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**Role of the Resid Solvent in Catalytic Coprocessing  
with Finely Divided Catalysts**

**Final Report**

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# The Role of the Resid Solvent in Catalytic Coprocessing with Finely Divided Catalysts

## Abstract

The role of the resid in coprocessing coal with petroleum resid has been investigated using model systems. The primary question being investigated is whether resid is participating in reactions with coal or if the resid is acting simply as a diluent. Since hydrogen transfer is an important mechanism by which solvent interacts with coal, hydrogen transfer between naphthenes, saturated alicyclic molecules, that represent resid and aromatic molecules that represent coal were examined in reactions with a high pressure  $H_2$  atmosphere that is typical of actual coprocessing. The model naphthene, perhydrophyrene, was chosen as the donor species and the models, anthracene, phenanthrene, and benzophenone, were chosen as the acceptor species. Reactions were performed with individual species and with combinations of donor and acceptor at 430 °C and 8.7 MPa  $H_2$  pressure introduced at ambient. Reactions were also performed in  $N_2$  and were used as references. In  $H_2$ , the predominant source of hydrogenation for all of the acceptors was molecular  $H_2$ . Small amounts of  $H_2$  were donated from perhydrophyrene as evidenced by the formation of pyrene and partially saturated pyrenes. The reactions at 440 °C with the acceptor phenanthrene were positively affected by the presence of perhydrophyrene, resulting in increased phenanthrene conversion. By contrast, neither anthracene nor benzophenone was. In  $N_2$  hydrogen donation and apparent transfer occurred in reactions of perhydrophyrene and phenanthrene as well as in reactions at 400 °C of benzophenone and perhydrophyrene. Molybdenum naphthenate reacted with sulfur promoted hydrogenation of the acceptors and in the reactions with phenanthrene and perhydrophyrene promoted

transfer between those two species. Nickel octoate, which also used as a catalyst, showed much less activity for hydrogenation.

Coprocessing reactions of coal with petroleum resid were performed to evaluate the effect of the chemistry of both constituents on coal conversion and the upgrading of the heavy resid. Three heavy resids, Maya, FHC-623 and Manji were used as the whole resid and as fractions that had been separated into hexane solubles and saturate fractions. The separation into hexane solubles removed the asphaltenes and silica gel chromatography of the hexane solubles removed some of the aromatic compounds leaving a solvent that was rich in saturates and naphthenes. These three resids and their respective fractions were reacted with three coals of different levels of reactivity, Pittsburgh No. 8, Blind Canyon DECS-17, and Illinois No. 6.

The conditions for the coprocessing reactions were 400 °C and a H<sub>2</sub> atmosphere for 30 min. Both thermal and catalytic reactions were performed. The catalyst used was a slurry phase hydrotreating catalyst, Mo naphthenate and elemental sulfur. The effect of the resid and the resid fractions on the conversion of coal to soluble products was determined both thermally and catalytically. Similarly, the conversion of the resids and their fractions to lighter boiling constituents was also examined. Both solvent and catalysis effects were observed. The coals with lesser reactivity showed the larger catalysis effect. The solvent effect was strongly dependent on coal-resid interactions that were specific to the specific combination's chemistry and composition. The whole resids and hexane soluble fractions were more conducive to coal conversion while the saturates were less effective solvents.

Reactions of the whole resids and the resid fractions with anthracene showed a substantial effect of the catalyst on the amount of hydrogen being accepted by anthracene. Anthracene

hydrogenated to form dihydroanthracene (DHA) and tetrahydroanthracene (THA) when reacted catalytically alone or with perhydropyrene (PHP). Catalytic reactions with resids or resid fractions resulted in less THA being formed. The whole resids and hexane solubles transferred more hydrogen resulting in the production of more partially hydrogenated anthracene compounds than reactions with saturates.

## Part I

### An Investigation of Hydrogen Donation and Transfer by Model Naphthenes During Thermal and Catalytic Coprocessing

#### Introduction

The goal of coprocessing coal with petroleum resid (Moschopedis et al., 1980; Mochida et al., 1992; Yan and Espenschied, 1983; Curtis and Huang, 1992; Ting et al., 1992; Olson et al., 1993) is to process coal with another readily available and low quality material and to upgrade both materials simultaneously. One desirable aspect of coprocessing is that it relieves the stringent requirement of direct coal liquefaction of having to produce a stable and a high quality recycle stream. Since resid is composed of myriad chemical structures that are dependent upon their origins and since resids have a predominance of aliphatic rather than aromatic structures, using resid as a solvent for coal raises interesting questions concerning the role of the resid in coprocessing. Since these aliphatic compounds are hydrogen-rich compared to coal, then in the reaction it would be desirable for the resid compounds to transfer hydrogen to coal and serve as active participants in the reaction. H-transfer reactions have been shown to be beneficial in converting coal to liquefied products (Bockrath, 1982; Derbyshire and Whitehurst, 1981).

A number of researchers have studied the mechanism of H-transfer in coal liquefaction (Derbyshire et al., 1982; Curran et al., 1967; Virk, 1979; Virk et al., 1979; Bass and Virk, 1980; King and Stock, 1980, 1981, 1982; McMillen et al., 1987a; McMillen et al., 1987b). Coprocessing presents a somewhat different system in that the coal-derived recycle solvent is replaced by a petroleum resid that is H-rich and which contains a substantial amount of nonaromatic species, principally naphthenes and other aliphatic structures. Previous research by Clarke (1984) suggested

that H-transfer occurred between naphthenes and coal under thermal liquefaction conditions. Increased coal conversion was obtained and the naphthenes produced aromatic compounds. McMillen and coworkers (1991) analyzed the experimental results of Clarke et al. (1984) and developed a mechanism for the H-transfer from naphthene to coal that they postulated would occur in coprocessing.

Rudnick (1986 a,b) has patented a process of catalyzing H-transfer from alicyclic to aromatic compounds by introducing thiophenol at temperatures and pressures typical of coal liquefaction. Rudnick (1986 a,b) performed a series of reactions with perhydrophyrene (PHP) a model naphthene and benzophenone, a model acceptor. Reactions of PHP with benzophenone at 440 °C with an unspecified superatmospheric pressure for 1 h did not yield any conversion of benzophenone. However, when 0.51 wt % thiophenol was added, benzophenone was hydrogenated producing 94.7 % diphenylmethane (DPM). Wang and Curtis (1994) repeated these experiments using the reaction conditions of 500 and 1250 psig either of N<sub>2</sub> or H<sub>2</sub> introduced at ambient temperature, 440 °C, with thiophenol being added at 0.51 wt %. In these reactions, the PHP to benzophenone ratio was 0.42. Catalysis by thiophenol enhanced conversion of benzophenone to DPM; this enhancement was greater at 380 °C in N<sub>2</sub> than at 440 °C. None of the reaction conditions were able to replicate the large production of DPM reported by Rudnick.(1986 a,b)

Recent research by Owens and Curtis (1994) investigated H-transfer from model naphthene compounds to model coal compounds during coprocessing. These reactions were performed in a N<sub>2</sub> atmosphere at 430 °C and used as a model naphthene and potential donor, PHP, and aromatics, coal, resid, and coal plus resid as acceptors. Reactions between PHP and anthracene (ANT) resulted in the production of pyrene, dihydroanthracene, and tetrahydroanthracene, respectively. Reactions of

coal with PHP yielded much higher coal conversions than reactions with ANT or pyrene while reactions of PHP with resid resulted in less retrogressive reactions.

Combining PHP with either aromatic compound in reactions with coal, resid, or coal and resid yielded higher coal conversions and less retrogressive reactions than when these reactions were performed without PHP. In  $N_2$ , H-transfer occurred from PHP to ANT or pyrene as evidenced by the formation of dehydrogenation products from PHP and from hydrogenation products from the aromatics. H-transfer also occurred from PHP to resid or coal as shown by increased coal conversion, fewer retrogressive reactions as evinced by decreased insolubles in resid, and the production of pyrene from PHP. H-transfer also occurred between the resid and ANT or the coal and ANT as indicated by the production of partially hydrogenated ANT.

The H-donability of three hydrogen-rich species, cyclic olefins, hydroaromatics, and naphthenes, were compared by Wang and Curtis (1994). Anthracene and pyrene were used as H-acceptors. Hydrogen was transferred most readily at coprocessing conditions by cyclic olefins, then by hydroaromatics, and the least by naphthenes. The dehydrogenation products from the H-donor and from the H-acceptors were analyzed to determine the amount of H-transfer that actually occurred. More H-transfer was observed between model donors and acceptors in  $N_2$  atmospheres than in  $H_2$  atmospheres where molecular  $H_2$  was the predominant  $H_2$  source.

The goal of this research was to evaluate the role that petroleum resid plays in the coprocessing of coal with resid. The primary question being investigated was whether resid participated in the reaction or if resid served just as a diluent in the reaction. One of the primary reactions that coprocessing solvents can undergo is donating and transferring hydrogen from the solvent to coal. Therefore, reactions using model species were performed in this study to evaluate

whether H-transfer occurred from the naphthenic model donor representative of resid to the model acceptors representative of coal under the temperature, atmosphere, catalyst, and pressure conditions typical of coprocessing.

### Experimental

**Materials.** The chemicals used in these experiments included anthracene (ANT, 99%), phenanthrene (PHEN, 98+ %), dihydrophenanthrene (DHPN), hexahydrophenanthrene (HHPN) biphenyl, dihydroanthracene (DHA) hexahydroanthracene (HHA), pyrene (PYR), hexahdropyrene (HHP), and perhydropyrene (PHP). These chemicals were obtained from Aldrich Chemical Company and were used as received. The slurry phase catalysts, molybdenum naphthenate (MoNaph, 6 wt % Mo) and nickel octate (NiOct, 12 wt% Ni) were obtained from Shepherd Chemical Company and were used as received. Sulfur was added to the catalytic reactions with MoNaph but not with NiOct. The sulfur was introduced as elemental sulfur and was obtained from Aldrich. The solvent used to recover the reaction products was HPLC grade tetrahydrofuran (THF) from Fisher Scientific Company.

**Reaction Procedures.** 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 N<sub>2</sub> or H<sub>2</sub> 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 400 and 440 °C for 30 min. The reactors were placed 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 with 5 mL of THF and the recovery obtained is given in the data tables.

Catalytic reactions were performed with MoNaph and NiOct being charged to the reactors at a loading levels 500 and 1000 ppm of Mo or Ni on a total reactant charge basis. Elemental sulfur was added to MoNaph reaction in a 3:1 S to Mo ratio since MoS<sub>2</sub> has been shown to be produced under these reaction conditions (Kim et al., 1989). The catalyst generated in situ at reaction temperature formed finely divided catalyst particles.

The THF soluble reaction products were analyzed on a Varian Model 3300 gas chromatograph equipped with an SGE HT-5 column, flame ionization detector and He as the carrier gas. The HT-5 column had a 0.1 μm coating thickness, 0.33 mm diameter and 25 m 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. Quantitation was performed using the internal standard method with biphenyl as the internal standard. Products were identified by GC-mass spectrometry using a VG 70 EHF mass spectrometer.

### **Results and Discussion**

Coprocessing of coal and petroleum resid is typically performed at temperatures ranging from 400 to 440 °C under a H<sub>2</sub> pressure of 18 to 20 MPa at reaction temperature. Since the primary question being addressed is whether naphthenic compounds transfer hydrogen to coal molecules at these conditions, these conditions were used for the model study. The model naphthene used was perhydrophyrene and the model acceptors were anthracene, phenanthrene, and benzophenone. The reactions involved either a model donor, model acceptor, or a combination of the two. The reactions were performed without a solvent in order to remove any influence the solvent might have on the

reactants. Some reactions were performed in a N<sub>2</sub> atmosphere to provide a baseline level of H-donability and acceptance in an inert atmosphere.

The reaction products obtained under these reaction conditions from anthracene (ANT) were dihydroanthracene (DHA) and tetrahydroanthracene (THA); from phenanthrene (PHEN), dihydrophenanthrene (DPHN) and tetrahydrophenanthrene (TPHN); from benzophenone (BENZ), diphenylmethane (DPM); from perhydropyrene (PHP), pyrene and partially saturated pyrenes, most commonly decahydropyrene (DCP), hexahydropyrene (HHP), tetrahydropyrene (THP), and dihydropyrene (DHP). The production of high molecular weight compounds from the individual reactants was monitored but none were detected. The information given in the data tables include the type of reaction that the compound underwent, either thermal or catalytic and either individual or combined with another species, the pressure and type of atmosphere and the temperature used, the product distribution from one of the components in the reaction, recovery, conversion, and the amount of H<sub>2</sub> accepted or donated which was calculated on a basis of 100 moles of acceptor or donor charged as reactants.

**Reactions of Anthracene.** Anthracene was reactive in thermal reactions with a H<sub>2</sub> atmosphere, yielding nearly 86% conversion to DHA and THA at both 400 and 440 °C as shown in Table 1. The primary product at both temperatures was DHA, yielding ~80.9% at 440 °C and 67.5% at 400 °C. The secondary product in both cases was THA with a higher production occurring at the lower temperature. Since more conversion to THA occurred at 400 °C, the amount of H<sub>2</sub> accepted per 100 moles of ANT was greater at 400 °C. Anthracene reacting in N<sub>2</sub> at 400 °C resulted in a only 1.7% conversion which was most likely caused by the dimerization or trimerization of ANT and

subsequent release of H<sub>2</sub>, although higher molecular weight products were not detected by gas chromatographic analysis.

Catalytic reactions of ANT with slurry phase catalyst, MoNaph + S, at the same reaction temperatures and pressure as the thermal reactions resulted in small increases in the ANT conversion but larger increases in THA production. The amount of H<sub>2</sub> accepted per 100 moles of ANT increased from 104.3 to 123.2 moles at 400 °C and from 90.8 to 136.6 moles at 440 °C. Hence, MoNaph + S was more active for hydrogenating ANT to THA at 440 °C than at 400 °C.

**Reactions of Phenanthrene.** Phenanthrene, in contrast to ANT, had a lesser propensity for accepting molecular H<sub>2</sub> in thermal reactions at 400 and 440 °C as evidenced by the conversion of phenanthrene being 4.7% and 9.1%, respectively (Table 2). This difference in reactivity has been well-documented in the literature (Song et al., 1991; Orare, 1983). 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. Phenanthrene was totally nonreactive in N<sub>2</sub> under both thermal and catalytic conditions at both 400 and 440 °C. This lower proclivity for accepting molecular H<sub>2</sub> made PHEN the reactant of choice in the reactions with the naphthene perhydropyrene. The donation of H<sub>2</sub> from PHP and acceptance of H<sub>2</sub> by the model acceptor would be more apparent when hydrogenation from molecular H<sub>2</sub> was minimized.

Catalytic reactions of PHEN with MoNaph + S nearly doubled the overall conversion compared to the thermal reactions. Dihydrophenanthrene was the primary product. The amount of H<sub>2</sub> accepted per 100 moles of PHEN also doubled compared to the thermal reaction. However, the amount of H<sub>2</sub> accepted at 400 °C was 12.0 moles of PHEN per 100 mol which was considerably less

than the corresponding ANT reaction which had 123.2 moles of H<sub>2</sub> accepted per 100 moles of ANT. Similar differences were observed at 440 °C.

**Reactions of Benzophenone.** Benzophenone has been used in the coal literature as a H-acceptor species to determine the H-donor ability of different potential donors (Raaen and Roark, 1978). Typically, these H-donor tests were performed in an inert atmosphere such as N<sub>2</sub> which allowed all of the H-transferred to be derived from the donor species. The BENZ reaction system was readily definable since the primary product is diphenylmethane (DPM). In the current study, reactions of BENZ were performed in both N<sub>2</sub> and H<sub>2</sub> atmospheres to determine the ease with which BENZ hydrogenated in a reducing atmosphere.

Benzophenone was quite reactive in a thermal reaction with a H<sub>2</sub> atmosphere, yielding 30.6% conversion at 400 °C and 65.0% at 440 °C when reacted with an initial H<sub>2</sub> pressure of 3.3 MPa as shown in Table 3. When the initial H<sub>2</sub> pressure was raised to 8.7 MPa, BENZ conversion increased to 77.1%. Since only one product was obtained, the H<sub>2</sub> accepted followed the conversion exactly. In a N<sub>2</sub> atmosphere, BENZ showed little reactivity, giving only 2.5 and 1.1% conversion, respectively, at 400 and 440 °C.

Catalytic reactions of BENZ were performed with two levels of MoNaph, 500 and 1000 ppm, at both reaction temperatures. In all reactions using H<sub>2</sub>, the catalyst increased conversion of BENZ to DPM, with conversions ranging from ~95 to 100%. The largest increases were observed with 500 ppm of MoNaph; at 400 and 440 °C, the conversions increased from the thermal 30.6% to the catalytic 100% and from 77.1% to 99.8%, respectively. The initial H<sub>2</sub> pressure in the catalytic reaction also affected the conversion somewhat, giving slightly lower conversions with higher H<sub>2</sub> pressure.

**Reactions of the Model Donor.** Perhydropyrene was used in the current study as a model naphthene and donor molecule to examine if hydrogen transfer occurred between the model naphthene and aromatic species in H<sub>2</sub> and N<sub>2</sub> atmospheres. Perhydropyrene, when reacted alone in H<sub>2</sub> and N<sub>2</sub> atmospheres thermally and catalytically at 400 and 440 °C, was stable showing almost no reactivity at these conditions (Table 4). At 400 °C in N<sub>2</sub>, no conversion of PHP occurred thermally while with MoNaph+S only 1% conversion to pyrene occurred; at 440 °C in N<sub>2</sub> the thermal and catalytic conversions of PHP were 0.5 and 5.6%, respectively. In H<sub>2</sub> at 440 °C, PHP in thermal reactions yielded at most 3% conversion and the catalytic reaction yielded less at 400 °C.

**Reactions of Model Donor and Acceptors.** Reactions that combined the model donor perhydropyrene with the model acceptors, anthracene, phenanthrene and benzophenone, were performed to determine the amount of H-donation from PHP to the acceptor. The reactions of PHP with the model acceptors at 1:1 and 5:1 weight ratio under thermal and catalytic conditions are given in Tables 1-3. The moles of H<sub>2</sub> accepted per 100 moles of ANT, PHEN or BENZ charged as well as the conversion of the model acceptors served as a measure of the activity of the system.

**Reactions of Perhydropyrene and Anthracene.** The thermal reaction of PHP with ANT at 400 °C in H<sub>2</sub> with a 1:1 ratio gave 103.9 moles of H<sub>2</sub> accepted while the addition of MoNaph+S increased the moles of H<sub>2</sub> accepted to 120.9. Increasing the ratio of PHP to ANT to 5:1 gave similar values for the moles of H<sub>2</sub> accepted; the moles of H<sub>2</sub> accepted in the thermal reaction was 104.0 while the addition of MoNaph+S increased H<sub>2</sub> 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 moles of H<sub>2</sub> accepted values were similar to those obtained without PHP at 400 °C.

When PHP was reacted with ANT in N<sub>2</sub>, the product pyrene was formed as shown in Table 5. The reactions at 440 °C in N<sub>2</sub> converted more PHP to pyrene than did the reactions at 400 °C. The moles of H<sub>2</sub> accepted per 100 moles of ANT were similar for all of the reactions. However, the moles of H<sub>2</sub> donated per 100 moles of PHP based on the formation and detection of pyrene varied considerably. One reason for this variance is that for perhydropyrene to dehydrogenate to form pyrene, 8 moles of H<sub>2</sub> must be released; therefore, small changes or errors in analyzing the moles of pyrene produced resulted in fairly large changes in the moles of H<sub>2</sub> donated. In contrast to the N<sub>2</sub> reactions, the reactions of PHP and ANT in H<sub>2</sub> did not produce any detectable amount of pyrene.

**Reactions of Phenanthrene and Perhydropyrene.** Although the reactivity of PHEN was much lower than that of ANT, reactions of PHEN with PHP were affected by the presence of PHP, reaction temperature, and presence of a catalyst (Table 2). Comparison of the conversion and H<sub>2</sub> accepted values at 400 and 440 °C but at otherwise equivalent conditions showed that the higher temperature promoted higher levels of conversion and moles of H<sub>2</sub> accepted.

Notable differences in reactivity were observed in the thermal reactions of PHEN and PHP at 400 °C compared to those containing MoNaph+S. Thermal reactions at 400 °C in H<sub>2</sub> with a 1:1 ratio of PHP to PHEN converted 2.9% PHEN while the 5:1 ratio converted 4.6%. The moles of H<sub>2</sub> accepted gave corresponding amounts of 4.4 and 7.4 moles of H<sub>2</sub> accepted per 100 moles of PHEN charged. In the catalytic reactions, the conversion of PHEN increased at both the 1:1 and 5:1 PHP to PHEN ratios, while the 5:1 ratio yielded the highest conversion. The moles of H<sub>2</sub> accepted were 17.2 and 23.7, respectively. Comparing the combined thermal reactions to those of PHEN alone showed that the presence of PHP did not increase either PHEN conversion or the moles of H<sub>2</sub>

accepted. By contrast, the addition of MoNaph+S to the PHP/PHEN reactions increased both quantities compared to the catalytic reaction of PHEN alone.

Reactions of PHP and PHEN in N<sub>2</sub> at 400 °C yielded a small amount of conversion of PHP to pyrene and of PHEN to TPHN. By contrast, when PHEN was reacted alone under these conditions, no PHEN conversion occurred. Therefore, the H<sub>2</sub> donated by PHP was transferred to PHEN when the reaction was performed in N<sub>2</sub> and when there was no competition for hydrogenation by molecular H<sub>2</sub>. When reacted at the higher ratio of PHP to PHEN, the moles accepted by the PHEN increased, indicating that additional H<sub>2</sub> was donated by PHP and transferred to PHEN.

Reactions of PHP and PHEN at 440 °C (Table 2) showed higher reactivity than those at 400 °C at corresponding reaction conditions. In N<sub>2</sub> with MoNaph+S at 440 °C, the amount of PHEN conversion to DHPN and THPN was 2.2%. The source of H<sub>2</sub> in the reaction was H<sub>2</sub> donated from PHP since the reaction of PHEN alone at equivalent reaction conditions yielded no conversion. In the reaction PHP produced pyrene and several partially saturated pyrene compounds, thereby donating 8.0 moles of H<sub>2</sub> of which 3.9 moles were accepted. In H<sub>2</sub> at 440 °C, the ratio of PHP to PHEN affected the amount of PHEN conversion as well as the amount of H<sub>2</sub> accepted. Both thermal and catalytic reactions at the 5:1 donor to acceptor ratio resulted in higher conversion and moles of H<sub>2</sub> accepted than at the 1:1 ratio. The thermal reaction at 440 °C yielded 9.3 moles of H<sub>2</sub> accepted at the 1:1 ratio while 16.8 moles of H<sub>2</sub> were accepted at the 5:1 ratio. Addition of MoNaph+S promoted hydrogenation of PHEN at both ratios, yielding at the 1:1 ratio 15.8 moles of H<sub>2</sub> accepted while at the 5:1 ratio 26.2 moles of H<sub>2</sub> were accepted.

Perhydropyrene reacted in these reactions with PHEN to form decahydropyrene (DCP), hexahydropyrene (HHP), tetrahydropyrene (THP), dihydropyrene (DHP), and pyrene (PYR) (Table

6). By comparison, when PHP was reacted alone in H<sub>2</sub>, only pyrene was produced catalytically at 400 °C and thermally at 440 °C, while at 440 °C with MoNaph + S a wider variety of products was formed (Table 4). When reacted with PHEN in a H<sub>2</sub> at 400 °C, the moles of H<sub>2</sub> donated by PHP ranged from 1.2 to 1.8 in thermal reactions while the catalytic reactions increased the moles of H<sub>2</sub> donated to 6.1 to 6.3. The ratio of donor to acceptor only increased the moles of H<sub>2</sub> donated slightly at both temperatures. At 440 °C, the moles of H<sub>2</sub> donated varied according to the reaction condition.

**Reactions of Perhydropyrene and Benzophenone.** Benzophenone was also chosen as a hydrogen acceptor because its previous use as a model acceptor to evaluate the propensity of donor to donate hydrogen to coal (Raaen and Roark, 1978; Curtis et al., 1984). These previous experiments were performed in an inert atmosphere, typically N<sub>2</sub>, in order to eliminate molecular H<sub>2</sub> as a source of hydrogen. Hydrogen donors were often ranked according to their propensity to release hydrogen and to transfer that hydrogen to the acceptor. In addition, in patents by Rudnick(1986 a,b) BENZ was used as an acceptor for PHP. At the reaction conditions used and using thiophenol as a catalyst, substantial conversion of BENZ to DPM by H-transfer from PHP was claimed; however, attempts to replicate the results in our laboratory yielded much smaller amount of the product, DPM.(Wang and Curtis, 1994) One of the reasons for this lack of success was the lack of definition of the gaseous atmosphere used in the patent and our consequent inability to replicate it exactly.

The reactions of PHP and BENZ in this study were performed at 400 and 440 °C in N<sub>2</sub> and H<sub>2</sub> at two pressures, 3.3 and 8.7 MPa, under thermal and catalytic conditions using 500 or 1000 ppm of Mo. Thermal reactions of PHP and BENZ at 400 °C in N<sub>2</sub> converted 5.5% of BENZ to DPM while the reaction without PHP only converted 2.5%. Similarly, at 400 °C with MoNaph + S at 1000 ppm, the conversion of BENZ was 7.6% to DPM when PHP was present while without PHP only

2.2% BENZ was converted. Hence, in a  $N_2$  atmosphere, PHP donated  $H_2$  that was accepted by BENZ. By contrast, raising the temperature to 440 °C and reacting with MoNaph + S resulted in similar conversions: 5.8% without PHP and 6.0% with PHP. In these systems the amount of conversion directly related to the moles of  $H_2$  accepted per 100 moles of BENZ. Consequently, for the reactions at 400 °C, the presence of PHP increased the moles of  $H_2$  accepted by 3.0 moles in the thermal reaction and by 5.4 moles in the catalytic reaction. When the small error obtained in determining the products in these reactions is considered, these differences in moles of  $H_2$  accepted were outside the range of error. Hence, PHP donated  $H_2$  to BENZ in  $N_2$  at these reaction conditions. At higher temperature, the thermal reaction of BENZ undergoing reaction and releasing  $H_2$  became more dominant, thereby reducing the effect of H-donation from PHP.

Catalytic reactions of BENZ with PHP at 440 °C with 500 ppm of Mo as MoNaph yielded less conversion to DPM than the correspondent reactions without PHP. The effect of increasing the  $H_2$  pressure was a decrease in conversion which resulted in a larger effect when PHP was present. The reactions of BENZ with 1000 ppm of Mo with PHP were performed only in a  $N_2$  reaction since the reactions with BENZ alone in  $H_2$  produced very high conversions, thereby not allowing PHP to have much opportunity for transferring  $H_2$  to BENZ.

The reaction products produced from PHP when reacted with BENZ included the partially saturated DCP, HHP, THP, DHP, and pyrene as presented in Table 7. The amount of each of these products was small in all reactions but varied in quantity according to the reaction conditions used. The moles of  $H_2$  donated per 100 moles of PHP charged are also given in Table 7. When the moles of  $H_2$  donated are compared to the moles of  $H_2$  accepted in Table 3, more moles of  $H_2$  were donated in the  $N_2$  atmosphere reaction than moles of  $H_2$  accepted. By contrast in the reactions with  $H_2$ ,

substantially more  $H_2$  was accepted than was donated, indicating that most of the hydrogenation of BENZ resulted from molecular  $H_2$ .

**Reactions with Nickel Octoate.** Reactions of PHEN alone and of PHEN with PHP were performed thermally and catalytically with nickel octoate (NiOct) to determine the efficacy of NiOct for promoting H-transfer from PHP to PHEN. The thermal reactions yielded 4.7% conversion of PHEN when reacted alone and 3.0% for the 1:1PHP: PHEN ratio and 4.6% for the 5:1 ratio. The two reaction products were DHPN and THPN. With NiOct present, PHEN conversion of 1.6% was less than the thermal reaction while the conversion at a 1:1 ratio was equivalent to the thermal case. Increasing the ratio to 5:1 at 400 °C resulted in 5.8% conversion which was slightly higher than the thermal case, while increasing the temperature to 440 °C resulted in increased conversion of 13.0%. The activity of NiOct for promoting hydrogenation in this system was less than that of MoNaph + S.

### Summary and Conclusions

The propensity for perhydropyrene, a compound representative of H-rich naphthenes in resids, to donate  $H_2$  to model acceptors under coprocessing conditions with a  $H_2$  atmosphere was low. The predominant source for hydrogenating all three acceptors, anthracene, phenanthrene, and benzophenone, under thermal or catalytic conditions was molecular  $H_2$ , although these different acceptors had much different reactivities for accepting hydrogen at these reaction conditions. Hydrogenation of phenanthrene was increased in the presence of perhydropyrene when reacted in  $H_2$  at 440 °C; both conversion of phenanthrene and the moles of  $H_2$  accepted increased when perhydropyrene was present in the reaction. None of the other acceptors were influenced by the presence of perhydropyrene when reacted in  $H_2$ . The catalyst, molybdenum naphthenate plus

elemental sulfur, promoted hydrogenation in both H<sub>2</sub> and N<sub>2</sub> atmospheres, while the other catalyst, nickel octoate had much less activity for hydrogenation in these reaction systems.

Only in reactions with N<sub>2</sub> atmospheres did the amount of H<sub>2</sub> donated from perhydropyrene exceed that amount of H<sub>2</sub> accepted by the acceptor. In addition, the amount of hydrogenated acceptor produced in the reactions of perhydropyrene with the acceptor was greater than that when the acceptor was reacted alone, evincing that perhydropyrene donated and transferred H<sub>2</sub> to the acceptors when reacted in N<sub>2</sub>. The molybdenum naphthenate plus sulfur catalyst promoted H-transfer from perhydropyrene to the acceptor in reactions with N<sub>2</sub> atmospheres.

The role of hydrogen transfer by naphthenic compounds that are present in resids during coprocessing was minimal. Hydrogenation of model acceptors occurred primarily by molecular H<sub>2</sub> while any transfer of H<sub>2</sub> from naphthenic compounds was only supplemental. The receptiveness of the H<sub>2</sub> acceptor for H<sub>2</sub> transferred from resid naphthenes was dependent upon the chemistry of the particular acceptor.

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**Table I. 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 <sub>2</sub> Accepted <sup>d</sup>	H <sub>2</sub> Donated <sup>e</sup>
				ANT	DHA	THA				
Thermal	ANT	N <sub>2</sub>	400	98.3±0.17	1.70±0.17	0.0±0.0	92.5	1.7	NA <sup>a</sup>	
Thermal	ANT	H <sub>2</sub>	400	14.1±0.8	67.5±0.4	18.4±1.2	90.1	104.3	NA	
MoNaph + S	ANT	H <sub>2</sub>	400	11.4±0.6	70.0±9.3	26.6±8.6	94.4	123.2	NA	
Thermal	ANT	H <sub>2</sub>	440	14.2±0.40	80.9±0.42	4.9±0.82	84.4	90.75	NA	
MoNaph + S <sup>b</sup>	ANT	H <sub>2</sub>	440	3.8±0.06	55.8±0.62	40.4±2.1	80.1	136.58	NA	
Thermal	PHP: ANT 1:1	N <sub>2</sub> <sup>f</sup>	400	94.0±1.8	6.0±1.8	0.0±0.0	82.5	6.5±0.7	0.0±0.0	
MoNaph + S	PHP: ANT 1:1	N <sub>2</sub> <sup>f</sup>	400	95.4±1.1	3.2±1.2	1.4±0.1	85.2	6.0±0.9	3.2±0.5	
Thermal	PHP: ANT 1:1	N <sub>2</sub> <sup>f</sup>	440	94.4±0.4	4.6±0.1	1.0±0.3	83.8	6.5±0.7	15.2±0.5	
MoNaph + S	PHP: ANT 1:1	N <sub>2</sub> <sup>f</sup>	440	96.3±0.1	3.7±0.1	0.0±0.0	87.1	4.3±0.3	9.6±0.5	
Thermal	PHP: ANT 1:1	H <sub>2</sub> <sup>g</sup>	400	5.9±0.5	84.3±4.5	9.8±4.0	98.2	103.9	0.0±0.0	
MoNaph + S	PHP: ANT 1:1	H <sub>2</sub> <sup>g</sup>	400	3.4±0.8	72.5±5.2	24.1±6.0	96.8	120.9	0.0±0.0	
Thermal	PHP: ANT 5:1	H <sub>2</sub> <sup>g</sup>	400	6.3±2.1	83.4±0.6	10.3±2.7	92.2	104.0	0.0±0.0	
MoNaph + S	PHP: ANT 5:1	H <sub>2</sub> <sup>g</sup>	400	5.3±2.0	68.2±6.5	26.6±4.5	82.9	121.2	0.0±0.0	

<sup>a</sup> Reaction Conditions: 30 min; 8.7 MPa H<sub>2</sub> or N<sub>2</sub> introduced at ambient temperature; Reactant loading approximately 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<sub>2</sub> and 6 wt% Mo in Mo naphthenate.

<sup>b</sup> MoNaph + S = Mo naphthenate with added elemental S.

<sup>c</sup> ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; H<sub>R</sub> = (1 × DHA mol% + 2 × THA mol%) × 100.

<sup>d</sup> Perhydropyrene product distributions are given in Table 4.

<sup>e</sup> Moles of H<sub>2</sub> Donated per 100 moles of PHP; H<sub>2</sub> Donated = (3 × DCP mol% + 5 × HHP mol% + 6 × THP mol% + 7 × DHP mol% + 8 × PYR mol%) × 100.

<sup>f</sup> Product distributions for perhydropyrene are given in Table 2.

<sup>g</sup> No perhydropyrene reaction products were observed.

<sup>h</sup> NA = not applicable

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

Reaction Condition	Reactant	Atmosphere	T(°C)	Product Distribution (mol %)			Recovery (%)	PHEN Conversion (%)	H <sub>2</sub> Accepted <sup>b</sup>	H <sub>2</sub> Donated <sup>c</sup>
				PHEN	DHPN	THPN				
Thermal	PHEN	N <sub>2</sub>	400	100±0.0	0.0	0.0	86.6	0.0	NA <sup>a</sup>	
MoNaph	PHEN	N <sub>2</sub>	400	100±0.0	0.0	0.0	85.5	0.0	NA	
Thermal	PHEN	H <sub>2</sub>	400	95.3±0.7	2.6±0.5	2.1±0.2	83.5	6.8±0.9	NA	
MoNaph+S <sup>b</sup>	PHEN	H <sub>2</sub>	400	91.0±0.0	6.0±0.0	3.0±0.1	87.3	12.0±0.1	NA	
Thermal	PHEN	N <sub>2</sub>	440	100±0.0	0.0	0.0	87.6	0.0	NA	
MoNaph+S	PHEN	N <sub>2</sub>	440	100±0.0	0.0	0.0	85.3	0.0	NA	
Thermal	PHEN	H <sub>2</sub>	440	90.9±1.2	5.9±0.7	3.2±0.5	91.8	12.3±1.7	NA	
MoNaph+S	PHEN	H <sub>2</sub>	440	81.3±3.8	12.8±2.4	5.9±1.4	82.0	24.6±5.2	NA	
Thermal	PHP: PHEN1:1	H <sub>2</sub>	400 <sup>d</sup>	97.1±0.2	1.5±0.0	1.4±0.2	88.5	4.4±0.3	1.2±0.1	
MoNaph+S	PHP: PHEN1:1	H <sub>2</sub>	400 <sup>d</sup>	86.9±2.0	9.0±1.5	4.1±0.5	90.0	17.2±2.5	6.2±0.0	
Thermal	PHP: PHEN5:1	N <sub>2</sub>	400 <sup>d</sup>	98.4±0.2	0.0±0.0	1.6±0.2	92.3	3.2±0.4	3.8±0.0	
MoNaph+S	PHP: PHEN5:1	N <sub>2</sub>	400 <sup>d</sup>	99.0±0.0	0.0±0.0	1.0±0.0	86.6	2.0±0.0	3.9±0.0	
Thermal	PHP: PHEN5:1	H <sub>2</sub>	400 <sup>d</sup>	95.4±0.2	1.8±0.4	2.8±0.8	86.9	7.4±2.1	1.8±0.0	
MoNaph+S <sup>b</sup>	PHP: PHEN5:1	H <sub>2</sub>	400 <sup>d</sup>	82.8±0.1	10.7±0.6	6.5±0.1	92.9	23.7±0.1	6.3±0.0	
Thermal	PHP: PHEN 1:1	H <sub>2</sub>	440 <sup>d</sup>	93.2±1.4	4.4±0.8	2.4±0.6	92.5	9.3±2.1	0.9±0.1	
MoNaph+S	PHP: PHEN 1:1	H <sub>2</sub>	440 <sup>d</sup>	87.2±1.3	9.9±0.7	2.9±0.6	94.8	15.8±1.9	7.5±0.1	
Thermal	PHP: PHEN 5:1	H <sub>2</sub>	440 <sup>d</sup>	87.1±1.1	9.0±0.0	3.9±1.2	86.0	16.8±2.3	3.0±0.1	
MoNaph+S <sup>b</sup>	PHP: PHEN 5:1	H <sub>2</sub>	440 <sup>d</sup>	79.5±3.6	14.9±2.1	5.6±1.5	80.0	26.2±5.1	4.9±0.1	
MoNaph+S	PHP: PHEN 5:1	N <sub>2</sub>	440 <sup>d</sup>	97.8±0.2	0.5±0.1	1.7±0.7	86.4	3.9±1.0	8.0±0.1	

<sup>a</sup> Reaction Conditions: 30 min; 8.7 MPa H<sub>2</sub> or N<sub>2</sub> introduced at ambient temperature; catalyst loading is 1000 ppm on total reactant charge basis; the total amount of reactant charged is approximately 0.1 g.

<sup>b</sup> Moles of H<sub>2</sub> Accepted per 100 moles of PHEN; H<sub>2</sub> accepted = (2 × THPN mol% + 1 × DHPN mol%) × 100.

<sup>c</sup> Moles of H<sub>2</sub> Donated per 100 moles of PHP; H<sub>2</sub> Donated = (3 × DCP mol% + 5 × HHP mol% + 6 × THP mol% + 7 × DHP mol% + 8 × PYR mol%) × 100.

<sup>d</sup> Perhydropryrene product distributions are given in Table 4.

• NA = not applicable

**Table I. 3. Conversion and Product Distribution of Benzophenone from Reactions of Benzophenone with Perhydropyrene<sup>a</sup>**

Reactants	Atmosphere	Temperature (°C)	Pressure (MPa)	Product Distribution, %		BENZ Conversion (%)	H <sub>2</sub> Accepted per 100 moles of BENZ
				BENZ	DPM		
<b>No Catalyst</b>							
BENZ <sup>b</sup>	N <sub>2</sub>	400	3.3	97.5±0.8	2.5±0.8	2.5	2.5
BENZ	N <sub>2</sub>	440	3.3	98.9±0.0	1.1±0.0	1.1	1.1
BENZ	H <sub>2</sub>	400	3.3	69.4±4.0	30.6±4.0	30.6	30.6
BENZ	H <sub>2</sub>	440	3.3	35.0±6.2	65.0±6.2	65.0	65.0
BENZ	H <sub>2</sub>	440	8.7	22.9±2.5	77.1±2.5	77.1	77.1
BENZ / PHP	N <sub>2</sub>	440	3.3	94.5±0.0	5.5±0.0	5.5	5.5
BENZ / PHP	H <sub>2</sub>	400	3.3	82.6±5.4	17.4±5.4	17.4	17.4
BENZ / PHP	H <sub>2</sub>	440	3.3	51.4±0.4	48.6±0.4	48.6	48.6
BENZ / PHP	H <sub>2</sub>	440	8.7	45.2±1.3	54.8±1.3	54.8	54.8
<b>500 ppm Mo</b>							
BENZ	H <sub>2</sub>	440	3.3	0.0±0.0	100.0±0.0	100.0	100.0
BENZ	H <sub>2</sub>	440	8.7	0.2±0.0	99.8±0.0	99.8	99.8
BENZ / PHP	H <sub>2</sub>	440	3.3	0.2±0.1	99.8±0.1	99.8	99.8
BENZ / PHP	H <sub>2</sub>	440	8.7	9.0±1.3	91.0±1.3	91.0	91.0
<b>1000 ppm Mo</b>							
BENZ	N <sub>2</sub>	400	3.3	97.8±0.5	2.2±0.5	2.2	2.2
BENZ	N <sub>2</sub>	440	3.3	94.2±0.7	5.8±0.7	5.8	5.8
BENZ	H <sub>2</sub>	400	3.3	4.2±0.8	95.8±0.8	95.8	95.8
BENZ	H <sub>2</sub>	440	3.3	0.4±0.2	99.6±0.2	99.6	99.6
BENZ	H <sub>2</sub>	440	8.7	1.8±0.1	98.2±0.1	98.2	98.2
BENZ / PHP	N <sub>2</sub>	400	3.3	92.4±0.0	7.6±0.0	7.6	7.6
BENZ / PHP	N <sub>2</sub>	440	3.3	94.0±0.4	6.0±0.4	6.0	6.0
BENZ / PHP	N <sub>2</sub>	400	8.7	96.2±0.1	3.8±0.1	3.8	3.8

<sup>a</sup> Reaction time = 30 min.

<sup>b</sup> BENZ = benzophenone, PHP = perhydropyrene

<sup>c</sup> H<sub>2</sub> Accepted = H<sub>2</sub> Accepted per 100 moles of BENZ

**Table I. 4. Product Distribution of Perhydropyrene from Thermal and Catalytic Reactions at 400 and 440 °C<sup>a</sup>**

Reaction Conditions	Atmosphere	Temperature (°C)	Catalyst Loading (ppm)	Product Distribution (wt%)			Recovery (%)	PHP Conversion (%)
				PHP	PYR	Others		
Thermal	N <sub>2</sub>	400	0	100.0±0.0	0.0±0.0	0	85.5	0.0
Mo Naph+S	N <sub>2</sub>	400	1000	99.0±0.5	1.0±0.5	0	82.5	1.0
Thermal	N <sub>2</sub>	440	0	99.5±0.8	0.5±0.8	0	88.1	0.5
Mo Naph+S	N <sub>2</sub>	440	1000	94.4±0.1	1.6±0.4	4.0±0.4	82.6	5.6
Thermal	H <sub>2</sub>	400	0	100.0±0.0	0.0±0.0	0	82.1	0.0
Mo Naph+S	H <sub>2</sub>	400	1000	99.8±0.0	0.2±0.0	0	78.3	0.2
Thermal	H <sub>2</sub>	440	0	97.0±0.0	3.0±0.0	0	87.3	3.0
Mo Naph + S	H <sub>2</sub>	440	1000	97.9±0.3	0.4±0.1 <sup>c</sup>	1.7±0.2 <sup>d</sup>	85.8	2.1

<sup>a</sup> Reaction Conditions: 30 min, 8.7 MPa H<sub>2</sub> introduced at ambient temperature. <sup>b</sup> PHP = perhydropyrene; PYR = pyrene. <sup>c</sup> 0.4±1 is the wt % of HHP.

<sup>d</sup> Other unidentifiable peaks.

**Table I. 5. Product Distributions of Perhydropyrene from Reactions of Anthracene with Perhydropyrene**

Reaction Conditions	Catalyst Loading (ppm)	Atmosphere	Reaction Temperature (°C)	Product Distribution (mole %)			Recovery (%)	H <sub>2</sub> Accepted <sup>a</sup> moles of H <sub>2</sub> Accepted per 100 moles of ANI	H <sub>2</sub> Donated <sup>a</sup> moles of H <sub>2</sub> Donated per 100 moles of PHP
				PHP	PYR	Others			
Thermal	0	N <sub>2</sub>	400	100±0	0	0	87.3	0.0±0.0	
MoNaph+S	1000	N <sub>2</sub>	400	99.6±0.5	0.4±0.5	0	82.0	3.2±0.5	
Thermal	0	N <sub>2</sub>	440	98.1±0.5	1.9±0.5	0	83.8	15.2±0.5	
MoNaph+S	1000	N <sub>2</sub>	440	98.8±0.3	1.2±0.3	0	83.9	9.6±0.3	

<sup>a</sup> H<sub>2</sub> Accepted = (1 × DHA mol % + 2 × THA mol %) × 100. <sup>b</sup> H<sub>2</sub> Donated = (8 × PYR mol %) × 100.

Table I. 6. Dehydrogenated Products of PHP from Reactions with PHEN at 400 and 440 °C

Reaction Condition	Reactants	Atmosphere	Temperature (°C)	Product Distribution, %				H <sub>2</sub> Donated
				PHP	DCP	HHP	THP	
Thermal	PHP: PHEN 1:1	H <sub>2</sub>	400	99.7±0.1	0.15±0.0	0.15±0.1	0.0±0.0	1.2
MoNaph + S	PHP: PHEN 1:1	H <sub>2</sub>	400	98.3±0.0	1.2±0.0	0.5±0.0	0.0±0.0	6.1
Thermal	PHP: PHEN 5:1	N <sub>2</sub>	400	98.7±0.0	1.3±0.0	0.0±0.0	0.0±0.0	3.9
MoNaph + S	PHP: PHEN 5:1	N <sub>2</sub>	400	98.7±0.0	1.3±0.0	0.0±0.0	0.0±0.0	3.9
Thermal	PHP: PHEN 5:1	H <sub>2</sub>	400	99.4±0.0	0.6±0.0	0.0±0.0	0.0±0.0	1.8
MoNaph + S	PHP: PHEN 5:1	H <sub>2</sub>	400	98.1±0.0	1.48±0.0	0.38±0.0	0.0±0.0	6.3
Thermal	PHP: PHEN 1:1	H <sub>2</sub>	440	99.7±0.1	0.3±0.1	0.0±0.0	0.0±0.0	0.9
MoNaph + S	PHP: PHEN 1:1	H <sub>2</sub>	440	98.4±0.1	0.8±0.0	0.45±0.1	0.35±0.0	7.5
Thermal	PHP: PHEN 5:1	H <sub>2</sub>	440	99.0±0.0	1.0±0.0	0.0±0.0	0.0±0.0	3.0
MoNaph + S	PHP: PHEN 5:1	H <sub>2</sub>	440	98.5±0.1	1.3±0.1	0.2±0.0	0.0±0.0	4.9
MoNaph + S	PHP: PHEN 5:1	N <sub>2</sub>	440	98.3±0.0	0.6±0.0	0.6±0.0	0.4±0.0	8.0

\* Reaction Conditions: 30 min; 8.7 MPa H<sub>2</sub> or N<sub>2</sub> introduced at ambient temperature; catalyst loading is 1000 ppm Mo on total reactant charge; the total amount of reactant charged is approximately 0.1 g.

b PHP = perhydropyrene, DCP = decahydropyrene, HHP = hexahydropyrene, PYR = pyrene

o H<sub>2</sub> Donated = (8 × PYR mol %) × 100.

Table I. 7. Conversion and Product Distribution of Perhydropyrene from Reactions of Benzophenone and Perhydropyrene<sup>a</sup>

Reactants	Atmosphere	Temperature (°C)	Pressure (MPa)	Product Distribution, %						PHP Conversion (%)	H <sub>2</sub> Donated
				PHP	BCP	HHP	THP	DHP	PYP		
No Catalyst											
BENZ / PHP	N <sub>2</sub>	440	3.3	98.3±0.0	0.6±0.0	0.3±0.0	0.0±0.0	0.3±0.0	0.5±0.0	1.7	9.4
BENZ / PHP	H <sub>2</sub>	400	3.3	99.6±0.0	0.4±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.4	1.2
BENZ / PHP	H <sub>2</sub>	440	3.3	97.0±0.3	0.9±0.1	0.7±0.0	0.7±0.1	0.0±0.0	0.7±0.1	3.0	16.0
BENZ / PHP	H <sub>2</sub>	440	8.7	99.1±0.5	0.6±0.0	0.2±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.9	3.6
500 ppm Mo											
BENZ / PHP	H <sub>2</sub>	440	3.3	96.4±0.3	1.1±0.0	1.3±0.1	0.0±0.0	0.0±0.0	1.2±0.3	3.6	19.4
BENZ / PHP	H <sub>2</sub>	440	8.7	97.8±0.5	0.7±0.0	0.4±0.0	0.3±0.0	0.0±0.0	0.8±0.0	2.2	12.2
1000 ppm Mo											
BENZ / PHP	N <sub>2</sub>	400	3.3	98.1±0.0	0.3±0.0	0.4±0.0	0.2±0.0	0.0±0.0	0.9±0.0	1.9	11.3
BENZ / PHP	N <sub>2</sub>	440	3.3	98.0±0.3	0.3±0.1	0.8±0.1	0.0±0.0	0.0±0.0	0.9±0.3	2.0	12.1
BENZ / PHP	N <sub>2</sub>	400	8.7	97.2±1.5	0.5±0.1	1.5±0.1	0.0±0.0	0.0±0.0	0.8±0.4	2.8	15.4

<sup>a</sup> Reaction time = 30 min.

<sup>b</sup> BENZ = benzophenone, PHP = perhydropyrene, DCP = decahydropyrene, HHP = hexahydropyrene, THP = tetrahydropyrene, DHP = dihydropyrene, PYP = pyrene.

<sup>c</sup> H<sub>2</sub> Donated = moles of hydrogen donated per 100 moles of PHP; H<sub>2</sub> Donated = (3 × DCP mol% + 5 × HHP mol% + 6 × THP mol% + 7 DHP mol% + 8 × PYP mol%) × 100.

Table I. 8. Nickel Octoate Catalysis of Perhydropyrene and Phenanthrene Reactions<sup>a</sup>

Reaction Condition	Reactant	Temperature (°C)	Product Distribution, %			PHEN Conversion (%)	H <sub>2</sub> Accepted <sup>b</sup>
			PHEN	DEPN	EPHN		
PHEN	NiOct	400	98.4±0.4	0.7±0.4	0.9±0.0	1.6	2.5
PHP: PHEN 1:1	NiOct	400	97.9±0.1	1.1±0.3	1.0±0.3	2.1	3.1
PHP: PHEN 5:1	NiOct	400	94.2±0.1	2.0±0.1	3.8±0.0	5.8	9.6
PHP: PHEN 5:1	NiOct	440	87.0±3.4	9.0±1.3	4.0±2.1	13.0	17.0
PHEN	Thermal	400	95.3±0.7	2.6±0.5	2.1±0.2	4.7	6.8
PHP: PHEN 1:1	Thermal	400	97.09±0.2	1.6±0.1	1.4±0.3	3.0	4.4
PHP: PHEN 5:1	Thermal	400	95.4±0.2	1.8±0.4	2.8±0.8	4.6	7.4

<sup>a</sup> Reaction Conditions: 8.7 MPa H<sub>2</sub> pressure introduced at ambient temperature; 30 min.

<sup>b</sup> H<sub>2</sub> Accepted: moles of hydrogen accepted per 100 moles of PHEN.

## Part II

### The Role of the Resid Solvent in the Coprocessing of Coal and Petroleum Resid

#### Introduction

Coprocessing coal and petroleum resid offers an opportunity to upgrade two relatively low value materials simultaneously to higher value products. The question has consistently been asked as to what role the resid solvent plays in coprocessing. The obvious advantages of providing a solvent for the slurry coal and for improving mass transfer of the three phase system are well known but the chemical interaction of the resid solvent with coal is not known and has been the object of this study.

The coprocessing of coal with petroleum resid has been investigated by a number of researchers who have evaluated a number of different coal and resid systems under a variety of thermal and catalytic reaction conditions. The study undertaken in this research was an evaluation of the chemical role of naphthenes present in resids as potential hydrogen donors to coal during coprocessing. Previous research (Owens and Curtis, 1994) has shown that under a N<sub>2</sub> atmosphere naphthenic compounds have the ability to act as H-donors to aromatic species such as anthracene and pyrene and to coal, increasing coal conversion. When naphthenic compounds were ranked with other model compounds as H-donors (Wang and Curtis, 1994), their propensity for donating hydrogen was much less than their hydroaromatic or cyclic olefin analogues. In Part I of this research, the propensity for the naphthenic compound, perhydropyrene, to donate hydrogen was greater under a N<sub>2</sub> atmosphere than under a H<sub>2</sub> atmosphere.

Petroleum resids are generally considered to be poorer solvents for than heavy coal-derived liquids (Tsai et al., 1987; Curtis et al., 1987;). The hydrogen donor ability of resids have been improved by pretreating the resid with a Birch reduction (Olsen et al. 1993; Wang and Curtis, 1984). Further research was performed in this study to examine under equivalent reaction conditions the hydrogen donor ability of the resids using acceptor, anthracene, and reacting each

of the three resids with three different coals and determining the amount of coal conversion. In this study, three petroleum resids and three coal were carefully selected to represent the different types of chemistry and potential interactions that could occur in coprocessing. The coals used were Pittsburgh No. 8, Blind Canyon DECS-17 and Illinois No. 6. The petroleum resids used were Manji, FHC-623, and Maya which had different asphaltene and metal contents. Each of the resids were used as either whole resids or as solubility fractions of hexane solubles or as saturates, chromatographically separated using a silica gel column.

Two sets of reactions were performed: (1) one set involved the reaction of the whole resid and the resid fractions with anthracene and the amount of anthracene conversion and the yield of partially hydrogenated reaction products being determined; and (2) the other involved thermal and catalytic reaction of the whole resid and the resid solubility fractions with coal. The products from the coprocessing reactions of coal and resid were analyzed for their solubility in THF and the THF soluble material were analyzed by simulated distillation. The effect of having a catalyst and a solvent present in the reaction was determined.

### **Experimental**

**Materials.** The coals used in the coprocessing reactions were Pittsburgh No. 8 and Illinois No. 6 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 used as received. Analyses of these coals are given in Table II. 1.

The resids used in the coprocessing reactions were Maya, Manji, and FHC-623, all 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 the whole resid into hexane solubles and insolubles, and then taking the hexane soluble fraction and separating the saturates by preparative liquid chromatography. 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. These analyses are given in Table II. 2.

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.

**Analysis of the Resids and Resid Fractions.** The fractionation of the resids into fractions was accomplished by dissolving 10 g of each resid into 150 mL of hexane and sonicating for 15 min. The solution was centrifuged for 30 min and the hexane solubles were decanted, thereby separating them from the insoluble materials. The procedure was repeated a second and third time. The remaining solids were extracted with toluene and THF sequentially, using the same procedures as was used for hexane. Three other fractions were also obtained: toluene soluble, hexane insoluble material, THF soluble, toluene insoluble and THF insolubles. The fractions obtained in sequence were termed oils, asphaltenes, preasphaltenes, and insoluble organic matter. The solvent from the three soluble fractions were then evaporated using a rotary evaporator; the condensed fractions were collected in flasks and placed in a vacuum oven at 50 °C for 24 hr. The solubility distribution for the different resids is given in Table II.3.

The hexane soluble fraction was further fractionated by preparative liquid chromatography into saturates and aromatics using a method modelled after ASTM D 2549-8. The separation was performed by using a silica gel column and cyclohexane as the eluent. The silica gel was activated in a drying oven at 240 °C for at least 24 hr before use. The Pyrex chromatography column (76 cm in length and 9.5 mm I. D.) was prepared by washing the column with detergent and water and thoroughly rinsing it with distilled water prior to use. The activated silica gel was poured into the Pyrex column with an Al-Mg filter plugging the end, packed by tapping the column gently, and then wetted with solvent.

A model mixture was separated prior to the resids separation to ascertain the efficacy of the procedure for separating saturates which contain naphthenes from aromatics in the hexane solubles. The model system was composed of a mixture of naphthenic and hydroaromatic species including decalin, anthracene, dihydroanthracene, octahydroanthracene, and pyrene. The procedure involved dissolving 5 g of hexane soluble material into 20 ml of cyclohexane and then eluting the solution through a packed column using 200 mL of cyclohexane. The eluate was collected as the saturates. Then 200 mL of chloroform were added to the column and the eluate collected was labeled as aromatics. The fraction collected during the transition when both solvents were present in the column was labeled intermediates. The results from the model compound separation is given in Tables II. 4 a, b, and c.

The hexane soluble fractions of the resids were separated using silica gel as the stationary phase and three eluting solvents: cyclohexane, chloroform, and THF. The procedure was similar to the model system with minor modifications. Two grams of hexane soluble fractions from each of the resids were dissolved in 10 mL of cyclohexane and the solution was placed on the top of the prewetted silica column. An elution sequence of 200 mL cyclohexane, 200 mL chloroform, followed by THF to remove any residuals from the column was performed to obtain saturates, aromatics, and residuals, respectively. The solvents from the eluate fractions were evaporated and the remaining material was vacuum dried at 50 °C for 24 hr. The dried fractions were then weighed and recoveries determined.

The resids and resids fractions were analyzed by  $^1\text{H}$  NMR analysis to obtain information on the types of hydrogen atoms present in each of these materials. Since obtaining direct information on skeletal carbon by using  $^{13}\text{C}$  NMR is very time consuming, the assignment of peaks and the calculation structural parameters were based on the Brown-Ladner method (Brown et al. 1960; Brown and Ladner, 1960) Bartle et al. (1979) compared Brown-Landner method with  $^{13}\text{C}$  NMR spectroscopy and found that the two methods were in agreement and recommended  $^1\text{H}$  NMR for

resid characterization provided that the Brown-Ladner parameters were modified slightly. By applying Brown-Ladner's equation, the skeletal carbon types and contents could be calculated satisfactorily. The chemical shifts and assignments are in Table II. 5.

Theoretically, to apply the Brown-Ladner equations the molecular weight and formula of samples analyzed by  $^1\text{H}$  NMR must be known, for the sample could possibly contain heteroatoms. However, in the case of the resids and resid fractions the heteroatom content (O, N and S) was generally known and usually quite small ( $0 < 1.0$  wt%,  $S \approx 3$  wt%,  $N < 0.5$  wt%). Therefore, a resid molecule model can be represented by assuming that an average molecule contains carbon and hydrogen elements only and that the number of hydrogen atoms is 100. By using this molecular model, the process of characterizing resids is significantly simplified.

The resid molecular model contains the following elements

$$H_{\alpha} + H_{\eta} + H_{\beta} + H_{\tau} + H_{ar} = 100$$

$$C_{al} + C_R = C_E$$

where  $H_{\alpha}$ ,  $H_{\eta}$ ,  $H_{\beta}$ ,  $H_{\tau}$  and  $H_{ar}$  represent different types of hydrogen atom (see the preceding table).

$C_{al}$ ,  $C_R$  and  $C_E$  represent the number of aliphatic, aromatic, and total carbon number, respectively.

According to Brown and Ladner method the alkyl and naphthenic carbon,  $C_{al}$  is given by

$$C_{al} = \frac{H_{\alpha}}{a} + \frac{H_{\eta}}{b} + \frac{H_{\beta}}{c} + \frac{H_{\tau}}{d}$$

In the above equation, a, b, c and d are parameters that relate hydrogen to skeletal carbon, and the parameters are:

$$a = 2.2 - 2.6; b = 1.8 - 2.0; c = 1.8 - 2.8 \text{ and } d = 3$$

Aromaticity, according to the Brown and Ladner method, is defined as:

$$f_a = C_R/C_E$$

where  $f_a$  represents the aromatic carbon content of a resid molecule. Conversely,  $1-f_a$  represents the combined content of naphthenic and paraffinic carbon atoms.

In the current study, a standard mixture of anthracene and hexahydroanthracene, whose compositions and concentrations were known, was analyzed by  $^1\text{H}$  NMR as calibration to examine the validity of operating parameters in Brown-Ladner equation. The percentage of different hydrogen types in the standard, such as aromatic, naphthenic or olefinic hydrogen, were calculated and then compared with the results achieved by  $^1\text{H}$  NMR. The results obtained by  $^1\text{H}$  NMR, which are listed in Table II. 6. agreed well with the theoretical values, demonstrating that Brown-Ladner equation and operating parameters employed in our experiment were appropriate. The  $^1\text{H}$  NMR spectra of the whole resid and resid fractions were performed and analyzed according to the Brown-Ladner method. The analysis was performed by first dissolving 0.01 g of sample (whole resid, hexane solubles and saturates) in 5 ml of  $\text{CDCl}_3$  with 1 wt% of TMS added as an internal marker. The concentration of a sample in  $\text{CDCl}_3$  for  $^1\text{H}$  NMR analysis was approximately 0.002 M. These prepared samples were analyzed using a Bruker AC 250 FT NMR spectrometer. The analytical results of Maya, FHC-623, and Manji are listed in Table II. 7.

**Reaction Procedures for Coprocessing Reactions.** Catalytic and thermal coprocessing reactions were performed using  $\sim 20\text{ cm}^3$  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  $\text{H}_2$  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 by applying the following equations:

$$\text{Conversion} = \left( 1 - \frac{g(IOM)_{maf}}{g(\text{coal charged})_{maf}} \right) \times 100 \%$$

The simplified formulas for the individual coals are given as follows:

Pittsburgh No. 8:

$$\text{Conversion} = \left( 1.102 - 1.120 \times \frac{g(IOM)}{g(\text{coal charged})} \right) \times 100 \%$$

Blind Canyon DECS-17:

$$\text{Conversion} = \left( 1.070 - 1.112 \times \frac{g(IOM)}{g(\text{coal charged})} \right) \times 100 \%$$

Illinois No. 6:

$$\text{Conversion} = \left( 1.183 - 1.286 \times \frac{g(IOM)}{g(\text{coal charged})} \right) \times 100 \%$$

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<sub>2</sub> was shown to be produced under these reaction conditions (Kim et al., 1989). 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  $\mu\text{m}$  coating thickness, 0.33 mm in diameter and 25 m in length. The temperature program started at 60  $^{\circ}\text{C}$  with a final temperature of 320  $^{\circ}\text{C}$  and with a program rate of 2.5  $^{\circ}\text{C}/\text{min}$ . The temperatures of the injector and detector were 320 and 325  $^{\circ}\text{C}$ , respectively. Biphenyl was used as the internal standard.

**Analysis of Reaction Products by Simulated Distillation.** The boiling point distribution of the THF soluble recovered products, resid and/or coal whichever were present as reactants, was obtained by simulated distillation(GC/SD). The sample for GC/SD was prepared by dissolving the recovered product in THF and injecting about 0.5 microliter of the THF solubles into the GC column. The column was temperature programmed starting from 100  $^{\circ}\text{C}$  and ending at 320  $^{\circ}\text{C}$  with a temperature program rate of 2.5  $^{\circ}\text{C}/\text{min}$ . The injected sample volume threshold was chosen such that as many peaks as possible could be detected in the chromatogram. Since the approximate boiling point range of resid was given by the supplier, Amoco, the column programming was designed to observe the gas chromatographic peak of the highest boiling point component in the resid sample.

Coal liquefaction products was also analyzed by GC/SD using the same method; but it was found that the coal liquids generated under the reaction condition used in this research contained very heavy components that were not detectable by GC/SD. Usually only one peak was observed, although for some samples two peaks were obtained. These peaks were subtracted from the GC/SD chromatogram of coprocessing products in order to obtain data that pertained to the resids and resid fractions.

The calibration curve of GC/SD was established by chromatographing an authentic compound mixture containing aromatic and hydroaromatic compounds whose boiling points and amounts were known. To obtain a baseline, the signals from a blank-sample run were subtracted

from the sample signals being run under the same conditions. A linear relation between boiling-point and retention time was achieved.

The validity of the calibration curve was examined by analyzing a standard mixture obtained from Supelco. The standard mixture was characterized by its initial boiling point and correspondent volume distribution of the components present. (Table II. 8.) The boiling points of the authentic compounds and their corresponding samples weight percent that was calculated by interpolation from Table II. 8. is compared in Table II. 9. The comparison clearly demonstrated that GC/SD characterized boiling point distribution of the standard mixture well.

The GC/SD analysis of heavy resid utilized a data sampling system composed of a HP 3396 A integrator and Peak 9600 software. All signals from the flame ionization detector were recorded at a frequency of 5 Hz. Since the total analysis time was 50 min, the total sampling number was 15,000; these signals were transferred to a personal computer and processed using Excel. Cumulative areas of any retention time segment were computed in Excel using Simpson's Method. The boiling point distribution of resids were computed using the retention time versus boiling point analysis of the calibration curve as markers.

### **Results and Discussion**

The goal of the research performed with the coal and resids was to ascertain the interaction between the two materials during coprocessing and to determine if the resids or resid fractions were effective in transferring H or otherwise affecting coal conversion. Three sets of experiments were performed: (1) analysis of the resids and coal prior to coprocessing to determine the type and reactivity of the starting material; (2) reactions of resids and resid fractions with anthracene to determine the amount of H-transfer that occurred from the resid and resid fractions to the anthracene; and (3) reactions of resids and resid fractions to determine the interactions between the solvent medium and coal during coprocessing. The effect of each of these experiments was evaluated in the following ways. The resids and resid fractions were analyzed by simulated

distillation before and after reaction at coprocessing conditions and the differences in the boiling point distribution were determined. The unreacted and reacted coal was analyzed by solubility in THF. The anthracene was analyzed after reaction and the anthracene conversion and the production of partially saturated products were determined in order to ascertain the amount of H-transfer that occurred. In the coprocessing reactions, the amount of coal that was converted to THF soluble products was determined as well as the boiling point distribution of the resid solvent.

**Coal Reactivity in Coprocessing Reactions.** The coals were reacted thermally and catalytically without solvent under coprocessing conditions and their conversions to THF soluble materials were measured. Each of the three coals displayed a different reactivity. Illinois No. 6 displayed the highest thermal coal conversion at 62.8%; Pittsburgh No. 8 yielded 44.8% conversion while Blind Canyon DECS-17 produced the least at 26.4% (Table II. 10). The addition of the slurry phase catalyst Mo naphthenate plus elemental sulfur to the coal reaction without a solvent resulted in different effects of the catalyst on coal conversion depending on the reactivity of the particular coal under these conditions. Pittsburgh No. 8 and Illinois No.6 coals gave similar conversion of 61.7% whereas DECS-17 yielded 45.3%. The catalyst was effective for increasing the conversion for Pittsburgh No. 8 and DECS-17 but not Illinois No.6 coal. The composition, rank, and reactivity of the coals themselves affected their conversion and their response to the Mo naphthenate plus sulfur catalyst.

These reactions performed without a solvent were influenced by limitations in the mass transfer of the gaseous hydrogen and the dispersion of the slurry phase catalyst in the reacting system. The mass transfer of these coal systems at coprocessing conditions can be improved by the inclusion of a solvent. An inert solvent, hexadecane, was added and reacted under thermal and catalytic conditions to test the effect of including a solvent under these reaction on coal conversion. The results from these reactions with the three coals are given in Table II.10 and serve as a base line for the reactions with resid or the resid fractions.

Each of the three coals, Illinois No. 6, Pittsburgh No. 8, and DECS-17 was reacted with each of the resids and resid fractions. The amount of coal conversion to THF solubles was determined and is presented in Table II.10 for reactions with Maya resid and its fractions, in Table II.11 for reactions with FHC-623 resid and its fractions, and in Table II.12 for reactions with Manji resid and its fractions. A summary of the coal conversion obtained using each of the three coals with each of the three resids is given in Table II. 13. This summary allows a direct comparison of the coal conversion obtained to be made among the different combinations of coals and resids.

Both the catalyst and the solvent had an effect on the amount of coal conversion obtained. Pittsburgh No. 8 coal showed the largest effect of the catalyst on conversion regardless of the type of solvent used while Illinois No. 6 coal showed the least. The presence of a solvent was beneficial for almost all of the reactions performed. However, each coal interacted differently with each resid and resid fraction; likewise, a given resid or resid fraction interacted differently with each coal. In the catalytic reactions with Illinois No. 6 coal, Maya resid and its fractions yielded the highest conversion; in catalytic reactions with Pittsburgh No. 8, FHC-623 whole resid was the most effective of all of the whole resids, and, in catalytic reactions with DECS-17 coal, FHC-623 whole resid was the most effective. Typically, the whole resid was most effective solvent for catalytic coal conversion among the three materials used from each resid, the hexane solubles were intermediate and the saturates were least effective, although there were notable exceptions with Manji and DECS-17 coal and FHC-623 and Illinois No. 6 coal. Individual levels of reactivity varied depending upon the specific interactions between the resid and coal during coprocessing.

These effects were explored further by evaluating the effects of the catalyst and solvent individually on coal conversion; these results were calculated and are presented in two separate tables. Table II. 14 presents the effect of the catalyst on coal conversion by comparing the conversion obtained in the catalytic reaction to that obtained in the thermal reaction for each solvent used. Similarly, Table II. 15 presents the effect of the solvent by comparing the conversion

obtained in thermal reactions with a solvent to that obtained in thermal reactions without a solvent. This comparison was also made for catalytic reactions.

*Effect of Catalysis.* The catalysis effect in these coprocessing experiments is defined as the difference in coal conversion to THF solubles between a catalytic reaction and a thermal reaction when all reaction conditions were kept constant ( Table II.14). A large catalysis effect resulted from a strong effect of the catalyst on the reaction system as well as positive interactions between the coal and catalyst or the solvent and catalyst. Similarly, a small catalysis effect resulted from a weak effect of the catalyst on the reaction system and small contributions from the interaction between the coal and catalyst and /or the solvent and catalyst. Although all of the coprocessing reactions showed positive catalysis effects except for one, the amount varied widely in the different reactions, ranging from 3.3% to 54.8%. The one exception was Illinois No. 6 coal that was reacted without a solvent which yielded a -1%, which most resulted from poor dispersion of the slurry phase catalyst in the reaction system.

The catalysis effect was strongly affected by the rank and inherent reactivity of coal used in the coprocessing reactions. Pittsburgh No.8 and Blind Canyon DECS-17 coals exhibited more than twice the activity than did Illinois No. 6 coal. The magnitude of the effect for a given coal is shown in the total column given in Table II.14 which is the sum of all of the catalysis effect for a given coal. The values for Pittsburgh No.8 and DECS-17 were nearly equal totaling 288.8 and 287.6%, respectively, while Illinois No. 6 coal gave a much smaller value of 116%. A partial explanation for these differences is that Illinois No. 6 coal is inherently more reactive than either of the other two coals, showing substantially more thermal conversion. Since the thermal conversion was higher, the catalyst had a smaller effect on the reactions system since the molecular species were already reacting in the thermal environment.

The presence of a solvent and the chemistry of that solvent also affected the activity of the catalyst in the coprocessing reaction systems. Hexadecane, an inert solvent, had a large catalysis

effect with all three coals; hexadecane served as a dispersing medium for the slurry phase catalyst but did not participate in the reaction or deactivate the catalyst. The resid solvents were not necessarily inert in these reactions, having the potential to be upgraded, interact with coal, transfer hydrogen, and poison the catalyst. Even so, when a resid solvent was present, either the whole resid or its hexane soluble or saturate fraction, the catalysis effect was different than that in the coal reaction without solvent.

The three resids and their fractions exerted unique effects on each coal in terms of the effect of catalysis. For example, when Maya resid and its fractions were coprocessed with Pittsburgh No.8 and DECS-17 coals, the whole resid displayed a higher catalysis effect than either the hexane soluble or saturate fractions. By contrast, when Maya was coprocessed with Illinois No. 6 coal the hexane soluble fraction yielded the highest catalysis effect. In coprocessing reactions of all three coals with FHC-623 resid and its fractions, the saturates displayed the greatest catalysis effect for Pittsburgh No. 8 and DECS-17 while the saturates displayed the highest catalysis effect for Illinois No. 6 coal.

*Solvent Effect.* The solvent effect in these coprocessing reactions is defined as the difference between the coal conversion to THF solubles when the coal was reacted alone and when coal was reacted with a solvent under equivalent reaction conditions. Table II.15 presents the changes in conversion caused by the addition of the solvent. The positive numbers in the table indicate an increase in coal conversion resulting from the addition of the solvent while the negative numbers represent a decrease in coal conversion.

When the base line solvent hexadecane was added to the coal reactions, all of the coal conversions increased except for the thermal reaction with Illinois No. 6 coal. The amount of the increase caused by introduction of hexadecane varied according to the coal present in the reaction. The reaction of hexadecane and DECS-17 coal, little interaction among hexadecane, coal and catalyst was observed, for the solvent effect was 5.5% percent for thermal reaction and 3.1%for

catalytic reaction. Both of these values are within experimental error. However, when reacted with Pittsburgh No. 8 coal, hexadecane displayed higher solvent effect in the catalytic reactions than in the reactions giving values of 23.3% and 14.3%, respectively. The solvent's presence provides a medium for the dissolution of H<sub>2</sub> gas and as such provide for better contact between the dissolving coal molecules and the H<sub>2</sub> molecules. However, the effect of hexadecane on the thermal reaction and conversion of Illinois No. 6 coal was negative, indicating that hexadecane suppressed any hydrogen transfer or positive reactions between the hydrogen-rich and hydrogen deficient portions of the coal as well as serving as an antisolvent for the dissolution of Illinois No. 6 coal. Hexadecane increased the amount of catalyst dispersion in the catalytic Illinois No. 6 reaction and resulted in higher coal conversion.

The reactions of the resids and the resid fractions with the different coals were unique indicating that the interactions were specific in terms of the chemistry and composition of the solvent and coal involved in the coprocessing reactions. The specifics of the interactions between the resids and resid fractions and each coal are described separately for each resid type.

*Coprocessing of Maya Resid and its Fractions with Coal.* The addition of Maya whole and the hexane soluble fraction increased the conversions of all three coals, except for the thermal reaction with Illinois No. 6 coal which showed a small negative value that was within experimental error of being zero. By contrast, the saturate fraction decreased coal conversion of Pittsburgh No. 8 and Illinois No.6 compared to reactions without solvent, indicating that the saturate fraction served as antisolvent in the reactions. The catalytic reactions with the whole resid showed a larger solvent effect than the thermal reactions. For the reactions with the Maya hexane soluble fraction, reactions with Pittsburgh No.8 and Illinois No.6 gave increased solvents effects with reacted catalytically rather than thermally. The opposite was true for DECS-17 coal. The fact that these hexane solubles reacted so differently with the three coals indicated that the chemistry of the Maya hexane solubles interacted differently with the chemistry of the three coals and affected the activity

of the catalyst in the individual systems. In summary, Maya whole resid and its fractions interacted with the coal and catalyst during the coprocessing reaction, for some promoting the reaction and conversion of the coal and for others being detrimental to the conversion of the coal.

*Coprocessing of FHC-623 Resid and its Fractions with Coal.* FHC-623 whole resid and its fractions showed a higher solvent effect for converting coals, especially in coprocessing reactions with DECS-17 coal. The differences in the solvent effect between the thermal and catalytic were less with FHC-623 systems than in the Maya systems. The FHC-623 hexane solubles showed less effect of the solvent than did the whole resid for correspondent reactions. In the Pittsburgh No.8 coprocessing system, the hexane solubles had essentially no effect on the conversion in either the thermal or catalytic reaction. In the Illinois No. 6 system, the solvent effect in the thermal reaction was small while the catalytic system gave a positive effect of 17.4. FHC-623 hexane solubles influenced both the thermal and catalytic DECS-17 reactions substantially, giving solvent effects of 17.2 and 18.1, respectively. By contrast to the solvent effect displayed by the FHC-623 whole resid and hexane solubles, the saturates yielded negative solvent values for Pittsburgh No. 8 and Illinois No.6 and low positive values for DECS-17. For all coals, the thermal values for the saturates were lower than the catalytic values indicating that there was some positive interactions among the coal, solvent, and catalyst.

*Coprocessing of Manji Resid and its Fractions with Coal.* Manji whole resid and its fractions showed strong coal-solvent-catalyst interaction; in each Manji solvent with each coal, the solvent effect was substantially more in the catalytic than in the thermal reactions. In all of the thermal reactions except one, the solvent effect was negative indicating that Manji whole resid and its fractions were detrimental to coal conversion compared to the conversion obtained without solvent. The saturate fraction was the least effective solvent and yielded the most negative solvent effect for each coal. The one exception was the thermal reaction with whole Manji resid and Illinois No. 6 coal, but in that case the positive value was 2.0 which was within experimental error of

having no effect. The catalytic reactions showed positive solvent effects except for the saturate fraction with Pittsburgh No. 8 coal, which gave a value of -21.4. The other catalytic systems yielded solvent effects that were substantially higher than the thermal; one notable synergetic effect was the interaction between the hexane soluble fraction and DECS-17 coal. This solvent effect was 33.4 which was the highest of any the solvent effects obtained, indicating that the hexane solubles interacted positively with the coal and catalyst.

**Summary of Coal and Resid Coprocessing Reactions.** The coal and resid coprocessing reactions clearly showed the positive effect of having Mo naphthenate catalyst present on coal conversion to THF solubles. Strong interactions occurred among the coal, catalyst, and solvent, regardless of the type of the solvent, hexadecane, resid, or resid fraction. The presence of a solvent increased the catalyst's efficiency by providing adequate mass transfer conditions. The ability of the resids or resid fractions to influence positively the conversion of the system was affected by the chemistry and composition of the resid medium. The saturates fraction was detrimental to coal conversion while the hexane soluble fraction was much more conducive to providing a good medium for converting coal. Similarly, the chemistry and composition of the coal in conjunction with the resid solvent affected coal conversion. Of the three coals tested, DECS-17 was the least susceptible to solvent-coal interactions while the conversion of Pittsburgh No.8 and Illinois No.6 coals was the most influenced by the solvent-coal interactions.

**Coprocessing of Resid with Anthracene.** In order to more fully understand the effect of the composition of each of the resids and resid fractions on the conversion, each resid and resid fraction was reacted with the model acceptor, anthracene (ANT). The amount of hydrogen transfer from the resid or resid fraction to ANT was determined by analyzing the amount of ANT conversion and the amount of hydrogenation to partially hydrogenated products. The products observed from ANT hydrogenation were dihydroanthracene (DHA) and tetrahydroanthracene (THA) with DHA being the predominant product. The amount of hydrogen transferred to the ANT

from the resid was calculated by determining the moles of H<sub>2</sub> accepted by ANT in terms of its partially hydrogenated products. The H<sub>2</sub> accepted by ANT is presented in terms of the amount accepted per 100 moles of starting ANT.

The reactions of ANT with resid or resid fractions were performed thermally and catalytically in a H<sub>2</sub> atmosphere at 400 °C for 30 min. The ANT product distributions and the H<sub>2</sub> accepted per 100 moles of ANT are given in Table II. 16. In addition, reactions of ANT with perhydropyrene (PHP) and hexadecane (HEX) individually and ANT alone are presented to provide a baseline for analyses. For comparisons H<sub>2</sub> acceptance data and the conversion of ANT are compared in Table II. 17.

The amount of H<sub>2</sub> accepted by ANT from the resid and resid fractions was dependent on the reactions conditions. In the thermal reactions, the maximum amount of H<sub>2</sub> accepted by ANT was in the reaction with FHC-623 whole resid where 96.9 moles of H<sub>2</sub> was accepted per 100 moles of ANT while the minimum was in the reaction with Manji hexane solubles where 47.9 moles were accepted. The range between the maximum and minimum was much smaller in the catalytic reactions than in the thermal, indicating that the catalyst influenced the hydrogenation reaction regardless of the solvent present. In the catalytic reactions ANT accepted the maximum amount of H<sub>2</sub> when reacted with the Maya hexane solubles where 111.7 moles were accepted and the minimum (95.7 moles) when reacted with Manji saturates.

The amount of H<sub>2</sub> accepted by ANT was also dependent on the composition of the resid solvent. The saturate fraction showed the least propensity for donating hydrogen to ANT when compared to the whole resid and the hexane soluble fraction. The saturate fraction contained the least amount of aromatic material and the highest proportion of saturated aliphatic compounds of the three materials. Although the composition of the resid saturate fraction varied among the three resids used, each of the three resids exhibited the same order of hydrogen donor propensity and

order of solvating ability based on the amount of H<sub>2</sub> accepted by ANT. The order was hexane solubles > whole resid > saturates.

Of the three resids, the behavior of Mnaji was unique. In the catalytic reactions with whole Manji resid and the two fractions ANT accepted a similar amount of H<sub>2</sub> as the as the other three resids. However, when Manji whole resid and its fractions were reacted thermally with ANT, ANT accepted markedly less H<sub>2</sub> than when ANT was reacted with Maya and FHC-623 and their respective fractions. Similar results were obtained from the reactions with Pittsburgh No.8 and DECS-17 coals.

The previously stated order reflected the effect of each resid material's composition on the ability of ANT to accept hydrogen and be hydrogenated in these reactions. The whole resid contained the asphaltene fraction composed of larger molecules that have higher aromaticity and heteroatom and metal contents. These compounds are consumers of hydrogen at these reaction conditions and compete for H<sub>2</sub> being donated from other parts of the resid and from molecular H<sub>2</sub>, thereby reducing the amount of H<sub>2</sub> available to ANT. By contrast, the asphaltenes had been removed from the hexane soluble fraction, leaving aromatic, hydroaromatic and saturated compounds. Since the asphaltenes were not present, the competition for H<sub>2</sub> was less than in the whole resid and any detrimental effects that the asphaltenes had on the catalyst were also removed. The saturates, by comparison, were less effective solvents for ANT since they contained less aromatics and hydroaromatic compounds that would solvate and transfer H<sub>2</sub> to ANT. The saturates contained the largest proportion of aliphatic and naphthenic compounds of the three resid materials and, thereby, did not provide as effective a solvating medium for ANT and less H<sub>2</sub> for transfer.

Thermal and catalytic reactions in which ANT was reacted alone and with either PHP or HEX were also performed in order to provide a comparison to the resid solvents. As was observed in Part I of this report, ANT hydrogenated more when ANT was reacted alone without a solvent. The addition of a solvent decreased the amount of hydrogenation from molecular H<sub>2</sub> because of a

dilution effect. The addition of HEX to ANT resulted in lower amounts of H<sub>2</sub> accepted by ANT in both the thermal and catalytic reactions compared to that in the ANT alone reaction. Hexadecane is a straight alkane that is basically nonreactive at 400 °C and does not have any propensity to donate or transfer H<sub>2</sub> under these reaction conditions. The amount of H<sub>2</sub> accepted by ANT per 100 moles of ANT when reacted with ANT was 89 moles for the thermal reaction and 108.9 for the catalytic reaction. These values can be considered the baseline values for ANT reactions at these reaction conditions with a nonreactive and nonhydrogen consuming solvent. The addition of PHP, a naphthene, to the ANT reaction under the same reaction conditions showed higher levels of H<sub>2</sub> acceptance in both thermal and catalytic reactions. In the thermal reaction 103.9 moles of H<sub>2</sub> and in the catalytic reaction 120.9 moles of H<sub>2</sub> was accepted per 100 moles of ANT. If the reaction of HEX with ANT is accepted as a baseline reaction for reactions of H<sub>2</sub> within a solvent system, then the reaction with PHP showed H-transfer between PHP and ANT. Since none of the detrimental chemical components or chemical competitors were present in PHP, higher ANT conversion and more hydrogenation to partially saturated products occurred. In fact, the reaction of ANT with PHP yielded the highest conversion to THA of any of the catalytic reactions of ANT with a solvent regardless of the solvent type.

**Summary of the Anthracene Reactions.** The presence of the resid solvents increased ANT conversion compared to the reaction of ANT alone under equivalent conditions. The addition of Mo naphthenate plus sulfur as a catalyst increased ANT conversion compared to no catalyst being present, whenever a solvent was used, either HEX, PHP or the resids. Resids undergo some of the same types of reactions that coal undergoes during coprocessing including hydrogenation, hydrocracking, heteroatom removal, and isomerization. Since coprocessing inevitably changes the chemical composition and size of the resid molecules, some of the changes that occur during coprocessing can be examined by analyzing the boiling point distribution of the resid or resid fraction before and after the coprocessing reaction.

**Boiling Point Distributions of Resids and Resid Fractions.** In this study, the boiling point distribution of the three whole resids and their respective fractions before and after reaction were determined. The boiling point distribution is defined as the percent of resid components with boiling point temperatures at certain temperature and gives a measure of the proportion of heavy and light compounds in a resid. When the heavier compounds of a resid are cracked or hydrocracked to form lighter components, the resid shows a higher proportion of its components at lower boiling point ranges and is said to be upgraded.

The petroleum resids used in this study (Maya, FHC-623, and Manji) were heavy vacuum resids with 97% of the material having boiling points over 1000 °F (537 °C) according to Amoco, the supplier of these resids. Since these resids are so heavy, substantial amounts of the resids will be retained on the gas chromatographic column used in the simulated distillation analysis used to determine the boiling point distribution. Only the lighter components can elute from the column and, therefore, the recovery of the resids from the gas chromatographic column was limited. The recovery of the resids and the resid fractions from the column was determined by using biphenyl as an internal standard. Prior to analysis, the resid and biphenyl were carefully weighed. The sample was then injected in to the gas chromatograph for simulated distillation analysis and the areas of biphenyl and of the resids were measured by an integrator. The recovery was calculated using the internal standard method with biphenyl as the internal standard. The data obtained from the simulated distillation analysis was sampled and transferred by using Peak 96 which was obtained from Hewlett Packard. All signals from the gas chromatograph were sampled at a frequency of 5 Hz. A calibration curve was developed that assigned retention times to boiling point temperatures. The spreadsheet program Excel was used to compute the cumulative area and the area ratio of any desired temperature segment. The boiling point ranges of the eluant of the coprocessing products are listed in Tables II. 18 and 19.

When the temperature program was properly set up and the analysis was correctly performed, the tail at the end of the chromatogram became smooth and sloped downward becoming gradually horizontal. That behavior indicated that all of the volatile components of resid had eluted from the column. The fraction remaining in the column consisted of heavy components with boiling points above the specified temperature as determined by the calibration curve. Therefore, the boiling point distribution that was obtained was of the eluant from the column which was only a small portion of the total sample. Most of the sample was retained on the column.

Boiling point distributions for the entire resid were calculated by multiplying the recovery by the boiling point distribution obtained from the eluant. Tables II.17 and 18 give the raw data for the boiling point distribution curves from the analysis of Maya resid and the reaction products from coprocessing reactions of Maya resid and coal. Tables 19 and 20 are derived from Tables II.17 and 18; the values were obtained by multiplying the recovery of each resid from the chromatography column with each number in the same row.

In this work a resid is defined as being upgraded if the resid contains more light (low boiling) components after coprocessing than before coprocessing as measured by the boiling point distribution. The boiling point distributions of the different coprocessing reactions are shown in Figures II.4 to II.36. In Figures II.1 and II.2 the boiling point distributions are given for thermal and catalytic coprocessing reactions of Maya resid and resid fractions with DECS-17 coals. The boiling point distributions of resids and resid fractions before and after coprocessing reactions with coal are given in Figures II.3 through II.14. Figures II.15 through II.23 describe the boiling point distribution of each resid and its respective resid fractions with each coal. In Figures II.24 through II.33 the boiling point distributions of the different resids and resid fractions after being coprocessed with the same coal are given.

The boiling point distribution of the resids and their fractions differed from each other because of their different compositions; however some common characteristics were observed

among them. (1) First, prior to reaction, the boiling point distribution of the resids and resid fractions showed the same order of the proportion of light components contained within each material. The fractions were ranked in order of light components as saturates > hexane solubles > untreated whole resids. This ranking showed that the saturates and hexane solubles contained a higher proportion of lighter species than did the parent whole resids, indicating that the separation process removed the lighter components from the resid. (2) Second, the boiling point distributions of all resids and resid fractions after coprocessing reactions shifted toward lower point ranges compared to the corresponding unreacted fraction. This result indicated that the larger molecules in the resid and resid fractions were broken down into smaller molecules during the reaction. (3) Third, the type and rank of coal affected the resid upgrading process and resulted in different boiling point distributions from a given resid. Coprocessing reactions of whole resids with DECS-17 coal resulted in the most upgrading of the resid. DECS-17 was also the least reactive coal, indicating that it competed less for the hydrogen, regardless of type in the system allowing the resid to utilize the hydrogen.

The boiling point distributions given in Figures II.15 through II.23 present the coprocessing result of each resid and resid fraction with the three coals. The amount of resid upgrading that occurred depended upon the type and rank of the coal. The order of a given resid and resid fractions upgrading varied according to the type of coal used in the coprocessing reaction. For example, upgrading of Manji resid after reaction with Illinois No. 6 coal ranked in the order of saturates > hexane solubles > whole resid, while the order was reversed for the reaction of Manji with DECS-17 coal. The same types of results were obtained with Maya and FHC-623. The conclusion can be made that coal-resid interactions not only influenced the amount of coal conversion achieved but also influenced the amount of resid upgrading that occurred.

The influence of resid compositions on the boiling point distributions from different resids and resid fractions after being reacted with the same coal are displayed in Figure II.24 through

II.33. The proportion of light components contained in the whole resids after coprocessing were in the order of Manji > Maya > FHC-623; a similar ranking occurred for the hexane solubles and saturate fractions. Although there were differences among the proportion of light components present in correspondent resids and resid fractions, the actual amount of material that eluted from the column in the 300 to 700 °C range was very similar. The differences of light component proportions between various resid fractions were usually less than 15 percentage points, and some were very small, close to zero.

**Summary of the Boiling Point Distributions.** The whole resid was the most reactive fraction in upgrading coal, in terms of promoting coal conversion. The source of the resid's ability to convert coal most likely came from the whole resid's chemical composition and aromaticity as well as its hydrogen donor or shuttling capability. The whole resids converted to lower boiling point material by hydrocracking and hydrogenation in the hydrotreating environment of the coprocessing system.

Fractionation of the resids by solvents and chromatographic separation resulted in two fractions including hexane solubles in which the asphaltenes were removed but contained a substantial amount of aromatic compounds and the other fraction in which the hexane solubles were further separated by a silica gel column into saturates which still contained some aromatics but less than in the hexane solubles. The saturate fraction which contained a substantial portion of saturated and naphthenic compounds was the least reactive of the three resid materials. The reactions with ANT also showed that the saturate fraction was the least likely to donate hydrogen. The hexane soluble fraction contained more aromatics than did the saturates and by proportion less saturated and naphthenic compounds. The hexane solubles showed the maximum ability to donate hydrogen to ANT but in coprocessing with coal only showed an intermediate activity for converting coal.

The resids and resid fractions participated in the reaction with coal during coprocessing in the sense that the resid molecules were mutually upgraded and some hydrogen transfer occurred.

The conclusion was based on the reactions performed between the resids and resid fractions and ANT. The resid solvent strongly affected the conversion of coal in the coprocessing reactions but, by contrast, the resids and resid fractions were upgraded forming lighter products during coprocessing. This upgrading occurred regardless of the coal present. All resid and resid fractions after coprocessing consisted of similar proportions of light components in the range of 300 to 700 °C. When the resids and resid fractions were compared before and after coprocessing, the resids showed substantial upgrading, resulting in the production of much lighter species from the resid.

### **Summary and Conclusions**

Coal and resid coprocessing reactions were performed thermally and catalytically to evaluate the effect of the resid solvent on coal conversion to THF solubles. The catalyst, Mo naphthenate plus sulfur, increased the amount of coal conversion in comparison to the thermal reactions, particularly when a solvent was present. The solvent increased the catalyst's efficiency by dispersing the slurry phase catalyst so that the catalyst was more accessible to the dissolving coal molecules and the upgrading resid molecules. Even with the catalyst present, the type of coal and the resid chemistry and characteristics affected the amount of coal conversion under the conditions typically used for coprocessing. The resids used were the whole resid and fractions separated into hexane solubles and saturates. The saturate fractions from all three resids was the least effective for converting coal during coprocessing compared to the whole resid and the hexane solubles from the resid. The whole resid and hexane solubles behaved similarly in terms of converting coal to THF solubles.

The chemical composition of the resids affected the amount of coal conversion as well as the overall reactivity of the coprocessing system. The coal solvating characteristics of each resid and resid fraction were influenced by the aromaticity of the resid and the amount of heavy components in the solvent as demonstrated by the coal conversion achieved with the three whole resids and their respective hexane soluble fractions. The resid solvents showed limited ability to donate hydrogen

in reactions with ANT. The resids and resid fractions influenced the degree of saturation achieved in the ANT hydrogenation reaction. When resid were present, lesser amounts of THA were produced than when ANT was reacted alone or with PHP as a model naphthene donor. The suppression of THA production may have resulted from the competition that the resids displayed for the molecular H<sub>2</sub> or may have resulted from catalyst poisoning caused by the resids' heavier components.

The whole resids and their fractions were upgraded under coprocessing conditions, both in the presence of coal and in the absence of coal. When the degree of upgrading was measured in terms of the boiling point distribution, the whole resids and the resid fractions each showed a higher proportion of lower boiling constituents after reaction. The extent of upgrading of the whole resid and resid fractions were similar. The similar boiling point distributions of the whole and resid fractions indicated that the coal type and coal-resid interactions did not have a substantial influence upon resid upgrading. The resid as a solvent did not readily donate H<sub>2</sub> to coal, but because the resid was upgraded simultaneously with coal, the lower boiling point products from both materials contributed to the products produced. Coprocessing resulted in a higher quality end product that contained a higher hydrogen content, than the products obtained from direct liquefaction.

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**Table II. 1. Analysis of Pittsburgh No. 8, Blind Canyon DECS-17 and Illinois No. 6**

	Pittsburgh No. 8	Blind Canyon DECS-17	Illinois No. 6
<b>Proximate Analysis, % (As Received)</b>			
Moisture	1.65	3.74	7.97
Ash	9.1	6.32	14.25
volatile Matter	37.2	45.0	36.86
<b>Ultimate Analysis (maf basis), wt%</b>			
Carbon, %	83.2	82.1	77.67
Hydrogen, %	5.3	6.2	5.00
Nitrogen, %	1.6	1.4	1.37
Chlorine, %	0.12	0.12	0.06
Pyritic Sulfur, %	1.4	0.02	2.81
Sulfate Sulfur, %	0.01	0.01	0.01
Organic Sulfur, %	0.8	0.41	2.01
Oxygen, %	8.83		13.51
H/C ratio	0.77	0.91	0.77
Dry Btu	13629	13826	11951
Rank	HVB	HVBA	HVB
Fe, (Calculated from FeS <sub>2</sub> )	1.23	0.01	2.46

**Table II. 2. Analysis of Maya, FHC-623 and Manji Resids**

Elemental Analysis	C, %	H, %	S, %	NL, ppm	Y, ppm	H/C
Maya Whole	83.7	9.8	4.68	118	680	1.41
Maya Hexane Solubles	83.8	10.8	4.11	94	140	1.55
Maya Saturates	82.23	9.95	3.63	131	724	1.45
FHC-623 Whole	84.2	10.4	3.73	84	240	1.48
FHC-623 Hexane Solubles	84.5	11.1	3.27	93	93	1.57
FHC-623 Saturates	84.05	11.76	3.14	18	81	1.68
Manji Whole	84.15	10.80	2.63	222	235	1.54
Manji Hexane Solubles	84.40	11.03	2.62	170	160	1.57
Manji Saturates	84.51	11.16	2.27	170	190	1.58

**Table II. 3. Fractions of Maya, FHC-623 and Manji Resids**

	Hexane Solubles	Toluene Solubles	THF Solubles	Recovery (%)
Maya	62.9(1.1)	37.1(1.1)	0.0(0.0)	99.8(0.9)
FHC-623	83.3(1.1)	14.9(0.4)	1.8(0.8)	99.9(0.9)
Manji	86.2(0.7)	13.9(0.7)	0.0(0.0)	99.9(0.7)

**Table II. 4a. Composition of Model Mixture**

compositions	DEC	DHA	HHA	ANT	PYR
wt%	40.4	15.1	15.0	14.4	15.1

Note:saturate: DEC=decalin;  
hydroaromatics:DHA=dihydroanthracene; HHA=hexahydroanthracene;  
aromatics: ANT=anthracene; PYR=pyrene;  
mixture amount=2.0012 g;  
saturate=40.4%, hydroaromatics=30.1%, aromatics=29.5%

**Table II.4b. Distribution of Model Mixture Components after Chromatographic Separation\***

Fractions	DEC	DHA	HHA	ANT	PYR	Total
Saturates <sup>b</sup>	99.0%	-	-	-	1.0%	100%
Intermediates <sup>c</sup>	54.5%	7.9%	15.2%	7.4%	14.9%	99.9%
Aromatics <sup>d</sup>	1.35%	26.0%	23.8%	24.9%	23.9%	99.9%
Component Recovery%	100	98.4	98.2	98.6	100	

column length = 76 cm; silica gel loading = 36 g.

<sup>b</sup> Saturates are compounds eluted with cyclohexane.

<sup>c</sup> Intermediates are compounds eluted when chloroform begins eluting.

<sup>d</sup> Aromatics are compounds eluted with chloroform only; all cyclohexane has been removed from the column.

**Table II. 4c. Fractional Distribution Model Mixture**

	Fractions		
	Saturates	Intermediates	Aromatics
Theoretical wt% of Fractions	40.4		59.6
Recovered wt% of Fractions	32.4	14.4	53.1
wt% of Saturated Component Recovered in each Fraction	80.0	19.2	10.9
wt% of Aromatic Component Recovered in each Fraction	1.1	10.9	87.8

Table II. 5. Structural Parameters from <sup>1</sup>H NMR

Sample	C <sub>E</sub> '	H <sub>E</sub> '	C <sub>A</sub> '	C <sub>R</sub> '	f <sub>a</sub>
Maya whole resid	71.71	100.04	42.52	29.19	0.41
Maya hexane solubles	65.03	100.04	42.41	22.62	0.35
Maya saturate fraction	63.91	99.96	42.73	21.18	0.32
FHC-623 whole resid	68.18	100.00	40.99	27.19	0.39
FHC-623 hexane solubles	64.13	100.05	41.79	22.34	0.32
FHC-623 saturate fraction	60.57	100.00	43.22	17.35	0.28
Manji whole resid	67.69	100.00	35.20	31.86	0.46
Manji hexane solubles	63.77	100.00	35.08	28.15	0.44
Manji saturate fraction	63.10	100.00	35.50	27.04	0.42

Note: C<sub>E</sub>' = Total carbon number of an averaged molecule.  
H<sub>E</sub>' = Total hydrogen number of an averaged molecule.  
C<sub>E</sub>' and H<sub>E</sub>' are normalized by setting H<sub>E</sub>' = 100 per molecule.  
C<sub>A</sub>' = Alkyl and naphthenic carbon number of an average molecule.  
C<sub>R</sub>' = Aromatic and ring joining carbon number of an averaged molecule.  
f<sub>a</sub> = Aromaticity, defined as C<sub>R</sub>'/C<sub>E</sub>'

**Table II. 6. Calibration of <sup>1</sup>H NMR Analysis**

Hydrogen Type	Theoretical Concentration	<sup>1</sup> H NMR results	Error
attached to a aromatic ring	37.9%	37.6%	0.3%
attached to a C=C bond	15.5%	15.3%	0.2%
naphthenic	46.6%	47.1%	0.6%

Note: the composition of standard:

Anthracene=49.45 mol%, hexahydroanthracene=50.55 mol%

**Table II. 7. Structural parameters from <sup>1</sup>H NMR**

Sample	C <sub>E</sub>	H <sub>E</sub>	C <sub>A</sub>	C <sub>R</sub>	f <sub>A</sub>
Maya whole resid	71.71	100.04	42.52	29.19	0.41
Maya hexane solubles	65.03	100.04	42.41	22.62	0.35
Maya saturate fraction	63.91	99.96	42.73	21.18	0.32
FHC-623 whole resid	68.18	100.00	40.99	27.19	0.39
FHC-623 hexane solubles	64.13	100.05	41.79	22.34	0.32
FHC-623 saturate fraction	60.57	100.00	43.22	17.35	0.28
Manji whole resid	67.69	100.00	35.20	31.86	0.46
Manji hexane solubles	63.77	100.00	35.08	28.15	0.44
Manji saturate fraction	63.10	100.00	35.50	27.04	0.42

Note: C<sub>E</sub> = Total carbon number of an averaged molecule.

H<sub>E</sub> = Total hydrogen number of an averaged molecule.

C<sub>E</sub> and H<sub>E</sub> are normalized by setting H<sub>E</sub> = 100 per molecule.

C<sub>A</sub> = Alkyl and naphthenic carbon number of an average molecule.

C<sub>R</sub> = Aromatic and ring joining carbon number of an averaged molecule.

f<sub>A</sub> = Aromaticity, defined as C<sub>R</sub>/C<sub>E</sub>

Table II. 8. ASTM D2887-89 Consensus Values

sample volume %	ASTM consensus b.p. (°C)
initial boiling point	114
5	142
10	169
15	196
20	220
30	257
40	287
50	312
60	331
70	354
80	376
85	389
90	404
95	425
final boiling point	475

Data from Supelco Company.

Table II. 9. Calibration of Simulated Distillation

RT (min)	b.p.(°C)	sample wt%		reference chemical
		std <sup>a</sup>	std <sup>b</sup>	
3.45	193	15	17.0(0.4) <sup>c</sup>	cis-decalin
5.92	255	30	31.5(3.2)	biphenyl
7.35	284	40	36.3(3.4)	bibenzyl
9.23	305	45	49.6(1.2)	benzophenone
11.2	340	65	61.6(0.7)	anthracene
15.0	392	85	83.1(0.7)	pyrene
18.12	448	96	93.8(0.6)	chrysene

- Using calibration curve to analyze standard mixture.
- data provided with standard mixture. Some points are rounded.
- analyzed with calibration curve.
- mean(std) calibration curve:  $b.p. (°C) = 16.58 \times RT(\text{min}) + 150.81$

**Table II. 10. Complete Reaction Matrix of Maya Resid with Coals**

Reactants	Reaction Conditions	Product Distribution (wt%)		Coal Conversion (wt%)	Recovery (wt%)
		THF Solubles	ICM		
<b>Pittsburgh No. 8 Coal</b>					
Coal	thermal	41.6(1.9)*	58.4(1.9)	44.8(2.1)	95.9
Coal	catalytic	56.7 (3.8)	43.3(3.8)	61.7(4.2)	96.9
Coal + Hexadecane	thermal	54.4 (4.2)	45.6(4.2)	59.1(4.7)	84.7
Coal + Hexadecane	catalytic	77.4 (2.9)	22.6(2.9)	84.9(3.3)	98.1
Coal + Whole Resid	thermal	51.8 (4.6)	48.2(4.6)	56.2(5.2)	90.4
Coal + Whole Resid	catalytic	81.3 (1.0)	18.7(1.0)	89.3(1.1)	96.7
Coal + Hexane Solubles	thermal	45.5 (2.0)	54.5(2.0)	49.2(2.2)	92.9
Coal + Hexane Solubles	catalytic	75.6 (2.2)	24.4(2.0)	82.9(2.2)	88.9
Coal + Saturate Fraction	thermal	34.8 (1.3)	65.2(1.3)	37.2(1.4)	89.3
Coal + Saturate Fraction	catalytic	55.0 (1.3)	45.0(1.3)	59.8(1.4)	95.0
<b>Blind Canyon (DECS-17) Coal</b>					
Coal	thermal	27.5 (0.3)	72.5(0.3)	26.4(0.4)	87.4
Coal	catalytic	44.5 (0.6)	55.5(0.6)	45.3(0.8)	89.3
Coal + Hexadecane	thermal	32.5(0.5)	67.5(0.5)	31.9(0.6)	86.7
Coal + Hexadecane	catalytic	47.3 (1.0)	52.7(1.0)	48.4(1.1)	82.8
Coal + Whole Resid	thermal	31.8 (1.9)	68.2(1.9)	31.2(2.2)	80.0
Coal + Whole Resid	catalytic	61.3 (2.0)	38.7(2.0)	64.0(2.3)	87.3
Coal + Hexane Solubles	thermal	40.0 (0.6)	60.0(0.6)	40.5(0.7)	87.4
Coal + Hexane Solubles	catalytic	48.0 (0.2)	52.0(0.2)	49.2(0.2)	91.8
Coal + Saturate Fraction	thermal	34.4 (1.6)	65.6(1.6)	37.7(1.8)	91.3
Coal + Saturate Fraction	catalytic	58.0 (1.6)	42.0 (1.6)	60.3(1.7)	96.1
<b>Illinois No. 6 Coal</b>					
Coal	thermal	56.8(0.6)	43.2(0.6)	62.8(0.8)	84.2
Coal	catalytic	56.0(1.3)	44.0(1.3)	61.8(1.6)	88.6
Coal + Hexadecane	thermal	44.3(0.7)	55.7(0.7)	46.7(0.9)	79.4
Coal + Hexadecane	catalytic	64.5(0.6)	35.5(0.6)	72.7(0.8)	82.0
Coal + Whole Resid	thermal	55.8(1.1)	44.2(1.1)	61.4(1.3)	86.9
Coal + Whole Resid	catalytic	59.3(2.8)	40.7(2.8)	65.9(2.8)	88.5
Coal + Hexane Solubles	thermal	61.7(1.8)	38.3(1.8)	69.0(2.3)	98.0
Coal + Hexane Solubles	catalytic	71.5(0.2)	28.5(0.2)	81.6(0.3)	93.1
Coal + Saturates	thermal	27.0(0.6)	73.0(0.6)	24.4(0.8)	94.1
Coal + Saturates	catalytic	36.2(1.3)	63.8(1.3)	36.2(1.7)	95.7

\* Standard deviation in parenthesis

Table II. 11. Complete Reaction Matrix of FHC-623 with Coals

Reactants	Reaction Conditions	Product Distribution (wt%)		Coal Conversion (wt%)	Recovery (wt%)
		THF Solubles	IOM		
<b>Pittsburgh No. 8 Coal</b>					
Coal	thermal	41.6 (1.9)*	58.4 (1.9)	44.8(2.1)	95.9
Coal	catalytic	56.7 (3.8)	43.3 (3.8)	61.7(4.2)	96.9
Coal + Hexadecane	thermal	54.4 (4.2)	45.6 (4.2)	59.1(4.7)	84.7
Coal+ Hexadecane	catalytic	77.4 (2.9)	22.6 (2.9)	84.9 (3.3)	98.1
Coal + Whole Resid	thermal	62.7 (3.7)	37.3(3.7)	68.4(4.1)	81.2
Coal + Whole Resid	catalytic	71.2 (1.5)	28.8(1.5)	77.9(1.8)	96.1
Coal + Hexane Solubles	thermal	41.2 (3.9)	58.8(3.9)	44.3(4.4)	87.8
Coal + Hexane Solubles	catalytic	57.3 (2.6)	42.7(2.6)	62.4(2.9)	95.1
Coal + Saturate Fraction	thermal	29.8 (0.8)	70.2(0.8)	31.6(0.9)	102.0
Coal + Saturate Fraction	catalytic	52.4 (5.3)	47.6(5.3)	56.9(5.9)	88.3
<b>Blind Canyon (DECS-17) Coal</b>					
Coal	thermal	27.5 (0.3)	72.5 (0.3)	26.4(0.4)	87.4
Coal	catalytic	44.5 (0.6)	55.5 (0.6)	45.3(0.8)	89.3
Coal + Hexadecane	thermal	32.5 (0.5)	67.5 (0.5)	31.9(0.6)	86.7
Coal + Hexadecane	catalytic	47.3 (1.0)	52.7 (1.0)	48.4(1.1)	82.8
Coal + Whole Resid	thermal	48.0 (0.2)	52.0(0.2)	49.2(0.2)	91.8
Coal + Whole Resid	catalytic	69.3 (1.3)	30.7(1.3)	72.9(1.4)	91.7
Coal + Hexane Solubles	thermal	43.0 (0.6)	57.0(0.6)	43.6(0.7)	88.4
Coal + Hexane Solubles	catalytic	61.8 (0.5)	39.2(0.5)	63.4(0.6)	84.0
Coal + Saturate Fraction	thermal	28.7 (2.7)	71.3(2.7)	27.7(3.0)	100.3
Coal + Saturate Fraction	catalytic	52.2 (1.9)	47.8(1.9)	53.9(2.1)	94.6
<b>Illinois No. 6 Coal</b>					
Coal	thermal	56.8(0.6)	43.2(0.6)	62.8(0.8)	84.2
Coal	catalytic	56.0(1.3)	44.0(1.3)	61.8(1.6)	88.6
Coal + Hexadecane	thermal	44.3(0.7)	55.7(0.7)	46.7(0.9)	79.4
Coal + Hexadecane	catalytic	64.5(0.6)	35.5(0.6)	72.7(0.8)	82.0
Coal + Whole Resid	thermal	59.7(3.3)	40.3(3.3)	66.4(4.2)	88.8
Coal + Whole Resid	catalytic	62.6(0.6)	37.4(0.6)	70.2(0.7)	90.9
Coal + Hexane Solubles	thermal	60.5(2.2)	39.5(2.2)	67.4(2.8)	89.2
Coal + Hexane Solubles	catalytic	69.6(1.1)	30.4(1.1)	79.2(1.4)	88.2
Coal + Saturate Fraction	thermal	41.5(1.7)	58.5(1.7)	43.0(2.2)	93.1
Coal + Saturate Fraction	catalytic	51.6(3.3)	48.4(3.3)	56.1(4.2)	86.8

\* Standard in parenthesis.

**Table II. 12. Reaction Matrix of Manji with Coals**

Reactants	Reaction Conditions	Product Distribution (wt%)		Coal Conversion (wt%)	Recovery (%)
		THF Solubles	IOM		
<b>Pittsburgh No. 8 Coal</b>					
Coal	thermal	41.6(1.9)	58.4(1.9)	44.8(2.1)	95.6
Coal	catalytic	56.7(3.8)	43.3(3.8)	61.7(4.2)	96.9
Coal + Hexadecane	thermal	54.4(4.2)	45.6(4.2)	59.1(4.7)	84.7
Coal + Hexadecane	catalytic	77.4(2.9)	22.6(2.9)	84.9(3.3)	98.1
Coal + Whole Resid	thermal	32.8(4.2)	67.2(4.2)	34.9(4.7)	90.2
Coal + Whole Resid	catalytic	69.2(2.6)	30.8(2.6)	75.8(2.9)	93.2
Coal + Hexane Solubles	thermal	27.8(0.3)	72.2(0.3)	29.3(0.4)	96.6
Coal + Hexane Solubles	catalytic	70.8(3.0)	29.2(3.0)	77.5(3.3)	97.0
Coal + Saturate Fraction	thermal	24.5(0.5)	75.5(0.5)	25.6(0.5)	87.1
Coal + Saturate Fraction	catalytic	37.6(0.8)	62.4(0.8)	40.3(1.0)	87.3
<b>Blind Canyon DECS-17 Coal</b>					
Coal	thermal	27.5(0.3)	72.5(0.3)	26.4(0.4)	87.4
Coal	catalytic	44.5(0.6)	55.5(0.6)	45.3(0.8)	89.3
Coal + Hexadecane	thermal	32.5(0.5)	67.5(0.5)	31.9(0.6)	86.7
Coal + Hexadecane	catalytic	47.3(1.0)	52.7(1.0)	48.4(1.1)	82.8
Coal + Whole Resid	thermal	25.3(2.2)	74.4(2.2)	23.9(2.5)	87.8
Coal + Whole Resid	catalytic	50.5(2.0)	49.5(2.0)	51.9(2.3)	91.7
Coal + Hexane Solubles	thermal	25.3(0.3)	74.7(0.3)	23.9(0.4)	89.7
Coal + Hexane Solubles	catalytic	74.6(3.2)	25.4(3.2)	78.7(3.5)	91.4
Coal + Saturate Fraction	thermal	12.2(2.9)	87.8(2.9)	9.4(3.3)	82.7
Coal + Saturate Fraction	catalytic	51.0(1.3)	49.0(1.3)	52.6(1.5)	99.0
<b>Illinois No. 6 Coal</b>					
Coal	thermal	56.8(0.6)	43.2(0.8)	62.8(0.8)	84.2
Coal	catalytic	56.0(1.3)	44.0(1.3)	61.8(1.6)	88.6
Coal + Hexadecane	thermal	44.3(0.7)	55.7(0.7)	46.7(0.9)	79.4
Coal + Hexadecane	catalytic	64.5(0.6)	35.5(0.6)	72.7(0.8)	82.0
Coal + Whole Resid	thermal	58.4(0.8)	41.6(0.8)	64.8(1.1)	90.6
Coal + Whole Resid	catalytic	61.0(0.6)	39.0(0.6)	68.1(0.8)	88.5
Coal + Hexane Solubles	thermal	49.7(1.3)	50.3(1.3)	53.7(1.6)	86.7
Coal + Hexane Solubles	catalytic	58.8(1.3)	41.2(1.3)	65.3(1.8)	81.0
Coal + Saturate Fraction	thermal	48.8(0.2)	51.2(0.2)	52.4(0.3)	93.3
Coal + Saturate Fraction	catalytic	63.1(1.2)	36.9(1.2)	70.9(1.6)	91.8

\* Standard in parenthesis.

Table II. 13. Coal Conversion in Coprocessing with Three Resids

Reactants	Coal Conversion (%)					
	Pittsburgh, No. 8		Blind Canyon, BECS-17		Illinois #6	
	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
Coal	44.8(2.1)*	61.7(4.2)	26.4(0.4)	45.3(0.8)	62.8(0.8)	61.8(1.6)
Coal + Hexadecane	59.1(4.7)	84.9(3.3)	31.9(0.6)	48.4(1.1)	46.7(0.9)	72.7(0.8)
Maya Complete Reaction Matrix						
Coal + Whole Resid	56.2(5.2)	89.3(1.1)	31.8(2.2)	64.0(2.3)	61.4(1.3)	65.9(3.7)
Coal + Hexane Solubles	49.2(2.2)	82.9(2.2)	40.5(0.7)	49.2(0.2)	69.0(2.3)	81.6(0.3)
Coal + Saturate Fraction	37.2(1.4)	59.8(1.4)	37.7(1.8)	60.3(1.7)	24.4(0.8)	36.2(1.7)
FHC-623 Complete Reaction Matrix						
Coal + Whole Resid	68.4(4.1)	77.9(1.8)	49.2(0.2)	72.9(1.4)	66.4(4.2)	70.2(0.7)
Coal + Hexane Solubles	44.3(4.4)	62.4(2.9)	43.6(0.7)	63.4(0.6)	67.4(2.8)	79.2(1.4)
Coal + Saturate Fraction	31.6(0.9)	56.9(5.6)	27.7(3.0)	53.9(2.1)	43.0(2.2)	56.1(4.2)
Manji Complete Reaction Matrix						
Coal + Whole Resid	34.9(4.7)	75.8(2.9)	23.9(2.5)	51.9(2.3)	64.8(1.1)	68.1(0.8)
Coal + Hexane Solubles	29.3(0.4)	77.5(3.3)	23.9(0.4)	78.7(3.5)	53.7(1.6)	65.3(1.8)
Coal + Saturate Fraction	25.6(0.6)	40.3(1.0)	9.4(3.3)	52.6(1.5)	52.4(0.2)	70.9(1.6)

Note: reaction condition: 400 °C, reaction time 30 min, under H<sub>2</sub> atmosphere, initial pressure=1250 psig  
 \* standard deviation in parenthesis.

**Table II. 14. Increase in Coal Conversion Caused by Slurry Phase Catalysis**

	Pittsburgh No. 8 (%)	Blind Canyon DECS-17 (%)	Illinois No. 6 (%)
Coal	16.9±6.3	11.9±1.2	-1.0±2.4
Coal + Hexadecane	25.8±8.0	16.5±1.7	26.0±1.7
<b>Maya Reaction Matrix</b>			
Coal + Whole Resid	33.1±6.3	32.2±4.5	4.5±5.0
Coal + Hexane Solubles	33.7±4.4	8.7±0.9	12.6±2.6
Coal + Saturate Fraction	22.6±2.8	22.6±3.5	11.8±2.5
<b>FHC-623 Reaction Matrix</b>			
Coal + Whole Resid	9.5±5.9	23.7±1.6	3.8±4.9
Coal + Hexane Solubles	18.1±7.3	19.8±1.3	11.8±4.2
Coal + Saturate Fraction	25.3±6.5	26.2±5.1	13.1±6.4
<b>Manji Reaction Matrix</b>			
Coal + Whole Resid	40.9±7.6	28.0±4.8	3.3±1.9
Coal + Hexane Solubles	48.2±3.7	54.8±3.9	11.6±3.4
Coal + Saturate Fraction	14.7±1.6	43.2±4.8	18.5±1.8
Total	288.8	287.6	116.0

Note: This table is derived from Table II. 13. The increases in coal conversion are obtained by subtracting coal conversions at thermal conditions from the corresponding conversions at catalytic conditions.

Table II. 15. Increase in Coal Conversion Caused by Addition of Solvent

Reactions	Coal Conversion (%)					
	Pittsburgh No. 8		Blind Canyon DECS-17		Illinois No. 6 Coal	
	Thermal	Catalytic	Thermal	Catalytic	Thermal	Catalytic
Coal	-	-	-	-	-	-
Coal + Hexadecane	14.3±6.8	23.2±7.5	5.5±1.0	3.1±1.9	-16.1±1.7	10.9±2.4
<b>Maya Complete Reaction Matrix</b>						
Coal + Whole Resid	11.4±7.3	27.6±5.3	5.4±2.6	18.7±3.1	-1.4±2.1	4.1±5.3
Coal + Hexane Solubles	4.4±4.3	21.2±6.4	14.1±1.1	3.9±1.0	6.2±3.1	16.8±1.9
Coal + Saturates	-7.6±3.5	-1.9±5.6	11.3±2.2	15.0±2.5	-38.4±1.6	-25.6±3.3
<b>FHC-623 Complete Reaction Matrix</b>						
Coal + Whole Resid	23.6±6.2	16.2±6.0	22.8±0.6	27.6±2.2	3.8±5.0	8.4±2.3
Coal + Hexane Solubles	-0.5±6.5	0.7±7.1	17.2±1.1	18.1±1.4	4.6±3.6	17.4±3.0
Coal + Saturates	-13.2±3.0	-4.8±9.8	1.3±3.4	8.6±2.9	-19.8±3.0	-5.7±5.8
<b>Manji Complete Reaction Matrix</b>						
Coal + Whole Resid	-9.9±6.8	14.1±7.1	-2.5±2.9	6.6±3.1	2.0±1.9	6.3±2.4
Coal + Hexane Solubles	-15.5±2.5	15.8±7.5	-2.5±0.8	33.4±4.3	-9.1±2.4	3.5±3.4
Coal + Saturates	-19.2±2.7	-21.4±5.2	-17.0±3.7	7.3±2.3	-10.4±1.0	9.1±3.2

Note: This table is derived from Table II. 13. The increases in coal conversion are obtained by subtracting coal conversions when reacting by itself from the corresponding conversions when reacting with a solvent.

Example: the conversion increase caused by Maya whole resid: 56.2-44.8=11.4

**Table II. 16. Product Distribution of Anthracene in Reactions with Maya, FHC-623 and Manji Resids**

Resid	Catalytic or Thermal	mol%			H <sub>2</sub> accepted per 100 mol of ANT, H <sub>2</sub>
		ANT	DHA	THA	
ANT	thermal	14.1(0.8)	67.5(0.4)	18.4(1.2)	104.3
ANT	catalytic	11.4(0.6)	70.0(9.3)	26.6(8.6)	123.2
PHP+ANT	thermal	5.9(0.5)	84.3(4.5)	9.8(4.0)	103.9
PHP+ANT	catalytic	3.4(0.8)	72.5(5.2)	24.1(6.0)	120.9
C-16+ANT	thermal	19.9(3.3)	71.2(3.8)	8.9(0.5)	89.0
C-16+ANT	catalytic	5.8(1.7)	79.6(5.4)	14.6(3.8)	108.8
Maya Whole	thermal	15.4(2.3)*	74.3(2.6)	10.4(0.5)	95.1
Maya Whole	catalytic	7.3(0.5)	78.5(0.7)	14.2(1.2)	106.9
Maya Hexane Solubles	thermal	22.0(3.4)	68.3(2.0)	9.7(1.4)	87.7
Maya Hexane Solubles	catalytic	10.1(0.1)	68.1(0.6)	21.8(0.6)	111.7
Maya Saturates	thermal	12.5(1.7)	79.5(0.1)	8.0(1.5)	95.5
Maya Saturates	catalytic	7.6(1.6)	81.4(1.1)	11.0(0.5)	103.4
FHC-623 Whole	thermal	11.9(2.2)	79.3(1.6)	8.8(0.6)	96.9
FHC-623 Whole	catalytic	7.4(0.1)	79.6(1.6)	12.8(1.5)	105.4
FHC-623 Hexane Solubles	thermal	16.0(0.4)	75.8(0.2)	8.2(0.6)	92.2
FHC-623 Hexane Solubles	catalytic	6.9(0.6)	79.8(0.3)	13.3(0.9)	106.4
FHC-623 Saturates	thermal	14.9(1.1)	75.3(3.7)	9.8(2.5)	94.9
FHC-623 Saturates	catalytic	9.7(3.2)	79.7(2.2)	10.6(1.0)	100.9
Manji Whole	thermal	45.0(0.5)	49.7(2.2)	5.3(2.7)	60.3
Manji Whole	catalytic	7.0(0.8)	85.5(0.3)	7.5(0.5)	100.5
Manji Hexane Solubles	thermal	58.7(3.8)	34.7(3.2)	6.6(0.6)	47.9
Manji Hexane Solubles	catalytic	11.3(0.7)	73.6(1.1)	15.1(0.4)	103.8
Manji Saturates	thermal	34.6(1.8)	59.4(1.5)	6.0(0.3)	71.4
Manji Saturates	catalytic	12.4(0.1)	79.5(0.7)	8.1(0.8)	95.7

Note: Reaction condition: 400 °C, 30 min. H<sub>2</sub> charged to 1250 psig at ambient temperature.  
 Catalyst= Mo naphthenate + sulfur, loading 1000 ppm Mo to total reactant charge.  
 \* mean(STD).  
 ANT = anthracene  
 PHP = perhydropyrene

Table II. 17. Hydrogen Acceptance by and Conversion of ANT in Reactions with Donors

Reaction	H <sub>2</sub> accepted per 100 mol of ANT, H <sub>2</sub>		ANT Conversion %	
	Thermal	Catalytic	Thermal	Catalytic
ANT	104.3	123.2	85.9	88.6
PHP + ANT <sup>a</sup>	103.9	120.9	94.1	96.6
C-16 + ANT	89.0	108.8	80.1	94.2
Maya Whole + ANT	95.1	106.9	84.6	92.7
Maya Hexane Solubles + ANT	87.7	111.7	78.0	89.9
Maya Saturates + ANT	95.5	103.4	87.5	92.4
FHC-623 Whole + ANT	96.9	105.4	88.1	92.6
FHC-623 Hexane Solubles + ANT	92.2	106.4	84.0	93.1
FHC-623 Saturates + ANT	94.9	100.9	85.9	90.3
Manji Whole + ANT	60.3	100.5	55.0	93.0
Manji Hexane Solubles + ANT	47.9	103.8	41.3	88.7
Manji Saturates + ANT	71.4	95.7	65.4	87.6

<sup>a</sup> The loading weight ratio ANT to the other reactant is 1:1.  
ANT = anthracene

Table II. 18. Boiling Point Distribution of the Eluants of Maya Resid and Blind Canyon DECS-17 Coal Coprocessing Product

Reactions	Type of Reaction	B.P. Distribution (%)					Recovery <sup>3</sup>	<1000 °F <sup>4</sup>
		<300 °C	<400 °C	<500 °C	<600 °C	<700 °C		
Whole	unreacted <sup>1</sup>	3.1	4.8	8.2	36.2	74.8	22.9%	11.2
Hexane Solubles	unreacted <sup>1</sup>	2.5	7.4	16.6	53.0	82.3	22.6%	22.4
Whole + Coal	thermal	4.8 <sup>2</sup> (0.1)	22.5 (0.1)	47.8 (1.9)	75.5 (4.4)	90.4 (3.6)	37.4%	56.2
Whole + Coal	catalytic	4.4 (0.6)	19.6 (4.2)	43.2 (8.6)	71.3 (10.4)	90.2 (3.9)	34.2%	48.6
Hexane Solubles + Coal	thermal	2.1 (0)	12.4 (1.7)	34.2 (1.7)	71.0 (1.2)	92.5 (0.6)	41.1%	43.1
Hexane Solubles + Coal	catalytic	2.6 (0.1)	12.5 (0.6)	32.1 (2.8)	67.1 (2.6)	88.1 (1.5)	34.5%	40.7
Saturates + Coal	thermal	4.3 (0.6)	18.0 (2.3)	43.2 (4.8)	76.0 (6.1)	90.2 (3.5)	23.9%	52.7
Saturates + Coal	catalytic	2.7 (0.3)	15.6 (0.6)	40.0 (0.6)	75.1 (2.3)	94.6 (1.9)	26.2%	49.3

Note: <sup>1</sup> only one sample analyzed.

<sup>2</sup> mean(STD) of duplicated reaction, all in per cent.

<sup>3</sup> recovery is assumed 100% for comparison on the same recovery basis.

<sup>4</sup> 1000 °F is the conventional cutting point used in industry. The value is obtained by interpolation from the boiling point distribution of resids.

Table II.19. Boiling Point Distribution of the Eluants of Maya and Pittsburgh No. 8 Coal Coprocessing Products

Reactions	Type of Reaction	B.P. Distribution, %					Recovery	<1000 °F
		<300 °C	<400 °C	<500 °C	<600 °C	<700 °C		
Whole	unreacted <sup>1</sup>	3.1	4.8	8.2	36.2	74.8	22.9%	11.2
Hexane solubles	unreacted <sup>1</sup>	2.5	7.4	16.6	53.0	82.3	22.6%	22.4
Whole + Coal	thermal	3.5 <sup>2</sup> (1.1)	16.6 (2.8)	38.0 (4.5)	68.8 (7.2)	86.6 (5.3)	44.1%	45.9
Whole + Coal,	catalytic	7.8	21.3	34.8	59.6	79.8	12.5%	40.2
Hexane Solubles + Coal	thermal	2.7 (0.0)	12.0 (0.3)	34.5 (0.8)	74.3 (1.0)	95.0 (0.6)	39.7%	43.7
Hexane Solubles + Coal	catalytic	4.6 (1.3)	15.8 (2.2)	33.5 (1.9)	68.3 (2.8)	88.3 (2.2)	16.7%	41.1
Saturates + Coal	thermal	3.3 (1.7)	8.9 (2.1)	31.9 (1.6)	66.9 (7.4)	85.1 (3.6)	27.8%	41.1
Saturates + Coal	catalytic	3.9 (1.3)	19.8 (7.4)	42.8 (6.4)	74.4 (3.6)	90.7 (0.8)	26.1%	51.0

Note: <sup>1</sup> only one sample analyzed.

<sup>2</sup> mean(STD) of duplicated reactions, all numbers in per cent.

Table II. 20. Boiling Point Distribution of Products of Maya Resid and Bind Canyon  
DECS-17 Coal Coprocessing

Reaction	Type of Reaction	BP Distribution, %							Recovery	Yield
		<40 °C	40-50 °C	50-60 °C	60-70 °C	70-80 °C	80-90 °C	>90 °C		
Whole	unreacted <sup>1</sup>	0.7	1.1	1.9	8.4	17.2	82.8	22.9%	2.6	
Hexane Solubles	unreacted <sup>1</sup>	0.6	1.7	3.8	12.0	18.6	81.4	22.6%	5.1	
Whole + Coal	thermal	1.8 <sup>2</sup> (0.1)	8.4 (0.5)	18.0 (0.3)	28.3 (0.2)	33.7 (0.4)	67.3	37.4%	21.0	
Whole + Coal	catalytic	1.6 (0.1)	6.9 (2.7)	14.6 (5.4)	24.6 (6.6)	30.6 (7.6)	69.4	34.2%	17.2	
Hexane Solubles+Coal	thermal	0.9 (0.0)	5.1 (0.7)	14.2 (0.9)	29.4 (0.1)	38.2 (0.6)	61.8	41.1%	17.8	
Hexane Solubles+Coal	catalytic	0.9 (0.0)	4.4 (0.2)	11.1 (0.1)	23.2 (1.1)	30.4 (0.2)	69.6	34.5%	14.1	
Saturates + Coal	thermal	1.0 (0.1)	4.3 (0.4)	10.3 (0.6)	18.1 (0.6)	21.5 (0.2)	78.5	23.9%	12.6	
Saturates + Coal	catalytic	0.7 (0.1)	4.1 (0.3)	10.5 (0.2)	19.7 (0.1)	24.7 (0.4)	75.3	26.2%	12.9	

Note: <sup>1</sup> only one sample analyzed.

<sup>2</sup> mean(STD) of duplicated reaction, all in per cent.

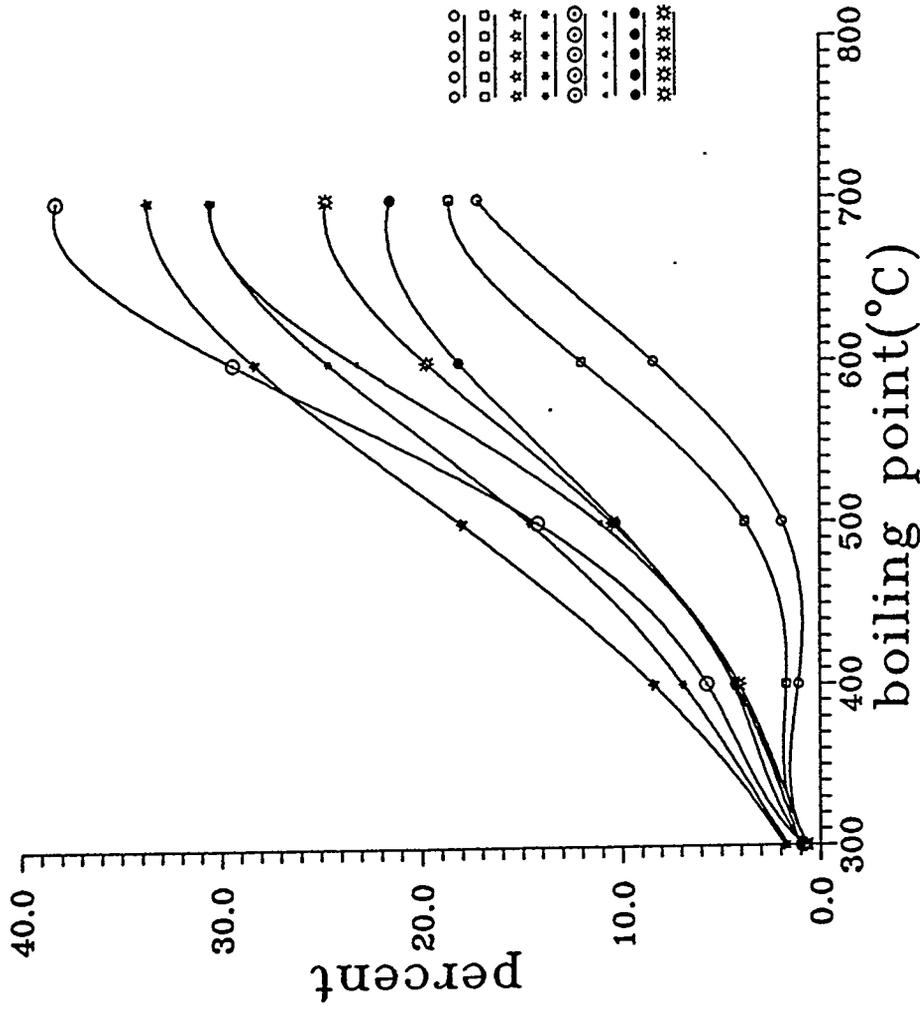


Figure II.1. Maya Resid and DECS-17 Coal Coprocessing Product Boiling Point Distribution

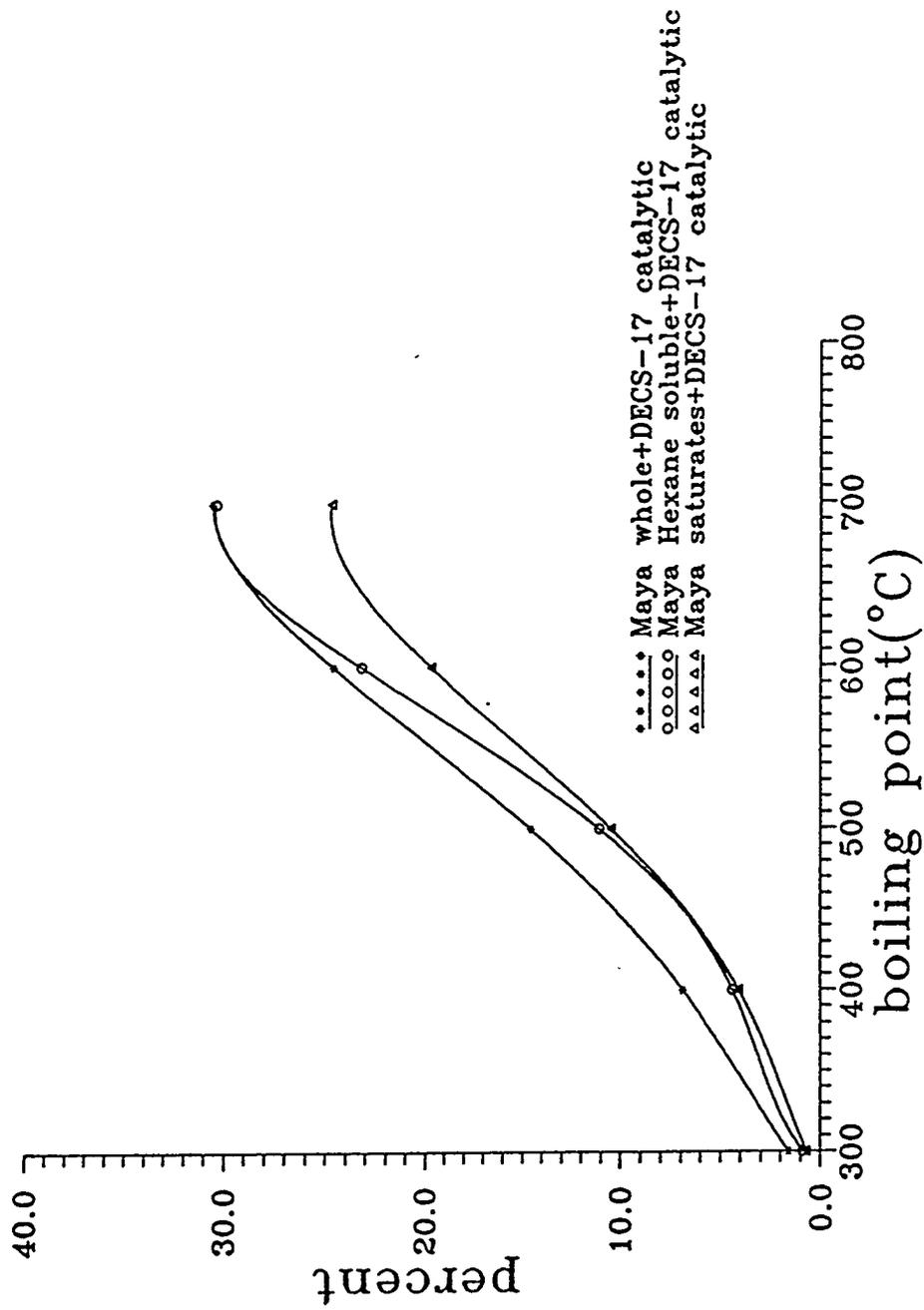


Figure II.2. Maya Resid - DECS-17 Coal Catalytic Reaction  
Product Boiling Point Distribution

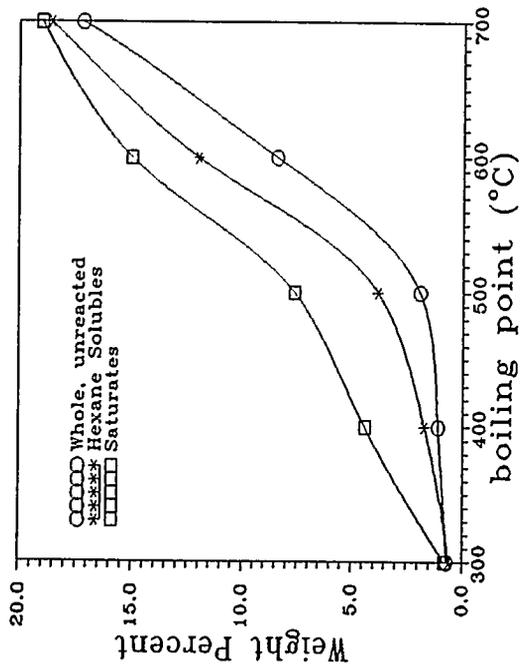


Figure II.3. Maya Resid and Resid Fraction

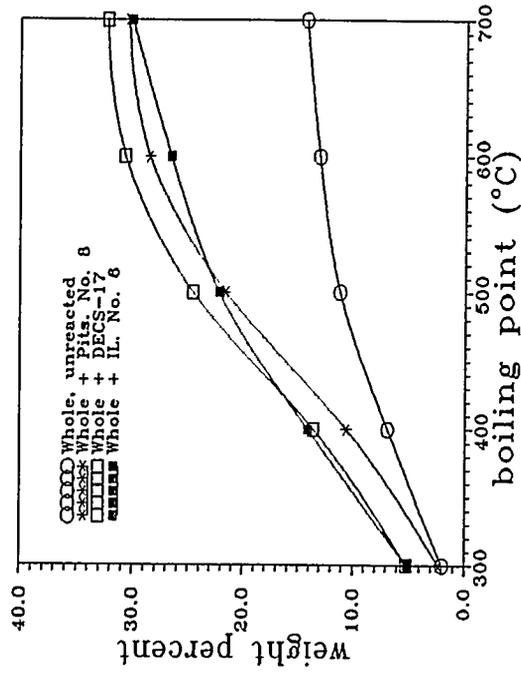


Figure II.4. Catalytic Reactions of Maya Whole Resid

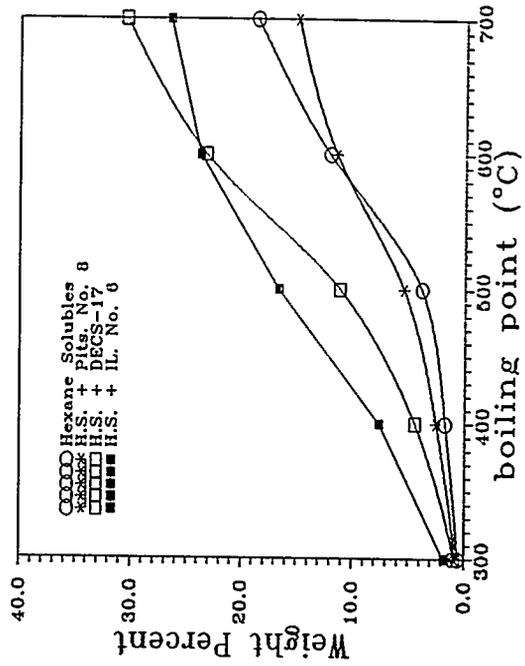


Figure II.5. Catalytic Coprocessing of Maya Hexane Solubles

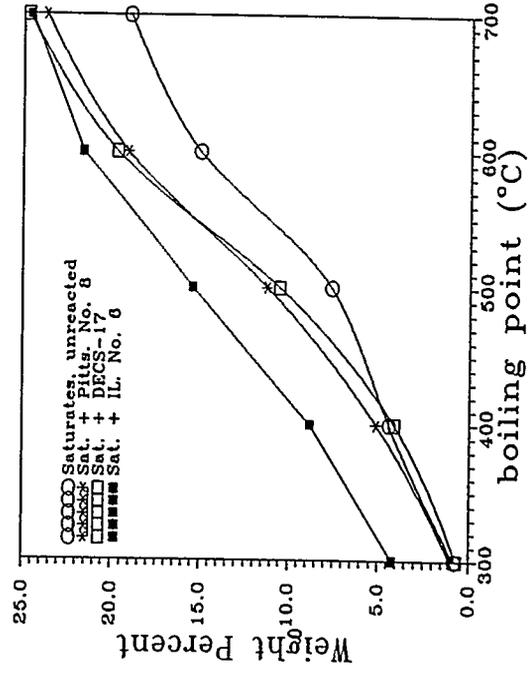


Figure II.6. Catalytic Reaction of Maya Saturates

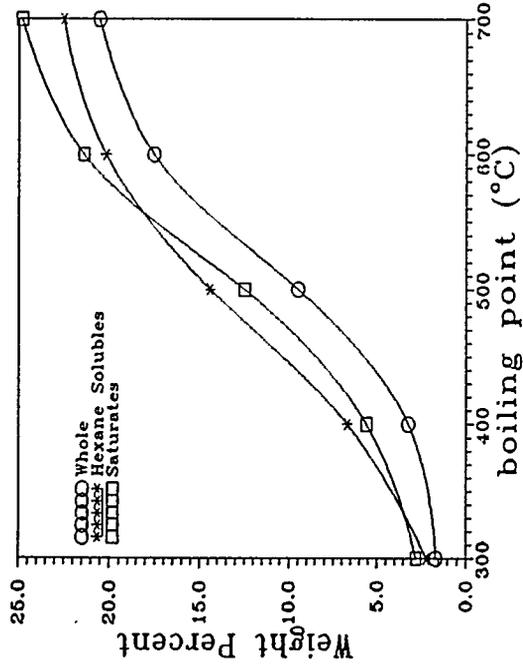


Figure II.7. FHC-623 Resid and Resid Fractions

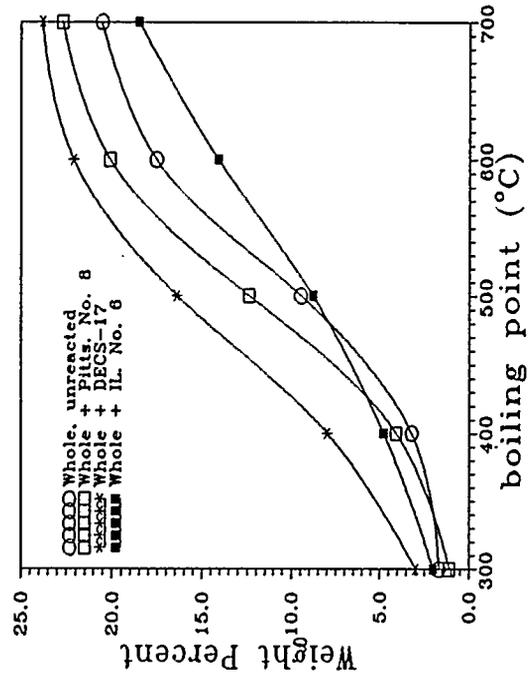


Figure II.8. Catalytic Reactions of FHC-623 Whole Resids

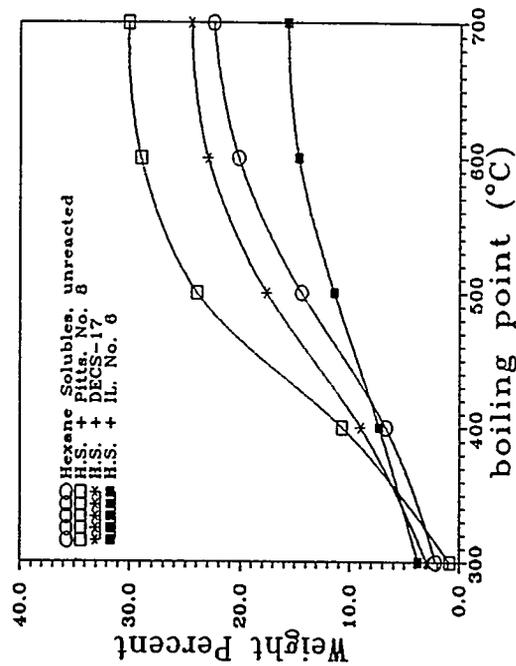


Figure II.9. Catalytic Reaction of FHC-623 Hexane Solubles

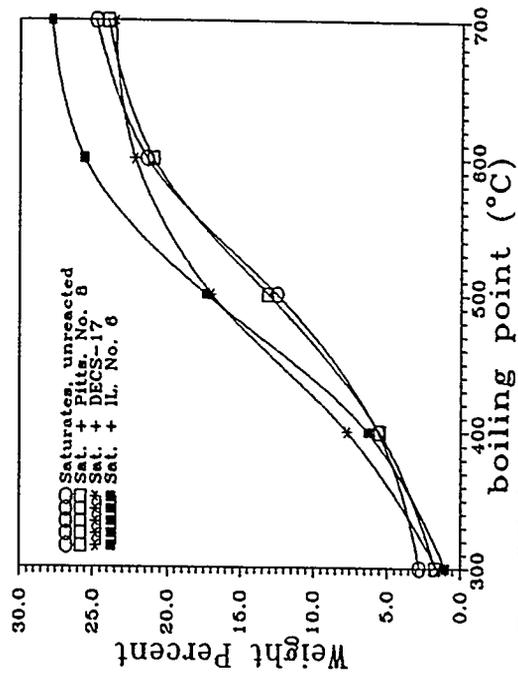


Figure II.10. Catalytic Reactions of FHC-623 Saturates

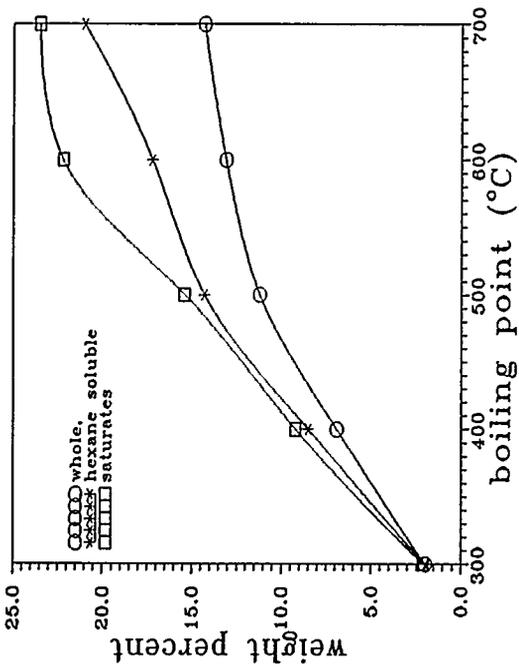


Figure II.11. Manji Resid and Resid Fractions

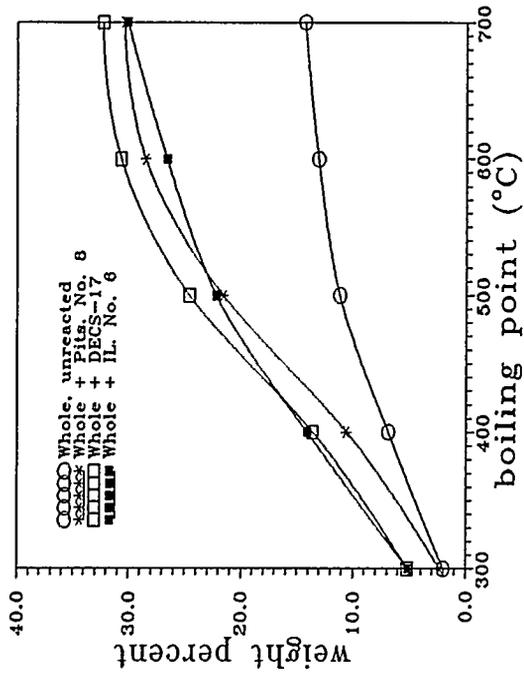


Figure II.12. Catalytic Reaction of Manji Whole Resid

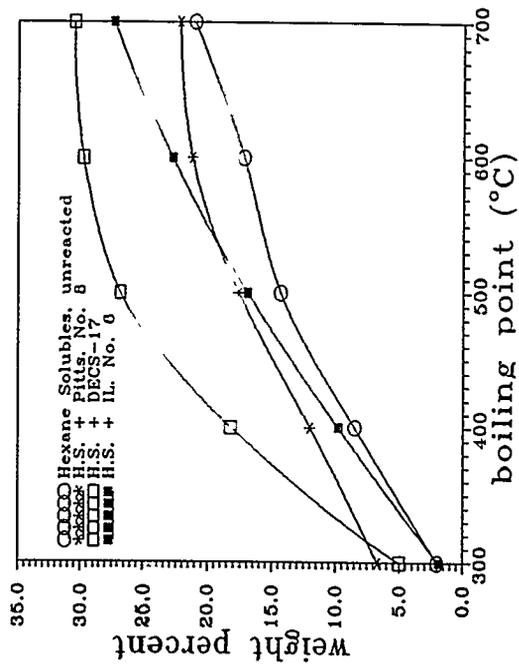


Figure II.13. Catalytic Reactions of Manji Hexane Solubles

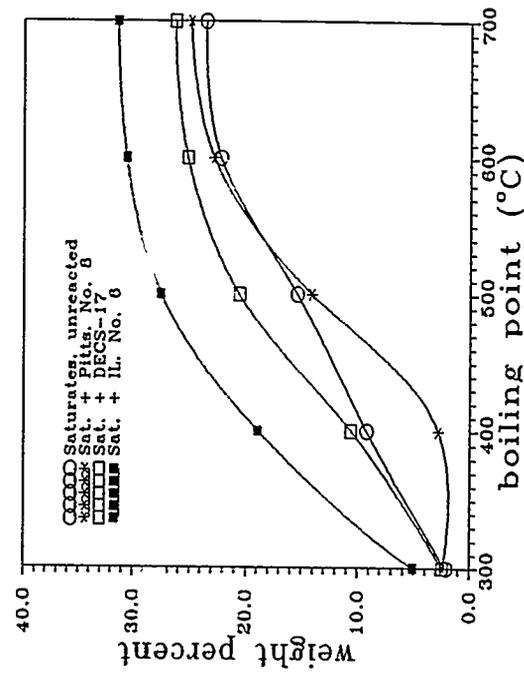


Figure II.14. Catalytic Reaction of Manji Saturates

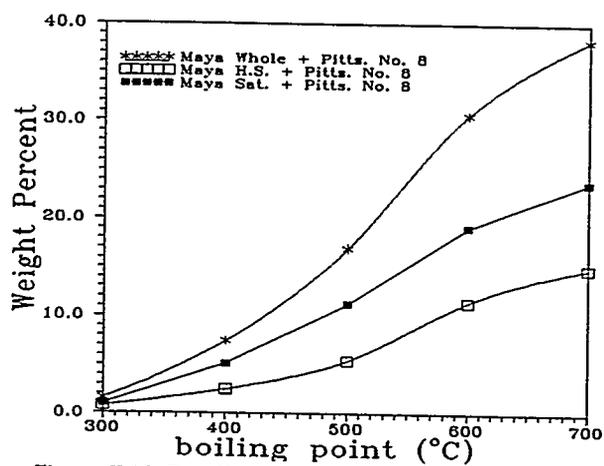


Figure II.15. Reaction of Maya and Pittsburgh No. 8

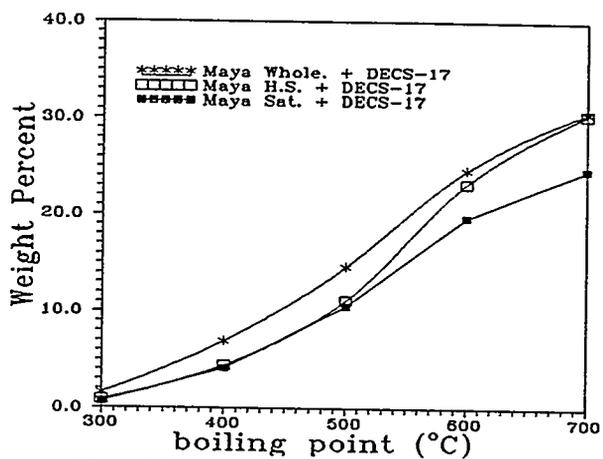


Figure II.16 Reaction of Maya with DECS-17

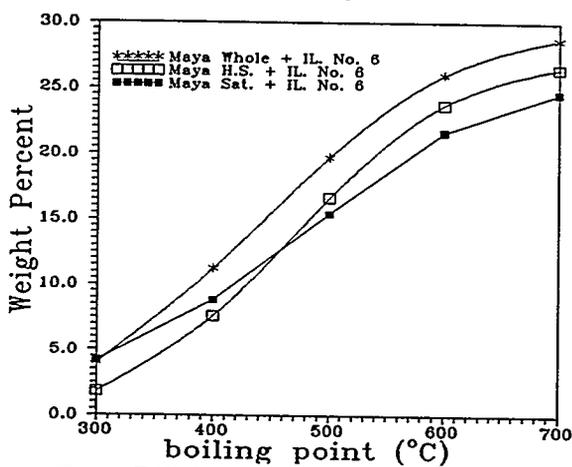


Figure II.17. Reaction of Maya with IL No. 6

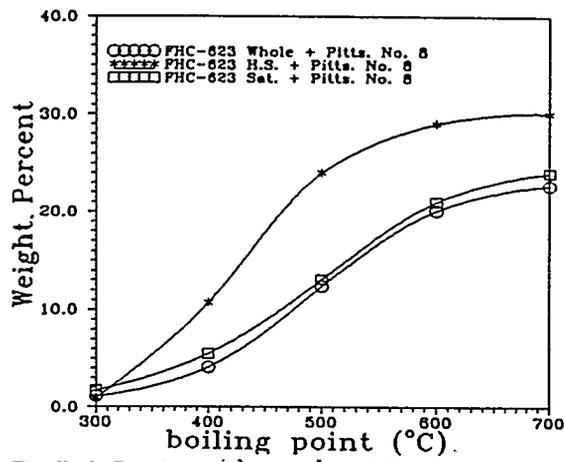


Fig. II.18. Reaction of FHC-623 and Pittsburgh No. 8

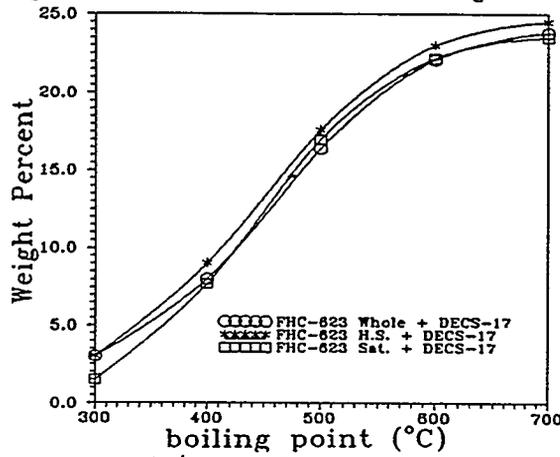


Fig. II.19. Reaction of FHC-623 and DECS-17

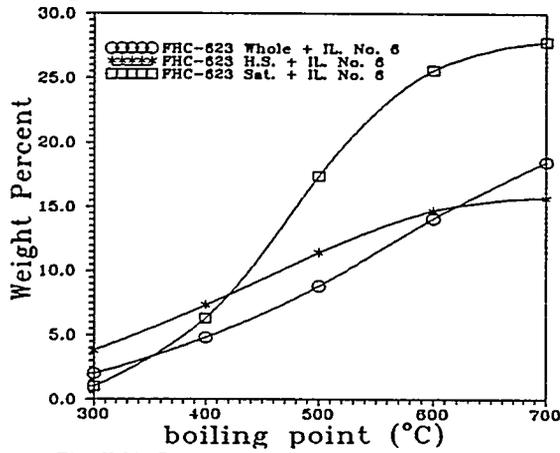


Fig. II.20. Reaction of FHC-623 and IL No.6

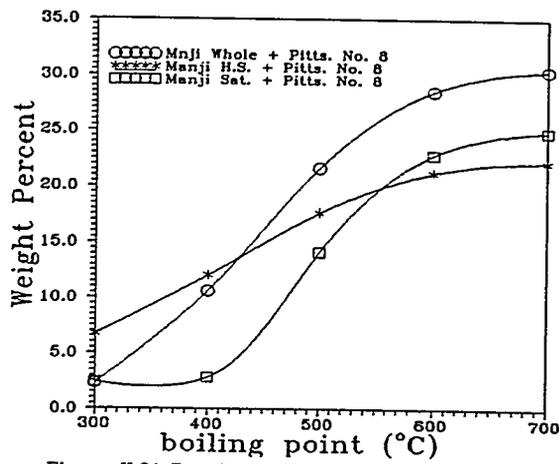


Figure II.21 Reaction of Manji and Pitts. No 8

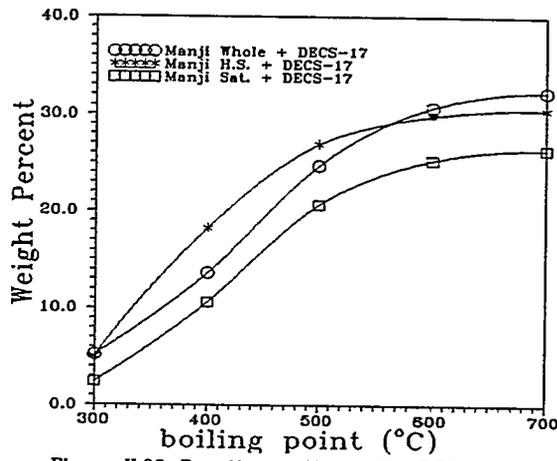


Figure II.22. Reaction of Manji with DECS-17

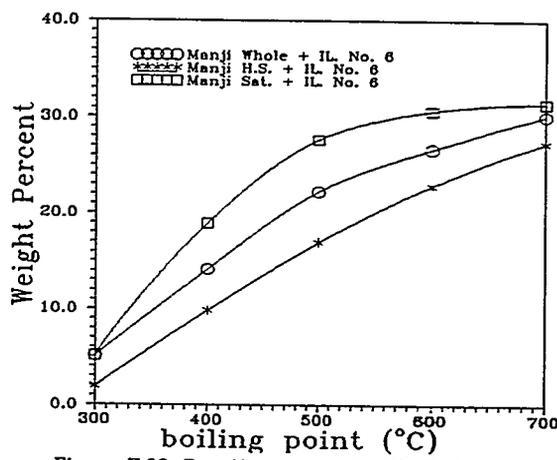


Figure II.23. Reaction of Manji with IL No. 6

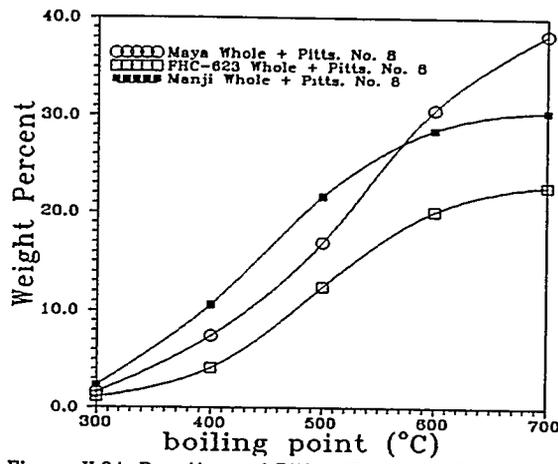


Figure II.24. Reactions of Pitts. #8 and Whole Resids

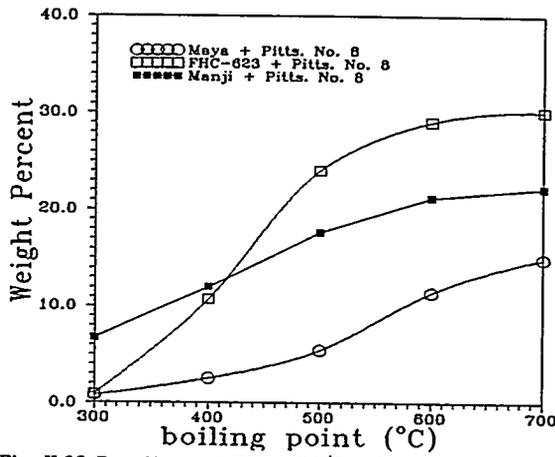


Fig. II.25 Reactions of Pitts. #8/Resid Hexane Solubles

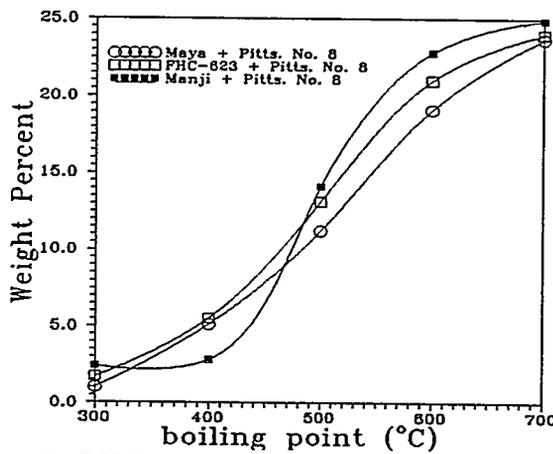


Fig. II.26 Reactions of Pitts. #8/Resid Saturates

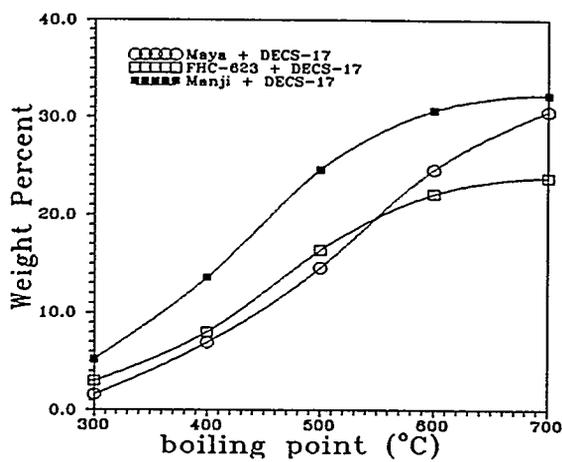


Fig. II.27. Reactions of DECS-17/Whole Resid

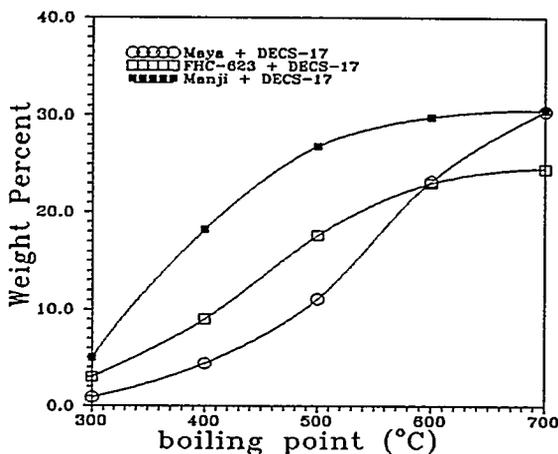


Fig. II.28. Reactions of DECS-17/Hexane Solubles

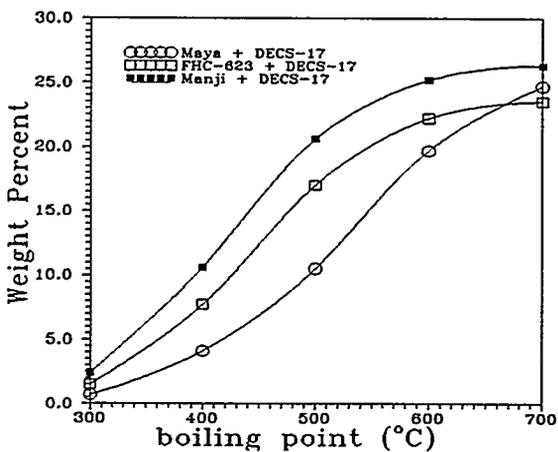


Fig. II.29. Reaction of DECS-17/Resid Saturates

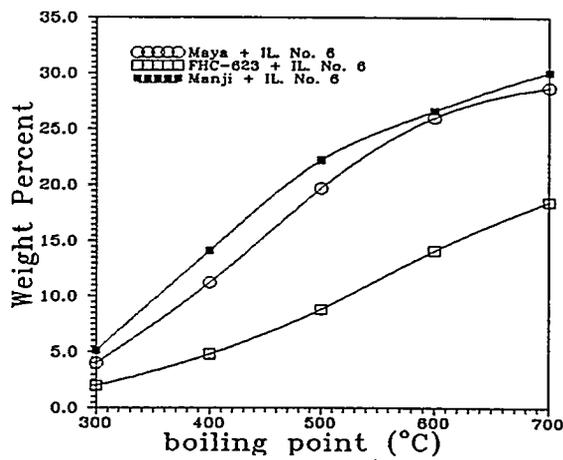


Fig. II.30. Reactions of IL #6/Whole Resid

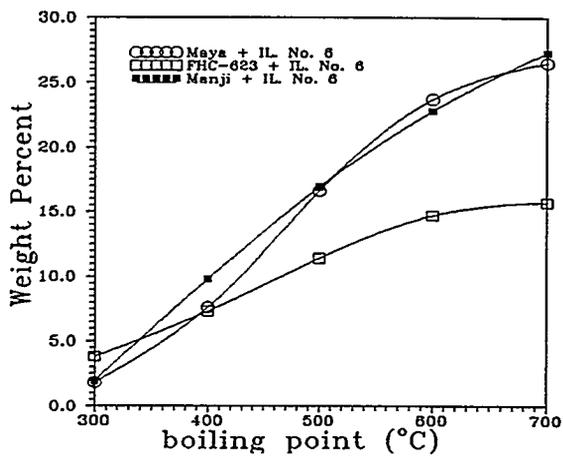


Fig. II.31. Reactions of IL #6/Hexane Solubles

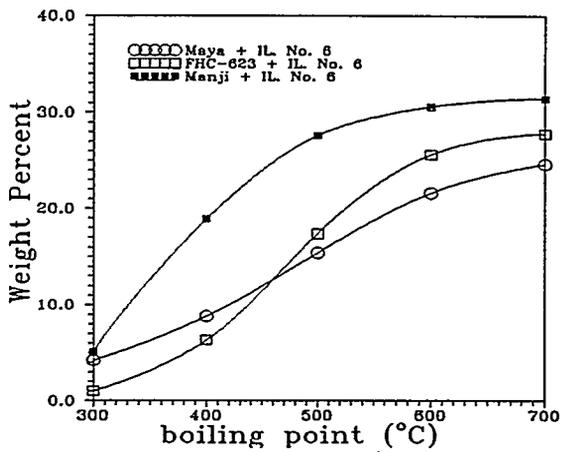


Fig. II.32. Reactions of IL #6/Saturates