TITLE: **The Role of the Resid Solvent in Coprocessing**

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OBJECTIVE: The objective of this project is to determine the role of petroleum resid in coprocessing of coal and resid. The question being asked is whether the resid is a reactant in the system or whether the resid is a merely a diluent that is being simultaneously upgraded? To fulfill the objective the hydrogen transfer from model compounds, naphthenes that represent petroleum resids to model acceptors is being determined. The specificity of different catalytic systems for promoting the hydrogen transfer from naphthenes to model acceptors and to coal is also being determined. In addition the efficacy of hydrogen transfer from and solvancy of whole and specific resid fractions under coprocessing conditions is being determined.

ACCOMPLISHMENTS & CONCLUSIONS:

The objective of this research was to evaluate the role of the resid in the coprocessing of coal and petroleum resid. An effective means of determining whether resid participates in the reactions at coprocessing conditions is to use model systems and trace their reaction pathways. The research performed in this study evaluated the hydrogen donability of a naphthenic compound perhydropyrene, a compound type prevalent in resids that are hydrogen-rich. Model species were also used as acceptors that represented the aromatic aspect of coal. The model acceptors that were used were anthracene and phenanthrene. In addition, coprocessing reactions using whole resids and resid fractions with coal and with a model acceptor were performed to evaluate hydrogen transfer and the solvancy ability of the resids.

Perhydropyrene has been used previously as a model donor representing resids.[1,2] In a N_2 atmosphere, perhydropyrene donated hydrogen to anthracene, increased the conversion of coal to THF soluble material, and reduced retrogressive reactions of petroleum resid in both thermal and catalytic reactions. Reactions of a number of hydrogen donor compounds such as cyclic olefins, hydroaromatic compounds, and naphthenes like perhydropyrene under equivalent reaction conditions showed that perhydropyrene had the least propensity for hydrogen donation among those compounds in both N_2 and H_2 atmospheres.[2] Since the naphthenic content of resids is significant, understanding how resids and their naphthenic content react in coal-resid coprocessing is important even though naphthenes exhibited the least hydrogen donating propensity of any of the hydrogen donors tested. In the current study, the model perhydropyrene was used to represent petroleum resid and was reacted individually and with model acceptors primarily in a H_2 atmosphere to simulate coprocessing reaction although some reactions were performed in N_2 to provide a reference point.

The model acceptors that were used included anthracene and phenanthrene, both of which are aromatic and represent molecules typically found in coal. Anthracene and phenanthrene have been used as coal model compounds and evaluated according to their ability to accept hydrogen from either a model donor or molecular hydrogen.[3-8] Hydrogenation reactions of anthracene and phenanthrene were performed at temperatures of 325 °C[3] and 400 °C[4-8] for 60 min with a hydrogen pressure of 5 to 9.8 MPa at ambient temperature. Different catalysts were used by the researchers including $NiMo/Al_2O_3$, $NiCl_2$, and sulfided $NiMo/Al_2O_3$ at loadings of 10 to 15 % on a reactant charge basis. MoNaph has been used extensively in coal and resid coprocessing reactions.[9-15] The catalyst used in this study was a slurry phase catalyst molybdenum naphthenate (MoNaph) which was added directly to the reactor contents along with excess sulfur.

The objective of the research involving coal and resid was to determine the role of resid in the coprocessing of coal and resid: basically, is resid serving as a reactant reacting with and trasferring hydrogen to coal to produce a product or is resid serving as a diluent for coal that is simultaneously upgraded? Coprocessing reactions were performed using three different resids, Maya, FHC-623, and Manji, each of which have different characteristics in terms of the amount of asphaltenes, metals such as Ni and V, and saturates containing naphthenes. These resids were used as either whole resid, hexane solubles of the resid, or the saturate fraction of the hexane soluble fraction. The resids and resid fractions were used in coprocessing reactions with coal and with the model acceptor, anthracene. The purpose of performing these reactions was to determine if hydrogen donation was occurring from the whole resid or resid fraction to the coal or anthracene. A second purpose was to determine the effect of the resid composition on its ability to solvate coal. Two bituminous coals, Pittsburgh No. 8 and Blind Canyon, were used in this study. The amount of coal conversion to THF solubles achieved in thermal and catalytic coprocessing reactions was determined and correlated to the type of resid fraction used. In the resid reactions with anthracene, the amount of conversion of anthracene to partially saturated products was determined and the amount of H_2 accepted by anthracene was calculated to evaluate the hydrogen donating ability of the resids.

Experimental

Materials. The chemicals used in the model experiments included anthracene (ANT, 99%), phenanthrene (PHEN, 98+ %), dihydrophenanthrene (DHPN), hexahydrophenanthrene (HHPN) biphenyl, dihydroanthracene (DHA) hexahydroanthrancene (HHA), pyrene (PYR), hexahydropyrene (HHP), and perhydropyrene (PHP). These chemicals were obtained from Aldrich Chemical Company and were used as received. The slurry phase catalyst, molybdenum naphthenate (MoNaph, 6 wt % Mo), was obtained from Shepherd Chemical Company and was used as received. Sulfur added to the catalytic reactions was introduced as elemental sulfur and was obtained from Aldrich. The solvent used to recover the reaction products was HPLC grade THF from Fisher Scientific Company.

The coals used in the coprocessing reactions were Pittsburgh No. 8 obtained from the Argonne Premium Coal Sample Bank and Blind Canyon (DECS-17) bituminous coal from the Penn State Coal Sample Bank. The coal was 200 mesh and was dried before being used.

The resids used in the coprocessing reactions were Maya and FHC-623, both supplied by Amoco. The resids were used as either whole resids, hexane soluble fractions or saturate fractions of the resid in the coprocessing reactions. The fractions were produced by fractionating into hexane solubles and insolubles, and then taking the hexane soluble fraction and separating the saturates by preparative liquid chromatography. The procedure involved dissolving 5 g of hexane soluble material into 20 ml of cyclohexane and the eluting the solution through a packed silica gel column. The solution was eluted with 150 ml of cyclohexane and the eluent collected was the saturated fraction after evaporation of the solvent. The compositions of the resids and resid fractions are given in Table 6. The carbon, hydrogen, nickel, and vanadium contents were measured by Galbraith Laboratory, Knoxville, TN. The sulfur content was determined using a Leco Model SC 32 sulfur analyzer. The MoNaph catalyst was in the same manner as in the model reactions used.

Reaction Procedures for Model Systems. The model reactions were conducted for 30 min in stainless steel tubular microreactors with a volume of ~20 mL. Each reaction was duplicated. The reactors were charged with the model reactants and with H_2 at 3.4 or 8.7 MPa at ambient temperature. When reacted individually, the model donor or model acceptors were added at ~ 0.1 g each of the donor or acceptor. When the donor and acceptor were charged simultaneously at a 1:1 weight ratio, each reactant was charged at 0.05 g, but when the weight ratio charged was 5:1, then 0.1 g of donor and ~ 0.02 g of acceptor were added. The reactions were performed at two different temperatures: 400 and 440 °C. The reactors were situated horizontally in a heated sand bath and were agitated at 400 cpm during the reaction. The liquid and solid products were removed from the reactor after being washed with 5 mL of THF and recovery obtained is given in the data tables.

Catalytic reactions were performed with MoNaph being charged to the reactors at a loading level of 1000 ppm of Mo on a total reactant charge basis. Elemental sulfur was added to MoNaph reaction in a 3:1 S to Mo ratio since MoS_2 was shown to be produced under these reaction conditions.[14] The catalyst generated in situ at reaction temperature formed finely divided catalyst particles.

The products that were recovered with THF from the reaction were analyzed on a Varian Model 3300 gas chromatograph equipped with an SGE HT-5 column and flame ionization detector. The HT-5 column had a 0.1 μm coating thickness, 0.33 mm in diameter and 25 m in length. The temperature program started at 60 °C with a final temperature of 320 °C and with a program rate of 2.5 °C/min. The temperatures of the injector and detector were 320 and 325 °C, respectively. Biphenyl was used as the internal standard.

Reaction Procedures for Coprocessing Reactions. Catalytic and thermal coprocessing reactions were performed using ~20 cm^3 stainless steel tubular microreactors. For each reaction, approximately 1 g of resid (weighed accurately to 0.0001 g) dissolved in 5 ml of THF was introduced into the reactor. The THF was evaporated by placing the microreactor in a vacuum oven overnight; coal was added to the system after the THF evaporated. In the catalytic reactions, MoNaph was introduced at a loading of 1000 ppm Mo on total reactor charge with a 3:1, S to Mo charge.

The coprocessing reaction conditions were 400 °C, for 30 min, 8.7 MPa H_2 introduced at ambient temperature, with horizontal agitation of 400 cpm. All reactions were duplicated. The reaction products were removed from the reactor by washing with several 10 mL aliquots of THF. The recovery typically obtained from these reactions ranged from 85 to 100% for resid reactions and 82 to 100% for coal and resid reactions. Conversion of the reaction products to THF soluble material was determined.

Results and Discussion

Model Naphthene and Model Acceptor Reactions

The reactions were conducted at liquefaction conditions and in the absence of a solvent. The reaction systems were composed of the model donor and model acceptors reacted individually and combinatorially under thermal and catalytic conditions. The model donor used in all of this work was perhydropyrene and the two model acceptors were anthracene and phenanthrene.

Reactions of the Model Acceptors. The two model acceptors used in this study had different propensities for accepting H_2 from the naphthenic donor and from molecular H_2. Reactions of anthracene and phenanthrene were performed individually in N_2 and H_2 at 400 and 440 °C and are described in Tables 1 and 2. Reactions of anthracene in N_2 resulted in less than 2% conversion of anthracene to DHA. The source of the hydrogen most likely came from anthracene itself when anthracene dimerized and the released H_2 which hydrogenated anthracene to form DHA.

Coprocessing of coal and petroleum resid is typically performed at temperatures ranging from 400 to 440 °C and under a H_2 pressure of 18 to 20 MPa at reaction temperature. H_2 pressure was used in these model reactions to simulate actual reaction conditions. Therefore, reactions of the two model acceptors were performed in H_2 at temperatures of 400 and 440 °C and at H_2 pressures of 18 to 20 MPa at reaction temperature. (The corresponding pressure at ambient temperature is 8.7 MPa.) The reaction products obtained from anthracene were DHA and THA as verified by GC mass spectrometry; the products from phenanthrene were dihydrophenanthrene (DHPN) and tetrahydrophenanthrene (THPN). The amount of H_2 that was accepted in each reaction is given in the tables by the column headed by the "H_2 accepted" which is the moles of H_2 accepted per 100 moles of acceptor. Comparison of these quantities gives a measure of the amount of H_2 that had been accepted by the given acceptor under specific reaction conditions.

Anthracene was reactive in a thermal reaction with molecular H_2 present, yielding nearly 86% conversion to partially saturated products at both 400 and 440 °C (Table 1). The primary product formed was DHA at 440 °C which accounted for nearly 81% of the product; the minor product was THA which only accounted for about 5% of the product. At 400 °C, the same products were formed although the quantities were somewhat different; a lesser amount of DHA, 67.5%, and greater amount of THA, 18.4%, were formed. The results from these reactions showed that although anthracene conversion remained relatively constant at 400 and 440 °C, the amount of DHA being hydrogenated to THA increased. Therefore, the amount of H_2 accepted per 100 moles of anthracene was greater at 400 °C than at 440 °C.

Phenanthrene, in contrast to anthracene, had a lesser propensity for accepting molecular H_2 at 400 and 440 °C as evidenced by the conversion of phenanthrene being 4.7% and 9.1%, respectively (Table 2). The products from phenanthrene were DHPN and THPN which were produced in equivalent amounts in the 400 °C reaction and in an almost 2:1 ratio of DHPN to THPN in the 440 °C reaction. This lower proclivity for accepting molecular H_2 made phenanthrene the reactant of choice in the reactions with the naphthene perhydropyrene. The donation of H_2 from perhydrophyrene and acceptance of H_2 by the model acceptor would be more apparent when hydrogenation from molecular H_2 was minimized.

These model acceptors were also reacted with the slurry phase catalyst, MoNaph+S, at the same temperatures and pressures as the thermal reactions; the result of these reactions are shown in Table 1 for anthracene and Table 2 for phenanthrene at 400 and 440 °C. Although fairly small increases in the conversion were obtained in the reactions with anthracene and phenanthrene, the catalyst promoted hydrogenation of the model acceptors. For example, the conversion for phenanthrene increased from 4.7 to 9.0% at 400 °C and from 9.1 to 18.7% at 440 °C with the addition of MoNaph+S. Similarly, the conversion of anthrancene increased at both reaction temperatures; the increase at 400 °C was from 85.9 to 88.6% conversion, while at 440 °C the increase was from 85.8 to 96.9% conversion.

Reaction of the Model Donor. The model donor used in this study was a naphthene, perhydropyrene. Perhydropyrene was used in the current study as a test naphthene molecule to examine if hydrogen transfer occurred between the model naphthene and aromatic species in H_2 and N_2 atmospheres. Perhydropyrene when reacted alone in H_2 and N_2 atmospheres thermally and catalytically at 400 and 440 °C was stable showing almost no reactivity at these conditions (Table 3). At 400 °C in N_2, no conversion of perhydropyrene occurred thermally while with MoNaph+S only 1% conversion to pyrene occurred; the thermal and catalytic conversions of PHP were 0.5% and 5.6%, respectively. At 440 °C in N_2, slightly higher conversion of perhydropyrene occurred. In H_2 at both 400 and 440 °C, perhydrophyrene was stable in noncatalytic reactions yielding at most 3% conversion. The MoNaph+S catalyst promoted conversion.

Reactions of Model Donor and Acceptors. Reactions were performed that combined the model donor perhydropyrene with the model acceptors anthracene and phenanthrene. The reactions of perhydropyrene with anthracene at 1:1 and 5:1 weight ratio under thermal and catalytic conditions are given in Table 1. The moles of H_2 accepted per 100 moles of anthracene or phenanthrene as well as the conversion of anthracene or phenanthrene served as a measure of the activity of the system.

The thermal reaction of perhydropyrene with anthracene at 400 °C and a 1:1 ratio gave a H_2 accepted of 103.9 while the addition of MoNaph+S increased the amount of H_2 accepted to 120.9. Increasing the ratio of perhydropyrene to ANT to 5:1 did not change the amount of H_2 accepted; the H_2 accepted in the thermal reaction was 104.0 while the addition of MoNaph+S increased H_2 accepted to 121.2. The primary product in all of these reactions was DHA, but the addition of MoNaph+S increased the amount of THA produced. These conversion and H_2 accepted values were nearly equivalent to those obtained without perhydropyrene at 400 °C.

Phenanthrene accepted much less donor and molecular H_2 than anthracene at equivalent reaction conditions. For example, when perhydropyrene and phenanthrene were reacted together thermally at a 1:1 and 5:1 ratio at 400 °C, the amount of conversion was 2.9 and 4.6% and the H_2 accepted was 4.4 and 7.4 moles, respectively, as shown in Table 2. The respective values for anthracene ranged from 80 to 95% conversion and 104 to 120 moles of H_2 accepted. The primary product from phenanthrene was usually DHPN with THPN being the secondary product.

Although the reactivity of phenanthrene was much lower than that of anthracene, reactions of phenanthrene with perhydropyrene responded to the presence of perhydropyrene, to change in reaction temperature, and to the type of catalyst used (Table 2). Comparison of the conversion and H_2 acceptance values at two different temperatures but at otherwise equivalent conditions showed that reactions at 440 °C promoted a higher level of conversion and H_2 accepted than those at 400 °C.

Despite the lower reactivity at 400 °C, notable differences in the reactivity were observed in the thermal reactions of phenanthrene and perhydropyrene compared to catalytic reactions containing MoNaph+S. Reactions at 5:1 ratio of donor to acceptor in N_2 at 400 °C showed that a small amount of perhydropyrene donated H_2 to phenanthrene yielding THPN as product. By comparison, the reaction of phenanthrene alone in N_2 at 400 °C did not convert any phenanthrene and, hence, did not yield any hydrogenated product. Thermal reactions at 400 °C in H_2 with a 1:1 ratio of perhydropyrene to phenanthrene converted 2.9% phenanthrene while the 5:1 ratio converted 4.6%. The amount of H_2 accepted gave a corresponding amount of 4.4 and 7.4 moles of H_2 accepted per 100 moles of phenanthrene. The increased amount of naphthene present in the reaction at 400 °C increased the amount H_2 accepted by phenanthrene, indicating that the increased hydrogen accepted was donated by perhydrophyrene. Hydrogen was released from perhydropyrene since pyrene was formed.

In the catalytic reactions using MoNaph+S, an excess amount of perhydropyrene at 400 °C also increased the amount of phenanthrene conversion and the amount of H_2 accepted by phenanthrene. MoNaph+S promoted hydrogenation of phenanthrene to DHPH and THPN. Comparing the combined donor and acceptor reactions to the acceptor reaction alone showed that perhydropyrene being present in the thermal reaction did not increase either phenanthrene conversion or the amount H_2 accepted. However, the addition of MoNaph+S with perhydropyrene present increased both conversion and H_2 accepted at 400 °C when compared to the catalytic reaction with phenanthrene alone.

Reactions of perhydropyrene and phenanthrene at 440 °C (Table 2) showed an overall higher reactivity than those at 400 °C at corresponding reaction conditions. In N_2 with MoNaph+S at 440 °C, the amount of phenanthrene conversion to DHPN and THPN was 2.2%. The source of H_2 in the reaction was H_2 donated from perhydropyrene. In the reaction perhydropyrene produced pyrene and several partially saturated pyrene compounds, thereby donating 8.9 moles of H_2 per 100 moles of perhydropyrene. In H_2 at 440 °C, the ratio of perhydropyrene to phenanthrene affected the amount of phenanthrene conversion as well as the amount of H_2 accepted. Both the thermal and catalytic reactions at the higher ratio gave larger amounts of these quantities than at the lower l:1 ratio. The thermal reaction at 440 °C resulted in 9.3 moles of H_2 accepted per 100 moles of phenanthrene at the 1:1 perhydrophrene to phenanthrene ratio and 16.8 moles of H_2 were accepted at the 5:1 ratio. The MoNaph+S catalyst promoted hydrogenation of phenanthrene at both ratios, yielding at the 1:1 ratio 15.8 moles of H_2 accepted by phenanthrene while at the 5:1 ratio 26.2 moles of H_2 were accepted.

Perhydropyrene reacted in these reactions with phenanthrene to form decahydropyrene (DCP), hexahydropyene (HHA), tetrahydropyrene (THP), dihydropyrene (DHP), and pyrene (PYR). When perhydropyrene was reacted alone, at 400 °C only pyrene was produced while at 440 °C with MoNaph + S a wider variety of products were formed (Table 3). Table 4 presents typical product distribution from reactions of perhydropyrene with anthracene. A calculation of the amount of H_2 donated from these products is given in the tables and is designated as the moles of H_2 donated per 100 moles of perhydropyrene or H_2 donated. In the H_2 atmosphere at 400 °C, the amount of H_2 donated from perhydropyrene remained nearly the same except for reactions containing MoNaph+S which increased H_2 donated to 6.3 from 1 to 2 in the thermal reactions. At 440 °C, higher amounts of H_2 were donated from perhydropyrene to the acceptors.

Role of Resid in Coprocessing

Thermal and catalytic coprocessing reactions of coal with whole resid and two resid fractions, hexane solubles and saturates from hexane solubles, were performed to evaluate the effect of solvent composition on solvating Pittsburgh No. 8 and Blind Canyon coal during coprocessing. In addition, these resid fractions were reacted with the hydrogen acceptor, anthracene; the amount of partially saturated products produced from anthracene in thermal and catalytic reactions was determined and the relative hydrogen donating ability of the different resid fractions was evaluated. Slurry phase MoNaph + S was the catalyst used in all of these reactions.

Characterization of the Resids. The resids chosen in this study have quite different compositions; Maya has the highest asphaltene content of 37.1% and less hexane solubles 62.9% than the other two resids as shown in Table 5. Maya also has the highest Ramsbottom carbon and metals content of Ni and V compared to the other two resids. Fractionating the resids affected the composition of the material produced. When the asphaltenes were separated from both resids by fractionating with hexane and analyzing the hexane solubles, the V content of Maya decreased from 680 to 140 ppm and of FHC-623 from 240 to 93 ppm. The Ni content did not change substantially with the separation indicating that the compounds containing Ni were fairly evenly distributed among all the compound types in the resids. The sulfur content of the whole resids ranged from 3 to nearly 5 %. Solvent fractionation reduced the sulfur content in both Maya and FHC-623 resids. The aromaticity f_a as measured by ^1H NMR decreased for both resids from the whole resid to the hexane solubles to the saturate fraction.

Coprocessing Reactions of Coal and Resid. Coprocessing reactions were performed thermally and catalytically with Pittsburgh No. 8 and Blind Canyon coals using three resids and their resids fractions as solvents as shown in Table 6. Hexadecane served as base line solvent. The coals were also reacted without solvent. Comparison of the reactivity of the coals reacted at equivalent reaction conditions showed that Pittsburgh No. 8 was more reactive than Blind Canyon coal when reacted alone or with hexadecane as the solvent.

Coprocessing reactions of three whole resids and their fractions with Pittsburgh No. 8 and Blind Canyon coals resulted in substantial differences in the coprocessing behavior between the two coals. Compilations of the effect of the catalyst and solvent on the coprocessing reactions are given in Tables 7 and 8. In Table 7, the values for determining the effect of the catalyst were obtained by subtracting the coal conversions obtained in the thermal reactions from those obtained in corresponding catalytic reactions. Positive values indicated that the catalyst increased coal conversion compared to the thermal reaction. In Table 8, the values were obtained by subtracting the coal conversions obtained when reacting coal by itself without a solvent from coal conversion obtained when coprocessing the coal with a solvent. The addition of hexadecane increased Pittsburgh No. 8 coal conversion by 12 and 13% in both thermal and catalytic reactions; whereas, in reactions with Blind Canyon coal the addition of hexadecane only increased coal conversion by 3 to 5 %.

The slurry phase catalyst MoNaph + S was equally effective in the reactions of both coals with the whole resid and saturate fraction. However, the catalyst was much more effective in the reaction of Maya hexane solubles with Pittsburgh No. 8 than with Blind Canyon coal. A similar effect was observed with FHC-623 resid, where the hexane soluble fraction was catalyzed more with Pittsburgh No. 8 than with Blind Canyon coal. The catalytic reaction of FHC-623 whole resid converted Pittsburgh No.8 coal more than Blind Canyon coal although after the asphaltenes were removed the hexane soluble fraction was a more effective solvent in the catalytic reaction with Pittsburgh No. 8 than with Blind Canyon. After the aromatic compounds were removed from the hexane soluble fraction, the FHC-623 saturates were equally effective as solvents in catalytic reaction of both coals. In coprocessing reactions of with Manji resid and its fractions, the resid asphaltenes also appeared to have a direct influence on the resids' ability to convert in catalytic reactions coal. The whole resid was more effective solvent for converting Pittsburgh No. 8 coal while Blind Canyon coal was converted better by Manji hexane soluble fraction.

The composition of the resid solvent had a noticeable effect on the coal conversions in both the thermal and catalytic coprocessing reactions (Table 8). As in evaluating the effect of the slurry phase catalyst, the effect of the solvent was dependent on both the compositions of the resids and the coal. Maya resid, for example, positively affected the coal conversion as a whole resid and as hexane solubles for both coals; however, the Maya saturates were detrimental to coal conversion for Pittsburgh No. 8 coal giving negative values while for Blind Canyon coal the saturates promoted coal conversion giving positive values of 11 to 12 %. The FHC-623 resid was also a better solvent for Blind Canyon coal than Pittsburgh No. 8. The whole resid gave the largest increase compared to no solvent; the hexane solubles were next followed by the saturates which gave just marginally positive values. In contrast, with Pittsburgh No. 8 coal the thermal reaction with FHC-623 hexane solubles and both thermal and catalytic reactions with FHC-623 saturates were negative. The thermal reaction of Manji whole resids yielded negative values for both coals which indicated that having Manji whole resid present in the reaction was detrimental to coal conversion. The same was true for Manji hexane solubles reacted with Pittsburgh No. 8 while the error involved in the corresponding reaction with Blind Canyon coal precludes any conclusions. The catalytic reaction with Manji whole resid and hexane solubles promoted conversion compared to no solvent being present.

The whole resids and resid fractions had distinctive abilities to convert coal. In the thermal reactions of Pittsburgh No. 8 coal, the whole resids were more effective than the hexane solubles followed by the saturates. In catalytic reactions, both the whole resids and hexane solubles were equally effective for coal conversion, while the saturates were much less effective. A different sequencing of the resid effectiveness was observed in both the thermal and catalytic reactions. The hexane solubles of some of the resids were more effective in thermal and catalytic reactions than the corresponding whole resid. The saturate fractions ranged from being very poor solvents to being similar in solvating ability as the whole resids and hexane soluble fractions.

Evaluation of Hydrogen Transfer from Resids and Resid Fractions to Anthracene. In the above described coprocessing reactions, not only did the whole resids' or resid fractions' composition affect the amount of coal conversion, but the coal's chemistry and reactivity also affected the amount of coal conversion achieved. Therefore, the effect of the resid or resid fraction itself on converting coal was difficult to discern. And, since the resid or resid fractions may serve as both solvating agents and as hydrogen donors to coal, experiments were performed with the whole resid and resid fractions using anthracene as a model acceptor to evaluate the propensity of these resid solvents to transfer hydrogen under coprocessing reaction conditions. Reactions were performed with anthracene alone and with perhydropyrene plus anthracene and hexadecane plus anthracene. These reactions showed the effect of the reaction conditions as well as the effect of having an additional hydrocarbon species present in the reaction. Table 9 presents the H_2 accepted by anthracene in these reactions; H_2 accepted is defined as the moles of H_2 accepted per 100 moles of anthracene.

Thermal reactions of anthracene alone and with the resid, resid fractions and hydrocarbons resulted in less H_2 being accepted by anthracene than in the catalytic reactions. The presence of MoNaph + S promoted hydrogenation of anthracene from molecular H_2 as shown by the increase H_2 accepted from 104.3 to 123.2 when anthracene was reacted alone in molecular H_2. The addition of a hydrocarbon solvent such as hexadecane or perhydropyrene decreased the amount of H_2 accepted by anthracene. The straight chain hydrocarbon, hexadecane, decreased the amount of H_2 accepted more than the naphthene, perhydropyrene. In fact, at a 1:1 ratio perhydropyrene only minimally reduced the amount of H_2 accepted. Two obvious factors affected the amount of H_2 accepted in these reactions: the diluent effect of adding a solvent and the amount of hydrogen that can be released from the solvent and donated to anthracene.

Introduction of Maya whole resid and resid fractions decreased the amount of H_2 accepted in both thermal and catalytic reactions compared to the anthracene alone reaction and the anthracene with perhydropyrene reaction. However, the amount of H_2 accepted was similar to that of the hexadecane reaction. For the Maya reactions, the whole resid and saturate fraction gave similar H_2 accepted in the thermal and catalytic reactions with anthracene while the H_2 accepted in the reactions with the hexane soluble fraction was less in the thermal reaction and more in the catalytic reaction than the other two resid materials. The FHC-623 whole resid and resid fractions gave very similar values for H_2 accepted in the thermal and catalytic reactions.

The diluent factor that reduced the amount of H_2 accepted was apparent in the addition of the whole resids and resid fractions to the anthracene reaction. The composition of the resids and the compatibility between the chemistry of the resid material and the catalyst were also factors that affected the amount of coal conversion achieved in these reactions.

Summary

Determining whether hydrogen donation occurred from perhydropyrene as a representative of a resid naphthene at typical coprocessing conditions was a goal of this investigation. The reactions of the model naphthene perhydropyrene and the model acceptors, anthracene and phenanthrene, clearly showed that different chemical species present in the coal have different propensities for accepting H_2 regardless of its source, molecular or donor. The model naphthene under some circumstances, like in the anthracene reaction, was a positive influence on the reaction, causing the overall amount of H_2 accepted to increase. Catalytic reactions with MoNaph+S also promoted the apparent transfer of H_2 from perhydropyrene to anthracene. Phenanthrene was not as active an acceptor as anthracene. Thermal hydrogenation of anthracene and phenanthrene with molecular hydrogen at 400 °C yielded 85% and 4.7% conversion, respectively. Excess donor model was required to observe a positive effect of the naphthene on the H_2 accepted by the model acceptor.

Coprocessing reactions of coal and petroleum resid and resid fractions showed substantial differences in the amount of conversion obtained in thermal and catalytic reactions depending on the composition of the resid solvent. The presence of the asphaltenes in the whole resid promoted coal conversion by providing a solvent that was conducive to coal conversion. Although catalysis by the slurry phase molybdenum naphthenate catalyst increased conversion for all of the fractions, catalysis improved disproportionately the ability of the hexane soluble fraction of all three resids to convert bituminous coals. Both Pittsburgh No. 8 and Blind Canyon coals' conversions were increased by catalysis although Pittsburgh No. 8 was somewhat more sensitive and yielded relatively higher conversions under catalytic conditions. The addition of a solvent to coal during these reactions resulted in more coal conversion if the solvent promoted coal conversion. The relatively inert hexadecane provided a solvent that helped to disperse the coal and the catalyst when a catalyst was used. The whole resids and most of the hexane soluble fractions promoted coal conversion; however the saturate fraction was usually detrimental to coal conversion. The composition of the resid solvent affected coal conversion and the compatibility between the resid and the catalyst. Hydrogen donation did appear to be a major factor in promoting conversion since the none of the resid materials appeared to promote coal conversion to a significant extent.

References

1. Owens, R.; Curtis, C.W. *Energy Fuels, 8*, 823, 1994.
2. Wang S.L.; Curtis, C.W. *Energy Fuels, 8*, 446, 1994.
3. Salim, S.S. and Bell, A.T. *Fuel,* 1984, Vol 63, April, 469-476.
4. Nakatsuji, Y., Kubo, T., Nomura, M., and Kikkawa, S., *Bulletin of the Chemical Society of Japan,* Vol. 51 (2), 618-624, 1978.
5. Song, C.; Nomura, M. and Ono, T. *Preprint - Am. Chem. Soc. Div. Fuel Chem., 36, 2,* 586-596,1991.
6. Song, C.; Ono, T.; and Nomura, M. *Bulletin Chemical Society Japan 62,* 630-632, 1989.
7. Fixari, B. and Perchec, P.L., *Fuel,* 1989, Vo. 68, February, 218-221.
8. Miyak, M., Sakashita, H., Norura, M. and Kikkawa, S. *Fuel,* 1982, Vol 61, February, 124-128.
9. Cassell, F.N.; Curtis, C.W. *Energy Fuels, 2,* 1, 1988.
10. Pellegrino, J.L.; Curtis, C.W. *Energy Fuels, 3,* 160, 1989.
11. Kim, H.; Curtis, C.W. *Energy Fuels, 4,* 214, 1990a; Kim, H.; Curtis, C.W. *Energy Fuels, 4,* 206, 1990b.
12. Ting, P.S.; Curtis, C.W.; Cronauer, D.C. *Energy Fuels, 6,* 511, 1992.
13. Kim, H.; Curtis, C.W. *Fuel Sci. Tech Intl. 9,* 229, 1991.
14. Kim, H.; Curtis, C.W.; Cronauer, D.C.; Sajkowski, D.J. ACS Fuel Div. Prep. 34, 4, 1446, 1989.
15. Brannan, C.J.; Curtis, C.W.; Cronauer, D.C. *Fuel Proc. Tech.* in press, 1995.

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Table 1. Anthracene at Reactions 400 °C and 440 °C: Reacted Alone and With Perhydropyrene

Reaction Condition	Reactants	Atmosphere	T (°C)	Product Distribution (mol%)			Recovery (%)	ANT Conversion, %	H_2 Accepted H_2 Donated
				ANT[c]	DHA	THA			
Thermal	ANT	N_2	400	98.3±0.17	1.70±0.17	0±0	92.5	1.7	1.7
Thermal	ANT	H_2	400	14.1±0.8	67.5±0.4	18.4±1.2	90.1	85.9	104.3
MoNaph + S	ANT	H_2	400	11.4±0.6	70.0±9.3	26.6±8.6	94.4	88.6	123.2
Thermal	ANT	H_2	440	14.2±0.40	80.9±0.42	4.9±0.82	84.4	85.8	90.75
MoNaph + S[b]	ANT	H_2	440	3.8±0.06	55.8±0.62	40.4±2.1	80.1	96.9	136.58
Thermal	PHP: ANT 1:1	N_2	400	94.0±1.8	6.0±1.8	0.0±0.0	82.5	6.0	6.5±0.7
MoNaph + S	PHP: ANT 1:1	N_2	400	95.4±1.1	3.2±1.2	1.4±0.1	85.2	4.6	6.0±0.9
Thermal	PHP: ANT 1:1	N_2	440	94.4±0.4	4.6±0.1	1.0±0.3	83.8	5.6	6.5±0.7
MoNaph + S	PHP: ANT 1:1	N_2	440	96.3±0.1	3.7±0.1	0.0±0.0	87.1	3.7	4.3±0.3
Thermal	PHP: ANT 1:1	H_2	400	5.9±0.5	84.3±4.5	9.8±4.0	98.2	94.1	103.9
MoNaph + S	PHP: ANT 1:1	H_2	400	3.4±0.8	72.5±5.2	24.1±6.0	96.8	96.6	120.9
Thermal	PHP: ANT 5:1	H_2	400	6.3±2.1	83.4±0.6	10.3±2.7	92.2	93.7	104.0
MoNaph + S	PHP: ANT 5:1	H_2	400	5.3±2.0	68.2±6.5	26.6±4.5	82.9	94.7	121.2

[a] Reaction time = 30 min; 8.7 MPa H_2 or N_2 at room temperature.

[b] MoNaph + S = Mo naphthenate with added elemental S.

[c] ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; H_R = (1 x DHA mol% + 2 x THA mol%) x 100.

[d] Reactant loading: Aproximately 0.05 g of each ANT and PHP in PHP:ANT = 1:1 thermal and catalytic reactions; Approximately 0.02 g of ANT and 0.1 g of PHP in PHP:ANT = 5:1 thermal and catalytic reactions.
Mo naphthenate loading is approximately 0.0017 g = total reactant charge (0.1 g)/ 60, computed according to 1000 ppm MoS_2 and 6 wt% Mo in Mo naphthenate.

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Table 2. Phenanthrene Reactions at 400 and 440 °C: Reacted Alone and With Perhydropyrene

Reaction Condition	Reactant	Atmosphere	T(°C)	Product Distribution (mol %)			Recovery (%)	PHEN Conversion (%)	H_2 Accepted[b]	H_2 Donated[c]
				PHEN	DHPN	THPN				
Thermal	PHEN	N_2	400	100±0.0	0.0	0.0	86.6	0.0	0.0	NA[d]
MoNaph	PHEN	N_2	400	100±0.0	0.0	0.0	85.5	0.0	0.0	NA
Thermal	PHEN	H_2	400	95.3±0.7	2.6±0.5	2.1±0.2	83.5	4.7	6.8±0.9	NA
MoNaph+S[b]	PHEN	H_2	400	91.0±0.0	6.0±0.0	3.0±0.1	87.3	9.0	12.0±0.1	NA
Thermal	PHEN	N_2	440	100 ±0.0	0.0	0.0	87.6	0.0	0.0	NA
MoNaph+S	PHEN	N_2	440	100 ±0.0	0.0	0.0	85.3	0.0	0.0	NA
Thermal	PHEN	H_2	440	90.9±1.2	5.9±0.7	3.2±0.5	91.8	9.1	12.3±1.7	NA
MoNaph+S	PHEN	H_2	440	81.3±3.8	12.8±2.4	5.9±1.4	82.0	18.7	24.6±5.2	NA
Thermal	PHP: PHEN 1:1	H_2	400	97.1±0.2	1.5±0.0	1.4±0.2	88.5	2.9	4.4±0.3	1.2±0.1
MoNaph+S	PHP: PHEN 1:1	H_2	400	86.9±2.0	9.0±1.5	4.1±0.5	90.0	13.1	17.2±2.5	6.2±0.0
Thermal	PHP: PHEN 5:1	N_2	400	98.4±0.2	0.0±0.0	1.6±0.2	92.3	1.6	3.2±0.4	3.8±0.0
MoNaph+S	PHP: PHEN 5:1	N_2	400	99.0±0.0	0.0±0.0	1.0±0.0	86.6	1.0	2.0±0.0	3.9±0.0
Thermal	PHP: PHEN 5:1	H_2	400	95.4±0.2	1.8±0.4	2.8±0.8	86.9	4.6	7.4±2.1	1.8±0.0
MoNaph+S[b]	PHP: PHEN 5:1	H_2	400	82.8±0.1	10.7±0.6	6.5±0.1	92.9	17.2	23.7±0.1	6.3±0.0
Thermal	PHP: PHEN 1:1	H_2	440	93.2±1.4	4.4±0.8	2.4±0.6	92.5	6.8	9.3±2.1	0.9±0.1
MoNaph+S	PHP: PHEN 1:1	H_2	440	87.2±1.3	9.9±0.7	2.9±0.6	94.8	12.8	15.8±1.9	7.5±0.1
Thermal	PHP: PHEN 5:1	H_2	440	87.1±1.1	9.0±0.0	3.9±1.2	86.0	12.9	16.8±2.3	8.6±0.1
MoNaph+S[b]	PHP: PHEN 5:1	H_2	440	79.5±3.6	14.9±2.1	5.6±1.5	80.0	20.5	26.2±5.1	10.7±0.6
MoNaph+S	PHP: PHEN 5:1	N_2	440	97.8±0.2	0.5±0.1	1.7±0.7	86.4	2.2	3.9±1.0	8.9±0.1

[a] Reaction Conditions: 30 min; 8.7 MPa H_2 or N_2 introduced at ambient temperature; catalyst loading = 1000 ppm on total reactant charge basis; the total amount of reactant charged is approximately 0.1 g.

[b] Moles of H_2 Accepted per 100 moles of PHEN; H_2 accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100.

[c] Moles of H_2 Donated per 100 moles of PHP; H_2 Donated = (3 x DCP mol% + 5 x HHP mol% + 6 x THP mol% + 7 x DHP mol% + 8 x PYR mol%) x 100.

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Table 3. Product Distribution of Perhydropyrene from Thermal and Catalytic Reactions at 400 and 440 °C[a]

Reaction Conditions	Atmosphere	Temperature (°C)	Catalyst Loading (ppm)	Product Distribution (wt%)			Recovery (%)	PHP Conversion (%)
				PHP	PYR	Others		
Thermal	N_2	400	0	100.0±0.0	0.0±0.0	0	85.5	0.0
Mo Naph+S	N_2	400	1000	99.0±0.5	1.0±0.5	0	82.5	1.0
Thermal	N_2	440	0	99.5±0.8	0.5±0.8	0	88.1	0.5
Mo Naph+S	N_2	440	1000	94.4±0.1	1.6±0.4	4.0±0.4	82.6	5.6
Thermal	H_2	400	0	100.0±0.0	0.0±0.0	0	82.1	0.0
Mo Naph+S	H_2	400	1000	99.8±0.0	0.2±0.0	0	78.3	0.2
Thermal	H_2	440	0	97.0±0.0	3.0±0.0	0	87.3	3.0
Mo Naph + S	H_2	440	1000	97.9±0.3	0.4±0.1[c]	1.7±0.2[d]	85.8	2.1

[a] Reaction Conditions: 30 min, 8.7 MPa H_2 introduced at ambient temperature. [b] PHP = perhydropyrene; PYR = pyrene. [c] 0.4±1 is the wt % of HHP.
[d] Other unidentitiable peaks.

Table 4. Product Distributions of Perhydropyrene from Reactions of Anthracene with Perhydropyrene

Reaction Conditions	Catalyst Loading (ppm)	Atmosphere	Reaction Temperature (°C)	Product Distribution (mole %)			Recovery (%)	H_2 Accepted:[e] moles of H_2 Accepted per 100 moles of ANT	H_2 Donated:[f] moles of H_2 Donated per 100 moles of PHP
				PHP	PYR	Others			
Thermal	0	N_2	400	100±0	0	0	87.3	6.0±1.8	0.0±0.0
MoNaph+S	1000	N_2	400	99.6±0.5	0.4±0.5	0	82.0	6.0±0.9	3.2±0.5
Thermal	0	N_2	440	98.1±0.5	1.9±0.5	0	83.8	6.5±0.7	15.2±0.5
MoNaph+S	1000	N_2	440	98.8±0.3	1.2±0.3	0	83.9	4.3±0.3	9.6±0.3

[e] H_2 Accepted = (1 x DHA mol % + 2 x THA mol %) x 100. [f] H_2 Donated = (8 x PYR mol %) x 100.

Table 5. Characteristics of Resids and Resid Fractions

Resid	Fractions (wt %)[a]			Elemental Analysis				Ramsbottom Carbon (wt%)	Metals (ppm)		
	Hexane Solubles	Toluene Solubles	THF Solubles	C	H	H/C	S		V	Ni	Fe
Maya	62.9±1.1	37.1±1.1	0.0	83.4[b]	9.5	1.4	5.2	28.3[b]	660[b]	123	20
Manji	86.1±0.7	13.9±0.7	0.0	85.1[b]	10.8	1.5	2.6	16.2	235	222	22
FHC-623	83.3±1.1	14.9±0.4	1.8±0.8	86.2[c]	10.4	1.5	3.7	NA	240[c]	84	NA

[a] Analyzed, [b] Data provided by Amoco, [c] Analyzed at Galbraith Laboratories, Knoxville, TN.

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Table 6. Coprocessing Reactions of Coals and Resids

Reactions	Coal Conversion (%)			
	Pittsburgh No. 8		Blind Canyon DECS-17	
	Thermal	Catalytic	Thermal	Catalytic
Coal	44.8±2.1[a]	61.7±4.2	26.4±0.4	45.3±0.8
Coal + Hexadecane	59.1±4.7	84.9±3.3	31.9±0.6	48.4±1.1
Maya Complete Reaction Matrix				
Coal + Whole Resid	56.2±5.2	89.3±1.1	31.8±2.2	64.0±2.3
Coal + Hexane Solubles	49.2±2.2	82.9±2.2	40.5±0.7	49.2±0.2
Coal + Saturate Fraction	37.2±1.4	59.8±1.4	37.7±1.8	57.7±7.4
FHC-623 Complete Reaction Matrix				
Coal + Whole Resid	68.4±4.1	77.9±1.4	49.2±0.2	72.9±1.4
Coal + Hexane Solubles	44.3±4.4	77.8±6.6	43.6±0.7	63.4±0.6
Coal + Saturate Fraction	29.9±5.1	56.9±5.6	27.7±3.0	53.9±2.1
Manji Complete Reaction Matrix				
Coal + Whole Resid	34.9±4.7	75.8±2.9	23.9±2.5	51.9±2.3
Coal + Hexane Solubles	29.3±0.4	77.5±3.3	50.1±11.2	78.7±3.5
Coal + Saturate Fraction	25.6±0.6	32.7±9.8	9.4±3.3	52.6±1.6

[a] Reaction Conditions: 400 °C, 30 min, 8.7 MPa H_2 introduced at ambient temperature.

Table 7. Increase in Coal Conversion Caused by Slurry Phase Catalysis

	Pittsburgh No. 8 (%)	Blind Canyon DECS-17 (%)
Coal	16.9	18.9
Coal + Hexadecane	25.8	16.5
Maya Reacton Matrix		
Coal + Whole Resid	33.1	32.2
Coal + Hexane Solubles	33.7	8.7
Coal + Saturates	22.6	20.0
FHC-623 Reaction Matrix		
Coal + Whole Resid	9.5	23.7
Coal + Hexane Solubles	33.5	19.8
Coal + Saturates	27.0	26.2
Manji Reaction Matrix		
Coal + Whole Resid	40.9	28.0
Coal + Hexane Solubles	48.2	28.6
Coal + Saturates	14.7	43.2

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Table 8. Increase in Coal Conversion Caused by Addition of Solvent

Reactions	Coal Conversion (%)			
	Pittsburgh No. 8		Blind Canyon DECS-17	
	Thermal	Catalytic	Thermal	Catalytic
Coal	–	–	–	–
Coal + Hexadecane	14.3	23.2	5.5	3.1
Maya Complete Reaction Matrix				
Coal + Whole Resid	11.4	27.6	5.4	18.7
Coal + Hexane Solubles	4.4	21.2	14.1	3.9
Coal + Saturates	-7.6	-1.9	11.3	12.4
FHC-623 Complete Reaction Matrix				
Coal + Whole Resid	23.6	16.2	22.8	27.6
Coal + Hexane Solubles	-0.5	16.1	17.2	18.1
Coal + Saturates	-14.9	-4.8	1.3	8.6
Manji Complete Reaction Matrix				
Coal + Whole Resid	-9.9	14.1	-2.5	6.6
Coal + Hexane Solubles	-15.5	15.8	23.7	33.4
Coal + Saturates	-19.2	-21.4	-17.0	7.3

Table 9. Hydrogen Accepted in Reactions with Hydrogen Donors

Reactions	H_2 Accepted[a]	
	Thermal	Catalytic
ANT	104.3	123.2
PHP + ANT (1:1)	103.9	120.9
Hexadecane + ANT (1:1)	89.0	108.8
Maya Whole + ANT (1:1)	95.1	106.9
Maya Hexane Solubles + ANT (1:1)	87.7	111.7
Maya Saturates + ANT (1:1)	95.5	103.5
FHC-623 Whole + ANT (1:1)	96.9	105.4
FHC-623 Hexane Solubles + ANT (1:1)	92.2	106.4
FHC- 623 Saturates + ANT (1:1)	94.9	100.9

[a] H_2 accepted per 100 mol of ANT

[b] Reaction Conditions: 400 °C, 30 min, 8.7 MPa H_2 introduced at ambient temperature.

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