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THE ROLE OF THE RESID SOLVENT IN CO-PROCESSING WITH FINELY DIVIDED CATALYSTS

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INTRODUCTION

The overall objective of this project is to evaluate the role of the resid in coprocessing. The primary purpose of this initial work was to establish under thermal and catalytic reaction conditions whether hydrogen transfer occurred between cycloalkane type structures that are present in resids and aromatics that are present in coal and liquefied coal.

The research this quarter focused upon evaluating different reaction systems for performing model donor and model acceptor studies. The first system that was evaluated involved anthracene (ANT) as the model acceptor. Previous results had shown that ANT did not convert substantially in a thermal reaction at 380° C (Wang 1992); however, more was converted (about 50%) at 440 °C. The results from the reactions performed last quarter indicated that substantial hydrogenation of ANT occurred thermally at 440 °C; more than had been observed previously. The reactors that were used, though, had contained substantial amounts of catalysts prior to the performance of the thermal reactions. Hence, the passivity of the reactors was questioned and new reactors were fabricated. Some of the reactions using ANT were performed again and are reported herein.

The second part of the work performed this quarter was to evaluate hydrogen transfer from the cycloalkane, perhydropyrene (PHP), to the aromatic phenanthrene (PHEN). Reactions were performed at a 1:1 PHP to PHEN weight ratio and with a 5:1 PHP to PHEN ratio. The reactions were performed thermally and catalytically at 400 and 425 °C using molybdenum naphthenate and nickel octoate as catalysts. Reactions were also performed with added sulfur either as elemental sulfur or benzothiophene.

EXPERIMENTAL

Anthracene Reactions

Anthracene thermal hydrogenation reactions were performed at 400 °C, for 30 min, with 1250 psig H_2 at ambient temperature. Reactions were performed in N_2 also introduced at 1250 psig at ambient temperature. The reaction products were collected and analyzed by gas chromatography (GC) using a Varian 3300 gas chromatograph equipped with a flame ionization detector and HT-5 column. Quantitation was performed by using the internal standard method with biphenyl as the internal standard. The retention time and response factors for the reactant and product peaks were established by analyzing authentic materials. The unknown product peaks in the chromatogram were analyzed by GC-mass spectrometry.

Perhydropyrene and Phenanthrene Reactions

The reactants, phenanthrene and perhydropyrene, were obtained from Aldrich Chemical Company. Phenanthrene, purchased at 98% purity, was recrystallized from ethanol prior to being used in model coprocessing reactions. Perhydropyrene was used as received. Two catalysts were used for this study: molybdenum naphthenate and nickel octoate. Each catalyst was introduced at 1000 ppm level. Both of these catalysts were obtained from Shepherd Chemical Company. The catalyst precursor, molybdenum naphthenate, was introduced with excess elemental sulfur being present in the reactor. The sulfur was added as 0.12 times the weight of molybdenum naphthenate, which was usually about 0.0004 g of sulfur. Sulfur was also tested as a catalytic material and was introduced either as elemental sulfur or as benzothiophene.

The model coprocessing reactions were conducted in ~20 cm^3 stainless steel tubular microreactors. The reactor was charged with 0.1 g of each reactant for the reactions performed with a 1:1 weight ratio of perhydropyrene:phenanthrene; the reactions that contained a 5:1 weight ratio of perhydropyrene to phenanthrene contained between 0.03 to 0.1 g of perhydropyrene and 0.15 to 1.0 g of phenanthrene. Hydrogen or nitrogen, at a pressure of 1250 psig at ambient temperature, was also charged. The reactions were conducted at 400 or 440 °C for 30 min at an agitation rate of 450 rpm. The reactors were shaken horizontally. After reaction, the reactor was quenched in room temperature water. The gaseous products were released and the solid and liquid products were recovered by tetrahydrofuran.

RESULTS AND DISCUSSION

Anthracene Reactions

The anthracene thermal hydrogenation (HYD) reactions given in Table 1 were performed at 400 °C. The HYD of ANT was substantial and averaged 87% conversion of ANT to hydrogenated products of dihydroanthracene (DHA) and tetrahydroanthracene (THA). DHA was the predominant product. A search of the literature showed that the HYD of ANT under thermal reaction conditions at 400 °C yielded 85.6% conversion with 69 wt % DHA being formed as the primary product and ~15% THA formed as the secondary product (Song, et al., 1988). Reactions of ANT were also performed in a N_2 atmosphere to ascertain if ANT had little or no reactivity without hydrogen being present. These results are also given in Table 1. Approximately 6% conversion of ANT occurred in N_2.

The choice of ANT as a hydrogen acceptor is questionable because ANT is quite reactive under thermal hydrogenation conditions. ANT was also very reactive under catalytic conditions. ANT totally converted to hydrogenated products in the presence of $NiMo/Al_2O_3$ (Song et al., 1988). Hence, other hydrogen acceptor compounds were investigated. ANT as a three-ring aromatic was more easily hydrogenated thermally and catalytically with $NiMo/Al_2O_3$ than the three-ring PHEN (Song et al., 1988). Phenanthrene showed much less conversion of ~4% thermally than did ANT and only ~80% conversion in the presence of $NiMo/Al_2O_3$. Therefore, PHEN was chosen as a possible model.

Perhydropyrene and Phenanthrene Reactions

The research performed this quarter involved evaluating PHEN as a model acceptor at coprocessing reaction conditions. PHEN was reacted in the presence of hydrogen with and without a cycloalkane hydrogen donor. The research performed with PHEN was at 400 and 440 °C, and the results are given in Table 2.

PHEN was tested under a variety of reaction conditions as presented in Table 2. Thermal reactions, reactions with elemental sulfur, reactions with Mo naphthenate (MoNaph) and with Ni octoate were performed in a hydrogen atmosphere at 400 °C. The hydrogenation reaction products formed were dihydrophenanthrene (DHPN) and tetrahydrophenanthrene (THPN). Under any of these reaction conditions, the hydrogen acceptance of PHEN of molecular H_2 was much less than observed with anthracene. Low conversions of PHEN were observed in the thermal reactions, in the reactions with elemental sulfur and in the reactions with Ni octoate (NiOct). In the presence of MoNaph and excess sulfur, the conversion of PHEN was

the greatest but was less than 10 wt %, indicating that PHEN does not readily hydrogenate, even in the presence of a relatively active catalyst.

Table 3 presents the reactions of PHP performed catalytically and thermally at 400 °C in hydrogen. The two catalysts used were MoNaph and NiOct. With MoNaph, excess sulfur, in the form of elemental sulfur, was added to the system. Sufficient excess sulfur was added so that 3:1 times the amount of sulfur needed to form MoS_2 was present. No sulfur was added to the reaction containing NiOct. Under these reaction conditions, both catalytic and thermal at 400 °C, PHP did not react substantially. Only in several reactions did a small amount of pyrene (PYR) form, usually 0.3% or less; in reactions with both catalysts, a small amount of decahydropyrene (DCHP) was formed; and with MoNaph, 0.3% or less of hexahydropyrene (HHP) was formed. The recoveries from both the thermal and MoNaph reactions of PHP were in the high 70% range while higher recoveries (in the low 90% range) were obtained with NiOct.

Reactions of PHP and PHEN together were performed at 400 °C in hydrogen with the following conditions: thermal, thermal with sulfur present as benzothiophene, thermal with sulfur present as elemental sulfur, catalytically with MoNaph with excess sulfur and catalytically with NiOct. The PHP:PHEN weight ratio was kept at either 1:1 or 5:1. A trace amount of PYR was occasionally observed from PHP, but in most of the reactions, no PYR was observed. Other dehydrogenation products of HHP and DCHP were formed. The amount of HHP and DCHP formed varied from reaction to reaction, depending upon the particular conditions of that reaction. The most HHP and DCHP formed occurred with MoNaph and excess sulfur at both the 1:1 and 5:1 PHP:PHEN ratios.

Reactions performed at 440 °C with PHP and PHEN are presented in Table 5. Again both 1:1 and 5:1 weight ratios of PHP to PHEN were used. The reaction products observed from PHP were PYR, DCHP, and HHP. The total amount of these products ranged from 1 to 3 wt %. PHEN was hydrogenated under the reaction conditions and produced both DHPN and THPN as the reaction products. The hydrogenation appeared to be sequential with DHPN being produced first and then THPN being produced from DHPN.

The degree of reactivity of PHEN reacted with PHP varied according to the reaction conditions used. Thermal reactions yielded 4.7% conversion with a 5:1 PHP:PHEN ratio and 1.7% conversion with a 1:1 ratio. The reaction with NiOct showed more conversion at the 5:1 ratio than at the 1:1 ratio. However, the effect of PHP being present in the reactor was very small since PHEN hydrogenated with NiOct without any PHP present yielded the same conversion as the 1:1 ratio. MoNaph+S present in the reactor was most effective for HYD of PHEN. The conversion increased from the reaction of PHEN alone at 9.7% (Table 2) to 13.3% with a 1:1 PHP:PHEN ratio to 17.5% with a 5:1 PHP:PHEN ratio (Table 4). Hence, the addition of PHP to the PHEN system with MoNaph+S had a positive effect on the amount PHEN hydrogenated.

The reactions performed in N_2 showed low reactivity regardless of the ratio of PHP: PHEN. Conversions of 4% or less of PHEN were observed. Although no PYR was observed in the reaction products, DCHP was formed as a dehydrogenation product from PHP. Hydrogen for PHEN HYD came from the hydrogenation released from PHP to form DCHP.

Reactions were also performed with PHP and PHEN at 440 °C in both H_2 and N_2 atmospheres as presented in Table 5. The conversion levels of PHEN ranked as reactions

containing MoNaph+S > NiOct > no catalyst when PHP was present in a 5:1 PHP:PHEN ratio. When the conversion of PHEN in the 5:1 ratio was compared to that in the 1:1 ratio, then the additional PHP appeared to increase the conversion of PHEN somewhat. However, the reaction with no PHP yielded almost the same conversion of PHEN as did the reaction with 5:1 PHP:PHEN.

A comparison of the HYD of PHEN with PHP and with PHP at 1:1 and 5:1 ratios at 400°C and 440 °C is given in Table 6. The only noticeable influence of PHP on the reaction was the enhancement caused by the PHP when MoNaph+S were present as the catalyst. This enhancement was observed in terms of both coal conversion and in the increased production of DHPN and THPN. This effect was obvioius at 400 °C. The reactions at 440 °C seemed to be more influenced by the increased temperature than by the presence of PHP.

Calculations were performed in order to describe more fully the reactivity of the PHP and PHEN systems. The moles of hydrogen accepted by PHEN was determined for each reaction. The HYD of PHEN was also determined and was based 100 mol of product. The degree of HYD is defined as being the sum of the mole percent of DHPN and two times the mole percent of THPN. The most hydrogenated product was considered to be THPN. The HYD of PHEN serves a measure for comparing the efficacy of the different systems for hydrogenating PHEN. The hydrogen efficiency of the reaction was also determined. Hydrogen efficiency is defined as the moles of hydrogen donated by PHP divided by the moles of hydrogen accepted by the model compounds.

The reactions of PHP and PHEN at 400 °C given in Table 7 gave a PHEN HYD of 23.7% with MoNaph+S for a 5:1 PHP:PHEN ratio and of 17.2% for a 1:1 ratio. The thermal

reactions and reactions with benzothiophene and NiOct all showed a HYD of less than 10%. Hence, the reaction with MoNaph+S was by far the most active system at 400 °C. At higher reaction temperature of 440 °C, the overall conversion and HYD increased compared to 400 °C as shown in Table 8. The effect of reaction temperature is shown on Figure 1. The thermal and NiOct systems were most influenced by temperature while the MoNaph+S system was much less affected. The reaction system with MoNaph+S at a 5:1 PHP:PHEN ratio at 440 °C yielded the most HYD of PHEN at 26.2% but the other systems at the 5:1 ratio were also quite reactive, yielding ~17% HYD. A comparison of the HYD of PHEN based on 100 moles of product for the two different weight ratios is given in Figure 2. The only system that was not sensitive to an increased PHP to PHEN ratio was NiOct at 440 °C.

The reaction of PHEN alone, as presented in Table 9, also showed high PHEN HYD at 400 °C when MoNaph+S was present, yielding 12.0%, while both the thermal and NiOct reactions gave much less HYD, 6.8% and 2.5%, respectively. Raising the temperature to 440°C increased the amount of HYD observed for all reactions. However, the system with MoNaph+S was still more reactive giving about twice the HYD of the thermal reaction.

SUMMARY

The phenanthrene and perhydropyrene reaction system in hydrogen appeared to be more affected by the presence of the hydrogen atmosphere than by the presence of perhydropyrene. The only system that appeared to be strongly affected by perhydropyrene was the reaction that contained Mo naphthenate and sulfur and a 1:1 ratio of perhydropyrene to phenanthrene. At this time, calculations are being made to determine the hydrogen efficiency of the system. The results of these calculations will be included in the next quarterly report.

References

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Table 1. Thermal Hydrogenation of Anthracene at 400°C

Reaction No.	Product Distribution, wt %				Recovery %
	ANT	DHA	THA	Others	
H_2 Atmosphere					
1	12.3	78.4	4.3	5.0	95.6
2	13.8	77.7	4.0	4.4	86.8
3	13.1	77.2	5.6	4.1	91.0
4	13.8	74.9	6.3	5.0	89.0
5	11.3	75.9	6.8	6.0	93.0
Average	12.9(1.07)	76.8(1.41)	5.4(1.2)	4.9(0.7)	
N_2 Atmosphere					
1	95.7	1.5		2.8	90.8
2	93.1	1.8		5.5	94.2
Average	94.4(1.8)	1.7(0.2)		4.2(1.9)	

Reaction Conditions: 400°C, 30 min, 1250 psig H_2 or N_2 at ambient temperature.

ANT = anthracene, DHA = dihydroanthracene, THA = tetrahydroanthracene
Others = unidentified GC peaks

Table 2. Product Distributions from Phenanthrene Reactions at 400 and 440°C in H_2

Reaction Condition	Catalyst Loading (ppm)	Temperature (°C)	Product Distribution (wt%)			Recovery (%)
			PHEN	DHPN	THPN	
Thermal	0 0	400	94.5 95.9	3.1 2.2	2.4 1.9	85.0 81.9
Elemental Sulfur	6116 5982	400	96.9 96.4	1.7 1.9	1.4 1.6	86.5 84.1
MoNaph+S	997 1014	400	90.9 90.6	6.1 6.0	3.0 3.1	88.5 86.0
NiOct	993 1000	400	98.0 98.7	1.1 0.4	0.9 0.9	97.3 90.2
MoNaph	978 968	400	82.0 90.0	13.1 7.0	4.9 3.0	86.5 82.9
Thermal	0 0	440	89.6 92.0	6.7 5.3	3.7 2.7	91.3 92.3
MoNaph+S	1003 993	440	77.2 84.9	15.1 12.4	7.4 5.3	97.6 86.9

Reaction Conditions: 440°C, 30 min, 1250 psi H_2 at ambient temperature
PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene

Table 3. Product Distribution of Perhydropyrene from Thermal and Catalytic Reactions at 400°C in H_2

Reaction Conditions	Catalyst Loading (ppm)	Product Distribution (wt %)				Recovery (%)
		PHP	HHP	DCHP	PYR	
Thermal	0 0	99.7 100.0	0.0 0.0	0.0 0.0	0.3 0.0	78.5 75.5
MoNaph+S	1164 1138	98.3 98.9	0.3 0.2	1.4 0.7	0.1 0.2	73.9 77.5
NiOct	1006 957	99.3 99.4	0.0 0.0	0.7 0.6	0.0 0.0	92.6 93.1

Reaction Conditions: 400°C, 30 min., 1250 psi H_2 at ambient temperature
PHP = perhydropyrene; PYR = pyrene; MoNaph = Mo naphthenate; NiOct = Ni octoate; S = sulfur

Table 4. Product Distributions of Reactions of Perhydropyrene with Phenanthrene at 400°C in H_2 and N_2 Atmospheres

Reaction Conditions	Catalyst Loading (ppm)	Weight Ratio PHP:PHEN	Atmosphere	Product Distribution (wt %)							Recovery (%)
				PHP	HHP	DCHP	PYR	PHEN	DHPN	THPN	
Thermal	0 0	5:1	H_2	99.4 99.6	0.0 0.0	0.6 0.6	0 0	96.6 94.1	1.4 2.2	2.0 3.7	89.3 84.5
Mo Naph	977 1004	5:1	H_2	99.0 99.1	0.0 0.0	1.0 0.9	0 0	91.8 90.8	4.1 5.6	4.1 3.6	82.6 90.7
MoNaph+S	1007 1003	5:1	H_2	98.2 98.2	0.4 0.3	1.4 1.5	0 0	82.5 82.6	10.8 10.7	6.7 6.6	91.3 94.5
NiOct	1031 999	5:1	H_2	99.6 99.3	0.0 0.0	0.4 0.7	0 0	94.0 94.5	2.1 1.6	3.9 3.9	76.8 75.6
Thermal	0 0	1:1	H_2	99.3 100	0.3 0.0	0.3 0.0	0.1 0	96.8 97.1	1.6 1.5	1.6 1.3	88.0 89.0
Elemental S	5112 5587	1:1	H_2	99.6 99.9	0.4 0.1	0.0 0.0	0 trace	95.6 96.9	2.2 1.4	2.2 1.7	94.2 95.4
Benzothiophene	4900 5587	1:1	H_2	100 100	0.0 0.0	0.0 0.0	0 0	97.6 98.6	1.1 0.6	1.3 0.8	89.0 89.2
MoNaph+S	1027 1014	1:1	H_2	98.6 97.9	0.5 0.5	0.7 1.6	0 0	84.8 88.7	10.5 7.5	4.7 3.7	90.0 90.0
NiOct	1019 1027	1:1	H_2	99.1 99.6	0.0 0.0	0.7 0.4	0.2 0	97.8 98.0	1.2 0.9	1.0 1.1	96.8 89.8
Thermal	0 0	5:1	N_2	98.9 99.6	0.0 0.0	1.1 0.4	0 0	98.1 98.5	0 0	1.9 1.5	99 85.6
MoNaph	1033 973	5:1	N_2	99.0 100	0.0 0.0	1.0 0.0	0 0	99 99	0 0	1 1	85.6 87.1

Reaction Conditions: 400°C, 30 min, 1250 psi H_2 or N_2 at ambient temperature.
PYR = pyrene; PHP = perhydropyrene; PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene
MoNaph = Mo naphthenate; NiOct = Ni octoate; S = sulfur

Table 5. Product Distribution from Reactions of Perhydropyrene and Phenanthrene at 440°C in H_2 and N_2 Atmospheres[a]

Reaction Condition	Catalyst Loading (ppm)	Atmos-phere	Weight Ratio PHP to PHEN	Product Distribution (wt%)							Recovery (%)
				PHP[b]	HHP	DCHP	PYR	PHEN	DHPN	THPN	
Thermal	0 0	H_2	5:1	99.0 98.9	1.0 1.1	1.0 1.1	0 0	85.8 88.1	9.0 9.1	5.2 2.8	84.9 87.1
NiOct	1014 1013	H_2	5:1	98.7 98.7	1.0 1.1	1.0 1.1	0 0	90.2 83.4	7.8 10.4	2.0 6.2	30.7 81.8
MoNaph+S	952 988	H_2	5:1	99.3 98.5	NA[c] 1.3	NA 1.3	0 0	75.6 82.9	17.1 12.9	7.3 4.2	86.1 73.2
MoNaph+S	1036 1009	N_2	5:1	98.3 98.1	0.6 0.6	0.6 0.9	0.4 0.4	98.0 97.5	1.0 0.0	1.0 2.5	70.0 86.9
Thermal	0 0	H_2	1:1	99.6 99.8	0.0 0.0	0.4 0.2	0.0 0.0	94.5 91.6	3.7 5.3	1.8 3.1	95.1 90.0
Elemental S	5426	H_2	1:1	98.1	0.5	1.3	0.1	93.3	5.2	1.5	89.7
MoNaph+S	968 1001	H_2	1:1	99.3 97.8	0.5 0.4	0.0 1.4	0.3 0.4	88.2 85.7	9.3 10.7	2.4 3.6	83.5 86.0

[a] Reaction Conditions: 440° C, 30 min., 1250 psi H_2 or N_2 at ambient temperature
[b] PHP = perhydropyrene; PYR = pyrene; PHEN = phenanthrene; DHPN = dihydrophhenanthrene; THPN = tetrahydrophenanthrene
MoNaph = Mo naphthenate; NiOct = Ni octoate; S = sulfur
[c] NA = not available

Table 6. Comparison of the Hydrogenation of Phenanthrene in the Presence and Absence of Perhydropyrene in a Hydrogen Atmosphere

Reaction Condition	Catalyst Loading (ppm)	Product Distribution (wt %)			Recovery (%)
		PHEN	DHPN	THPN	
Phenanthrene Hydrogenation Without Perhydropyrene at 400°C					
Thermal	0 0	94.5 95.9	3.1 2.2	2.4 1.9	85.0 81.9
MoNaph+S	997 1014	90.9 90.6	6.1 6.0	3.0 3.1	88.5 86.0
NiOct	993 1000	98.0 98.7	1.1 0.4	0.9 0.9	97.3 90.2
Phenanthrene Hydrogenation With Perhydropyrene at 1:1 Ratio at 400°C					
Thermal	0 0	96.8 97.1	1.6 1.5	1.6 1.3	89.1 88.0
MoNaph+S	1027 1014	84.8 88.7	10.5 7.5	4.7 3.7	90.0 90.0
NiOct	1019 1027	97.8 98.0	1.2 0.9	1.0 1.1	96.8 89.8
Phenanthrene Hydrogenation with Perhydropyrene at 5:1 Ratio					
Thermal	0 0	96.6 94.1	1.4 2.2	2.0 3.7	89.3 84.3
MoNaph+S	1007 1003	82.5 82.6	10.8 10.7	6.7 6.6	91.3 94.5
NiOct	1031 999	94.0 94.5	2.1 1.6	3.9 3.9	76.8 75.6

(Continued)

Reaction Conditions: 400°C, 30 min., 1250 psi H_2 at ambient temperature

PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene
NiOct = Ni octoate; MoNaph = Mo naphthenate; S = sulfur

Table 6. Comparison of the Hydrogenation of Phenanthrene in the Presence and Absence of Perhydropyrene in a Hydrogen Atmosphere (Continued)

Reaction Condition	Catalyst Loading (ppm)	Product Distribution (wt %)			Recovery (%)
		PHEN	DHPN	THPN	
Phenanthrene Hydrogenation Without Perhydropyrene at 440°C					
Thermal	0 0	89.6 92.0	6.7 5.3	3.7 2.7	91.3 92.3
MoNaph+S	1003 993	77.2 84.9	15.1 12.4	7.4 5.3	97.6 86.9
Phenanthrene Hydrogenation With Perhydropyrene at 1:1 Ratio at 440°C					
Thermal	0 0	94.5 91.6	3.7 5.3	1.8 3.1	95.1 90.0
MoNaph+S	968 1001	88.2 85.7	9.3 10.7	2.4 3.6	83.5 86.0
Phenanthrene Hydrogenation with Perhydropyrene at 5:1 Ratio at 440°C					
Thermal	0 0	85.8 88.1	9.0 9.1	5.2 2.8	84.9 87.1
MoNaph+S	952 988	75.6 82.9	17.1 12.9	7.3 4.2	86.1 73.2

Reaction Conditions: 440°C, 30 min., 1250 psi H_2 at ambient temperature

PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene;
MoNaph = Mo naphthenate; S = sulfur

Table 7. Reactions of Perhydropyrene and Phenanthrene at 400°C

Reaction Condition	Atmos-phere	PHP:PHEN Ratio	Product Distribution (mol%)			PHEN Conversion %	HYD (mol) Based on 100 mol Product	Hydrogen Accepted[a] (mol x 10^4)
			PHEN	DHPN	THPN			
Thermal	H_2	5:1	95.4(1.2)	1.8(0.4)	2.8(0.8)	4.6	7.4(2.1)	0.17(0.04)
MoNaph+S	H_2	5:1	82.8(0.1)	10.7(0.6)	6.5(0.1)	17.2	23.7(0.1)	0.51(0.07)
NiOct	H_2	5:1	94.2(0.1)	2.0(0.1)	3.8(0.0)	5.8	9.6(0.1)	0.29(0.07)
Thermal	H_2	1:1	97.1(0.2)	1.5(0.0)	1.4(0.2)	2.9	4.4(0.3)	0.22(0.02)
MoNaph+S	H_2	1:1	86.9(2.0)	8.9(1.5)	4.1(0.5)	13.1	17.2(2.5)	0.78(0.21)
NiOct	H_2	1:1	97.9(0.1)	0.8(0.3)	1.0(0.3)	2.1	2.9(0.7)	0.15(0.04)
Benzothiophene	H_2	1:1	98.1(0.5)	0.8(0.3)	1.0(0.3)	1.9	2.9(0.7)	0.15(0.04)
Thermal	N_2	5:1	98.4(0.2)	0.0	1.7(0.2)	1.6	3.3(0.4)	0.08(0.02)
MoNaph+S	N_2	5:1	99.0(0.0)	0.0	1.0(0.0)	1.0	2.0(0.0)	0.04(0.01)

[a] Amount of H_2 accepted by PHEN based on average loading.
Mo = Mo naphthenate
Ni = Ni octoate
S = sulfur

Reaction Conditions: 30 min; 1250 psig H_2 or N_2 at ambient temperature.

PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene

Table 8. Reactions of Perhydropyrene and Phenanthrene at 440°C

Reaction Condition	Atmosphere	PHP:PHEN Ratio	mol%			PHEN Conversion (%)	HYD (mol) Based on 100 mol Product	Hydrogen Accepted[a] (mol x 10^4)
			PHEN	DHPN	THPN			
Thermal	H_2	5:1	87.1(1.1)	9.0(0.0)	3.9(1.2)	12.9	16.8(2.3)	0.27(0.04)
MoNaph+S	H_2	5:1	79.5(3.6)	14.9(2.1)	5.6(1.5)	20.5	26.2(5.1)	0.30(0.06)
NiOct	H_2	5:1	87.0(3.4)	9.0(1.3)	4.0(2.1)	13.0	17.1(5.4)	0.35(0.07)
Thermal	H_2	1:1	93.2(1.4)	4.5(0.8)	2.4(0.6)	6.8	9.3(2.1)	0.48(0.10)
MoNaph+S	H_2	1:1	87.2(1.3)	9.9(0.7)	2.9(0.6)	12.8	15.8(1.9)	0.62(0.04)
S	H_2	1:1	93.3(0.0)	5.2(0.0)	1.5(0.0)	6.7	16.2(0.0)	0.37(0.0)
MoNaph+S	N_2	5:1	97.8(0.2)	0.5(0.1)	1.7(0.7)	2.2	3.9(1.0)	0.06(0.03)

[a] Amount of H_2 accepted by PHEN based on average loading.
MoNaph = Mo naphthenate
NiOct = Ni octoate
S = sulfur

Reaction Conditions: 30 min; 1250 psig H_2 or N_2 at ambient temperature.

PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene

Table 9. Reactions of Phenanthrene at 400 and 440°C

Reaction Condition	Atmos-phere	Tempera-ture (°C)	Product Distribution (mol %)			PHEN Conver-sion (%)	HYD (mol) Based on 100 mol Product	Hydrogen Accepted[a] (mol x 10^4)
			PHEN	DHPN	THPN			
Thermal	H_2	400	95.3(0.7)	2.6(0.5)	2.1(0.2)	4.7	6.8(0.9)	0.3(0.1)
MoNaph+S	H_2	400	91.0(0.0)	6.0(0.0)	3.0(0.1)	9.0	12.0(0.1)	0.6(0.0)
NiOct	H_2	400	98.4(0.4)	0.7(0.4)	0.9(0.0)	1.6	2.5(0.4)	0.2(0.1)
Thermal	H_2	440	90.9(1.2)	5.9(0.7)	3.1(0.5)	9.1	12.2(1.7)	0.6(0.1)
MoNaph+S	H_2	440	81.3(3.8)	12.8(2.4)	5.9(1.4)	18.7	24.6(5.2)	2.5(0.8)

[a] MoNaph = Mo naphthenate
NiOct = Ni octoate
S = sulfur

Reaction Conditions: 30 min; 1250 psig H_2 at ambient temperature.

PHEN = phenanthrene; DHPN = dihydrophenanthrene; THPN = tetrahydrophenanthrene; PHP = perhydropyrene

Figure 1. Reactions of Perhydropyrene and Phenanthrene at 400 and 440°C.

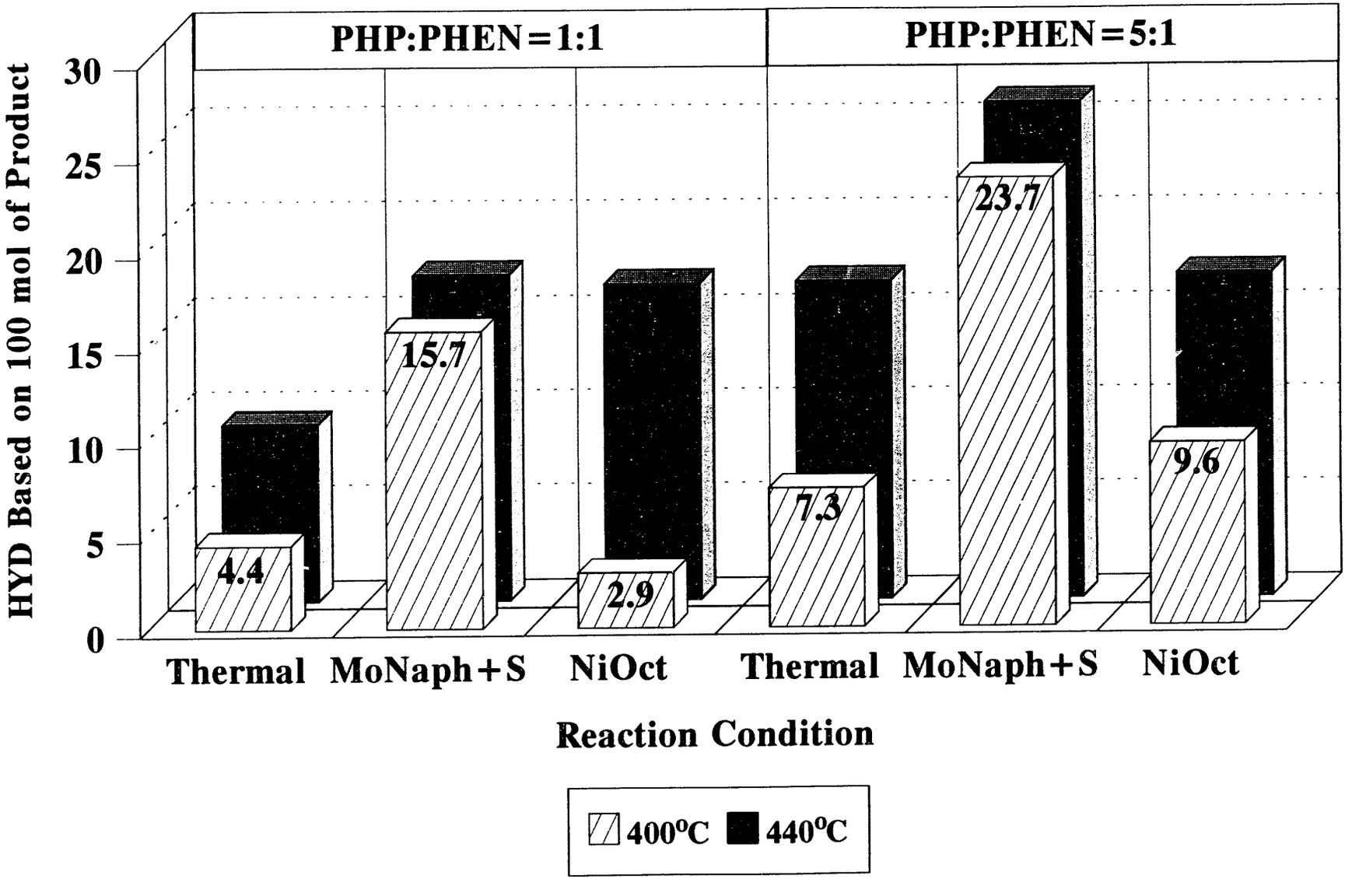
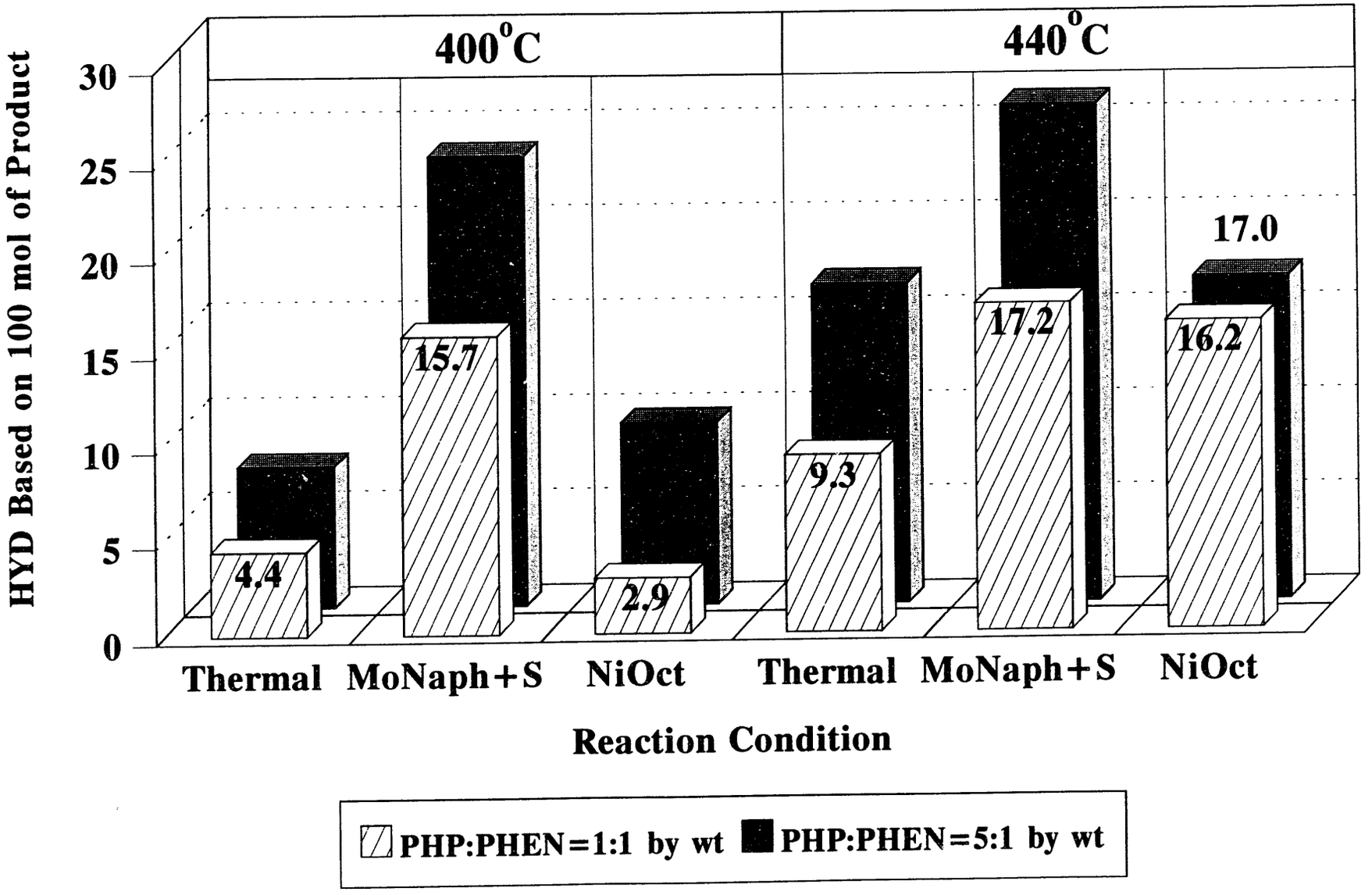


Figure 2. Reactions of Perhydropyrene and Phenanthrene at 400 and 440°C.



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