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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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Quarterly Report
January to March 1993

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Low Severity Liquefaction Promoted by Cyclic Olefins

PART I

LOW SEVERITY LIQUEFACTION STUDIES USING HEXAHYDROANTHRACENE

Introduction

Low-severity coal liquefaction allows for the solubilization of coal with reduced gas make. The idea being tested in this research is whether selective bond rupture occurs during liquefaction at low temperatures that can be satisfied by hydrogen donation from highly active hydrogen donor compounds. Promotion of coal solubilization through hydrogen transfer using highly active and effective hydrogen donors is the objective of this study.

The highly effective hydrogen donors being tested are cyclic olefins. Representative cyclic olefins are isotetralin (ISO), which is 1,4,5,8-tetrahydronaphthalene, and 1,4,5,8,9,10-hexahydroanthracene (HHA). These compounds have been shown to highly effective donors (Bedell and Curtis, 1991) which release their hydrogen at fairly low temperatures, in the 200 to 300 °C range. ISO has been shown to be much more effective than its hydroaromatic analogue tetralin (TET) in releasing hydrogen at low temperatures and transferring that hydrogen to an acceptor molecule or to coal (Bedell and Curtis, 1991). Likewise, at 380 °C, the ability of HHA to release hydrogen in both N_2 and H_2 atmospheres was greater than a comparative hydroaromatic compound, dihydroanthracene (DHA). However, when an acceptor molecule or coal was present, DHA was as or more active than HHA in transferring hydrogen (Bedell et al., 1993). In another study, at equivalent reaction conditions and in the presence

of anthracene (ANT) as a hydrogen acceptor, ISO released more than 200 times as much hydrogen as TET and HHA released 18 to 25 times as much hydrogen as DHA (Wang, 1992).

The objective of the research performed this quarter was to optimize the reaction parameters for maximizing coal conversion and hexane soluble production from low-severity reactions using Illinois No. 6 coal and HHA as the highly reactive hydrogen donor species. Previous reports have presented data on the reactions of HHA and ANT at low-severity liquefaction conditions (Curtis, 1992). An extensive set of reactions was performed in which Illinois No. 6 was reacted thermally and catalytically at low-severity conditions, with and without the reactive donor HHA. Individual reaction parameters were evaluated such as reaction temperature, reaction time, concentration of hydrogen donor, and hydrogen pressure. The research performed this quarter included combining two of the reaction parameters in order to achieve the highest possible level of coal conversion and hexane soluble fraction at 350 °C.

Experimental

A parametric evaluation of Illinois No. 6 coal reacted in the presence of hexahydroanthracene (97% purity from Aldrich) using hexadecane (99% purity from Aldrich) as solvent was performed. The reactions were performed thermally and catalytically using molybdenum naphthenate and excess sulfur. Molybdenum naphthenate, obtained from Shepherd Chemical Company, was 6% Mo and used as received.

Low-severity liquefaction reaction conditions were employed. The reactions were performed in ~50 ml stainless steel tubular reactors that were well agitated. The baseline conditions were 350 °C, 500 psig H_2 introduced at ambient temperature, and 0.5 wt % donable hydrogen from hexahydroanthracene. Molybdenum naphthenate was introduced at 500 ppm

with a sulfur level of 3:1 S to Mo stoichiometric ratio, presuming that finely divided MoS_2 would form during the reaction (Kim et al., 1989; Huffman and Huggins, 1993). Different combinations of reaction parameters were used which included reaction times of 60 min, catalyst loading of 1000 ppm of active metal, hydrogen pressures of 1000 ppm and donable hydrogen concentrations of 1.0 wt %. The different combinations of parameters used in reactions performed this quarter are presented in Table 1. In each reaction set, at least two parameters were changed from the baseline conditions.

After the reactions were performed at the chosen conditions, the reaction products were analyzed. The amount of coal conversion obtained was determined by evaluating the amount of coal converted to tetrahydrofuran soluble materials. The products from the liquefied coal were analyzed in terms of gas, oil (hexane soluble material), asphaltenes (toluene soluble material, hexane insoluble material), preasphaltenes (tetrahydrofuran soluble material, toluene insoluble material). The data presented in the report are given in terms of the total product distribution in grams, total product distribution normalized in weight percent, and the solvent-free distribution normalized in weight percent. The distribution of the reaction system prior to reaction is also given in weight percent.

The product analysis for hexahydroanthracene and its reaction products were conducted using a Varian 3700 gas chromatograph equipped with a Supelco DB5 column, septumless injector and a flame ionization detector. The hydrogenated products were qualitatively identified by spiking with authentic compounds and by analyzing with GC mass spectrometry using a VG 70 EHF-GC mass spectrometer. Quantitative analysis of the reaction products were achieved using the internal standard method with p-xylene as the internal standard.

were achieved using the internal standard method with p-xylene as the internal standard.

The following term, percent hydrogenation (% HYD), is defined to assist in comparing the results from a number of reactions. Percent hydrogenation is defined as the number of moles of hydrogen required to produce the liquid products as a percentage of the number of moles of hydrogen required to achieve the most hydrogenated product, in this case, perhydroanthracene.

Results and Discussion

The research performed this quarter focused upon evaluating the effect of different reaction parameters on the efficacy of coal liquefaction using cyclic olefins as donors. The cyclic olefin used in this particular set of experiments was 1,4,5,8,9,10-hexahydroanthracene (HHA). The first several sets of experiments evaluated single parameter effects. The majority of the experiments performed this quarter evaluated the effect of two parameters on the efficacy of low-severity coal liquefaction, particularly in terms of coal conversion and hexane soluble yields.

The data that are presented in the tables are given in terms of (1) total product distribution in grams; (2) total product distribution normalized in weight percent; (3) solvent-free product distribution normalized in weight percent; and (4) original distribution prior to reaction in weight percent. The reaction conditions for each reaction set are given in each table.

Table 1 summarizes the experiments that were performed with two parameters. These reaction sets are presented in Tables 4 through 9. The first two sets of data presented in Table 2 and 3 describe an experiment that evaluates the effect of catalyst loading on the thermal and catalytic reactions of Illinois No. 6 coal using HHA introduced at 0.5 wt % donable hydrogen.

This particular reaction was performed at 350 °C at 500 psi hydrogen introduced at ambient temperature for 30 min. Elemental sulfur was added to the catalytic reaction to promote the formation of finely divided MoS_2 from Mo naphthenate during the in situ reaction. Table 2 presents the data obtained this quarter, while Table 3 presents the data obtained last quarter. The primary data that was in question was the solvent-free product distribution normalized in weight percent that was presented last quarter. The data obtained this quarter in Table 2 are much more in line with other data obtained under similar reaction conditions. The data obtained for the 500 ppm level of catalyst were quite similar for the two quarters which indicates that at these low-severity conditions that reproducibility in product distributions can be readily achieved.

Effect of Combining Two Reaction Parameters on Low-Severity Coal Liquefaction. The combinations of two reaction parameters that were used this quarter are given in Table 1. The different sets of parameters included (Set I) 60 min, 500 ppm Mo as Mo naphthenate, 1000 psig H_2 at ambient temperature, and 0.5 wt% donable H; (Set II) 60 min, 500 ppm Mo as Mo naphthenate, 500 psig H_2 at ambient temperature, and 1.0 wt% donable H; (Set III) 60 min, 1000 ppm Mo as Mo naphthenate, 500 psig H_2 at ambient temperature, and 0.5 wt% donable H; and (Set IV) 30 min, 1000 ppm Mo as Mo naphthenate, 1000 psig H_2 at ambient temperature, and 0.5 wt% donable H.

Table 4 presents the Set I data. The reaction was conducted thermally and catalytically for 60 min at 500 and 1000 psig H_2 at ambient temperature. The lowest coal conversion at 46.1% was achieved during the thermal reaction at 500 psi H_2. The other three reactions, catalytic at 500 psig H_2 and thermal and catalytic at 1000 psig H_2, all had similar coal

conversions ranging from 50.2 to 52.2%. The primary difference between the two sets of reactions at 60 min was that the oil yield (hexane solubles) on a solvent free basis was ~25% for 1000 psi H_2 reaction while the amount was negative (-24% for thermal and -38% for catalytic) for the 500 psi reaction. Hence, the longer reaction time and the higher hydrogen pressure was beneficial for production of hexane soluble oil.

The effect of reaction time in conjunction with 1000 psig H_2 at ambient pressure (Set II) was examined in Table 5. The difference between 30 min and 60 min in terms of coal conversion and hexane soluble oil yield was substaintial. Thermal and catalytic coal conversions at 30 min were ~39% while at 60 min they were ~51%. Likewise, at 30 min the hexane soluble oils were negative on a solvent-free basis while at 60 min ~25% hexane soluble oils were produced. Hence, longer reaction time had a substantial effect on the low severity products produced even at the higher hydrogen pressure.

Hexahydroanthracene, being present in the low severity liquefaction reaction, has been shown to be highly effective for promoting coal conversion (Curtis, 1992). In Table 6 (Set III), the amount of donable hydrogen from HHA was doubled. Both the lower level of donable hydrogen (0.5 wt%) and the higher level (1.0 wt%) were reacted for 60 min. For both levels, thermal reaction yielded lower coal conversion than did the reaction with Mo naphthenate. Most coal conversion was obtained at 1.0 wt% donable hydrogen for 60 min with 500 ppm of Mo naphthenate, yielding 57.8% conversion. Hexane soluble yields on a solvent-free basis were also much greater for 1 wt% donable hydrogen level, for both thermal and catalytic reactions.

Table 7 presents the effect of two levels of catalyst loading with a hydrogen pressure of 1000 psig on the product distribution with 0.5 wt % donable hydrogen. The reactions were

performed for 30 min. The amount of coal conversion achieved for both the thermal and 500 ppm catalyst loading was nearly the same at ~39%. However, when the catalyst loading was increased to 1000 ppm the coal conversion increased to nearly 50%. A substantial difference was also observed in the hexane soluble oils on a solvent-free basis for both the thermal reaction and the reactions with 500 ppm Mo naphthenate, negative oil amounts were observed; however, the 1000 ppm Mo naphthenate reaction yielded an oil content of ~27% on a solvent-free basis.

When these same reactions with 0.5 wt % donable hydrogen were performed at 60 min with 500 psi H_2 at ambient temperature, the coal conversions were higher for each reaction. In fact, the thermal reaction gave a conversion of ~46%, the 500 ppm of ~50%, and the 1000 ppm of 55%. Only the 1000 ppm Mo naphthenate reaction yielded a positive oil yield on a solvent-free basis.

The product distributions obtained from HHA from all of the different reactions are presented in Tables 9 and 10. In all of the reactions, between 40 to 50% HHA remained. The primary product was DHA and the secondary products were octahydroanthracene (OHA) and anthracene (ANT). All of the reaction yielded a negative percent hydrogenation indicating that dehydrogenation of HHA occurred.

Summary

The parametric evaluation using the highly reactive cyclic olefin, hexahydroanthracene, showed that the hydrogen donor species were quite effective in promoting low-severity coal liquefaction. Different reaction parameters were evaluated. The most effective parameters were

longer reaction times up to 60 min, higher catalyst loading, and higher levels of donable hydrogen.

The future work that is planned is to evaluate the effect of the three most effective reaction parameters on the efficacy of low-severity coal liquefaction. Coal pretreatment will also be attempted to evaluate its effect on low-severity coal liquefaction. Two coals of lower rank, Beulah Zap and Wyodak, will also be used in order to evaluate the effective of the optimized reaction parameters with hexahydroanthracene present.

References

Bedell, M.W. and Curtis, C.W. *Energy and Fuels*, 5, 469, 1991.

Bedell, M.W., Curtis, C. W., and Hool, J.W. *Energy and Fuels,* 7, 200, 1993.

Curtis, C.W. Quarterly Reports, "Low Severity Coal Liquefaction Promoted by Cyclic Olefins," July-September, 1992; October-December 1992.

Huffman, G.P.; Ganguly, B.; Zhao, J.; Rao, K.R.P.; Shah, N.; Feng, Z; Huggins, F.E.; Taghiei, M.M.; Lu, F.; Wendu, I.; Pradhar, V.R.; Treiney, J.W.; Seehra, M.S.; Ibrahim, M.M.; Shabtai, J.; and Eyring, E.M. *Energy and Fuels,* 7, 285-296, 1993.

Kim, H.; Curtis, C.W.; Cronauer, D.C.; Saykowski, D.J. *Amer. Chem. Soc. Fuel Chem. Div. Prepr.*, 34(4):1431-1438, 1989.

Personal communication, Dr. G. P. Huffman and Dr. E. E. Huggins, 1993.

Table 1. Combination of Parameters Used in Reactions Performed This Quarter

Sample	1	2	3	4
Reaction Time, min	60	60	60	30
Catalyst Loading, ppm	500	500	1000	1000
Hydrogen Pressure, psig	1000	500	500	1000
HHA Concentration, wt% donable H	0.5	1.0	0.5	0.5

Table 2. Effect of Catalyst Loading on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal with Hexahydroanthracene (Reactions Performed This Quarter)[a]

Product Distribution	Mo Naphthenate	
	500 ppm Mo	1000 ppm Mo
Total Distribution Weight in Grams		
Gas	0.155±0.007	0.140±0.014
Oil	3.431±0.173	3.221±0.137
Asphaltenes	0.173±0.067	0.363±0.051
Preasphaltenes	0.823±0.032	1.067±0.096
IOM	0.921±0.014	0.822±0.009
Coal Conversion, %	41.2±0.6	47.2±0.6
Recovery, %	94.1±0.2	94.2±0.1
Total Distribution Normalized in Weight Percent		
Gas	2.53±0.13	2.20±0.11
Oil	61.50±0.37	57.26±1.24
Asphaltenes	2.70±0.92	5.74±0.78
Preasphaltenes	13.51±0.57	16.95±1.69
IOM	19.76±0.13	17.85±0.42
Solvent-Free Distribution Normalized in Weight Percent		
Gas	6.29±0.34	5.45±0.33
Oil	15.95±0.56	7.10±4.96
Asphaltenes	6.74±2.26	13.96±1.52
Preasphaltenes	33.79±1.56	41.40±5.15
IOM	37.23±0.20	32.09±1.66
Distribution Prior to Reaction in Weight Percent		
Gas	2.51±0.01	2.33±0.02
Oil		
HHA[b]	9.74±0.01	9.71±0.01
Hexadecane	54.96±0.01	54.64±0.01
Preasphaltenes & IOM	32.33±0.02	32.35±0.00
Catalyst	0.46±0.01	0.97±0.01

[a] Reaction Conditions: 350°C, 500 psi H_2 at ambient temperature (0.16 g), 30 min. 0.61 g HHA, 0.03 g of elemental S.

[b] HHA = hexahydroanthracene

Table 3. Effect of Catalyst Loading on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal with Hexahydroanthracene (Reactions Performed Last Quarter)[a]

Product Distribution	Mo Naphthenate	
	500 ppm Mo	1000 ppm Mo
Total Distribution Weight in Grams		
Gas	0.170±0.014	0.170±0.014
Oil	3.378±0.007	3.114±0.067
Asphaltenes	0.126±0.008	0.166±0.057
Preasphaltenes	0.965±0.233	1.421±0.167
IOM	0.843±0.013	0.766±0.040
Coal Conversion, %	45.8±0.81	50.1±2.6
Recovery, %	92.8±2.67	96.3±3.3
Total Distribution Normalized in Weight Percent		
Gas	2.91±0.16	2.88±0.21
Oil	64.11±3.29	57.16±2.71
Asphaltenes	2.16±0.21	2.81±0.93
Preasphaltenes	16.43±3.51	24.04±3.05
IOM	14.39±0.17	13.11±0.80
Solvent-Free Distribution Normalized in Weight Percent		
Gas	6.89±0.12	6.74±0.41
Oil	14.75±4.59	-0.58±7.71
Asphaltenes	5.13±0.67	6.58±2.10
Preasphaltenes	38.95±6.88	56.46±7.92
IOM	34.28±1.74	30.80±2.30
Distribution Prior to Reaction in Weight Percent		
Gas	2.82±0.00	2.83±0.07
Oil		
HHA	9.62±0.01	9.66±0.05
Hexadecane	54.78±0.02	54.34±0.08
Preasphaltenes & IOM	32.31±0.02	32.22±0.02
Catalyst	0.47±0.01	0.95±0.02

[a] Reaction Conditions: 350°C, 500 psi H_2 at ambient temperature (0.16 g) 30 min. 0.61 g HHA, 0.03 g of elemental S.

[b] HHA = hexahydroanthracene

Table 4. Effect of Hydrogen Pressure on the Product Distributions of Thermal and Catalytic Reaction of Illinois No. 6 Coal with Hexhydroanthracene[a]

Product Distribution	H_2 Pressure (500 psi)		H_2 Pressure (1000 psi)	
	Thermal	Mo Naphthenate 500 ppm	Thermal	Mo Naphthenate 500 ppm
Total Distribution Weight in Grams				
Gas	0.145±0.007	0.160±0.000	0.320±0.007	0.310±0.007
Oil	2.796±0.045	2.252±0.169	3.404±0.442	3.527±0.013
Asphaltenes	0.115±0.021	0.143±0.002	0.146±0.050	0.210±0.009
Preasphaltenes	1.874±0.034	2.350±0.008	0.823±0.020	0.732±0.068
IOM	0.841±0.004	0.775±0.046	0.708±0.021	0.750±0.025
Coal Conversion, %	46.1±0.5	50.2±3.1	52.2±1.4	50.8±2.7
Recovery, %	97.5±0.9	96.8±2.1	90.3±6.0	92.8±0.8
Total Distribution Normalized in Weight Percent				
Gas	2.49±0.14	2.72±0.00	5.20±0.11	5.08±0.06
Oil	48.89±0.42	41.67±0.05	67.16±0.16	66.66±0.62
Asphaltenes	1.98±0.34	2.44±0.03	2.36±0.83	3.50±0.11
Preasphaltenes	32.19±0.36	39.98±0.12	13.58±0.30	12.21±1.00
IOM	14.45±0.06	13.19±0.81	11.70±0.35	12.53±0.55
Solvent-Free Distribution Normalized in Weight Percent				
Gas	6.03±0.34	6.45±0.01	11.86±0.28	11.52±0.30
Oil	-23.71±1.20	-38.06±1.57	25.14±0.04	24.54±2.37
Asphaltenes	4.80±0.82	5.77±0.06	5.37±1.88	7.94±0.35
Preasphaltenes	77.92±0.81	94.62±0.25	30.97±0.75	27.67±2.62
IOM	34.96±0.08	31.22±1.88	26.66±0.81	28.33±0.90
Distribution Prior to Reaction in Weight Percent				
Gas	2.50±0.02	2.71±0.02	5.12±0.01	5.04±0.02
Oil				
HHA	9.72±0.02	9.71±0.02	9.21±0.02	9.17±0.01
Hexadecane	55.39±0.07	55.02±0.02	54.41±0.06	54.10±0.02
Preasphaltenes & IOM	32.39±0.08	32.09±0.02	31.26±0.03	31.21±0.02
Catalyst	0.0	0.47±0.01	0.0	0.48±0.01

[a] Reaction Conditions: 350°C, 60 min, 0.61 g HHA, 0.03 g of elemental S with 500 ppm Mo introduced as Mo naphthenate.

Table 5. Effect of Catalyst Loading on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal with Hexahydroanthracene [a]

Product Distribution	Reaction Time			
	30 min		60 min	
	Thermal	Mo Naphthenate, 500 ppm	Thermal	Mo Naphthenate, 500 ppm
Total Distribution Weight in Grams				
Gas	0.310±0.014	0.340±0.014	0.320±0.007	0.310±0.007
Oil	2.594±0.009	2.949±0.128	3.404±0.442	3.527±0.013
Asphaltenes	0.113±0.008	0.106±0.012	0.146±0.050	0.210±0.009
Preasphaltenes	1.349±0.041	1.449±0.055	0.823±0.020	0.732±0.68
IOM	0.951±0.056	0.951±0.036	0.708±0.021	0.750±0.025
Coal Conversion, %	38.9±3.5	38.8±2.3	52.2±1.4	50.8±2.7
Recovery, %	88.3±1.8	96.0±0.5	90.3±6.0	92.8±0.8
Total Distribution Normalized in Weight Percent				
Gas	5.12±0.22	5.62±0.23	5.20±0.11	5.08±0.06
Oil	55.07±1.85	52.92±1.56	67.16±0.16	66.66±0.62
Asphaltenes	1.86±0.12	1.76±0.21	2.36±0.83	3.50±0.11
Preasphaltenes	22.25±0.62	23.97±0.95	13.58±0.30	12.21±1.00
IOM	15.70±0.88	15.73±0.63	11.70±0.35	12.53±0.55
Solvent-Free Distribution Normalized in Weight Percent				
Gas	11.64±0.43	12.80±0.49	11.86±0.28	11.52±0.30
Oil	-2.16±3.61	-7.23±3.75	25.14±0.04	24.54±2.37
Asphaltenes	4.23±0.25	4.01±0.49	5.37±1.88	7.94±0.35
Preasphaltenes	50.60±1.12	54.58±2.27	30.97±0.75	27.67±2.62
IOM	35.69±1.80	35.84±1.49	26.66±0.81	28.33±0.90
Distribution Prior to Reaction in Weight Percent				
Gas	5.03±0.03	5.41±0.02	5.12±0.01	5.04±0.02
Oil				
HHA[b]	9.21±0.01	9.25±0.01	9.21±0.02	9.17±0.01
Hexadecane	54.49±0.04	53.79±0.03	54.41±0.06	54.10±0.02
Preasphaltenes & IOM	31.27±0.04	31.09±0.04	31.26±0.03	31.21±0.02
Catalyst	0.0	0.46±0.02	0.0	0.48±0.01

[a] Reaction Conditions: 350°C, 1000 psi H_2 at ambient temperature (0.32 g), 0.61 g HHA, 0.03 g of elemental S with 500 ppm Mo, hexadecane as solvent.

[b] HHA = hexahydroanthracene

Table 6. Effect of Hexahydroanthracene Concentration on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal for 60 Minutes[a]

Product Distribution	0.61 g of HHA		1.22 g of HHA	
	Thermal	Mo Naphthenate, 500 ppm	Thermal	Mo Naphthenate, 500 ppm
Total Distribution Weight in Grams				
Gas	0.145±0.007	0.160±0.000	0.300±0.000	0.300±0.014
Oil	2.796±0.045	2.252±0.169	3.623±0.027	3.511±0.086
Asphaltenes	0.115±0.021	0.143±0.002	0.259±0.062	0.215±0.057
Preasphaltenes	1.874±0.034	2.350±0.008	0.857±0.064	1.020±0.066
IOM	0.841±0.004	0.775±0.046	0.745±0.041	0.649±0.034
Coal Conversion, %	46.1±0.5	50.±3.1	52.2±2.8	57.8±2.0
Recovery, %	97.5±0.9	96.8±2.1	95.8±2.2	95.4±4.0
Total Distribution Normalized in Weight Percent				
Gas	2.49±0.14	2.72±0.00	2.76±0.00	2.32±0.16
Oil	48.89±0.42	41.67±0.05	64.69±2.76	64.59±1.82
Asphaltenes	1.89±0.34	2.44±0.03	4.78±1.83	3.91±1.01
Preasphaltenes	32.19±0.36	39.98±0.12	14.86±1.06	17.59±1.37
IOM	14.45±0.06	13.19±0.81	12.91±0.66	11.59±0.40
Solvent-Free Distribution Normalized in Weight Percent				
Gas	6.03±0.34	6.45±0.01	5.12±0.01	4.76±0.13
Oil	-23.71±1.20	-38.06±1.57	35.37±5.45	33.33±4.57
Asphaltenes	4.80±0.82	5.77±0.06	8.28±2.01	7.08±2.03
Preasphaltenes	77.92±0.81	94.62±0.25	27.40±2.09	33.52±2.87
IOM	34.96±0.08	31.22±1.88	23.83±1.34	21.31±0.20
Distribution Prior to Reaction in Weight Percent				
Gas	2.50±0.02	2.71±0.02	2.58±0.02	2.40±0.04
Oil				
HHA[b]	9.72±0.02	9.71±0.02	19.90±0.01	19.20±0.01
Hexadecane	55.39±0.07	55.02±0.02	45.21±0.09	45.70±0.01
Preasphaltenes & IOM	32.39±0.08	32.09±0.02	32.31±0.11	32.25±0.08
Catalyst	0.0	0.47±0.01	0.0	0.45±0.06

[a] Reaction Conditions: 350°C, 500 psi H_2 at ambient temperature (0.32 g), 0.61 g HHA, 0.03 g of elemental S with 500 ppm Mo, hexadecane as solvent.

[b] HHA = hexahydroanthracene

Table 7. Product Distributions for Thermal and Catalytic Reactions of Illinois No. 6 Coal at Different Catalyst Loading for 30 Minutes[a]

Product Distribution	Thermal	Mo Naphthenate, 500 ppm	Mo Naphthenate, 1000 ppm
Total Distribution Weight in Grams			
Gas	0.310±0.014	0.340±0.014	0.310±0.007
Oil	2.594±0.009	2.949±0.128	3.596±0.063
Asphaltenes	0.113±0.008	0.106±0.012	0.086±0.036
Preasphaltenes	1.349±0.041	1.449±0.055	0.659±0.052
IOM	0.951±0.056	0.951±0.036	0.786±0.041
Coal Conversion, %	38.9±3.5	38.8±2.3	49.5±2.6
Recovery, %	88.3±1.8	96.0±0.5	90.8±1.9
Total Distribution Normalized in Weight Percent			
Gas	5.12±0.22	5.62±023	5.17±0.16
Oil	55.07±1.85	52.92±1.56	68.70±0.34
Asphaltenes	1.86±0.12	1.76±0.21	1.46±0.62
Preasphaltenes	22.25±0.62	23.97±0.95	11.86±0.55
IOM	15.70±0.88	15.73±0.63	13.31±0.57
Solvent-Free Distribution Normalized in Weight Percent			
Gas	11.64±0.43	12.80±0.49	12.17±0.54
Oil	-2.16±3.61	-7.23±3.75	26.76±0.11
Asphaltenes	4.23±0.25	4.01±0.49	3.45±1.51
Preasphaltenes	50.60±1.12	54.58±2.27	26.28±0.98
IOM	35.69±1.80	35.84±1.49	31.34±0.96
Distribution Prior to Reaction in Weight Percent			
Gas	5.03±0.03	5.41±0.02	5.07±0.04
Oil			
HHA[b]	9.21±0.01	9.25±0.01	9.20±0.01
Hexadecane	54.49±0.04	53.79±0.03	53.45±0.01
Preasphaltenes & IOM	31.27±0.04	31.09±0.04	31.34±0.01
Catalyst	0.0	0.46±0.02	0.94±0.02

[a] Reaction Conditions: 350°C, 1000 psi H_2 at ambient temperature (0.32 g) 0.61 g HHA, 0.03 g of elemental S, hexadecane as solvent.

[b] HHA = hexahydroanthracene

Table 8. Product Distributions for Thermal and Catalytic Reactions of Illinois No. 6 Coal at Different Catalyst Loading for 60 Minutes[a]

Product Distribution	Thermal	Mo Naphthenate, 500 ppm	Mo Naphthenate, 1000 ppm
Total Distribution Weight in Grams			
Gas	0.145±0.007	0.160±0.000	0.160±0.007
Oil	2.796±0.045	2.252±0.169	3.471±0.022
Asphaltenes	0.115±0.021	0.143±0.002	0.148±0.027
Preasphaltenes	1.874±0.034	2.350±0.008	0.962±0.042
IOM	0.841±0.004	0.775±0.046	0.700±0.034
Coal Conversion, %	46.1±0.5	50.2±3.1	55.0±2.2
Recovery, %	97.5±0.9	96.8±2.1	92.5±0.3
Total Distribution Normalized in Weight Percent			
Gas	2.49±0.14	2.72±0.00	2.65±0.16
Oil	48.89±0.42	41.67±0.05	66.78±0.25
Asphaltenes	1.98±0.34	2.44±0.03	2.50±0.42
Preasphaltenes	32.19±0.36	39.98±0.12	16.22±0.94
IOM	14.45±0.06	13.19±0.81	11.85±0.42
Solvent-Free Distribution Normalized in Weight Percent			
Gas	6.03±0.34	6.45±0.01	5.99±0.61
Oil	-23.71±1.20	-38.06±1.57	24.14±3.75
Asphaltenes	4.80±0.82	5.77±0.06	5.71±0.73
Preasphaltenes	77.92±0.81	94.62±0.25	37.16±3.69
IOM	34.96±0.08	31.22±1.88	27.00±0.18
Distribution Prior to Reaction in Weight Percent			
Gas	2.50±0.02	2.71±0.02	2.57±0.04
Oil			
HHA	9.72±0.02	9.71±0.02	9.73±0.02
Hexadecane	55.39±0.07	55.02±0.02	54.38±0.06
Preasphaltenes & IOM	32.39±0.08	32.09±0.02	32.36±0.03
Catalyst	0.0	0.47±0.01	0.96±0.01

[a] Reaction Conditions: 350°C, 500 psi H_2 at ambient temperature (0.32 g) 0.631 g HHA, 0.03 g of elemental S, hexadecane as solvent.

[b] HHA = hexahydroanthracene

Table 9. Comparison of the Product Distributions from Hexahydroanthracene Reacted in the Presence of Illinois No. 6 Coal

Data	Catalyst Type	Catalyst Loading (ppm)	Reaction Time (min)	Pressure (psi)	Wt of HHA (g)	Product Distribution (wt %)				HYD (%)
						ANT[a]	DHA	HHA	OHA	
New	MoNaph+S[b]	500	30	500	0.61	10.0±0.6	34.7±0.1	46.0±1.5	9.3±0.3	-12.9
New	MoNaph+S	1000	30	500	0.61	9.9±0.1	32.4±0.8	49.0±1.1	8.7±0.4	-12.3
Old	MoNaph+S	500	30	500	0.61	13.9±1.0	26.2±0.7	50.4±0.3	9.6±1.2	-12.1
Old	MoNaph+S	1000	30	500	0.61	14.5±0.6	25.4±0.8	50.6±0.4	9.5±0.2	-12.1

[a] ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene
[b] MoNaph = molybdenum naphthenate

Table 10. Product Distribution of Hexahydroanthracene at Different Reaction Times Reacted in the Presence of Illinois No. 6 Coal

Catalyst Type	Catalyst Loading (ppm)	Reaction Time (min)	Pressure (psi)	Wt of HHA (g)	Product Distribution (wt %)				HYD (%)
					ANT[a]	DHA	HHA	OHA	
None	0	60	500	1.22	12.1±1.5	23.4±2.5	48.1±2.4	16.4±2.0	-9.5
MoNaph+S	500	60	500	1.22	8.1±0.6	32.6±0.6	46.5±0.8	12.9±0.5	-10.9
MoNaph+S	1000	30	1000	0.61	6.3±1.8	37.4±2.6	45.4±1.9	10.9±0.8	-11.8
MoNaph+S	1000	60	500	0.61	11.0±0.9	32.0±0.7	47.9±0.4	9.1±0.2	-12.5
None	0	60	1000	0.61	12.9±1.5	28.5±0.7	47.8±1.0	10.8±0.8	-12.1
MoNaph+S	500	60	1000	0.61	6.4±0.5	43.0±0.6	41.5±0.5	9.1±0.6	-13.8

[a] ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene
[b] MoNaph = molybdenum naphthenate

PART II
INFRARED STUDIES OF CYCLIC OLEFINS

Objective

To determine the feasibility of using Fourier transform infrared spectroscopy (FTIR) and a heated cell to observe and evaluate the extent of hydrogen donation by cyclic olefins to acceptor compounds representative of those found in coal.

Progress

In order to use FTIR as a tool for investigating hydrogen donation one must be able to observe spectroscopically the release of hydrogen from a donor compound. This may be done either directly or indirectly by spectroscopic examination of reactants and/or products. In the previous quarter's work, two groups of model compounds, naphthalene (NAP) series and anthracene (ANT) series, were chosen for investigation as possible hydrogen donors. FTIR spectra were obtained for each analog in the NAP and ANT series of possible hydrogen donors. Because of solubility problems, different solvents were used for the two series of compounds. The NAP series of compounds was analyzed in carbon tetrachloride while the ANT series was analyzed in carbon disulfide.

Unique absorption bands for each model compound in both series were determined for future use in ascertaining differences between individual model compounds and products produced in heated experiments. The major absorbance bands for all the NAP and ANT model compounds, in carbon tetrachloride and carbon disulfide, respectively, have been tabulated over the wavelength region of 3200 to 600 cm^{-1}. This library of data is presented in the attached tables. Unique absorption bands for individual model compounds can be determined from

these tables which will aid in determination of mechanistic pathways, by monitoring reactants, products, and possibly intermediates occurring in the hydrogen donation process. For example, if one was able to dehydrogenate tetralin (TET), the FTIR spectrum could show bands at 2820 cm^{-1} and/or bands at 2832 cm^{-1} which would indicate the dehydrogenated TET products of 1,4-dihydronaphthalene and 1,2-dihydronaphthalene, respectively. Alternatively, neither of these product bands would be available and all bands between 2935 cm^{-1} and 2500 cm^{-1} could be missing, leading to the result that TET was completely dehydrogenated to produce NAP.

Fluorolube was chosen and tested as a diluent for the heated experiments. Mixtures, 1% analytic in diluent, of each compound in the NAP series were prepared and analyzed. Examination of the major absorbance bands indicated very little difference in the spectra when compared to the solution spectra. It should be noted, that the use of fluorolube as a diluent, limits the spectral region of analysis for the hydrogen donors to the absorbance wavelength region between 3200 and 1500 cm^{-1}. Observation of absorbance bands outside of this region will require different diluent.

In preparation for the heated experiments, a fluorolube mull was heated in a water-cooled high-temperature cell equipped with NaCl windows. Spectra were acquired at a variety of temperatures between 60 and 250 °F for a variety of time periods. No chemical changes were observed in the fluorolube spectrum. Changes in intensities of the absorbance bands were observed that were attributed to leaking. A check with the manufacturer of the heated cell indicated that the O-rings had a temperature limit of 175 °F. O-rings capable of withstanding prolonged temperatures up to 300 °F were purchased. They will be tested in this quarter's work. Because of the toxicity of the chemical compounds and diluents that are utilized in the

heated experiments, additional work is now being put into building a safety hood for possible accidents occurring during the heated cell experiments.

Future Work

The heated temperature FTIR experiments will be performed this quarter. The temperature of the experiments will be extended to the upper limit of the O-rings, 300°F. Heated experiments on the diluent, fluorolube, will be repeated at the higher temperatures to insure that it will not interfere in the analysis of the model compounds. The feasibility of using the heated cell to determine if hydrogen release from the model compounds can be observed by FTIR will be examined. Heating experiments involving hexadecane as the diluent for the model compounds will also be performed and examined by FTIR for hydrogen release. The use of hexadecane as a solvent will allow additional spectral regions of the model compounds to be examined. All experiments will involve extended time periods, as well as, a variety of temperatures. Modifications to the heated cell unit may be required in order to achieve higher temperatures to effect hydrogen release in these experiments.

Time permitting, thin film experiments at elevated temperature will be implemented.

The ultimate goal of all experiments is to design and implement high temperature experiments in order to monitor hydrogen release and donation by cyclic olefins to coal.

Table 1. FTIR ABSORPTION WAVELENGTHS FOR NAPHTHALENE ANALOGS in CCl_4

Compound/(Purity)		Wavelengths (cm^{-1}) 3200-2800														
Naphthalene	(99)	****	*3092*	**3068**	**3053**	3035	*3021*	****	*2982*	*2964*	*2933*	****	****	****	****	****
1,2-Dihydronaphthalene	(75)	****	*3093*	**3069**	**3058**	**3036**	**3019**	****	****	****	**2934**	****	**2886**	****	2854	****
	(95)	****	*3093*	3069	3058	**3036**	**3019**	****	****	****	**2935**	****	**2886**	****	*2864*	****
1,4-Dihydronaphthalene	(92N)	****	****	*3077*	3062	**3030**	*3019*	****	*2981*	****	****	****	2883	2866	****	****
	(90)	****	****	*3077*	3065	**3034**	*3019*	****	*2984*	****	****	****	2886	2871	****	****
	(69N)	****	*3094*	*3070*	3057	**3032**	**3017**	****	****	****	**2932**	****	**2883**	****	**2859**	****
	(69)	****	****	3069	3059	3035	**3018**	****	****	****	**2935**	****	2886	****	2862	****
1,4-Tetrahydronaphthalene	(99)	****	****	*3075*	3061	*3042*	3018	****	****	****	**2931**	**2898**	**2885**	****	**2860**	2841
Isotetralin	(97)	****	****	*3067*	****	**3030**	****	****	2975	****	*2924*	****	****	**2875**	****	**2848**
	(88)	****	****	3066	****	**3031**	****	****	2975	2958	**2926**	****	****	**2875**	****	**2849**
Hexahydronaphthalene	(98)	****	****	****	****	**3029**	****	****	2973	****	**2928**	**2905**	**2884**	**2873**	**2859**	****
Octahydronaphthalene	(99)	****	****	****	****	****	****	****	****	****	**2928**	****	**2886**	**2866**	**2858**	****
Cis-Decalin	(99)	****	****	****	****	****	****	****	****	****	**2925**	****	****	****	**2860**	****
Trans-Decalin	(99)	****	****	****	****	****	****	****	****	****	**2920**	****	****	****	**2851**	****
Hexadecane	(99)	****	****	****	****	****	****	****	****	**2957**	**2926**	****	****	**2872**	**2854**	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 2. FTIR ABSORPTION WAVELENGTHS FOR NAPHTHALENE ANALOGS in CCl_4

Compound/(Purity)		Wavelengths (cm^{-1}) 2800-1485														
Naphthalene	(99)	****	****	****	****	****	****	****	****	****	****	****	1597	****	**1510**	****
1,2-Dihydronaphthalene	(75)	**2832**	****	****	****	****	****	****	****	****	****	****	****	****	****	**1485**
	(95)	**2832**	****	****	****	****	****	****	****	****	****	****	****	****	****	**1485**
1,4-Dihydronaphthalene	(92N)	****	**2820**	****	****	**1684**	**1666**	**1653**	**1646**	**1635**	**1617**	**1602**	**1597**	**1580**	**1497**	****
	(90)	****	**2823**	*1745*	**1718**	****	*1667*	****	****	****	****	****	****	*1582*	**1497**	****
	(69N)	**2830**	****	****	**1715**	****	****	****	****	****	****	****	****	****	**1493**	1485
	(69)	2833	****	**1745**	**1717**	1680	****	****	****	****	****	****	****	****	1493	1485
1-4-Tetrahydronaphthalene	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	**1495**	****
Isotetralin	(97)	****	**2816**	****	****	****	1662	****	****	****	****	****	****	****	****	****
	(88)	****	**2816**	****	****	****	1662	****	****	****	****	****	****	****	1497	****
Hexahydronaphthalene	(98)	**2832**	**2815**	****	****	****	****	1656	****	****	****	****	****	****	****	****
Octahydronaphthalene	(99)	**2831**	****	****	****	****	****	****	****	****	****	****	****	****	****	****
Cis-Decalin	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****
Trans-Decalin	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****
Hexadecane	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 3. FTIR ABSORPTION WAVELENGTHS FOR NAPHTHALENE ANALOGS in CCl_4

Compound/(Purity)		Wavelengths (cm^{-1}) 1485-1265														
Naphthalene	(99)	****	****	****	****	****	****	****	1389	****	****	****	****	****	****	1267
1,2-Dihydronaphthalene	(75)	*1466*	**1453**	****	**1439**	**1428**	****	****	****	****	****	****	*1327*	****	**1278**	****
	(95)	****	1453	****	1438	1428	****	****	****	****	****	****	****	****	1278	****
1,4-Dihydronaphthalene	(92N)	**1471**	**<u>1456</u>**	****	****	**<u>1426</u>**	****	****	1389	1359	1345	1342	****	1296	1279	1268
	(90)	*1468*	**1457**	****	****	**1427**	****	****	****	1359	****	****	****	****	****	****
	(69N)	****	**<u>1452</u>**	****	**<u>1438</u>**	**1428**	****	****	****	**<u>1360</u>**	****	****	*1327*	****	**1279**	****
	(69)	****	**1453**	****	**1438**	**1429**	1417	****	****	**<u>1360</u>**	****	****	1328	****	1279	****
1-4-Tetrahydronaphthalene	(99)	*1474*	**1453**	****	**1437**	****	****	****	****	*1354*	****	****	****	****	*1284*	****
Isotetralin	(97)	****	****	****	****	**<u>1431</u>**	****	*1398*	****	****	****	****	****	****	****	****
	(88)	*1466*	1457	****	****	**<u>1431</u>**	****	*1398*	****	****	****	****	****	****	****	****
Hexahydronaphthalene	(98)	****	1457	1448	**1439**	1425	****	****	****	****	*1339*	****	****	****	1273	****
Octahydronaphthalene	(99)	****	****	**1449**	**1440**	****	****	****	****	****	****	****	1323	****	1278	****
Cis-Decalin	(99)	1466	1460	**1447**	****	****	****	****	****	****	****	****	****	****	****	****
Trans-Decalin	(99)	****	1459	**<u>1449</u>**	****	****	****	****	****	****	*1346*	*1333*	****	*1306*	****	****
Hexadecane	(99)	**1467**	****	****	****	****	****	****	1378	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 4. FTIR ABSORPTION WAVELENGTHS FOR NAPHTHALENE ANALOGS in CCl_4

Compound/(Purity)		Wavelengths (cm^{-1}) 1265-960														
Naphthalene	(99)	****	****	*1210*	****	****	****	1128	****	****	****	****	1011	****	****	****
1,2-Dihydronaphthalene	(75)	****	*1223*	1206	*1194*	****	*1165*	****	*1115*	*1105*	1038	1027	1010	****	****	****
	(95)	****	****	****	****	****	****	****	****	****	1037	1026	1010	****	****	****
1,4-Dihydronaphthalene	(92N)	1254	****	****	1193	1184	****	****	****	****	1041	****	****	**0998**	****	****
	(90)	****	1218	****	*1193*	*1184*	****	****	****	****	1042	****	****	0999	****	****
	(69N)	****	**<u>1220</u>**	****	****	****	****	****	****	****	1037	1026	**1010**	****	****	****
	(69)	****	**<u>1218</u>**	****	1090	****	****	****	****	****	*1038*	*1026*	*1010*	****	****	****
1-4-Tetrahydronaphthalene	(99)	****	****	****	****	****	****	****	*1112*	****	*1037*	****	****	****	****	****
Isotetralin	(97)	****	****	****	****	****	****	*1134*	****	****	****	****	****	****	**0987**	**<u>0973</u>**
	(88)	****	****	****	****	****	****	*1134*	****	****	****	****	****	****	**0987**	**<u>0973</u>**
Hexahydronaphthalene	(98)	****	****	****	****	****	****	1125	****	****	****	****	****	0993	****	****
Octahydronaphthalene	(99)	****	****	****	****	****	1163	****	****	****	****	****	****	****	****	****
Cis-Decalin	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	0968
Trans-Decalin	(99)	*1253*	****	****	****	****	****	*1138*	****	****	****	****	****	****	****	*0972*
Hexadecane	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 5. FTIR ABSORPTION WAVELENGTHS FOR NAPHTHALENE ANALOGS in CCl_4

Compound/(Purity)		Wavelengths (cm^{-1}) 960-600														
Naphthalene	(99)	0958	****	****	****	****	****	****	****	****	****	****	****	****	****	0619
1,2-Dihydronaphthalene	(75)	*0956*	****	0939	****	****	0885	0868	****	****	****	****	****	**0692**	**0682**	****
	(95)	****	****	0939	****	****	0885	****	****	****	****	****	****	**0692**	0682	****
1,4-Dihydronaphthalene	(92N)	****	****	****	0920	****	****	****	****	****	****	**0785**	**0744**	****	****	**0660**
	(90)	****	****	****	0920	****	****	****	****	****	****	****	****	****	****	**0660**
	(69N)	****	****	0940	****	****	**0886**	****	****	****	0805	**0783**	**0746**	**0692**	**0683**	****
	(69)	****	****	*0939*	****	****	****	****	****	****	****	****	****	**0693**	0683	****
1-4-Tetrahydronaphthalene	(99)	****	*0947*	****	****	****	****	****	****	****	****	****	****	****	****	****
Isotetralin	(97)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	**0672**
	(88)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	**0672**
Hexahydronaphthalene	(98)	****	**0949**	****	****	*0899*	****	0872	****	****	****	****	****	****	****	**0663**
Octahydronaphthalene	(99)	****	****	****	****	****	****	****	*0851*	*0831*	****	****	****	****	****	****
Cis-Decalin	(99)	****	****	****	****	****	****	****	0854	****	****	****	****	****	****	****
Trans-Decalin	(99)	****	****	0925	****	****	****	****	****	****	****	****	****	****	****	****
Hexadecane	(99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 1. FTIR ABSORPTION WAVELENGTHS FOR ANTHRACENE ANALOGS in CS_2

Compound/(Purity)	Wavelengths (cm^{-1}) 3200-2830														
Anthracene (99)	****	****	**3053**	****	3023	3010	****	****	****	****	****	****	****	****	****
9,10-Dihydroanthracene (98)	3075	3064	****	3042	**3021**	****	****	****	2936	****	****	****	****	2854	****
1,4,5,8,9,10-Hexahydroanthracene (99)	****	*3063*	****	****	**<u>3026</u>**	****	*2986*	2972	****	****	****	****	**<u>2868</u>**	****	**<u>2837</u>**
1-8-Octahydroanthracene (99)	****	****	****	****	****	****	**2993**	****	**<u>2930</u>**	**<u>2922</u>**	****	**<u>2879</u>**	****	**<u>2853</u>**	**<u>2833</u>**
Perhydroanthracene (RO)	****	****	****	****	****	****	****	**<u>2970</u>**	**2931**	****	**2904**	****	**2869**	**2853**	****
Hexadecane (99)	****	****	****	****	****	****	****	**<u>2957</u>**	**<u>2926</u>**	****	****	**<u>2872</u>**	****	**<u>2854</u>**	****

Table 2. FTIR ABSORPTION WAVELENGTHS FOR ANTHRACENE ANALOGS in CS_2

Compound/(Purity)	Wavelengths (cm^{-1}) 2830-1620														
Anthracene (99)	****	****	****	****	****	****	****	*1935*	*1793*	****	****	*1705*	*1674*	****	1622
9,10-Dihydroanthracene (98)	2811	****	****	****	****	****	****	****	****	****	****	****	****	****	****
1,4,5,8,9,10-Hexahydroanthracene (99)	**<u>2809</u>**	*2756*	2735	2728	*2710*	*2666*	****	****	****	****	****	****	****	1656	****
1-8-Octahydroanthracene (99)	****	****	****	****	****	****	*2655*	****	****	****	****	****	****	****	****
Perhydroanthracene (RO)	****	****	****	****	****	****	****	****	****	1781	**<u>1729</u>**	****	****	****	****
Hexadecane (99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 3. FTIR ABSORPTION WAVELENGTHS FOR ANTHRACENE ANALOGS in CS_2

Compound/(Purity)	Wavelengths (cm^{-1}) 1620-1110														
Anthracene (99)	****	*1396*	****	****	****	1314	****	****	1270	****	****	****	1165	1146	****
9,10-Dihydroanthracene (98)	****	****	****	****	****	****	****	*1282*	****	****	1204	*1181*	****	*1151*	1119
1,4,5,8,9,10-Hexahydroanthracene (99)	****	1396	*1371*	****	1339	****	****	****	****	****	****	*1172*	****	****	*1113*
1-8-Octahydroanthracene (99)	****	****	****	1350	1337	****	1296	1288	****	1244	****	****	****	****	****
Perhydroanthracene (RO)	****	****	****	****	****	****	****	****	****	****	****	**1178**	**1159**	****	****
Hexadecane (99)	**1467**	****	1378	****	****	****	****	****	****	****	****	****	****	****	****

Table 4. FTIR ABSORPTION WAVELENGTHS FOR ANTHRACENE ANALOGS in CS_2

Compound/(Purity)	Wavelengths (cm^{-1}) 1110-770														
Anthracene (99)	****	****	****	0999	****	****	**0953**	****	*0907*	****	**0876**	****	****	****	****
9,10-Dihydroanthracene (98)	****	1039	****	****	****	****	**0953**	****	****	*0893*	****	****	****	****	*0779*
1,4,5,8,9,10-Hexahydroanthracene (99)	****	****	****	****	**0986**	**0976**	****	****	****	****	****	****	0844	****	0785
1-8-Octahydroanthracene (99)	****	****	****	****	*0982*	****	****	**0926**	****	****	****	**0855**	****	*0815*	****
Perhydroanthracene (RO)	**1070**	**1039**	1013	0993	****	****	****	****	**0912**	****	****	****	****	****	****
Hexadecane (99)	****	****	****	****	****	****	****	****	****	****	****	****	****	****	****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

Table 5. FTIR ABSORPTION WAVELENGTHS FOR ANTHRACENE ANALOGS in CS_2

Compound/(Purity)	Wavelengths (cm^{-1}) 770-600
Anthracene (99)	**** *0750* **** **** **** **0726** 0601
9,10-Dihydroanthracene (98)	**** **0756** **** **** **0745** **0729** **0607**
1,4,5,8,9,10-Hexahydroanthracene (99)	0785 **** *0765* **0658** **** **** ****
1-8-Octahydroanthracene (99)	**** **** **** **** **** **** ****
Perhydroanthracene (RO)	**** **** **** **** **** **** ****
Hexadecane (99)	**** **** **** **** **** **** ****

Italic => Shoulder or Trace Amount
Normal Print => 0.02 - 0.049 Absorbance
Bold Print => 0.050 - 0.099 Absorbance
Bold/Underline => $\geq$ 0.100 Absorbance

PART III

LITERATURE REVIEW

An Overview of Low Severity Liquefaction.

The vast wealth of coal in the United States has led to the investigation of different ways of utilizing this resource. The conversion of coals to transportation and heating fuels is one possibility. Coal liquefaction and gasification provide alternative fuels to oil and gas, currently produced from petroleum. Liquefaction of coal requires a conversion of a solid hydrocarbon to the liquid state, an increase in the hydrogen content, a decrease in the heteroatom content and a removal of the mineral matter.

The hydrogen content of gasoline is about 14% by weight while that of a typical bituminous coal is only 5%. The hydrogenation of coal is not an easy process and usually requires high temperatures and pressures (Hessley, 1986). Current liquefaction methods involve staged reaction conditions and multiple reactor systems. Conventional two-stage liquefaction utilizes a solubilization process in the first reactor under high temperature and pressure followed by a catalytic upgrading of the coal liquids in the second. These high-severity bench-scale processes have held the emphasis since the first German discoveries in the 1920's and 30's. These reactions take place well above the activation energies of the major reactions involved and often lead to high retrogressive condensation, cracking and an array of transalkylation reactions. The catalyst in the second stage reactor tends to deactivate because of coking. Coking occurs because of the high concentration of high molecular weight preasphaltenes in the products of the first step (Moroni, 1986).

The alternative to high severity reactions in the first step of this process is the use of reactions with low severity conditions (generally at temperatures below 350°C and pressures from 500-1500 psi) coupled with physical and chemical methods to optimize coal dissolution. These methods include use of catalysts, coprocessing with heavy oils, use of hydrogen donating species and pretreatment of the coal.

The low severity approach has revolutionized the whole thinking on coal liquefaction. Miller (1991) and Moroni (1986) suggest that low severity liquefaction holds many advantages over high severity methods:

- There is reduced hydrocarbon gas production which results in not only reduced feed gas consumption, but enhanced hydrogen utilization efficiency.
- The tendency towards retrogression of the primary coal dissolution products is reduced. The lack of retrogressive reactions increases the residuum product quality.
- The occurrence of low molecular weight reactive coal fragments in a solvent low in heteroatoms and high in hydroaromatics appears to show the success in processing both low and high reactivity coals. Both types yield similar conversions and product qualities, challenging the notion that conversion success is dependent on coal quality and not the procedure used.
- Coal extracts that are produced are low in heteroatom content and, therefore, less refractory. These extracts are more amenable to catalytic upgrading in a conventional catalytic cracker.
- There are less severe slurry handling and materials of construction problems due to lower operating temperatures and pressures.

- Conventional pipes, pumps, valves and fittings can be used in the reactor instead of expensive high-pressure, high-temperature equipment.

Low severity liquefaction is still very new. Reactivity of the coals, while often favorable, can be optimized through the use of the aforementioned methods. These chemical and physical promoters of coal dissolution must be investigated to find those that can achieve sufficient conversion in a reasonable amount of time.

Some success, in this regard, has been seen by Miller and Shams (1991) using pretreatment of the coal with a mild hydrochloric acid solution. The use of cyclic olefins as hydrogen donors has also been successful in improving reactivity of coals in low severity liquefaction. An investigation of mild acidic pretreatment followed by dissolution of the coal in the presence of cyclic olefins as hydrogen donors could provide even better results. If positive results are achieved, this procedure might be manipulated further, by varying acids and solvents used and pretreatment conditions, to achieve even better results. Such a possibility was not stumbled upon by chance. The science of low severity coal liquefaction is a rapidly developing one, and through experimentation with different methods a better understanding is growing.

Coal Structure and Low Severity Liquefaction

Many different avenues have been investigated to improve the conversion of coal under low severity conditions. The first step was to attempt to learn about the mechanisms involved. In the study done by Chakrabartty (1985), ways of increasing the extractability of carbon-hydrogen structured materials of coal were investigated to attempt to come to a better understanding of the chemistry of liquefaction of low rank coals. Solvolysis of an Alberta

subbituminous coal with tetralin as a solvent at ambient pressure and temperatures from 300 to 400 °C was carried out. The amount of tetrahydrofuran (THF) insolubles in the solvolysis products was then recorded. The physical effect of the swelling behavior of coals with different solvents was also observed by soaking them for 40 hr at ambient temperature. These were then refluxed for 4 hr in phenol with p-toluenesulfonic acid to determine the improved activity of the phenolation reactions. Both of these sets of experiments highlighted the role that surface reactions play in the yield and nature of reactions involved with liquefaction. Altering the layered structure of molecules could conceivably enhance coal solubilization.

Snape and coworkers (1991) investigated the influence of coal structure on primary conversions and oil yields in thermolytic extraction with different H-donor and non-H-donor solvents. The experiments were done using a Wyodak subbituminous coal, an Illinois No.6 coal and a United Kingdom bituminous coal (Point of Ayr) in a Lummus process-derived distillate (with a boiling range of 340-400 °C and 1% donable hydrogen) with tetralin (TET) at a short contact time. A temperature of 450 °C was used to increase oil yields without a hydrogen overpressure.

Extractions of two United Kingdom coals (Linby and Point of Ayr) at 400 °C using TET, naphthalene (NAP), 9,10-dihydrophenanthrene (DHA), phenanthrene (PHEN), and pyrene (PYR) as models for up to 30 min were performed to observe the factors involving initial dissolution. Some coal/solvent slurries were pre-soaked at 250 °C, and the effect of extraction of the Linby coal with THF prior to liquefaction was observed.

When the THF extractable materials in the Linby coal are removed prior to reaction, there was an increase in the primary conversions in the polynuclear aromatic compounds

(PAC's) investigated. It can be inferred that the mobile phase limits the accessibility of the PAC's within Linby and other lower rank coals. The conversion of the non-THF extracted Linby coal was greater with NAP than with PHEN and PYR. Even after THF extraction, NAP conversion was comparable to that of PYR. Pre-soaking had little effect. Pyrene seems to be an effective "hydrogen shuttler" because it causes the hydrogen in the Linby coal to be utilized more effectively than did the NAP or PHEN. Pyrene resulted in higher conversion. Tetralin and DHA gave much higher yields of THF solubles than all the PAC's but PYR which gave conversions close to those for DHA. Pre-soaking did not improve the short contact time conversion for TET as it did the DHA, presumably due to poorer physical contact between TET and the coal.

With this limited suite of coals, the yield of THF insolubles increased with increasing rank much more smoothly than if a wider range of coals was used. It was also determined that solvents with good physical contact were essential to slowing retrogressive reactions. Without good contact, it was difficult to see a definite correlation between coal rank and oil yield or total conversion. The oil yields did generally increase with decreasing rank in the presence of a good hydrogen donor and when a catalyst was used to prevent retrogressive reactions. Especially for low rank coal, it is important halt these retrogressive reactions to preserve the products of the initial stages of liquefaction.

Catalysis in Low Severity Liquefaction

Stansberry and coworkers (1984) had already discovered the importance of catalysts in liquefaction in their search to understand the mechanics of the process. They investigated the catalytic low-temperature hydrogenation of coal. Their purpose was to derive information

about the structures and interactions of the 'network' and 'mobile' phases of the coal and to determine the effect of catalytic pretreatment of the coal on liquefaction.

Samples of bituminous coals from the Pennsylvania State University Coal Sample Bank were suspended in an aqueous solution of ammonia heptamolybate ($(NH_4)_6Mo_7O_{24}\bullet 4H_2O$). Molybdenum catalyst was then impregnated onto the coal by mixing the slurry for 30 min at room temperature. After removing the excess water in vacuo, 98% of the catalyst remained on the coal. The reaction was carried out in a tubing bomb microreactor at a cold 1000 psig of reactant gas without use of a solvent. Conversion was measured by the amount of chloroform soluble extracts.

At above 325 °C, the presence of hydrogen gas caused an increase the total yield. The presence of the impregnated catalyst increased it even further. At 400 °C, the yield was 43.1% which was twice as high as hydrogen alone and four times as high as nitrogen alone. It is unclear whether with the catalyst there was more efficient liberation of the trapped species, or there was decomposition of the 'network'. It seems likely that the catalyst produced some products through the breaking of some strong chemical bonds. The mechanism is unusually subtle because the additional liquids generated through the use of the catalyst are very similar to those generated in its absence.

The catalysts studied in the work of Smith and Johnson (1990) also proved to be good hydrogen donors. They used intermetallic alloys to form reversible hydrides to store atomic hydrogen within their metal matrices. In some cases, these hydrides can store more atomic hydrogen than liquid hydrogen. FeTi, $LaNi_5$, $CaNi_5$, Mg_2Cu and Mg_2Ni were used to catalyze the coal liquefaction. Alabama Black Creek coal was used in a slurry with

1-methylnaphthalene. Five milliliter microreactors were used at temperatures of 316, 371, and 427 °C at 4.38 MPa. Effectiveness of the catalysts ranked according to $CaNi_5$ = $LaNi_5$ > FeTi > Mg_2Cu > Mg_2Ni. The first three gave greater than 60% conversion, and $CaNi_5$ gave 21, 49, and 62% catalyzed conversion at the three temperatures, compared to a non-catalyzed conversion of 18, 25, and 33%, respectively. These results can be accredited to the desorption isotherms and pure component hydrogenation properties of the catalysts. The most active catalysts have low temperature/low pressure desorption isotherms and also have components with known hydrogenation activity.

Coal and Oil Coprocessing

Coprocessing of coals with heavy oils has, in some cases, given larger distillate yields than oil or coal individually. Miller and Baldwin (1986) found shale oil to be quite useful in coprocessing due to its high heterocyclic nitrogen content. Wyodak subbituminous was used with oil from Colorado shale to determine the effectiveness of low severity coprocessing. The reactions were carried out in a 60 cm^3 stirred microautoclave heated by an external high temperature furnace. Carbon monoxide and water were used as a reducing agent. The range of temperatures was from 600 to 650 °C, and a range of pressures from 1000 to 1500 psig cold CO for 15 to 60 min. Distilled water (50 wt% of the dry feed coal) and iron sulfate as a disposable catalyst (5 wt% of the dry feed coal) were also used.

The increased hydrogen donability of hydrotreated shale oils and increased concentrations of partially hydrogenated nitrogen compounds which led to higher conversion showed the significance of prehydrotreatment of the shale oil. Lower reaction temperature and higher CO pressure causing the favorable thermodynamic equilibrium of the water-gas shift

reaction also increased the yield. 85% conversion was achieved from reactions at 600°C and 1500 psig CO.

Miller and Baldwin (1988) also had success using basic nitrogen dissolution promoters, such as 1,2,3,4-tetrahyroquinoline (THQ) and dipropylamine, in the coprocessing of coal with heavy oil. Kentucky 9 bituminous coal and Wyodak subbituminous coals were used as feed coals with Cold Lake atmospheric residuum as the coprocessing heavy oil. Along with the two nitrogen compounds already mentioned; 7,8-benzoquinoline, piperidine, 4-piperidinopyridine, 5,6-benzoquinoline and diphenylamine were used. The reactions took place in a 300 cm^3 autoclave reactor under hydrogen or carbon monoxide. The use of THQ and dipropylamine caused the greatest improvements in coal conversion. Piperidine, 4-piperidinopyrine and diphenylamine had little effect. This was due to the limited adduction of the THQ and dipropylamine. No relationship between yield structure and conversion improvement was obvious from these experiments. A comparison of the reactions at varying severities suggested that low severity dissolution followed by catalytic hydrocracking would be beneficial to coal conversion but also to reduction of nitrogen losses.

In follow-up work, Miller and Baldwin (1990) found that two-stage coprocessing in the presence of THQ by low severity dissolution and conventional catalytic hydrocracking yielded coal conversions and distillates similar to that of high severity liquefaction. This occurred without the hydrogen consumption and hydrocarbon gas production associated with the latter.

Improved Hydrogen Donors in Low Severity Liquefaction

It is obvious from each of these examples that a good source of hydrogen is key to successful liquefaction. The supply of hydrogen has to correspond with the demand. Some

of the most successful compounds used to donate hydrogen and improve conversion in low severity liquefaction coal liquefaction are cyclic olefins. Cyclic olefins are hydroaromatic species that do not contain aromatic rings. Bedell and Curtis (1991) used 1,4,5,8-tetrahydronaphthalene (isotetralin) and 1,4,5,8,9,10-hexahydroanthracene (HHA). These compounds release hydrogen more readily than the conventional hydroaromatics and increase the coal conversion.

These reactions were carried out in 20 cm^3 tubing bomb reactors at 380 °C and 1250 psig cold hydrogen or nitrogen pressure. Reaction times varied from 2 min to 1 hr and contained 2.0 g of hexadecane as the solvent and 3 wt% hydrogen donor (0.033 to 0.179 wt% donable hydrogen indicating the number of hydrogen atoms lost to produce the aromatic ring). Shell 324, $NiMo/Al_2O_3$, and Amocat 1B, Mo/Al_2O_3 were used to test donability under catalytic conditions.

The isotetralin was reactive under both atmospheres. At longer reaction times of 15 to 60 min in hydrogen and after 30 min in nitrogen, all of the isotetralin was converted. At 2 min, approximately 50% of the isotetralin remained in both cases. Under catalytic conditions, only trace amounts of the isotetralin remained after 2 min. Similar results were found for the HHA. At 2 min reaction times, 47% was left in nitrogen and 61% in hydrogen. The catalysts also converted the HHA almost totally.

The cyclic olefins converted their hydrogen more readily than their hydroaromatic analogues. As the temperature of the reaction increased, the difference lessened. In order to get the best results, matching between the kinetics of hydrogen donation and hydrogen acceptance must be done.

Improved Low Severity Liquefaction Through Pretreatment

Building on the results of researchers like Chakrabartty, the significance of chemical and physical pretreatment of the coal before reaction has been explored. Baldwin and coworkers (1991) investigated both solvent swelling and mild alkylation using selective and non-selective techniques. The effect was tested in direct hydroliquefaction and coal/oil coprocessing at high and low severity conditions. Two coals from the Argonne Premium Coal Collection Sample Bank, Illinois No.6 (hvb) and Wyodak subbituminous, were used. Dihydrophenanthrene was used for the direct liquefaction and Cold Lake resid was used in the coprocessing. All reactions were done in tubing bomb microautoclaves. Conversion was determined on the basis of THF solubility.

Selectively O-methylated alkylation was found to be more beneficial in enhancing the reactivity of the low rank Wyodak than the high ranking Illinois coal. The THF conversion increase was greatest at low severity (120% at 350 °C for 5 min) in dihydrophenanthrene. At intermediate severity, the yield for the resid was improved 100% at 350 °C for 30 min and 60% at 425 °C for 5 min. On the other hand, the reactivity of Illinois No. 6 decreased from only a 20% improvement as severity increased. Oxygen alkylation was completely ineffective for the high rank Illinois coal, but non-selective methylation improved the high rank coal conversion at high severity. It did not affect the Wyodak, though. The swelling of the coal with acetone improved the yield of hexane solubles for both coals.

Chemical pretreatment seems to improve conversion due to the minimization of organic oxygen coupling reactions early in the liquefaction process. With solvent swelling, this can

significantly increase conversion. There seems to be some optimal level for dissolution, since the effect decreases with increasing severity.

More recently, McArthur and coworkers (1992) worked with the pretreatment of coal with chlorobenzene. Polar pretreatment of coals is hard to interpret due to the removal of organic matter that occurs as changes in the macromolecular structure of the coal are made. Chlorobenzene extracts virtually no organic matter from the coal. This pretreatment was looked at in conjunction with coal liquefaction with a hydrogen donor solvent and dry solvent-free hydrogenations, each with and without dispersed molybdenum catalyst. Pittsburgh No. 8 from the Argonne Premium Sample Bank was used in all cases.

This pretreatment improved the conversion for tetralin extraction (20% increase in dichloromethane (DCM) solubles) and non-catalytic hydrogenation (increased from 19 and 31% DCM solubles). With catalyst, the effect was negative (25% less oil was produced as were 12-13% more DCM insolubles). The reduction in the amount of oils and DCM solubles produced may be due to the increased ability of the oil to be transported out of the macromolecular structure of the catalyst thereby decreasing the amount of bitumen remaining in the pore structure to transport hydrogen to reaction sites.

Chlorobenzene, since it is a low-swelling solvent, does not disrupt hydrogen bonding like most other polar solvents. It may bring about conformational changes in the coal. These changes may disrupt the non-covalent bonding between aromatics.

Pretreatment With Mild Acidic Solution

One of the newest and most promising pretreatment methods is that of Shams and coworkers (*Fuel*, 1992). This method involves the mild chemical pretreatment of coal using

methanol and a trace of hydrochloric acid. Following the lead of previous researchers, they investigated the increased reactivity of coals using this pretreatment method. Hydrochloric acid destroys ionic bridges and reduces coordination between oxygen-containing functional groups to allow better contact between coal and solvent. This process also removes alkaline and alkaline earth cations which inhibited hydrogen transfer. This chemistry can also alkylate sites in the coal which lead to retrogressive reactions. Another advantage of this pretreatment process is the lack of expense for materials.

In the initial study of Miller and Shams (1991), 0.1 cm^3 of concentrated hydrochloric acid and 40 cm^3 of methanol were used to suspend a 5 g coal sample. The sample was continuously stirred for 3 hr. Most of the solvent was then decanted off, and the coal was first rinsed with fresh solvent and then distilled water before the reaction. The sample was vacuum dried for 24 hr and agitated in a 20 cm^3 tubing bomb reactor for 30 min at 350 °C and 1000 psig cold hydrogen. Dihydrophenanthrene was used as donor solvent in all of these reactions. All eight of the Argonne Premium Coal Samples were used as feed coals.

Methanol and HCl pretreatment enhanced the low severity reactivity of all eight coals. Improvements from 5.5 wt % for Blind Canyon coal to 31.5 wt % for Wyodak coal were seen. There were no simple identifiable trends in the enhanced reactivity with increase in coal rank. Replacement of methanol with hexane also showed improvements in reactivity. They also observed that reactivity was significantly increased, although the samples pretreated had only been alkylated to a small extent.

From these results, they realized that there were many more effects at work than had been previously realized. Alkylation of oxygen and carbon sites in the coal structure is only

a part of the chemistry involved. Species such as calcium, iron or magnesium may be leached from the mineral matter in the coal. There could also be formation of chlorinated compounds like $FeCl_2$ which are proven dissolution catalysts.

In later work, Shams and Miller (*ACS Preprints*, 1992) tried to discern which part of the process had the greatest effect on the increased low severity reactivity. They varied acid concentration, pretreatment temperature and time and the separation method used. They also paid special attention to the effect of pretreatment on coal composition and the effect of calcium content on low severity reactivity.

The same basic process used before was used in their later work. Once again all eight coals from the Argonne bank were used. At 1.5 vol % HCl with methanol, reactivity was enhanced. The increases averaged 14.9 wt % with as much as 24.5 wt % for Wyodak to 28.4 wt % for Beulah-Zap to 5.2 wt% for Blind Canyon. Once again, no simple trends in accordance with physical or chemical properties. Replacing methanol with hexane and acetone also proved to be useful in increasing reactivity. No trends were found relating solvent properties either. Methanol alone did not increase reactivity, but HCl with distilled water did. This would seem to indicate that the HCl is the important component. Distilled water alone had no effect so an organic solvent needs to be present.

Several analytical techniques demonstrated that pyrite was unaffected by this pretreatment technique. This eliminates the possibility of the formation of $FeCl_3$, a known dissolution catalyst, influencing the liquefaction. Using X-ray diffraction of the ash, it was apparent that 90% of the calcium had been removed. Elemental analysis showed that not only was calcium leached, but also magnesium, potassium and sodium.

Increasing the amount of acid to remove more calcium caused an increase in reactivity. An equivalent amount of calcium carbonate was also added to coals that had their calcium removed. Doing this almost completely negated the effect of pretreatment. Sharma and Miller hypothesized that calcium can directly catalyze retrogressive reactions in low severity liquefaction.

About 2 vol % HCl in the reaction proved to be optimal. A pretreatment time of 3 hr proved long enough. Variation in these two parameters made little difference. Increasing reaction temperature, as expected, increased yield. Overall, pretreatment of the coals with the HCl/methanol solution improved conversion by low severity liquefaction over a wide range of conditions, meriting further study.

Current Research Emphasis

The combination of some of these methods could further improve low severity conversion. It seems logical that a combination of a proven pretreatment technique with a good dissolution catalyst or a good hydrogen donor would increase reactivity.

The importance of surface chemistry with yield and nature of reactions shown in early research indicates the physical importance of pretreatment. Swelling of the coal with an organic solvent improves the contact. This good contact is also important to slowing retrogressive reactions. The best conversions come when the initial products of liquefaction are preserved. In addition to the physical importance of pretreatment, there is a chemical advantage. Shams saw not only the effect of minimization of organic oxygen coupling reactions, but with his process there also seemed to be a demineralization. The minerals removed the catalysts for retrogressive reactions.

The chemistry of liquefaction is still not well understood. Stansberry's attempt to determine whether catalysts liberate species or just further decomposition was largely inconclusive. There was improvement in conversion so the catalysts seemingly assisted in bond breakage. These good catalytic effects were also seen in the work involving coprocessing.

The most compelling factor in each of these procedures, is the ability of the coal to receive the hydrogen that it needs to be liquefied. Bedell and Curtis (1991) found that cyclic olefins gave their hydrogen up much more readily than did hydroaromatics. The coal conversion was a significantly improved. The combination of retrogressive reaction suppression and good hydrogen donability should provide for good coal conversion. It was this reasoning that influenced the decision to investigate a combination of the HCl/methanol pretreatment and the usage of cyclic olefins as hydrogen donors. The increased reactivity of the pretreated coal should enhance the effect of the hydrogen donability of the cyclic olefins.

REFERENCES

1. Baldwin, Robert M.; Kennar, D. R.; Nguanprasert, O.; Miller, Ronald L. "Liquefaction Reactivity Enhancement of Coal by Mild Alkylation and Solvent Swelling Techniques," *Fuel*, 70(3), 1991, 429-433.

2. Bedell, Michael W.; Curtis, Christine W. "The Chemistry and Reactivity of Cyclic Olefins as Donors in Coal Liquefaction," *Energy and Fuels*, 5, 1991, 469.

3. Chakrabartty, Sujit K. "Search For Low Severity Liquefaction Concept," *Liquid Fuels Technology*, 3(1), 1985, 1-13.

4. Hessley, Rita K.; Reasoner, John W.; Riley, John T. *Coal Science: An Introduction to Chemistry Technology, and Utilization*, John Wiley & Sons, Inc., 1986.

5. McArthur, C. A.; Mackinnon, A. J.; Hall, P. J.; Snape, Colin E. "The Effects of Chlorobenzene Pretreatment on the Low Severity Liquefaction Behavior of Pittsburgh No. 8 Coal," *ACS Fuel Chemistry Preprints*, 37(2), 1992, 764-769.

6. Miller, Ronald L.; Baldwin, Robert M. "Liquefaction Co-processing of Coal and Shale Oil at Low Severity Conditions,"*ACS Fuel Chemistry Preprints*, 31(4), 1986, 152-160.

7. Miller, R. L.; Giacomelli, G. F.; Baldwin, R. M. "Low Severity Co-processing Using Homogeneous Basic Nitrogen Promoters," *ACS Fuel Chemistry Preprints*, 33(1), 1988, 154-162.

8. Miller, R. L.; Baldwin, R. M.; Kennar, D. R. "Addition of Basic Nitrogen Promoters to Enhance Low Severity Two-stage Coal Liquefaction and Coal/Oil Co-processing," *ACS Fuel Chemistry Preprints*, 35(1), 1990, 9-16.

9. Miller, R. L.; Shams, KayGhobad; Baldwin, R. M. "Mild Coal Pretreatment to Enhance Liquefaction Reactivity," *ACS Fuel Chemistry Preprints*, 36(1), 1991, 1-6.

10. Moroni, Eneo C. "Low Severity Coal Liquefaction: A Challenge to Coal Structure Dependency," *ACS Fuel Chemistry Preprints*, 31(4), 1986, 1-4

11. Shams, K.; Miller, R. L.; Baldwin, R. M. "Enhanced Low Severity Coal Liquefaction Using Selective Calcium Removal," *ACS Fuel Chemistry Preprints*, 37(2), 1992, 1017-1024.

12. Shams, K.; Miller, R. L.; Baldwin, R. M. "Enhancing Low Severity Coal Liquefaction Reactivity Using Mild Chemical Pretreatment," *Fuel*, 1992, 1015-1023.

13. Smith, James E., Jr.; Johnson, Scott D. "Low Severity Coal Liquefaction Using Intermetallic Hydrides as Both Catalysts and Hydrogen Distribution Agents," *ACS Fuel Chemistry Preprints*, 35(1), 1990, 23-30.

14. Snape, C. E.; Derbyshire, Frank J.; Stephens, Howard P.; Kottenstett, Richard J.; Smith, Neil W. "Influence of Organic Coal Structure on Liquefaction Behavior Under Low Severity Conditions," *ACS Symposium Series*, 461(Coal Science 2), 1991, 182-192.

15. Stansberry, P.; Terrer, M. T.; Derbyshire, F. J.; Finseth, D. H. "Low Severity Catalytic Hydrogenation of Coals in the Absence of Solvent," *ACS Fuel Chemistry Preprints*, 29(5), 1984, 67-75.

PART III.B.

FUTURE WORK IN THE STUDY OF THE EFFECTS OF MILD ACIDIC PRETREATMENT TO ENHANCE LOW SEVERITY COAL LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

Objective: The objective of this project is to study the effects of mild acidic pretreatment on the reactivity of feed coals of differing rank in low severity liquefaction reactions promoted by cyclic olefins.

FUTURE WORK

Since the pretreatment methods of Ronald Miller et al., of the Colorado School of Mines, and the use of cyclic olefins as hydrogen donors of Christine Curtis et al., of Auburn University, each improves low severity coal liquefaction, a combination of these two procedures will be used. It will be determined whether the reactivity of various Argonne coals with isotetralin, a cyclic olefin, may be enhanced through pretreatment with a dilute solution of hydrochloric acid in methanol. If time permits, these results with various ranks of coal will be studied. Due to improvements seen in pretreatment of lower rank coals, the emphasis will be placed on subbituminous coal [Wyodak] and lignite [Beulah-Zap]. If reactivity increases, the effect of different acid concentrations, different solvents and, due to the desire to avoid the usage of chlorine in manufacturing processes, different acids will also be studied.

Pretreatment will be accomplished by continuously stirring a 5-g sample of coal in 40 cm^3 of methanol with 0.1 cm^3 of concentrated hydrochloric acid for 3 hr. After pretreatment, the majority of the organic solvent will be decanted off, and the coal will be washed thoroughly first with pure solvent, then with distilled water to remove all of the residual acid. It will then be vacuum dried, as will untreated samples, for 24 hr.

These samples will then be placed into two tubular microreactors, attached to an agitator and immersed in a fluidized sand bath. Two identical reactions will be run to ensure good reproducibility. The reactions will take place at 350 °C and 500 psig initial cold hydrogen pressure for a reaction time of 30 min.

Coal conversion will be measured using THF extraction data corrected for the intrinsic solubilities of treated and untreated coals. Selected few reactions will undergo detailed analysis.

In order provide a reference for and ensure the validity of the results, preparatory work will need to be done. Each of these procedures; pretreatment, reaction and conversion analysis, will have to be practiced. An easily repeated, definite routine will have to be established for each process. One of the most important factors to be considered is good recovery throughout. A mass balance must be maintained from beginning to end.

In order to make an analysis of the reaction products, response factor data for gas chromatography using an internal standard must be done. A response factor graph for the isotetralin and for its products after hydrogen donation: naphthalene, decalin, and tetralin must be made. After this has been accomplished, each of these compounds individually will undergo reactions at the previously mentioned reaction conditions only in the presence of solvent. The products will undergo GC analysis. Each compound will then be reacted with the untreated highlighted coal, most likely Wyodak, at these conditions. These products will not only undergo GC analysis, coal conversion of each will also be determined. Then, HCl-methanol pretreated coal will be reacted with all of the compounds and the same analyses will be done.

After all of this has been completed, there are many parameters that may be altered to observe the effect. The use of different coals and different pretreatment will be explored. The emphasis will be placed on finding an alternate acid. The temperature and pressure of the reaction can also be changed. It is hoped that through this project the reactivity in low severity liquefaction can be improved, and the feasibility of low severity coal liquefaction increased.

PART III. APPENDIX

Procedure for Mild Chemical Pretreatment of Coal

1. Using standard weighing paper, weigh out 5 g of coal to be pretreated. Place this coal into a 125 ml Erlenmeyer flask with a stopper. To this add 40 ml of methanol (or other solvent) using a buret or other accurate measuring vessel. Using a syringe, add 0.4 ml of concentrated hydrochloric acid (or other acid) to the coal solution. Be sure to rinse the syringe immediately after use to prevent corrosion.
2. Place flask onto an orbital shaker with the stopper replaced to prevent evaporation of the solvent. Shake the solution vigorously (approximately 300 rpm) at room temperature for 3 hr.
3. After shaking the solution, transfer it to a centrifuge bottle. To ensure the transfer of all coal, more methanol may be added to the flask and poured into the centrifuge bottle. Centrifuge the solution for about 10 to 15 min (enough time to allow the coal to settle to the bottom).
4. Record the weight of one sheet of filter paper (11.0 cm Whatman 5 Qualitative or something of similar size and porosity). Place the filter paper into a large funnel with a fixed perforated filter plate (i.e., 114 mm Coors porcelain funnel) that has been sealed into a large vacuum flask with a rubber stopper. Place a vacuum hose onto the flask and open the line. Wet the filter paper with methanol to seal it to the funnel. Pour the solution out of the centrifuge bottle slowly onto the filter paper. If the solution is poured too quickly, the vacuum will not be able to draw it through the filter paper quickly enough and some of the coal will go past the edge of the filter paper and be

lost. Again, more methanol may be used to ensure that all of the coal is removed from the bottle. After all of the coal has been placed onto the filter paper, use a pipet to wash the coal. The coal should be washed first with 150 ml of methanol (in 25 or 50 ml increments) to rinse any remaining acid off of the coal. It should then be washed with 150 ml of distilled water to rinse all of the methanol off of the coal. Again this should be done slowly enough to allow the vacuum to draw the liquid through the filter so the coal does not run to the edge of the funnel. It is very likely that the vacuum flask, unless it is very large, will fill with liquid before the procedure is complete. If it begins to fill, halt the procedure, and empty it into a waste bottle.

5. Once the coal has been washed, the filter may be removed easily from the funnel by placing the vacuum hose onto the air line and opening it slightly to create a minor overpressure in the flask. Remove the filter paper carefully and place it onto a petri dish (11.0 cm paper will require a 150x15 dish). Place it into a vacuum oven at room temperature until it is used.

6. Untreated coal that it used to compare results should be dried under the same conditions.

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