the formation of pyrene (PYR) and dihydroanthracene (DHA). The weight percents of the products formed varied according to the ratio of ANT/PHP with a minimum appearing at a 2 to 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 Bank with PHP, ANT, and PYR resulted in higher coal conversion with PHP and lower with ANT and PYR. With PHP less retrogressive reactions occurred 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 in 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 naphthenic components in the resid would provide a valuable hydrogen resource for coal and alleviate some dependence on molecular hydrogen.

This research investigates the hydrogen transfer from naphthene type structures in the resid to hydrogen acceptors: aromatic species, coal, and the resid itself. Previous research by Clarke et al. (Fuel, 63, 1476, 1984) had pointed to the possibility that hydrogen transfer was occurring 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 then performed with both naphthenes and aromatics with Illinois No. 6 coal from the Argonne Premium Coal 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.

## Experimental

**Materials.** The chemicals used in this study included pyrene, perhydropyrene, and anthracene which were obtained from Aldrich Chemical at a purity of 99% or higher. The coal used was Illinois No. 6 from the Argonne National Laboratory Premium Coal Sample Program. The residuum used was Maya Resid from Amoco. 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 charged with nitrogen gas. The reaction conditions for the model reactions were temperature of 430°C, N<sub>2</sub> at 400 psig ambient, and reaction times of 60, 90 and 180 minutes. For the single component model reactants, 0.1 gram was charged. For the binary component model reactants, the amount of individual reactant used ranged from 0.1 to 0.6g with the total amount of reactant charged ranging from 0.4 to 1.0g. 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 gas chromatograph 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 minutes only. Each reactant was charged at a level of one gram. After reaction the liquid and solid products were extracted with toluene to yield toluene solubles and with THF to yield THF solubles and insoluble organic matter (IOM).

## Results and Discussion

**Hydrogen Transfer in Thermal Coprocessing.** A systematic set of experiments has been performed in our laboratory to evaluate whether hydrogen can be transferred directly from saturated naphthenes to coal and resid. The experiment performed evaluated the hydrogen transfer from naphthenic PHP to aromatics ANT or PYR. Reactions were then conducted to react PHP with Illinois No. 6 coal from the Argonne Premium Coal Bank, aromatics, ANT and PYR, with coal, and 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 that was performed involved naphthene, aromatic, coal and resid. Blank reactions were also performed with each individual material to evaluate the effect of the reaction conditions on the reactivity of the individual materials.

**Hydrogen Transfer in the Model Reactions.** The model systems that were used included the binary combinations of ANT with PHP and PYR with PHP. When reacted individually each of these reactants yielded no conversion. However, when reacted in combination the reactions involving ANT with PHP resulted in hydrogen transfer while no evidence of hydrogen transfer or any reactivity was observed with the PHP and PYR system.

The initial ANT and PHP reaction was performed with a 1 to 1 ratio of ANT to PHP. When reactivity was observed as the production of the partially saturated DHA and the formation of the unsaturated PYR, it was evident that hydrogen transfer had occurred since the only hydrogen available

was from PHP and that this reactive system should be further investigated. Three sets of experiments were performed at 60, 90 and 180 minutes with weight ratios of ANT to PHP ranging from 0.14 to ~ 10. Representative data are given in Table 1. Hydrogen transfer occurred at all of these conditions as evinced by the products formed. At 60 minute reaction time, DHA was formed at low ratios of ANT to PHP but decreased by two-thirds at an ANT/PHP weight ratio of 2 to 1. The weight ratio of DHA increased somewhat at higher ANT/PHP ratios as the production of tetrahydroanthracene (THA) began to be observed. At longer reaction times THA appeared at lower ANT to PHP weight ratios and more was formed. PYR was formed also during these reactions. The amount of PYR formed increased almost linearly with increasing ANT to PHP ratios. At the higher ANT to PHP ratios, the hydrogen donor PHP was limited while ANT was available in excess.

Given also in Table 1 are the percent hydrogenation (% HYD) and the hydrogen efficiency for these reactions. Percent HYD is defined as the moles of hydrogen needed to produce the liquid products as a percentage of those required to produce the most hydrogenated product, THA. Hydrogen efficiency is defined as the number of moles of hydrogen accepted to form a partially saturated species divided by the moles of hydrogen donated times 100%. Although some scatter appeared in these data, the % HYD appeared to the lowest and highest at low and high ratios of ANT to PHP. Hydrogen efficiency usually ranged from low to high with a minimum being present at a 2 to 1 ANT to PHP ratio. Higher hydrogen efficiencies were observed at higher ANT to PHP ratios where the stoichiometric weight ratio was approximately 6.3 to 1.

The data presented in Table 1 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 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 atmosphere so that hydrogen transfer occurred only as a result of interactions among the reactants.

For this study, coal conversion is defined as moisture and ash free (maf) coal minus IOM divided by maf coal charged and multiplied by 100. The resid conversion or that portion of the resid remaining THF soluble is defined as the resid minus IOM divided by the resid charged and multiplied by 100. The coal and resid conversion is defined as maf coal plus resid minus IOM divided by maf coal and resid charged and multiplied by 100. The liquid to solid ratio is defined as the amount of toluene solubles divided by the amount of toluene insolubles present. Another term describing 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. The degree of upgrading (TSD) is defined as the TOL solubles in the product minus the TOL solubles in the reactant divided by the upgradable materials. The upgradable materials are defined as maf coal for the coal reactions, resid for resid reactions and coal plus resid for the combined reaction. A positive number indicates that upgrading occurred while a negative number indicates retrogressive reactions.

Twelve different reaction systems were employed to evaluate hydrogen transfer between naphthenes and aromatics as shown in Tables 2 and 3. In addition, Illinois No. 6 coal and Maya resid were reacted individually to generate a baseline for their individual conversion and stability.

The binary coal systems ranked in reactivity as coal/PHP > coal/PYR > coal/ANT. The reaction of coal with PHP resulted in the highest coal conversion as compared to the coal systems with ANT and PYR. Neither ANT or PYR promoted coal conversion. In fact, ANT increased the amount of IOM present substantially, yielding very low coal conversion, less than the coal by itself, while coal/PYR system yielded 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 since PYR should have a higher solvating power for coal than PHP and higher conversion was obtained with PHP than PYR. Also, some PYR was produced indicating that dehydrogenation of PHP occurred as given in Table 3. Production of DHA and THA in the coal/ANT system indicated that hydrogen was transferred from coal to ANT.

Comparison of the ternary systems showed higher coal conversion for the system of coal/PHP/PYR than for coal/PHP/ANT, although little difference was observed in their toluene soluble yields. The effect of ANT in the system may be resultant from a lower solvating power for coal than pyrene or a higher propensity for retrogressive reactions. PHP added 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 resulting in DHA and THA. PYR was formed from PHP.

The ternary system employing coal/PYR/PHP yielded substantial coal conversion, ~ 83%, which was quite similar to that obtained for coal/PHP of 86%. However, it is difficult to ascertain what occurred with PYR and PHP. An equal weight amount was charged and no net change in their amounts was observed. However, the error in this reaction was much higher than other ternary and binary systems indicating variability in the products produced. The chemistry of the coal/PYR/PHP system 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.

The binary reactions of the model reactants with resid resulted in a substantial influence of the different reactants on the resid. Without added reactants, the resid underwent substantial retrogressive reactions causing 20% of the resid to become THF insoluble. The addition of PHP resulted in much more of the resid remaining THF soluble compared to the resid reacted alone. Neither the addition of ANT nor PYR blocked any of the retrogressive reactions; however, the binary system with PYR kept more of the resid THF soluble (~ 86%) than did the ANT at 79%. These binary systems yielded the same amount of THF solubles as did the resid alone. The ranking of the binary resid/model reactant systems was resid/PHP > resid/PYR > resid/ANT.

In the binary system, PHP transferred hydrogen to the resid with 7% PYR being formed. PYR showed no reactivity, but ANT underwent substantial hydrogenation, accepting hydrogen from the resid and forming both DHA and THA. The hydrogenated products showed some variability in the two different reactions, but regardless, even in the reaction with lowest reactivity, more than 13% hydrogenated products were formed.

The ternary systems involving resid had similar resid conversions of 97% for resid/PHP/PYR and 98% for resid/PHP/ANT. Likewise, 97% conversion was obtained with resid and PHP. Hence, regardless of additive the addition of PHP to resid enhanced resid upgrading and helped to inhibit retrogressive reactions. In the resid/ANT/PHP reaction more than 30% of the ANT hydrogenated yielding DHA and THA as products. More than 10% PYR was produced. The resid/PYR/PHP system, however, showed no net change in the quantity of PYR and PHP present.

The quaternary mixtures yielded similar coal conversions as the ternary system although the reaction with ANT did increase somewhat. Substantial hydrogenation of ANT occurred while 30% PYR was produced. ANT only accepted 22% of the hydrogen released thereby leaving substantial hydrogen for uptake by the coal and resid. In the quaternary systems with PYR and PHP, no net change in the weight percents of the reactants was observed; however, a large variability in the quantities was observed.

#### Summary and Conclusions

The effect of the different added species on the system performance can be evaluated by comparing the degree of upgrading, % TSD, occurring in each system. The highest degree of upgrading occurred in coal systems in which PHP was present. Likewise, the least amount of degrading occurred in those resid systems that contained PHP. For both coal and residuum PYR had a slightly positive effect on the system while ANT had a negative effect.

The hydrogen donor and acceptor ability of both coal and resid has been demonstrated in this study. When no other donor was present, both coal and resid transferred hydrogen to ANT, yielding partially saturated products. Reactions of PHP alone and in combination with hydrogen acceptors clearly showed that a hydrogen acceptor is required in order for PHP to act as a donor. Hydrogen transfer from PHP to aromatics, coal, and resid was obvious because of their respective conversion and the formation of PYR. The relative reactivity of ANT and PYR is of interest. ANT accepted hydrogen readily and quickly from whatever source was available while PYR was nearly unreactive. 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 involve themselves 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 Maya resid.

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**Table 1. Products Produced from Hydrogen Transfer in Reactions of Anthracene with Perhydropyrene**

Weight Ratio of ANT to PHP	Time (min)	Yield, %			%HYD	Hydrogen Efficiency
		DHA	THA	PYR		
0.166	60	13.3	0	0.34	6.7	101
0.51	60	6.9	0	1.2	3.4	38.1
1.0	60	6.4	0	2.8	3.2	31.2
2.1	60	4.3	0	3.0	2.2	44.9
5.0	60	5.7	0	7.0	4.5	104
6.5	60	5.0	1.0	7.7	3.5	83
9.2	60	4.2	0.8	7.8	2.9	111
0.52	90	6.5	0	1.6	3.3	33.6
1.02	90	4.7	0	2.9	2.4	19.4
2.06	90	4.3	0	3.5	2.2	46.0
5.0	90	6.1	2.0	12.8	5.1	72.0
8.0	90	6.0	2.5	13.2	5.5	108
0.51	180	10.4	0	1.9	5.2	41.7
2.08	180	3.7	0	6.3	1.8	21.2
5.26	180	4.1	0	10.1	2.1	34.3
8.52	180	6.9	1.8	16.1	5.3	81.6

Table 2. Coal and Resid Reaction Products from Thermal Coprocessing Reactions

System	Toluene Solubles (%)	THF Solubles (%)	IOM (%)	Conversion (%)	TSD (%)	Liquid to Solid Ratio
Coal/PHP	75.5±2.2	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±1.9	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±0.0	3.0±0.0	0.9±0.0	97.6±0.0	-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

ANT = anthracene; PHP = perhydropyrene; PYR = pyrene  
 Reaction Conditions: 430°C, 60 minutes, N<sub>2</sub> atmosphere

Table 3. Reactive Products from Model Donors and Acceptors Reactions in Thermal Coprocessing

System	ANT	DHA	THA	PHP	PYR	Hydrogen Efficiency
Coal/PHP	-	-	-	89.8±2.4	10.2±2.4	
Coal/ANT	89.6±0.1	7.3±0.1	3.1±1	-	-	
Coal/PYR	-	-	-	-	100.0±0	
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	
Resid/PHP	-	-	-	93.0±1.5	7.0±1.4	
Resid/ANT	82.8±4.2	13.4±4.4	3.8±0.2	-	-	60.6
Resid/PYR	-	-	-	-	100.0±0	
Resid/ANT/PHP	66.4±0.1	18.5±1.1	15.1±1.0	90.2±0.5	9.8±0.6	
Resid/PYR/PHP	-	-	-	47.8±5.3	52.4±5.4	
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	
Coal	-	-	-	-	-	
Resid	-	-	-	-	-	

\* -: none present