

AN INVESTIGATION OF HYDROGEN TRANSFER IN COPROCESSING USING MODELS AND REDUCED RESIDS

Shu-Li Wang and Christine W. Curtis
Chemical Engineering Department
Auburn University, AL 36849-5127

Abstract

Hydrogen donor reactions in the coprocessing of coal and petroleum resids have been investigated using different hydrogen-rich models and reduced resids as donors and aromatics as acceptors. Three hydrogen-rich donor species were compared: cyclic olefins, hydroaromatics, and cycloalkanes; the aromatic acceptors included pyrene and anthracene; and the resids were reduced by the Birch method. Hydrogen was transferred most readily at 380°C by cyclic olefins, followed by hydroaromatics, and the least was transferred by cycloalkanes. Catalysis by thiophenol promoted the hydrogen transfer by the cycloalkanes at 380°C but had little effect at 440°C. Reduced resids transferred substantially more hydrogen to an aromatic species than did the untreated resids. In a tertiary system of reduced resid, cycloalkane, and aromatic, the reduced resids yielded more hydrogen transfer and promoted hydrogen donation from the cycloalkanes in a nitrogen atmosphere. Reduction of resids by the Birch method appeared to be an effective means of increasing the hydrogen donor ability of resids.

Introduction

Hydrogen donor reactions are important in the transfer of hydrogen from hydrogen-rich compounds to aromatic species in the liquefaction of coal. Different hydrogen-rich compounds have different propensities for donating hydrogen under liquefaction conditions; just as different hydrogen acceptors have different propensities for accepting hydrogen. In this study, the ability of three different hydrogen donors to donate hydrogen and the efficiency of their hydrogen transfer to aromatic species were compared under both hydrogen and nitrogen atmospheres.

The compounds compared were cyclic olefins, which have been shown to release their hydrogen quickly under liquefaction conditions, hydroaromatics, that are typically present in coal liquids and are known hydrogen donors, and cycloalkanes, that are present in resids and do not readily donate their hydrogen. Promotion of hydrogen transfer from the hydrogen-rich cycloalkanes to aromatics is of special interest because these structures are prevalent in resids and offer an indigenous source of hydrogen. Rudnick [1986a,b] has shown that the introduction of an organic sulfur compound promotes this type of hydrogen transfer. In this work, catalytic reactions with organic sulfur were performed to evaluate the effect on the hydrogen transfer from cycloalkanes to aromatics at 380°C and 440°C under both nitrogen and hydrogen atmospheres. These results were compared to thermal reactions at the same conditions.

In the coprocessing of coal with resid, resids have limited ability to solvate coal and to donate hydrogen because of the predominance of indigenous saturated structures. Increasing the hydrogen donability of the chemical species of the resid should enhance the ability of the resid to solvate coal. This enhancement was induced by reducing resids by the Birch reduction method [Birch and Rao, 1972] which is known for producing cyclic olefinic structures from

aromatic species. The ability of these reduced resids to transfer hydrogen to aromatics was determined and compared to the parent resids.

Experimental

Materials and Analysis. Reactions were performed using the following hydrogen-rich compounds: cyclic olefins, isotetralin (ISO) which was synthesized in our laboratory, and hexahydroanthracene (HHA) from Aldrich; hydroaromatics, tetralin (TET) and 9,10-dihydroanthracene (DHA) both from Aldrich; and a cycloalkane, perhydropyrene (PHP) from Aldrich. The compounds used as hydrogen acceptors in these reactions were anthracene (ANT) and pyrene (PYR) both obtained from Aldrich. Thiophenol was used as a catalyst for promoting the transfer of hydrogen from cycloalkanes to aromatics. The catalyst was introduced at a level of 2,000 ppm of sulfur. The reaction products were analyzed by gas chromatography using a Varian 3300 gas chromatograph with FID detection and biphenyl as the internal standard. Qualitative analysis of the products was conducted with a VG70 EHF GC-mass spectrometer.

Thermal and catalytic reactions were performed with the parent resids and treated resids which had been reduced by the Birch method [Birch and Rao, 1972]. The Birch reduction method reduces aromatics in the resid to cyclic olefins and other partially saturated forms by adding Na, alcohol, and ammonia to the resid which is dissolved in tetrahydrofuran (THF) as the solvent. The resids that were used in these reactions were Maya obtained from Amoco Oil Co., a deasphalted resid from a deasphalting resid unit (DAU) from Exxon and south Louisiana resid (S. LA) also from Exxon; the hydrogen acceptor for the reactions was ANT; and the catalyst was 2000 ppm sulfur introduced at thiophenol. The products from these resid reactions were analyzed by gas chromatography to determine the reaction products from both the model donors and acceptors and by solvent fractionation to determine the products from the resid. The solvents used in the extraction of the thermal products were toluene (TOL) and THF, but in the catalytic reactions, hexane (HEX) was also used.

Reaction Procedures. Reactions were performed in 20 cm³ stainless steel tubular microreactors with single reactants charged at 0.1 g and with binary reactants charged at 0.1 g aromatic and the hydrogen-rich compound introduced at a 1:1 or 5:1 weight ratio to the aromatic. The reaction conditions for the thermal model reactions were 380°C, 30 minutes, nitrogen or hydrogen at 400 psi at ambient, and horizontal agitation at 435 rpm.

Definitions. The following definitions were used: Percent hydrogenation (% HYD) is defined as the moles of hydrogen required to achieve the liquid products as a percentage of the moles of hydrogen required to produce the most hydrogenated product. In the case of ANT, octahydroanthracene (OHA) was considered the most hydrogenated product; in the case of pyrene, the most hydrogenated product was taken to be hexahydropyrene (HHP). Hydrogen efficiency is defined as the moles of hydrogen accepted by the hydrogen acceptor divided by the moles of hydrogen released by the hydrogen donor. The amount of gaseous hydrogen that was accepted by the hydrogen donor is defined as the moles of hydrogen accepted by the hydrogen acceptor under a hydrogen atmosphere minus the moles of hydrogen accepted by the hydrogen acceptor under a nitrogen atmosphere.

Results and Discussion

Thermal Reactions of Hydrogen-Rich Compounds with Aromatics. Reactions of hydrogen-rich compounds, cyclic olefins, hydroaromatics and cycloalkanes, with aromatic species, ANT and PYR, were performed in N₂ and H₂ atmospheres. The purpose of these

experiments was to determine how much hydrogen was released from the hydrogen donor and how much of that hydrogen was accepted by the aromatic species. The reaction of the cyclic olefins with the aromatics resulted in the products of tetralin (TET), 1,2- and 1,4-dihydronaphthalene (DHN), and naphthalene (NAP) from ISO and of OHA, tetrahydroanthracene (THA), DHA and ANT from HHA. The hydroaromatics produced NAP from TET and THA plus ANT from DHA. The cycloalkane PHP only produced PYR as its product. The amount of hydrogen released from the hydrogen-rich compounds was in the order of cyclic olefins > hydroaromatics > cycloalkanes. The amount of hydrogen released from each species was dependent upon the type of atmosphere and acceptor present as well as upon the amount of hydrogen-rich compound present. These results are shown in Table 1.

ANT, as an acceptor, formed DHA and THA as products while PYR formed dihydropyrene (DHP), tetrahydropyrene (THP) and hexahydropyrene (HHP) as products. The % HYD of the aromatic species in individual reactions and in binary reactions with hydrogen-rich species is presented in Table 1. The most hydrogenation of the aromatic species occurred in the presence of the cyclic olefins and in a H₂ atmosphere. ANT was more reactive than PYR when reacted with the same hydrogen donor and at the same conditions.

The hydrogen efficiency of the systems was also compared in Table 1. As the value for hydrogen efficiency approached one, then the amount of hydrogen released was equal to the amount of hydrogen accepted. The hydrogen efficiency of the systems in the N₂ atmosphere showed that the cyclic olefins were the least efficient since they released substantially more hydrogen than the aromatic species was able to accept. In the H₂ atmosphere, hydrogen efficiencies of greater than one were obtained which indicated that gaseous hydrogen was participating in the reactions. The moles of gaseous H₂ incorporated into the reaction products from the hydrogen acceptor varied with the system as shown in Table 1.

Catalytic Reactions of Hydrogen-Rich Compounds with Aromatics. Catalytic reactions were performed with a reaction system of PHP with ANT at a weight ratio of PHP to ANT of 1:1 and 5:1 in both N₂ and H₂ atmospheres at reaction temperatures of 380 and 440°C. The catalyst was 2000 ppm of sulfur introduced as thiophenol. The products produced from PHP were HHP and PYR at both reaction temperatures; the products produced from ANT were DHA at 380°C and DHA, THA, and OHA at 440°C. The amount of hydrogen donated and accepted from these reactions was compared to that in the thermal reactions at the same conditions (Table 2).

The addition of the sulfur catalyst increased the amount of hydrogen donation from PHP. The catalyst also increased the amount of hydrogen acceptance and, hence, hydrogenation of ANT to DHA in both atmospheres. Under thermal conditions, PHP produced only PYR as the product while under catalytic conditions HHP was formed in larger amounts than PYR. The catalysis of hydrogen donation and acceptance by S was observed most in the PHP/ANT system at a 5:1 weight ratio at 380°C in H₂ and N₂ compared to the thermal reaction where a substantial increase in the hydrogenation of the aromatic was obtained compared to the thermal reaction. The promotion of the reaction by S was also observed in N₂ but not in H₂ at 440°C. The higher temperature of 440°C with H₂ as the atmosphere seemed to have more effect on hydrogen donation and acceptance than did the catalyst, because the % HYD's of ANT were equivalent in thermal and catalytic reactions.

The hydrogen efficiency in N₂ shown in Table 2 was always less than one with the hydrogen efficiency of 5:1 PHP to ANT reaction systems frequently having a higher efficiency than the 1:1 ratio. The hydrogen efficiencies for the reactions in the hydrogen atmosphere were always greater than one indicating incorporation of gaseous hydrogen into the reaction

products. The number of moles of gaseous hydrogen incorporated was substantially higher for the higher temperature reactions at 440°C than those at 380°C.

Hydrogen Transfer from Resids. The purpose of this work was to evaluate the efficacy of hydrogen transfer from hydrogen-enriched reduced resids to an aromatic species and to compare that to the hydrogen transfer from the parent resid. The systems used were the reduced and parent resids with the acceptor ANT and the ternary system of a reduced or parent resid with ANT and the hydrogen-rich species, PHP.

The reactions of the reduced and parent resids with ANT in both N₂ and H₂ atmospheres are presented in Table 3. All three of the reduced resids yielded substantially more hydrogenation of ANT to DHA and THA than did the parent resids. The hydrogen atmosphere promoted more hydrogenation of ANT than did nitrogen regardless of whether the resid was reduced or was the parent. The product distributions from each of the resid reactions are given in Table 4. The binary system of resid with ANT produced some THF soluble material and insoluble organic material (IOM) in each reaction regardless of resid or atmosphere. The reduced resids showed a higher propensity for having THF soluble materials in the presence of ANT than did the parent resids.

When PHP was added to the resid/ANT system, the change observed was fairly small in terms of the hydrogenation of ANT. However, more hydrogen uptake appeared to be achieved from hydrogen transferred from hydrogen-rich species than from gaseous hydrogen. The %HYD of ANT in N₂ was higher in the systems with PHP present than in those without PHP. Small increases in %HYD were also observed in the hydrogen atmosphere. The product distributions for the ternary systems (Table 4) showed that all of the resids remained toluene soluble. The amount of hexane solubles produced was greater in the hydrogen atmosphere than in the nitrogen for all but one of the systems.

Summary

Hydrogen donation from three types of hydrogen-rich species resulted in substantial hydrogen donation from cyclic olefins, less from hydroaromatic species, and a very small amount from cycloalkanes by comparison. The hydrogen transfer by cycloalkanes to aromatics was promoted by the presence of sulfur. This promotion, however, appeared to be condition specific with more catalysis apparent at 380°C in N₂ than at any other condition. Reduced resids produced by the Birch method were more effective hydrogen donors than their parent resids. Hydrogen enrichment of these resids produced a solvent more effective for the thermal hydrogenation of aromatic species such as are present in coal.

References

- Rudnick, L.R., European Patent 195, 541, 1986a; European Patent 195, 539, 1986b.
Birch, A.J., G.S. Rao, *Advances in Organic Chemistry, Methods and Results*, Vol. 8, E.C. Taylor, ed., Wiley Interscience, NY, NY, 1972.

Table 1. Thermal Reaction Systems

Reaction Conditions	Mole of Hydrogen Released x 10 ⁴		Percent Hydrogenation (%)		Hydrogen Efficiency		Moles of H ₂ From Gas-cous H ₂ Moles X 10 ⁴	
	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂
ISO	10.73(0.17)	11.39(0.06)						
ISO/ANT (1:1)	11.08(0.03)	17.00(0.06)	19.24(0.27)	18.32(0.14)	0.39(0.01)	0.24(0.00)	0.21(0.09)	
ISO/ANT (5:1)	44.69(0.61)	45.42(0.13)	24.88(0.07)	24.39(0.18)	0.12(0.00)	0.12(0.00)	0.12(0.05)	
TET	0.05(0.03)	0.03(0.00)						
TET/ANT (1:1)	0.05(0.02)	0.00(0.00)	4.53(0.26)	0.25(0.05)	19.77(2.89)	---	0.96(0.06)	
TET/ANT (5:1)	0.11(0.03)	0.39(0.03)	4.45(0.25)	0.93(0.07)	8.84(1.68)	0.54(0.14)	0.40(0.08)	
PHP	0.00(0.00)	0.00(0.00)						
PHP/ANT (1:1)	0.27(0.02)	0.28(0.05)	3.08(0.28)	0.46(0.17)	2.57(0.22)	0.35(0.09)	0.59(0.08)	
PHP/ANT (5:1)	0.18(0.01)	0.25(0.02)	3.97(0.42)	0.63(0.02)	4.91(0.84)	0.57(0.07)	0.74(0.09)	
ISO/PYR (1:1)	10.99(0.13)	11.80(0.19)	6.02(0.25)	4.11(0.30)	0.08(0.00)	0.05(0.00)	0.28(0.07)	
ISO/PYR (5:1)	49.46(0.79)	47.65(0.32)	17.30(0.27)	13.20(0.75)	0.05(0.00)	0.04(0.00)	0.61(0.15)	
TET/PYR (1:1)	0.00(0.00)	0.00(0.00)	0.00(0.00)	0.00(0.00)	---	---	0.00(0.00)	
TET/PYR (5:1)	0.07(0.00)	0.28(0.19)	0.41(0.09)	0.16(0.01)	0.79(0.18)	0.17(0.12)	0.02(0.01)	
HHA	9.95(0.31)	9.95(0.09)						
HHA/PYR (1:1)	9.93(0.01)	9.52(0.31)	13.59(0.23)	8.14(0.84)	0.20(0.00)	0.13(0.02)	0.81(0.15)	
HHA/PYR (5:1)	35.84(0.48)	43.67(0.82)	30.35(0.97)	10.40(2.48)	0.13(0.01)	0.04(0.01)	2.95(0.50)	
DHA	0.35(0.06)	0.28(0.00)						
DHA/PYR (1:1)	0.43(0.01)	0.52(0.05)	2.46(0.18)	1.63(0.85)	0.87(0.06)	0.44(0.20)	0.15(0.13)	
DHA/PYR (5:1)	1.96(0.03)	1.78(0.19)	11.27(0.35)	8.58(2.17)	0.85(0.04)	0.72(0.17)	0.40(0.37)	

* --- means no hydrogen was released in that condition.

ISO = isotetralin

PHP = perhydropyrene

ANT = anthracene

TET = tetralin

HHA = hexahydroanthracene

DHA = dihydroanthracene

Table 2. Catalytic Reaction Systems

Reaction Conditions	Mole of Hydrogen Released x 10 ⁴		Percent Hydrogenation (%)		Hydrogen Efficiency		Moles of H ₂ From Gas-ous H ₂ Moles X 10 ⁴	
	H ₂	N ₂	H ₂	N ₂	H ₂	N ₂	H ₂	H ₂
380°C Thermal								
PHP/ANT (1:1)	0.27(0.02)	0.28(0.05)	3.08(0.28)	0.46(0.17)	2.57(0.22)	0.35(0.09)	0.59(0.08)	
PHP/ANT (5:1)	0.18(0.01)	0.25(0.02)	3.97(0.42)	0.63(0.02)	4.91(0.84)	0.57(0.07)	0.74(0.09)	
380°C Catalytic								
PHP/ANT (1:1)	0.75(0.01)	0.71(0.16)	4.83(0.53)	0.96(0.14)	1.44(0.18)	0.31(0.91)	0.88(0.14)	
PHP/ANT (5:1)	1.05(0.14)	1.44(0.22)	11.11(0.60)	4.40(0.09)	2.38(0.28)	0.70(0.12)	1.49(0.13)	
440°C Thermal								
PHP/ANT (1:1)	0.24(0.13)	0.55(0.09)	15.44(0.64)	0.30(0.04)	14.13(0.27)	0.13(0.04)	3.40(0.14)	
PHP/ANT (5:1)	0.61(0.13)	0.77(0.15)	15.47(0.16)	2.60(0.19)	5.88(1.27)	0.78(0.15)	2.88(0.07)	
440°C Catalytic								
PHP/ANT (1:1)	0.61(0.03)	0.55(0.27)	14.93(0.19)	1.48(0.13)	5.48(0.30)	0.77(0.49)	3.01(0.09)	
PHP/ANT (5:1)	0.67(0.08)	1.18(0.22)	14.51(0.33)	3.25(0.22)	4.91(0.55)	0.64(0.17)	2.55(0.14)	

PHP = perhydropyrene ANT = anthracene

Table 3. Resid Reaction Systems

Reaction Conditions	Moles of Hydrogen Accepted x 10 ⁴		Percent Hydrogenation (%)		Moles of H ₂ From Gaseous H ₂ Moles X 10 ⁴	
	H ₂	N ₂	H ₂	N ₂	H ₂	H ₂
Maya/ANT (Reduced)	3.15(0.19)	1.62(0.07)	7.03(0.42)	3.61(0.16)	1.52(0.26)	
Maya/ANT (Reduced)	8.02(0.31)	4.26(0.06)	17.90(0.60)	9.50(0.15)	3.76(0.37)	
DAU/ANT (Reduced)	4.69(0.15)	1.61(0.11)	10.03(0.51)	3.59(0.23)	3.07(0.26)	
DAU/ANT (Reduced)	8.31(0.14)	5.08(0.15)	17.94(0.44)	11.34(0.34)	3.22(0.29)	
S.LA/ANT (Reduced)	3.26(0.05)	0.97(0.10)	7.28(0.11)	2.15(0.24)	2.29(0.15)	
S.LA/ANT (Reduced)	5.26(0.07)	3.25(0.17)	11.73(0.17)	7.24(0.38)	2.01(0.24)	
Maya/PHP/ANT (Reduced)	4.98(0.18)	3.09(0.36)	11.10(0.42)	6.90(0.81)	1.88(0.54)	
Maya/PHP/ANT (Reduced)	7.88(0.07)	5.84(0.21)	17.60(0.15)	13.03(0.47)	2.04(0.28)	
DAU/PHP/ANT (Reduced)	4.72(0.23)	3.59(0.09)	10.54(0.52)	8.02(0.21)	1.12(0.32)	
DAU/PHP/ANT (Reduced)	8.08(0.09)	5.85(0.04)	18.02(0.22)	13.06(0.08)	2.22(0.13)	
S.LA/PHP/ANT (Reduced)	3.02(0.17)	1.95(0.14)	6.73(0.38)	4.36(0.31)	1.06(0.31)	
S.LA/PHP/ANT (Reduced)	6.15(0.14)	5.06(0.13)	13.73(0.32)	11.29(0.29)	1.09(0.27)	

DAU = deasphalted resid
 S.LA = South Louisiana resid
 PHP = perhydropyrene
 ANT = anthracene