

INVESTIGATION OF HYDROGEN TRANSFER IN COPROCESSING USING MODEL SYSTEMS

Jing Shen and Christine W. Curtis
Chemical Engineering Department
Auburn University, AL 36849

Introduction

The objective of this research was to evaluate the role of the resid in the coprocessing of coal and petroleum resid. The question being asked was whether the resid is an active solvent in coprocessing reactions and whether resid donates any hydrogen to coal during coprocessing. An effective means of determining whether resid participates in the reactions at coprocessing conditions is to use model systems and trace their reaction pathways. The research performed in this study evaluated the hydrogen donability of a naphthenic compound perhydropyrene, a compound type prevalent in resids that are hydrogen-rich. Model species were also used as acceptors that represented the aromatic aspect of coal. The model acceptors that were used were anthracene and phenanthrene.

Perhydropyrene has been used previously as a model donor representing resids by Owens and Curtis (1994) and Wang and Curtis (1994). In a N_2 atmosphere, perhydropyrene donated hydrogen to anthracene, increased the conversion of coal to THF soluble material, and reduced retrogressive reactions of petroleum resid (Owens and Curtis, 1994). Reactions of a number of hydrogen donor compounds such as cyclic olefins, hydroaromatic compounds, and naphthenes like perhydropyrene under equivalent reaction conditions showed that perhydropyrene had the least propensity for hydrogen donation among those compounds in both N_2 and H_2 atmospheres (Wang and Curtis, 1994). In the current study, the model perhydropyrene was used to represent petroleum and was reacted individually and with model acceptors primarily in a H_2 atmosphere to simulate coprocessing although some reactions were performed in N_2 to provide a reference point.

The model acceptors that were used included anthracene and phenanthrene, both of which are aromatic and represent molecules typically found in coal. Anthracene and phenanthrene have been used as coal model compounds and evaluated according to their ability to accept hydrogen from either a model donor or molecular hydrogen. Hydrogenation reactions of anthracene and phenanthrene were performed at temperatures of 325 °C (Salim and Bell, 1984) and 400 °C (Nakatsuji et al., 1978; Song et al., 1989 and 1991; Fixari and Perchec, 1989; Miyak et al., 1982) for 60 min with a hydrogen pressure of 5 to 9.8 MPa at ambient temperature. Different catalysts were used by the researchers including NiMo/Al₂O₃, NiCl₂, and sulfided NiMo/Al₂O₃ at loadings of 10 to 15 % on a reactant charge basis. The catalyst used in this study was a slurry phase catalyst molybdenum naphthenate which was added directly to the reactor contents along with excess sulfur. Mo naphthenate has been used extensively in coal and resid coprocessing reactions (Cassell and Curtis, 1988; Pellegrino and Curtis, 1989; Kim and Curtis 1990, 1990a, 1990b, 1991; Ting et al. 1992; Brannan et al. 1995).

Experimental

Materials. The chemicals used in these experiments included anthracene (ANT, 99%), phenanthrene (PHEN, 98+ %), biphenyl, dihydroanthracene (DHA), pyrene (PYR), hexahydropyrene (HHP), and perhydropyrene (PHP). These chemicals were obtained from Aldrich Chemical Company and were used as received. The slurry phase catalyst, Mo naphthenate (MoNaph, Mo 6 wt %), was obtained from Shephard Chemical Company and was used as received. Sulfur added to the MoNaph 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.

Reaction Procedures. The reactions were conducted for 30 min in stainless steel tubular microreactors with a volume of ~20 mL. Each reaction was duplicated. The reactors were charged with the model reactants and with H_2 at 3.4 or 8.7 MPa at ambient temperature. When reacted individually, the model donor or model acceptors were added at ~ 0.1 g each of the donor or acceptor. When the donor and acceptor were charged simultaneously at a 1:1 ratio, each reactant was charged at 0.05 g, but when the ratio charged was 5:1, then 0.1 g of donor and ~ 0.02 g of acceptor were added. The reactions were performed at two different temperatures: 400 and 440 °C. The reactors were situated horizontally in a heated sand bath and were agitated at 400 rpm during the reaction. After 30 min of reaction the reactors were quickly quenched in

room temperature water. The liquid and solid products were removed from the reactor after being washed with 5 mL of THF and recovery obtained is given in the data tables.

Catalytic reactions were performed with MoNaph being charged to the reactors at a loading level of 1000 ppm of Mo on a total reactant charge basis. Elemental sulfur was added to MoNaph reaction in a 3:1 S to Mo ratio since MoS_2 was shown to be produced under these reaction conditions (Kim et al. 1989). The catalyst generated in situ at reaction temperature formed finely divided catalyst particles.

Analysis. 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°C with a final temperature of 320°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°C , respectively. Biphenyl was used as the internal standard.

Results and Discussion

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

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

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

Anthracene was reactive in a thermal reaction with molecular H_2 present, yielding nearly 86% conversion to partially saturated products at both 400 and 440°C (Table 1). The primary product formed was DHA at 440°C which accounted for nearly 81% of the product; the minor product was THA which only accounted for about 5% of the product. At 400°C , the same products were formed although the quantities were somewhat different; a lesser amount of DHA, 67.5%, and greater amount of THA, 18.4%, were formed.

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

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

temperatures; the increase at 400 °C was from 85.9 to 88.6% conversion, while at 440 °C the increase was from 85.8 to 96.9% conversion.

Reaction of the Model Donor. The model donor used in this study was the naphthene, perhydropyrene. Perhydropyrene was used in the current study as a test naphthene molecule to examine if hydrogen transfer occurred between the model naphthene and aromatic species in H₂ and N₂ atmospheres. Perhydropyrene was reacted alone in H₂ and N₂ atmospheres thermally and catalytically at 400 and 440 °C. Perhydropyrene was stable showing almost no reactivity at these conditions. At 400 °C in N₂, no conversion of perhydropyrene occurred thermally while with MoNaph+S 1% conversion to pyrene occurred. At 440 °C in N₂, slightly higher conversion of perhydropyrene occurred. In H₂ at both 400 and 440 °C, perhydropyrene was stable yielding at most 3% conversion. The MoNaph+S catalyst promoted conversion.

Reactions of Model Donor and Acceptors. Reactions were performed that combined the model donor perhydropyrene with the model acceptors anthracene and phenanthrene. The reactions of perhydropyrene with anthracene at 1:1 and 5:1 ratio under thermal and catalytic conditions are given in Table 1. The moles of H₂ accepted per 100 moles of anthracene or phenanthrene as well as the conversion of anthracene or phenanthrene served as a measure of the activity of the system.

The thermal reaction of perhydropyrene with anthracene at 400 °C and a 1:1 ratio gave a H₂ accepted of 103.9 while the addition of MoNaph+S increased the amount of H₂ accepted to 120.9. Increasing the ratio of perhydropyrene to ANT to 5:1 did not change the amount of H₂ accepted; the H₂ accepted in the thermal reaction was 104.0 while the addition of MoNaph+S increased H₂ 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 H₂ accepted values were nearly equivalent to those obtained without perhydropyrene at 400 °C.

Phenanthrene accepted much less donor and molecular H₂ than anthracene at equivalent reaction conditions. For example, when perhydropyrene and phenanthrene were reacted together thermally at a 1:1 and 5:1 ratio at 400 °C, the amount of conversion was 2.9 and 4.6% and the H₂ accepted was 1.2 and 1.8 moles, respectively, as shown in Table 2. The respective values for anthracene ranged from 80 to 95% conversion and 104 to 120 moles of H₂ accepted. The primary product from phenanthrene was usually DHPN with THPN being the secondary product.

Although the reactivity of phenanthrene was much lower than that of anthracene, reactions of phenanthrene with perhydropyrene responded to the presence of perhydropyrene, to change in reaction temperature, and to the type of catalyst used. The reactivity of the perhydropyrene and phenanthrene systems is given on Table 2. Comparison of the conversion and H₂ acceptance values at two different temperatures but at otherwise equivalent conditions showed that reactions at 440 °C promoted a higher level of conversion and H₂ accepted than those at 400 °C.

Despite this lower reactivity at 400 °C, notable differences in the reactivity were observed in the thermal reactions of phenanthrene and perhydropyrene compared to catalytic reactions containing MoNaph+S. Reactions at 5:1 ratio of donor to acceptor in N₂ at 400 °C showed that a small amount of perhydropyrene donated to phenanthrene yielding THPN as product. By comparison, the reaction of phenanthrene in N₂ at 400 °C did not convert any phenanthrene and, hence, did not yield any hydrogenated product. Thermal reactions at 400 °C in H₂ with a 1:1 ratio of perhydropyrene to phenanthrene converted 2.9% phenanthrene while the 5:1 ratio converted 4.6%. The amount of H₂ accepted gave a corresponding amount of 4.4 and 7.4 moles of H₂ accepted per 100 moles of phenanthrene. The increased amount of naphthene present in the reaction at 400 °C increased the amount H₂ accepted by phenanthrene.

In the catalytic reactions using MoNaph+S, an excess amount of perhydropyrene at 400 °C also increased the amount of phenanthrene conversion and the amount of H₂ accepted by phenanthrene. MoNaph+S promoted hydrogenation of phenanthrene to DHPN and THPN. Comparing the combined donor and acceptor reactions to the acceptor reaction alone showed that perhydropyrene being present in the thermal reaction did not increase either phenanthrene conversion or the amount H₂ accepted. However, the addition of MoNaph+S with perhydropyrene present increased both conversion and H₂ accepted at 400 °C when compared to the catalytic reaction with phenanthrene alone.

Reactions of perhydropyrene and phenanthrene at 440 °C (Table 2) showed an overall higher reactivity than at 400 °C at corresponding reaction conditions. In N₂ with MoNaph+S, the amount of phenanthrene conversion to DHPN and THPN was 2.2%. The source of H₂ in the reaction was H₂ donated from perhydropyrene. In the reaction perhydropyrene produced pyrene

and several partially saturated pyrene compounds, thereby donating 8.9 moles of H₂ per 100 moles of perhydropyrene. In H₂ at 440 °C, the ratio of perhydropyrene to phenanthrene affected the amount of phenanthrene conversion as well as the amount of H₂ accepted. Both the thermal and catalytic reactions at the higher ratio gave larger amounts of these quantities than at the lower 1:1 ratio. The thermal reaction at 400 °C resulted in 9.3 moles of H₂ accepted per 100 moles of phenanthrene while at 440 °C 16.8 moles of H₂ were accepted. The MoNaph+S catalyst promoted hydrogenation of phenanthrene at both ratios yielding at the 1:1 ratio 15.8 moles of H₂ accepted by phenanthrene while at the 5:1 ratio 26.2 moles of H₂ were accepted.

Perhydropyrene reacted in these reactions with phenanthrene to form decahydropyrene (DCP), hexahydropyrene (HHA), tetrahydropyrene (THP), dihydropyrene (DHP), and pyrene (PYR). More different products were made from perhydropyrene when phenanthrene was present than when perhydropyrene was reacted alone, where only pyrene was produced. A calculation of the amount of H₂ donated from these products is given in the tables and is designated as the moles of H₂ donated per 100 moles of donor or H₂ donated. In the H₂ atmosphere at 400 °C, the amount of H₂ donated from perhydropyrene remained nearly the same except for reactions containing MoNaph+S which increased H₂ donated to 6.3 from 1 to 2 in the thermal reactions. At 440 °C, higher amounts of H₂ were donated from perhydropyrene to the acceptors.

Summary

Determining whether hydrogen donation occurred from perhydropyrene as a representative of a resid naphthene at typical coprocessing conditions was a goal of this investigation. The reactions of the model naphthene perhydropyrene and the model acceptors, anthracene and phenanthrene, clearly showed that different chemical species present in the coal have different propensities for accepting H₂ regardless of its source, molecular or donor. The model naphthene under some circumstances, like in the anthracene reaction, was a positive influence on the reaction, causing the overall amount of H₂ accepted to increase. Catalytic reactions with MoNaph+S also promoted the apparent transfer of H₂ from perhydropyrene to anthracene. Phenanthrene was not as active an acceptor as anthracene. Thermal hydrogenation of anthracene and phenanthrene with molecular hydrogen at 400 °C yielded 85% and 4.7% conversion, respectively. Excess donor model was required to observe a positive effect of the naphthene on the H₂ accepted by the model acceptor.

References

- Cassel, F.N.; Curtis, C.W. *Energy Fuels*, 2, 1, 1988.
Faxari, B. and Perchec, P.L., *Fuel*, 1989, Vo. 68, February, 218-221.
Kamiya, Y., Futamura, S., Mizuki, T., Kajioka, M. and Koshi, K. *Fuel Processing Technology*, 14, 79-90, 1986.
Kim, H.; Curtis, C.W. *Energy Fuels*, 4, 214, 1990a.
Kim, H.; Curtis, C.W. *Energy Fuels*, 4, 206, 1990b.
Kim, H.; Curtis, C.W. *Fuel Sci. Tech Intl.* 9, 229, 1991.
Kim, H.; Curtis, C.W.; Cronauer, D.C.; Sajkowski, D.J. *ACS Fuel Dive Prep.* 34, 4, 1446, 1989.
Miyak, M., Sakashita, H., Norura, M. and Kikkawa, S. *Fuel*, 1982, Vol 61, February, 124-128.
Nakatsuji, Y., Kubo, T., Nomura, M., and Kikkawa, S., *Bulletin of the Chemical Society of Japan*, Vol. 51 (2), 618-624, 1978.
Owens, R.; Curtis, C.W. *Energy Fuels*, 8, 823, 1994.
Pellegrino, J.L.; Curtis, C.W. *Energy Fuels*, 3, 160, 1989.
Salim, S.S. and Bell, A.T. *Fuel*, 1984, Vol 63, April, 469-476.
Song, C.; Nomura, M. and Ono, T. *Preprint - Am. Chem. Soc. Div. Fuel Chem.*, 36, 2, 586-596, 1991.
Song, C.; Ono, T.; and Nomura, M. *Bulletin Chemical Society Japan* 62, 630-632, 1989.
Ting, P.S.; Curtis, C.W.; Cronauer, D.C. *Energy Fuels*, 6, 511, 1992.
Wang S.L.; Curtis, C.W. *Energy Fuels*, 8, 446, 1994.

Acknowledgements

The support of the United States Department of Energy under contract No. DE-AC22-91PC91055 for this work is greatly appreciated.

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

Reaction Condition	Reactants	Atmosphere	T (°C)	Product Distribution (mol%)			Recovery (%)	ANT Conversion, %	H ₂ Accepted H ₂ Donated
				ANT	DHA	THA			
Thermal	ANT	N ₂	400	98.3±0.17	1.70±0.17	0±0	92.5	1.7	
Thermal	ANT	H ₂	400	14.1±0.8	67.5±0.4	18.4±1.2	90.1	104.3	
MoNaph + S	ANT	H ₂	400	11.4±0.6	70.0±9.3	26.6±8.6	94.4	123.2	
Thermal	ANT	H ₂	440	14.2±0.40	80.9±0.42	4.9±0.82	84.4	90.75	
MoNaph + S ^b	ANT	H ₂	440	3.8±0.06	55.8±0.62	40.4±2.1	80.1	136.58	
Thermal	PHP: ANT 1:1	N ₂	400	94.0±1.8	6.0±1.8	0.0±0.0	82.5	6.5±0.7	
MoNaph + S	PHP: ANT 1:1	N ₂	400	95.4±1.1	3.2±1.2	1.4±0.1	85.2	6.0±0.9	
Thermal	PHP: ANT 1:1	N ₂	440	94.4±0.4	4.6±0.1	1.0±0.3	83.8	6.5±0.7	
MoNaph + S	PHP: ANT 1:1	N ₂	440	96.3±0.1	3.7±0.1	0.0±0.0	87.1	4.3±0.3	
Thermal	PHP: ANT 1:1	H ₂	400	5.9±0.5	84.9±4.5	9.8±4.0	98.2	103.9	
MoNaph + S	PHP: ANT 1:1	H ₂	400	3.4±0.8	72.5±5.2	24.1±6.0	96.8	120.9	
Thermal	PHP: ANT 5:1	H ₂	400	6.3±2.1	83.4±0.6	10.3±2.7	92.2	104.0	
MoNaph + S	PHP: ANT 5:1	H ₂	400	5.3±2.0	68.2±6.5	26.6±4.5	82.9	121.2	

^a Reaction time = 30 min; 8.7 MPa H₂ or N₂ at room temperature.

^b MoNaph + S = Mo naphthalene with added elemental S.

^c ANT = anthracene; DHA = dihydroanthracene; THA = tetrahydroanthracene; H₂ = (1 x DHA mol% + 2 x THA mol%) x 100

^d 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 naphthalene loading is approximately 0.0017 g = total reactant charge (0.1 g)/60, computed according to 1000 ppm MoS₂ and 6 wt% Mo in Mo naphthalene.

Table 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 ₂ Accepted ^b	H ₂ Donated ^c
				PHEN ^a	DHPN	THPN				
Thermal	PHEN	N ₂	400	100±0.0	0.0	0.0	86.6	0.0	NA ^a	
MoNaph	PHEN	N ₂	400	100±0.0	0.0	0.0	85.5	0.0	NA	
Thermal	PHEN	H ₂	400	95.3±0.7	2.6±0.5	2.1±0.2	83.5	6.8±0.9	NA	
MoNaph+S ^b	PHEN	H ₂	400	91.0±0.0	6.0±0.0	3.0±0.1	87.3	12.0±0.1	NA	
Thermal	PHEN	N ₂	440	100±0.0	0.0	0.0	87.6	0.0	NA	
MoNaph+S	PHEN	N ₂	440	100±0.0	0.0	0.0	85.3	0.0	NA	
Thermal	PHEN	H ₂	440	90.9±1.2	5.9±0.7	3.2±0.5	91.8	12.3±1.7	NA	
MoNaph+S	PHEN	H ₂	440	81.3±3.8	12.8±2.4	5.9±1.4	82.0	24.6±5.2	NA	
Thermal	PHP: PHEN 1:1	H ₂	400	97.1±0.2	1.5±0.0	1.4±0.2	88.5	4.4±0.3	1.2±0.1	
MoNaph+S	PHP: PHEN 1:1	H ₂	400	86.9±2.0	9.0±1.5	4.1±0.5	90.0	17.2±2.5	6.2±0.0	
Thermal	PHP: PHEN 5:1	N ₂	400	98.4±0.2	0.0±0.0	1.6±0.2	92.3	3.2±0.4	3.8±0.0	
MoNaph+S	PHP: PHEN 5:1	N ₂	400	99.0±0.0	0.0±0.0	1.0±0.0	86.6	2.0±0.0	3.9±0.0	
Thermal	PHP: PHEN 5:1	H ₂	400	95.4±0.2	1.8±0.4	2.8±0.8	86.9	7.4±2.1	1.8±0.0	
MoNaph+S ^b	PHP: PHEN 5:1	H ₂	400	82.8±0.1	10.7±0.6	6.5±0.1	92.9	23.7±0.1	6.3±0.0	
Thermal	PHP: PHEN 1:1	H ₂	440	93.2±1.4	4.4±0.8	2.4±0.6	92.5	9.3±2.1	0.9±0.1	
MoNaph+S	PHP: PHEN 1:1	H ₂	440	87.2±1.3	9.9±0.7	2.9±0.6	94.8	15.8±1.9	7.5±0.1	
Thermal	PHP: PHEN 5:1	H ₂	440	87.1±1.1	9.0±0.0	3.9±1.2	86.0	16.8±2.3	8.6±0.1	
MoNaph+S ^b	PHP: PHEN 5:1	H ₂	440	79.5±3.6	14.9±2.1	5.6±1.5	80.0	26.2±5.1	10.7±0.6	
MoNaph+S	PHP: PHEN 5:1	N ₂	440	97.8±0.2	0.5±0.1	1.7±0.7	86.4	3.9±1.0	8.9±0.1	

^a Reaction Conditions: 30 min; 8.7 MPa H₂ or N₂ at ambient temperature; catalyst loading = 1000 ppm on total reactant charge basis; the total amount of reactant charged is approximately 0.1 g.

^b Moles of H₂ Accepted per 100 moles of PHEN; H₂ accepted = (2 x THPN mol% + 1 x DHPN mol%) x 100.

^c Moles of H₂ Donated per 100 moles of PHP; H₂ Donated = (3 x DCP mol% + 5 x HHP mol% + 6 x THP mol% + 7 x DHP mol% + 8 x PYR mol%) x 100.