TECHNICAL PROGRESS REPORT

Coal Conversion Laboratory
CHEMICAL ENGINEERING DEPARTMENT
AUBURN UNIVERSITY
Auburn, Alabama 36830

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SOLVENT TAILORING IN COAL LIQUEFACTION

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OBJECTIVE

The objective of this research program is to determine the effects of phase behavior of process components on coal liquefaction and of solvent composition on coal-dissolution behavior as well as their combined effects on second-stage upgrading. Through understanding the fundamentals of coal dissolution, this research will provide data for tailoring solvents to attain higher reaction rates, increased conversion, and higher product selectivity.

ACKNOWLEDGEMENT

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PROJECT TITLE: Solvent Tailoring In Coal Liquefaction

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SUMMARY

The work discussed in this report was the first in the area of ranking model solvents in terms of their hydrogen donor ability. It was felt that results of this study would have important applications in later studies.

A series of twenty-three model donor solvents were used to rank their efficacy for the dissolution of Western Kentucky #9/14 coal. The transfer of hydrogen from the solvent to the coal fragments, as measured by coal conversion, was examined at three levels of available hydrogen. The hydrogen donors are ranked according to their ability to convert coal to THF solubles.

Aromatic analogs of the model donors showed little ability to convert coal to THF solubles. Factors which influence hydrogen donation include the presence of heteroatoms or substituents both internal and external to the aromatic or hydroaromatic rings, the degree of hydrogenation, the aromaticity or nonaromaticity of the hydroaromatics, and the presence of five-membered rings. A relationship between heats of formation and hydrogen donor ability was shown for hydroaromatics within two ring or three ring homologous series. A model hydrogen acceptor, benzophenone, was also used to rank model donors and a comparison was made with the model donor ranking by coal conversion.

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Introduction

Recent studies have shown the importance of hydrogen donors and hydrogen transfer reactions in the dissolution of coal (1-4). Curran et al. (3) has postulated that hydrogen transfer from solvent to coal during liquefaction proceeds via a free radical mechanism. By comparing the dissolution of a HVC bituminous coal in tetralin, naphthalene and dodecane, Neavel (4) has demonstrated that the presence of hydrogen donors substantially enhances coal conversion at reaction times greater than four minutes. Derbyshire and Whitehurst(5) have examined the stabilization of dissolving coal fragments by hydrogen transfer from the hydroaromatic fraction of the coal to an aromatic which, in turn, donates hydrogen to a coal free radical.

The basic premise that hydrogen transfer reactions play an important role in the dissolution of coal is generally well-accepted and serves as a starting point for this study. Many researchers (6-14) have attempted to qualitatively and quantitatively determine the hydrogen donors present in liquefaction solvents as well as to predict the efficacy of specific donors. The need to quantitate hydrogen donor ability of process solvents and the hydroaromaticity of coal has led to the development of several spectroscopic methods for determining the hydroaromaticity of process solvents (6-8). In addition, catalytic dehydrogenation has been used to determine the hydroaromatic content of coals (9-10) and of process solvents (11). Model hydrogen acceptors have been employed to rank the efficacy of process solvents as well as to rank the reactivity of individual hydrogen donor compounds. Comparisons of the stability of radical anions formed during

hydrogen abstraction has also been used to evaluate the relative propensity of hydrogen donation from different model donors (12-13). Thermodynamic considerations involving resonance energies of hydroaromatics and their aromatic analogs have been used to predict the hydrogen donor abilities of different hydroaromatics (14).

Process solvents are comprised of a number of different chemical entities with the compositions being dependent upon coal feed type and process conditions. It is highly desirable for such solvents to contain the optimal blend of hydrogen donors as well as compounds with active functional groups for maximal coal conversion. The objective of this study is to determine the ability of different model donors to convert coal to THF solubles during liquefaction and, thereby, rank their effectiveness. Although a number of hydrogen donors as well as aromatic compounds have been tested previously for their coal dissolution ability, their reactivity is difficult to compare due to the differing reaction conditions and coals used by the various investigators. This comprehensive study offers a systematic comparison of many hydrogen donors and their aromatic analogs under a single prescribed set of reaction conditions using the same bituminous coal. It is not suggested that the results obtained with this single coal will apply to all coals; however, by using the same coal for all donors, a significant variable in testing donor ability is eliminated. Determining the chemical characteristics of hydrogen donors most effective for coal conversion may elucidate the hydrogen donors desirable for maximal coal dissolution and may provide insight into the mechanism of hydrogen donation.

A related aspect of hydrogen transfer reactions explored in this study is to determine if model acceptor experiments effectively mimic the behavior of coal in liquefaction, and, if so, can they be utilized to rank solvents for their coal liquefaction effectiveness. A brief review of the literature shows that

a number of model acceptor systems have been studied including bibenzyl(15-16) benzophenone (17), 1,1-binaphthyl (18), and aromatics (14) such as anthracene and phenanthrene. The benzyl radical, generated thermally, has been used by Cronauer et al. (15) to study hydrogen transfer in model solvents such as tetralin, decalin and mesitylene and to determine the reactivity of various C-C and C-O functional groups likely to be encountered during liquefaction. Bockrath and associates (16) have also used the benzyl radical to study the effectiveness of both model donor and liquefaction process solvents. Raaen and Roark (17) have used benzophenone as a model acceptor to rank hydrogen donors, to determine the effect of hydroxyl substituents on the rate of hydrogen donation, and to measure the hydroaromaticity of coal. Ten hydrogen donors have been ranked by Kline and Harrison (18) using, 1,1 binaphthyl as an acceptor. This use of model acceptors is based on the hypothesis that the model acceptor reacts in a manner similar to that of coal at liquefaction conditions. The direct measurement of coal conversion for model donors in this work permits comparison with model acceptor results.

Experimental

Equipment and Analyses. A 15 cc stainless steel tubing bomb reactor described previously (19) was immersed in the temperature controlled fluidized sandbath and agitated vertically at 700 rpm during the reaction.

Coal Reactions. Reactions of Western Kentucky 9/14 coal with hydroaromatic and aromatic compounds were performed in a tubing bomb reactor for 30 minutes at 400 C in a nitrogen atmosphere while agitating at 700 rpm. For each reaction, two grams of Western Kentucky 9/14 coal (Table 1), ground to 20-270 mesh and dried in a vacuum oven overnight, and 4 grams of 1-methylnaphthalene were used. The moles of hydrogen donor model compound charged to the bomb was varied so that an equal amount of donor hydrogen was charged in each experiment. Experiments were performed using three levels of donor hydrogen, being one, two, or four times 4.39×10^{-3} moles.

Table 1

Ultimate and Proximate Analysis of Western Kentucky 9/14 Coal[a]

Ultimate Analysis (wt % maf)	
C	80.1
H	5.8
N	1.3
O	9.5
S	3.4

Proximate Analysis (wt % maf)	
Volatile matter	38.0
Fixed carbon	53.0
Ash	8.9
Moisture	4.2

[a]Wilsonville SRC Pilot Plant feed coal analyses

The aromatic compounds were typically introduced at the second level. Coal conversion was measured by an ash balance using tetrahydrofuran as the wash solvent.

Chemicals. The model compounds used in this study and their respective sources are listed in Table 2.

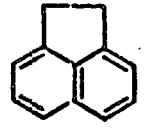
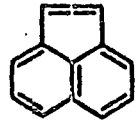
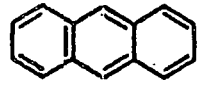
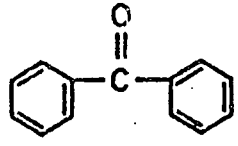
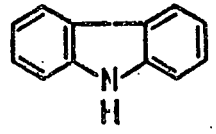
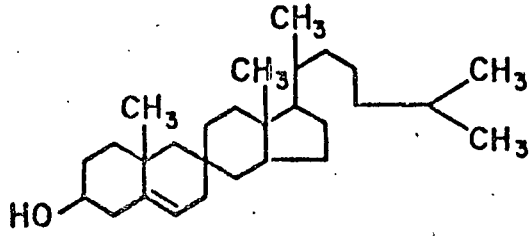
Benzophenone Reactions. Reactions of benzophenone with hydrogen donor compounds were performed in the above mentioned pressurized reactor using 5.5×10^{-4} moles of hydroaromatic compound, 5.5×10^{-4} moles of benzophenone, 1 gram of 1-methylnaphthalene as solvent and a nitrogen atmosphere. The reactions were performed for 60 minutes at 400°C while agitating at 700 rpm. Reaction products from benzophenone and the different hydrogen donors were analyzed by gas chromatography. Chromatographic analyses were performed on a Varian Model 3700 gas chromatograph using a flame ionization detector, an eight foot, 1/8 inch O.D. stainless steel column packed with SP 2250 obtained from Supelco. Temperature programming was used for some analyses.

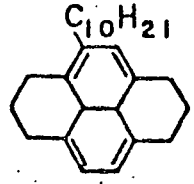
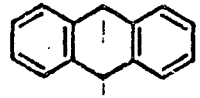
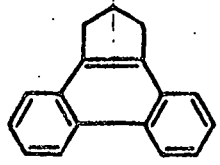
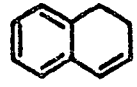
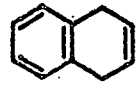
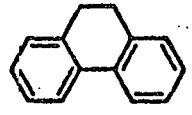
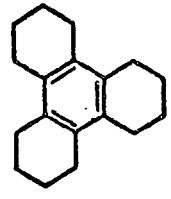
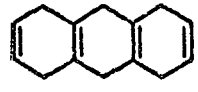
Results and Discussion

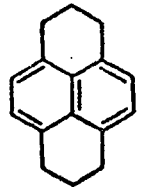
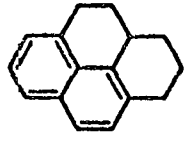
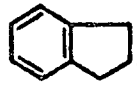
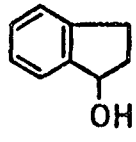
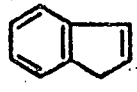
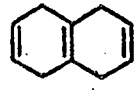
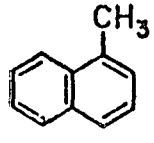
Reactions of Hydrogen Donors with Coal. A series of twenty-three model donor solvents were used to rank their efficacy for the dissolution of Western Kentucky #9/14 coal. Compounds with two, three and four rings with different degrees of hydrogenation were selected. In addition, some compounds with five-membered rings such as indan and acenaphthene were also used. Also included among these donors were compounds with ring nitrogens and with hydroxyl substituents. The ranking of model donors according to their reactivity for coal conversion at three levels of donatable hydrogen is given in Table 3. At the lowest level of donatable hydrogen, coal conversion varied from a low of 26% using 2,3-dihydro-1H-cyclopenta(L)-phenanthrene to a high of 48.6% conversion for 1,2,3,4-tetrahydrocarbazole. The low level of coal conversion obtained at this

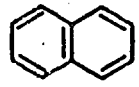
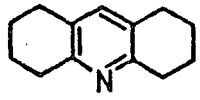
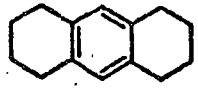
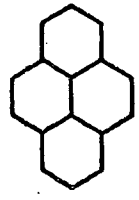
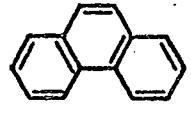
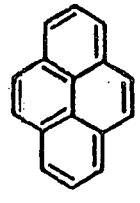
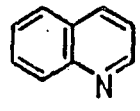
Table 2

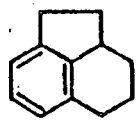
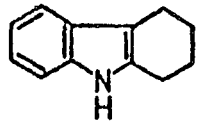
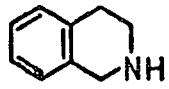
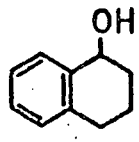
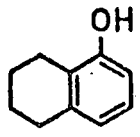
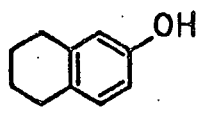
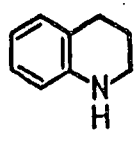
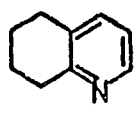
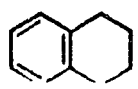
List of Model Compound Used, Their Structures, and Sources

Compound	Structural Formula	Purity	Source
Acenaphthene		+99.9	
Acenaphthylene		99.2	Aldrich
Anthracene		99.4	Aldrich
Benzophenone		+99	Aldrich
Carbazole		98.14	Aldrich
Cholesterol		94.5	Aldrich

Compound	Structural Formula	Purity	Source
1-n-decyl-3,4,5,8,9,10-hexahydropyrene		82.54	API-PSU*
9,10-Dihydroanthracene		98.5	Aldrich
2,3-Dihydro-1 H-cyclopenta (L) phenanthrene			Aldrich
1,2-Dihydronaphthalene		98.0	Aldrich
1,4-Dihydronaphthalene		92.9	Pfalty & Bauer
9,10-Dihydrophenanthrene		98.0	Aldrich
Dodecahydrotriphenylene		97.07	Aldrich
1,4,5,8,9,10-Hexahydroanthracene		99.04	Aldrich

Compound	Structural Formula	Purity	Source
1,2,3,6,7,8-Hexahydropyrene		98.55	Aldrich
1,2,2a,3,4,5-Hexahydropyrene		95.34	API-PSU*
Indan		98.1	Aldrich
1-Indanol		98.86	Aldrich
Indene		99.8	Aldrich
Isotetralin (1,4,5,8-tetrahydro-naphthalene)		99.48	Aldrich
1-Methylnaphthalene		99.3	Aldrich

Compound	Structural Formula	Purity	Source
Naphthalene		99.5	Fisher Scientific
1,2,3,4,5,6,7,8-Octahydroacridine		99.87	Aldrich
1,2,3,4,5,6,7,8-Octahydro-anthracene		99.06	Aldrich
Perhydropyrene		80.18	Aldrich
Phenanthrene		100	Aldrich
Pyrene		99.8	Aldrich
Quinoline		+99	Alfa

Compound	Structural Formula	Purity	Source
2a,3,4,5-Tetrahydroacenaphthene		99.99	Aldrich
1,2,3,4-Tetrahydrocarbazole		99.96	Aldrich
1,2,3,4-Tetrahydroisoquinoline		99.84	Aldrich
1,2,3,4-Tetrahydro-1-naphthol		98.98	Aldrich
5,6,7,8-Tetrahydro-1-naphthol		99.92	Aldrich
5,6,7,8-Tetrahydro-2-naphthol		99.24	Aldrich
1,2,3,4-Tetrahydroquinoline		99.84	Aldrich
5,6,7,8-Tetrahydroquinoline		99.94	Aldrich
Tetralin		98.71	Aldrich

*High Molecular Weight Hydrocarbon Bank
at Pennsylvania State University

Table 3

Coal Conversion in Hydrogen Donor Solvents

Hydrogen Donor Compounds	Coal Conversion Amount of Donatable Hydrogen ($\times 10^{-3}$ moles)		
	4.89	2 x 4.89	4 x 4.89
9,10 Dihydrophenanthrene	39.8	65.5	84.5
1,2,3,4-Tetrahydroquinoline	36.6	60.6	84.1
1,2,3,6,7,8-Hexahydropyrene	39.1	67.4	81.4
1,2,3,4-Tetrahydrocarbazole	48.6	67.8	81.1
Isotetralin	46.8	67.5	80.6
1,4,5,8,9,10-Hexahydroanthracene	48.3	65.4	77.8
Dodecahydrotriphenylene	44.1	59.4	71.0
9,10-Dihydroanthracene	39.0	57.7	70.4
2a,3,4,5-Tetrahydroacenaphthene	36.9	50.2	70.3
1,2,3,4-Tetrahydroisoquinoline	39.7	57.4	68.5
5,6,7,8-Tetrahydro-2-naphthol	39.5	53.1	68.4
5,6,7,8-Tetrahydro-1-naphthol	38.9	56.1	66.5
Octahydroanthracene	43.0	54.3	66.3
Octahydroacridine	40.0	53.6	65.1
1,2-Dihydronaphthalene	36.7	52.2	64.5
1,2,3,4-Tetrahydro-1-naphthol	34.6	44.4	58.7
Tetralin	35.0	43.6	58.0
5,6,7,8-Tetrahydroquinoline	34.6	43.0	46.8
Cholesterol	41.7	38.2	--
Acenaphthene	29.9	38.1	40.1
1-Indanol	28.1	33.4	39.0
Indan	26.9	34.1	38.4
2,3-Dihydro-1H-cyclopenta (L) phenanthrene	26.0	29.9	33.0
Blank	18.6	18.6	18.6

concentration indicates hydrogen deficiency in the reaction. Increased levels of donatable hydrogen produced increased levels of coal conversion with the low conversion being 29.9% and 33.0% for 2,3,-dihydro-1H-cyclopenta (L) phenanthrene for the second and third concentration levels, respectively, and the high being 67.8% for 1,2,3,4-tetrahydrocarbazole for the second level and 84.9% for 9,10-dihydrophenanthrene for the third level. Comparison of the ranking of the intermediate compounds shows few changes in reactivity at the three concentration levels.

In these reactions with coal, all solvents were compared at the same level of donatable hydrogen. A wide variation in coal conversion in solvents containing the same amount of donor hydrogen was observed. These results indicate that the hydrogen donor content of a solvent alone would not be sufficient to completely define its effectiveness as a coal liquefaction solvent. As a general rule, though, increased conversion resulted from increased hydrogen donor content for a particular solvent. Comparison of the donor ranking demonstrates certain chemical and functional group characteristics which are beneficial to coal dissolution. Comparison of 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroisoquinoline to tetralin and 5,6,7,8-tetrahydroquinoline indicates that a donor with nitrogen in a saturated ring increases coal conversion over a donor with nitrogen in the aromatic ring or the hydrocarbon counterpart. Position of the nitrogen in the saturated ring and associated electronic effects may also influence the donor reactivity in that the tetrahydroisoquinoline isomer converts less coal than does tetrahydroquinoline. Nonaromatic hydroaromatic isomers such as isotetralin and 1,4,5,8,9,10-hexahydroanthracene readily donate hydrogen. Isotetralin compared to tetralin is particularly illustrative of the increased reactivity with isotetralin yielding 80.6% conversion at the high concentration level while tetralin yields 58%.

Compounds containing saturated five-membered rings such as acenaphthene, indan, and 2,3,-dihydro-1H-cyclopenta (L) phenanthrene show low conversions for each hydrogen concentration level. The hydrogen donor ability of indan is of

interest in coal liquefaction due to the fact that tetralin, a compound commonly used as a hydrogen donor, can isomerize to form 1-methylindan whose hydrogen donor ability is questionable. Indan has been used in model acceptor experiments; its reactivity varied according to the model acceptor used. With benzophenone, indan gives no conversion, but with the benzyl radical indan donates hydrogen readily to form toluene. In a recent study using ESR spectroscopy by Kim et al. (13), indan quenched free radicals generated from bibenzyl more readily than did either hydrophenanthrene or tetralin. At all three donor levels, low levels of coal conversion were observed for indan, increasing from 26.9% to 38.4% with increasing concentration of indan. In this case, the ranking using the bibenzyl acceptor can lead to erroneous conclusions concerning indan's ability to dissolve coal. At the second concentration level, the unsaturated analog, indene, showed even lower conversion (Figure 1). The addition of an hydroxyl substituent on the unsaturated five-membered ring has little effect on coal conversion.

Addition of hydroxyl substituents to donor compounds have in some cases shown increased liquefaction yields for some coals (20). In this study, a comparison of the dissolution behavior for Western Kentucky #9/14 coal is made among tetralin, 1,2,3,4-tetrahydro-1-naphthol, with the hydroxyl on the saturated ring, and 5,6,7,8-tetrahydro-2-naphthol, on the aromatic ring. The coal dissolution ability of 1,2,3,4-tetrahydro-1-naphthol is essentially equivalent to tetralin. In contrast, the 2-naphthol shows an increase in conversion compared to the tetralin for the second and third concentration levels. Position of the hydroxyl evidently affects the chemical interactions between the coal and donor causing this increase in conversion.

Thermodynamic Considerations. The stability of different model donors can be examined thermodynamically by comparing their heats of formation. A number of

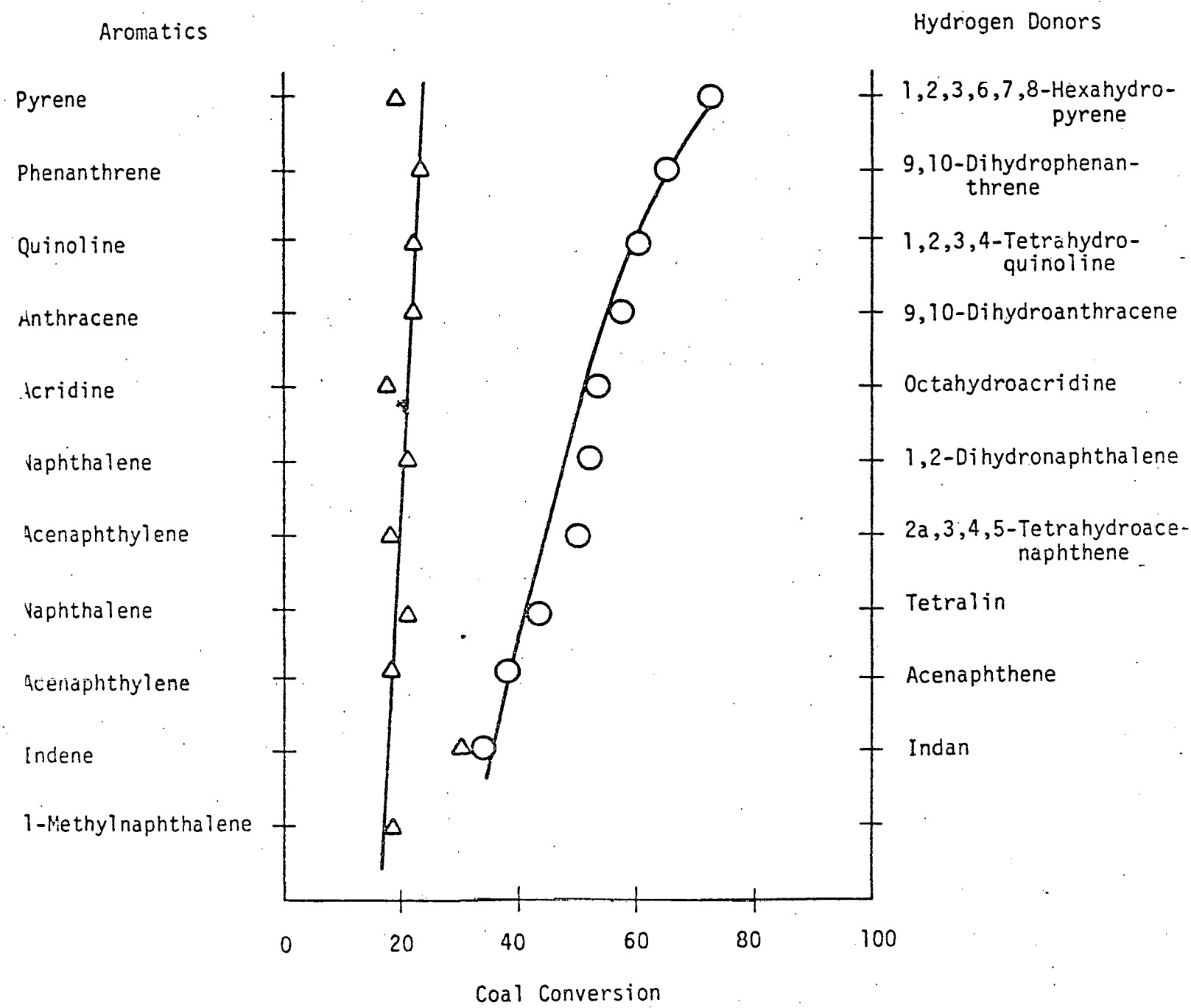


Figure 1: Coal Conversion Abilities of Hydrogen Donor Compounds and Their Aromatic Analogs.

heats of formation for hydrogen donors and aromatics have been developed and catalogued by Shaw et al. (21). Comparison of the heats of formation between either the two or three ring groupings may give an indication of reactivity and hence donor effectiveness.

Comparison of the stabilities of two-ring hydrogenated compounds listed in Table 6 ranks the reactivity of these compounds as

isotetralin > 1,4-dihydronaphthalene > 1,2-dihydronaphthalene > tetralin

The ranking of two ring donors based upon experimental coal conversion shows the same order of reactivity although sufficient quantity of 1,4-dihydronaphthalene was not available to permit coal conversion experiments. Both dihydronaphthalenes and tetralin were reacted with benzophenone and gave the same ranking as stated above (as will be described later).

According to heats of formation of the hydrogenated three ring compounds given in Table 4, 9,10-dihydroanthracene should be a better donor than octahydroanthracene. The coal conversions obtained from these donors are in agreement with the stability ranking. The high reactivity of 1,4,5,8,9,10-hexahydroanthracene in the experimental coal conversion is most likely due to the fact it is a nonaromatic hydroaromatic. The heats of formation of nonaromatic hydroaromatics are typically 20 to 30 kcal/mole (21) higher than that of the next least stable hydroaromatic, rendering the nonaromatic hydroaromatic highly unstable. Extrapolating from the heats of formation of similar compounds, it is likely that 1,4,5,8,9,10-hexahydroanthracene is less stable than 9,10-dihydroanthracene. The ranking according to reactivity then is

1,4,5,8,9,10-hexahydroanthracene >> 9,10-dihydroanthracene > octahydroanthracene

which is in accordance with experimental coal conversion. In reaction with benzophenone, 9,10-dihydroanthracene is more reactive than octahydroanthracene. Of the three ring phenanthrene series only 9,10-dihydrophenanthrene was used

Table 4

Stabilities of Selected Hydrogen Donor Compounds

Hydrogen Donors	ΔH_f° (kcal/mole)
Two Ring	
Isotetralin	38.0
1,4-Dihydronaphthalene	32.9
1,2-Dihydronaphthalene	31.6
Tetralin	6.0
Three Ring	
9,10-Dihydroanthracene	38.2
Octahydroanthracene	- 8.2
9,10-Dihydrophenanthrene	37.0

Table 5

Reactivity of Model Donors using Benzophenone as an Acceptor

Hydrogen Donor	Conversions	
	Benzophenone (Mole %)	Hydroaromatic (Weight %)
Cholesterol	25.1	96.6
1,2,2a,3,4,5-Hexahydropyrene	22.3	36.1
1,4-Dihydronaphthalene	19.2	100
1-n-Decyl-3,4,5,8,9,10 Hexahydropyrene	18.1	49.2
1,2,3,4-Tetrahydroquinoline	15.6	35.9
9,10-Dihydroanthracene	10.9	38.1
1,2-Dihydronaphthalene	9.8	83.2
9,10-Dihydrophenanthrene	8.1	21.9
2a,3,4,5-Tetrahydroacenaphthene	2.7	19.3
Acenaphthene	0.0	0.0
Octahydroanthracene	0.0	0.0
Tetralin	0.0	0.0
Indan	0.0	0.0
1-Methylnaphthalene	0.0	0.0

Table 6

Comparison of Hydrogen Donor Reactivity
Using Different Model Acceptors

Hydrogen Donor Compound	Model Acceptor: Benzophenone		Bibenzyl		1,1' Binaphthyl
	This Work	Raaen & Roark	Bockrath et al.		Kline and Harrison
	I	II	I	II	
Cholesterol	25.1	39			
Tetrahydrocarbazole		28			
1,2,2a,3,4,5-Hexahydropyrene	22.3				28.0
1,2,3,6,7,8-Hexahydropyrene					
1,4-Dihydronaphthalene	19.2				3.4
1-n-Decyl-3,4,5,8,9,10 Hexahydropyrene	18.1				
1,2,3,4-Tetrahydroquinoline	15.6	21	0.18	1.65	
9,10-Dihydroanthracene	10.9	13		36.9	17.7
1,2-Dihydronaphthalene	9.8	28			
9,10-Dihydrophenanthrene	8.1	20	0.31	1.67	3.1
2a,3,4,5-Tetrahydroacenaphthene	2.7				
Acenaphthene	0.0			1.36	
Octahydroanthracene	0.0				
Tetralin	0.0	17	0.27	1.17	6.3
Decalin		0.0			1.3
Indan	0.0		0.35	0.57	
1-Indanol			0.28	2.74	
2-Indanol			0.40	3.45	
1-Methylnaphthalene	0.0		0.13	0.15	
Blank					1.4

and has a similar heat of formation as its isomer, 9,10-dihydroanthracene. Comparison of the coal conversions of these isomers shows that 9,10-dihydrophenanthrene converts more coal, ∿84.5%, than 9,10-dihydroanthracene ∿70.4% at the highest donor level. The conversion of benzophenone by these isomers is also quite similar. The order of reactivity of the compounds is

9,10-dihydroanthracene ≅ 9,10-dihydrophenanthrene > octahydroanthracene

Although the reactivity of the hydrogen donors for coal conversion within a homologous ring series appears to correlate with the heats of formation, comparison of different homologous ring series such as the four ring series with the two ring series does not correlate.

Reaction of Aromatics with Coal. The aromatic analogs of selected hydroaromatics were tested for their ability to convert coal to THF solubles and were introduced at the middle concentration level. A comparison of coal solubility with hydrogen donors and their aromatic analogs is given in Figure 1. The aromatics which were reacted for 30 minutes in the inert atmosphere did not raise coal conversion significantly above that of the coal in 1-methylnaphthalene. As can be seen from Figure 1, the coal conversions by aromatics are essentially the same ranging from 17.7% to 22.7%. The reactivity of the different aromatics may have shown more differences if a freshly mined coal or a coal of different rank had been used.

Derbyshire and Whitehurst (5) have studied the conversion of a number of coals in pyrene using both argon and hydrogen atmospheres. In their investigation, they determined that coals of different rank convert to varying extents in pyrene with coals having carbon contents of 82-88 wt% maf dissolving most readily. However, a low degree of weathering of the coal was shown to be a principal requirement for good dissolution in pyrene. Coal, that has been

freshly mined and stored in argon, gave high dissolution while coal that had been oxidized by contact with air gave lower values. The difference in liquefaction behavior becomes appreciable at a carbon content above 80% as the more reactive coals have a greater sensitivity to mild oxidation conditions.

Benzophenone as a Model Acceptor. Benzophenone was chosen as a model acceptor for this work due to its several inherent advantages which include thermal stability, ease of analysis of the reaction products, and quantitative conversion into diphenylmethane and water. Thirteen model hydrogen donors were reacted with benzophenone at 400°C. The reactivity of each donor is ranked in Table 5 according to the amount of benzophenone conversion obtained. The conversion of the hydroaromatic species which occurred during the reaction was determined on an equivalent mole basis which caused the amount of donatable hydrogen to vary with the degree of hydrogenation of the model donor.

Examination of the ranking of model donors by benzophenone conversion shows that benzophenone conversion does not correlate with the amount of available hydrogen present. Several comparisons of benzophenone conversions by donors with different degrees of hydrogenation illustrate this point: 22.3% conversion of benzophenone by 1,2,3a,3,4,5-hexahydropyrene, 19.2% by 1,4-dihydronaphthalene and no conversion of benzophenone by either tetralin or octahydroanthracene. At increased reaction times, 120 and 180 minutes, tetralin yielded measurable conversions of benzophenone of 2.0% and 3.7% respectively. With the exception of 1,4-dihydronaphthalene, the hydrogen donors with four rings give up their hydrogen more readily than two or three ring donors.

Comparison of the conversion of hydroaromatics with benzophenone conversion indicates that some of the model donors are unstable at liquefaction conditions in that the conversion of some hydroaromatics far exceeds that of benzophenone. The products of the hydroaromatics were not determined in this study; however,

in cases with the highest discrepancy between the two conversions an explanation can be given. Cholesterol is highly unstable at high temperatures, undergoing facile dehydrogenation (17) and decomposing at 360C. Both dihydronaphthalenes are nearly totally converted, showing over twice the conversion required for the reaction with benzophenone indicating disproportionation into tetralin and naphthalene (22). The conversion of benzophenone is quite different for the two isomers with the conversion of the 1,4 isomer being more than double that of the 1,2 isomer. Tetralin, one of the disproportionation products of dihydronaphthalene, by itself yields no conversion of benzophenone under these reaction conditions. Thus, an active donor can be converted to an inactive donor. The high conversion of decylhexahydropyrene may well result from partial dealkylation at high reaction temperatures.

The literature is replete with model acceptor experiments which give the reactivity of model donors considered to be important in coal liquefaction. A comparison of model donors' reactivity ranked by several model acceptors is given in Table 6. In the first two columns, the ranking using benzophenone from this work and that from work by Raaen and Roark are compared. Although the reaction conditions are similar in the two series of experiments, they are not equivalent with the primary differences being that the donor was added in excess in Raaen's work compared to equal molar amounts in this work. Furthermore, the reaction time was 90 minutes in Raaen's experiments, 30 minutes longer than this work. Under those conditions of excess donor and longer reaction time, higher conversions of benzophenone were achieved. In both cases, however, cholesterol readily gave up its hydrogen and produced the highest conversion of benzophenone of any of the donors used; also, in both cases, tetralin was one of the least reactive compounds. The ranking of the intermediate compounds varied between the two studies. Ranking with 1,1-binaphthyl also showed tetralin to be less reactive than most of the other model donors.

Bockrath (16) estimated the ability of hydrogen donors to donate hydrogen to coal, by measuring the hydrogen donor acceptor ability of benzyl radicals generated by the thermolysis of dibenzylmercury and dibenzyldiazene. Bockrath (22) used a second method of estimating hydrogen donor ability by determining relative reaction rates by allowing the donor in question to compete with a reference donor for the benzyl radical. The ranking of the former are listed under column I of the bibenzyl group in Table 7 and the latter under column II. Comparison of the donor ability of the benzyl radical to the other model acceptors indicates little correlation with either the benzophenone or binaphthyl work. The donor index using bibenzyl shows tetrahydroquinoline to be a very poor solvent and also shows indan to have good donor ability in one case and poor donor ability in the second. Tetrahydroquinoline has been shown to be an effective donor for the dissolution of coal, in fact, being far more reactive than tetralin.

A comparison of coal conversion and benzophenone conversion by model hydrogen donors obtained in this study is presented in Table 7. No correlation is observed between the two rankings. Coal conversion shows a differentiation among each of the donors whereas benzophenone conversion ranks four compounds, octahydroanthracene, tetralin, acenaphthene, and indan, as being equivalently poor, even though their coal conversions are quite different. Benzophenone also has the ability to abstract hydrogen from cholesterol which decomposes under reaction conditions; however, coal at liquefaction conditions cannot readily abstract hydrogen thus generated, and hence yields low coal conversions.

Conclusion

The ranking of hydrogen donors at the same donatable hydrogen level for their ability to convert coal to THF solubles demonstrates that different donors have different abilities to liquefy coal. The presence of donatable hydrogen constitutes a necessary and important factor in coal conversion as evidenced by comparison with the conversion aromatic analogs. However, properties of

Table 7

Ranking of Model Donors

Donors	Conversions	
	Coal	Benzophenone
9,10-Dihydrophenanthrene	1	6
1,2,3,4-Tetrahydroquinoline	2	6
1,2,3,6,7,8-Hexahydropyrene	3	2
9,10-Dihydroanthracene	4	4
2a,3,4,5-Tetrahydroacenaphthene	5	7
Octahydroanthracene	6	8
1,2-Dihydronaphthalene	7	5
Tetralin	8	8
Cholesterol	9	1
Acenaphthene	10	8
Indan	11	8

the model donors other than the concentration of available hydrogen can affect THF solubles. The ease with which hydrogen is abstracted from a particular donor as well as the functional groups and heteroatoms present are significant factors affecting reactivity of the hydrogen donors during liquefaction. Ranking of hydrogen donor reactivity by coal conversion and by model acceptor experiments shows no direct correlation between the two.

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