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Low Severity Coal Liquefaction Promoted by Cyclic Olefins

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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 N₂ and H₂ 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). Last quarter research was performed in which two parameters were optimized. After performing this research, it was obvious that the combination of three parameters would probably be highly effective. Combinations of three reaction parameters were evaluated such as reaction temperature, reaction time, concentration of hydrogen donor, and hydrogen pressure. The research performed this quarter included combining three 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, contained 6% Mo and was used as received.

Low-severity liquefaction reaction conditions were employed. The reactions were performed in ~50 cm³ stainless steel tubular reactors that were well agitated. The reactor was charged with 2 g of coal and 4 g of solvent. The solvent was composed of hexadecane and hexahydroanthracene. When hexahydroanthracene was present at 0.5 wt% donable hydrogen, 0.61 g was introduced and at 1.0 wt% donable hydrogen, 1.22 g was introduced. In both cases, hexahydroanthracene composed the remainder of the solvent. The base line conditions were

350 °C, 500 psig H₂ 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 when Mo was introduced at 500 ppm, presuming that finely divided MoS₂ 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 three parameters were changed from the base line 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) and insoluble organic matter (THF insoluble and ash free). 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 was conducted using a Varian 3700 gas chromatograph equipped with a J&W DB-5 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 was

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

The following term, percent hydrogenation (% HYD) of hexahydroanthracene, 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). These reactions evaluated the effect of the combination of three 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.

The first two sets of data presented in Tables 2 and 3 describe an experiment that evaluated the effect of catalyst loading on reactions of Illinois No. 6 coal using HHA introduced at 0.5 wt% donable hydrogen. Thermal reactions were also performed at the same conditions of 350 °C, 500 psig H₂ introduced at ambient temperature, 60 min reaction time, and 0.5 wt% donable hydrogen. The experiments given in Table 2 were performed during this quarter to establish the effect of the reaction conditions on the amount of oil present in the

reaction products. The previous reactions given in Table 3 which were performed last quarter and gave aberrant results in terms of the amount of hexane soluble oil present in the product. The results obtained this quarter for the product oil in the thermal and catalytic reactions at 500 and 1000 ppm were reasonable and consistently increased with the severity of the reaction condition. Therefore, the results given in Table 2 will replace those given in Table 3.

Effect of Combining Three Reaction Parameters on Low-Severity Coal Liquefaction

Table 1 summarizes the experiments that were performed with three parameters. The reaction parameters evaluated were reaction time, catalyst loading, hydrogen pressure, and HHA concentration. The different sets of parameters included (1) Set I at 60 min, 1000 ppm of Mo, 1000 psig H₂ charged at ambient temperature and 0.5 wt% donable hydrogen; (2) Set II at 60 min, 500 ppm of Mo, 1000 psig H₂ charged at ambient temperature, and 1.0 wt% donable hydrogen; and (3) Set 3 at 60 min, 1000 ppm, 500 psig H₂ charged at ambient temperature, and 1 wt% donable hydrogen. The possible set of all the parameters being at their high level was not performed because the effect of the amount of H₂ gas charged either at 500 or 1000 psig was small in all the reactions previously performed.

Table 4 presents the Set I data. The reactions were conducted thermally and catalytically at 500 and 1000 ppm of Mo. The coal conversions that were achieved for the three different reaction conditions were very similar. At these reaction conditions, the presence of the Mo naphthenate catalyst had very little effect. However, the presence of hydrogen donor was very influential in promoting coal conversion. The product distributions given on a solvent-free basis were also very similar for all three reaction conditions. Hence, the presence of the hydrogen donor seemed to be the overriding effect.

The effect of HHA concentration at 0.5 wt% and 1.0 wt% of donable hydrogen on coal conversion and product distributions achieved in low severity reactions is presented in Table 5. Comparison of the effect of HHA concentration in the thermal reactions showed that the higher concentration yielded higher coal conversion, 55.0% versus 52.2%. The addition of Mo naphthenate and sulfur to the reaction at a level of 500 ppm Mo resulted in slightly more conversion of coal, 58.8%, than the thermal reaction at 55% with 1.0 wt% donable hydrogen. A larger difference was observed between the two catalytic reactions at the two different hydrogen donor concentration levels: 58.8% coal conversion with 1 wt% donable hydrogen compared to 50.8% conversion at 0.5 wt% donable hydrogen. An increase in the oil product was observed at the 1.0 wt% donable hydrogen level compared to 0.5 wt% for both thermal and catalytic reactions. The lower HHA concentration yielded approximately 25% oil for both thermal and catalytic reactions while the higher HHA concentration produced 33 and 36% oil for thermal and catalytic reactions, respectively.

Set III reaction data are presented in Table 6. All of the reaction parameters were at the high level except for the H₂ pressure which has previously been shown to be ineffective in changing either coal conversion or the oil level in low severity reactions with HHA present. The effect of increasing Mo naphthenate to 1000 ppm of Mo was substantial on both coal conversion and oil produced in the reaction products. Two sets of reactions were performed at these reaction conditions in order to validate the results. Each set consisted of two reactions and each set was performed at different times. The coal conversion achieved with the first set of replicates was 62.9% and with the second set 64.2%. These coal conversions were the highest achieved at any of the low severity reaction conditions. The amount of oil produced on a solvent-free basis, although somewhat variable, $42.5 \pm 0.3\%$ and $47.6 \pm 2.0\%$, was also the highest achieved. Hence, the reaction condition of 500 psi H₂ charged at ambient temperature,

60 min reaction time, 1.0 wt% donable hydrogen, and 1000 ppm Mo naphthenate promoted substantial coal conversion at 350 °C. Each of the reaction parameters at the higher level contributed to the overall coal conversion and oil yield.

Hexahydroanthracene Product Distributions. The product distributions obtained from HHA in the different reactions performed this quarter are presented in Tables 7 and 8. Product distributions achieved from HHA for the reactions performed at two catalyst loadings (data given in Tables 2 and 3) are given in Table 7. The reactions, performed this quarter designated as "new," yielded DHA as the primary product. The thermal reaction produced ~26% DHA while the catalytic reactions produced 34% and 36% DHA for the 500 and 1,000 ppm of Mo, respectively. More ANT was produced in the thermal reaction than in either of the catalytic reactions. The amount of HHA remaining was slightly less with the catalytic reactions than with the thermal reaction. The amount of octahydroanthracene (OHA) produced was equivalent for all three reaction conditions. The product distributions for the previously performed reactions designated as old, gave a high level of ANT and from Table 3 a very low oil content which indicates that the hydrogen charged to the reactors may have leaked out during the reaction.

Hexahydroanthracene product distributions for the reactions combining ternary parameters are given in Table 8. The amount of HHP that remains after reaction always was between 40 and 50%. The primary product produced in each reaction was DHA. Both ANT and OHA were secondary products. In the catalytic reactions less ANT was produced than in the thermal reactions. Likewise, more DHA was produced in the catalytic reactions than in the thermal reactions.

Summary

The low severity reactions using hexahydroanthracene at reaction parameters of 500 psi H₂ charged at ambient temperature, 60 min reaction time, 1.0 wt% donable hydrogen and 1,000 ppm Mo as Mo naphthenate reacted in the presence of excess sulfur gave a coal conversion of more than 62%. Two sets of duplicate reactions were performed at different times, both of which gave consistently high coal conversion and oil yield. Therefore, under the appropriate reaction conditions, hydrogen donation at low severity conditions can be optimized.

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Table 1. Combinations of Ternary Parameters Used This Quarter

Sample	1	2	3
Reaction Time, min	60	60	60
Catalyst Loading, ppm	1000	500	1000
Hydrogen Pressure, psig	1000	1000	500
HHA Concentration, wt% Donable Hydrogen	0.5	1	1

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

New Product Distribution	No Catalyst	Mo Naphthenate	
		500 ppm Mo	1000 ppm Mo
Total Product Distribution in Grams			
Gas	0.145±0.007	0.155±0.007	0.145±0.021
Oil	3.742±0.091	3.515±0.143	3.543±0.051
Asphaltenes	0.140±0.014	0.162±0.035	0.134±0.012
Preasphaltenes	0.714±0.060	0.708±0.040	0.893±0.010
IOM	0.787±0.008	0.779±0.037	0.739±0.002
Coal Conversion, %	49.22±0.52	49.94±2.36	52.92±2.18
Recovery, %	94.32±0.50	91.57±1.71	92.97±0.72
Total Distribution Normalized Weight Percent			
Gas	2.45±0.08	2.65±0.15	2.47±0.36
Oil	69.10±0.16	69.11±0.22	67.62±0.08
Asphaltenes	2.36±0.28	2.78±0.64	2.27±0.21
Preasphaltenes	12.79±0.69	12.12±0.54	15.18±0.19
IOM	13.30±0.33	13.34±0.47	12.46±0.05
Solvent-Free Product Distribution Normalized in Weight Percent			
Gas	5.84±0.18	6.35±0.48	5.83±0.85
Oil	26.23±0.39	26.19±0.74	23.40±0.17
Asphaltenes	5.65±0.65	6.66±1.63	5.39±0.49
Preasphaltenes	30.55±1.68	28.95±0.79	35.93±0.44
IOM	31.73±0.83	31.85±0.58	29.45±0.09
Distribution Prior to Reaction in Weight Percent			
Gas	2.57±0.03	2.59±0.00	2.59±0.01
Oil			
HHA	9.90±0.07	9.97±0.01	9.98±0.01
Hexadecane	55.35±0.45	54.49±0.01	53.98±0.01
Coal	32.18±0.35	32.43±0.01	32.43±0.01
Catalyst		0.52±0.01	1.02±0.01

^aReaction Conditions: 350°C, 500 psi H₂, 60 min, 0.61 g HHA, 0.03 g of elemental S.

Table 3. Effect of Catalyst Loading on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal with Hexahydroanthracene^a

Old Product Distribution	No Catalyst	Mo Naphthenate	
		500 ppm Mo	1000 ppm Mo
Total Product Distribution 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, %	46.10±0.53	50.16±3.06	55.00±2.18
Recovery, %	97.50±0.89	96.79±2.10	92.47±0.32
Total Distribution Normalized 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 Product 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
Coal	32.39±0.08	32.09±0.02	32.36±0.03
Catalyst		0.47±0.01	0.96±0.01

^aReaction Conditions: 350°C, 500 psi H₂, 60 min, 0.61 g HHA, 0.03 g of elemental S.

Table 4. Effect of Catalyst Loading on the Product Distributions of Thermal and Catalytic Reactions of Illinois No. 6 Coal with Hexahydroanthracene Using 1000 psi Hydrogen Pressure^a

Product Distribution	No Catalyst	Mo Naphthenate	
		500 ppm Mo	1000 ppm Mo
Total Product Distribution in Grams			
Gas	0.320±0.007	0.310±0.007	0.305±0.007
Oil	3.404±0.442	3.527±0.013	3.341±0.070
Asphaltenes	0.146±0.050	0.210±0.009	0.142±0.004
Preasphaltenes	0.823±0.020	0.732±0.068	0.887±0.259
IOM	0.708±0.021	0.750±0.025	0.716±0.020
Coal Conversion, %	52.17±1.36	50.78±2.73	53.99±1.33
Recovery, %	90.34±5.95	92.76±0.81	92.97±0.72
Total Distribution Normalized Weight Percent			
Gas	5.20±0.11	5.08±0.06	5.05±0.11
Oil	67.16±0.16	66.66±0.62	66.05±4.02
Asphaltenes	2.36±0.83	3.50±0.11	2.34±0.06
Preasphaltenes	13.58±0.30	12.21±1.00	14.70±4.19
IOM	11.70±0.35	12.53±0.55	11.86±0.34
Solvent-Free Product Distribution Normalized in Weight Percent			
Gas	11.86±0.28	11.52±0.30	11.34±0.05
Oil	25.14±0.04	24.54±2.37	23.92±5.19
Asphaltenes	5.37±1.88	7.94±0.35	5.26±0.01
Preasphaltenes	30.97±0.75	27.67±2.62	32.85±6.71
IOM	26.66±0.81	28.33±0.90	26.63±1.48
Distribution Prior to Reaction in Weight Percent			
Gas	5.12±0.01	5.04±0.02	5.06±0.01
Oil			
HHA	9.21±0.02	9.17±0.01	9.69±0.01
Hexadecane	54.41±0.06	54.10±0.02	52.59±0.03
Coal	31.26±0.03	31.21±0.02	31.64±0.01
Catalyst		0.48±0.01	1.02±0.03

^aReaction Conditions: 350°C, 1000 psi H₂, 60 min, 0.61 g HHA, 0.03 gS, 3.4 g hexadecane.

Table 5. Effect of Hexahydroanthracene Concentration on Thermal and Catalytic Reactions at 1000 psi Hydrogen Pressure^a

Reaction Condition	0.61g of HHA		1.22g of HHA	
Product Distribution	No Catalyst	Mo Naphthenate 500 ppm	No Catalyst	Mo Naphthenate 500 ppm
Total Product Distribution in Grams				
Gas	0.320±0.007	0.310±0.007	0.305±0.007	0.315±0.007
Oil	3.404±0.442	3.527±0.013	3.550±0.076	3.601±0.040
Asphaltenes	0.146±0.050	0.210±0.009	0.145±0.029	0.146±0.043
Preasphaltenes	0.823±0.020	0.732±0.068	1.070±0.142	0.978±0.021
IOM	0.708±0.021	0.750±0.025	0.642±0.008	0.643±0.051
Coal Conversion, %	52.17±1.36	50.78±2.73	55.02±3.26	58.76±3.32
Recovery, %	90.34±5.95	92.76±0.81	95.05±0.48	94.54±0.67
Total Product Distribution Normalized in Weight Percent				
Gas	5.20±0.11	5.08±0.06	5.07±0.01	5.22±0.11
Oil	67.16±0.42	66.66±0.62	64.08±0.98	65.42±0.01
Asphaltenes	2.36±0.83	3.50±0.11	2.42±0.56	2.42±0.72
Preasphaltenes	13.58±0.30	12.21±1.00	17.76±1.94	17.05±0.81
IOM	11.70±0.35	12.53±0.55	10.67±0.39	9.89±0.21
Solvent-Free Product Distribution Normalized in Weight Percent				
Gas	11.86±0.28	11.52±0.30	9.42±0.25	9.67±0.21
Oil	25.14±0.04	24.54±2.37	33.06±0.36	35.96±0.02
Asphaltenes	5.37±1.88	7.94±0.35	4.52±1.11	4.48±1.34
Preasphaltenes	30.97±0.75	27.67±2.62	33.07±1.11	30.02±0.69
IOM	26.66±0.81	28.33±0.90	19.92±1.16	19.87±1.80
Product Distribution Prior in Reaction in Weight Percent				
Gas	5.12±0.01	5.04±0.02	5.05±0.00	5.05±0.00
Oil				
HHA	9.21±0.02	9.17±0.01	19.38±0.02	19.38±0.01
Hexadecane	54.41±0.06	54.10±0.02	43.98±0.02	43.42±0.00
Coal	31.26±0.03	31.21±0.02	31.60±0.04	31.66±0.01
Catalyst		0.48±0.01		0.49±0.01

^aReaction Conditions: 350°C, 1000 psi H₂, 60 min, 0.03 g of elemental S, hexadecane as solvent.

Table 6. Effect of Catalyst Loading on the Product Distributions from Thermal and Catalytic Reactions of Illinois No. 6 Coal with 1% Donable Hydrogen

Product Distribution (weight in grams)	No Catalyst	Mo Naphthenate 1000 ppm	
		First Replicate	Second Replicate
Total Product Distribution in Grams			
Gas	0.155±0.007	0.155±0.007	0.145±0.007
Oil	3.623±0.027	3.538±0.039	3.740±0.074
Asphaltenes	0.259±0.062	0.330±0.007	0.235±0.033
Preasphaltenes	0.857±0.064	0.759±0.053	0.670±0.019
IOM	0.745±0.041	0.577±0.023	0.557±0.055
Coal Conversion, %	52.16±2.77	62.91±1.50	64.17±2.18
Recovery, %	95.78±2.17	91.63±1.22	92.84±1.43
Total Distribution Normalized Weight Percent			
Gas	2.76±0.00	2.64±0.11	2.50±0.08
Oil	64.69±2.76	69.02±0.39	70.75±7.09
Asphaltenes	4.78±1.03	5.62±0.09	4.16±0.68
Preasphaltenes	14.86±1.06	12.91±0.97	12.91±0.40
IOM	12.91±0.66	9.81±0.37	9.68±0.82
Solvent-Free Product Distribution Normalized in Weight Percent			
Gas	5.12±0.01	4.90±0.24	4.62±0.16
Oil	35.37±5.45	42.47±0.30	47.56±1.95
Asphaltenes	8.28±2.01	10.42±0.25	7.72±1.24
Preasphaltenes	27.40±2.09	23.97±1.61	22.33±0.93
IOM	23.83±1.34	18.24±0.82	17.77±1.48
Distribution Prior to Reaction in Weight Percent			
Gas	2.58±0.02	2.60±0.01	2.62±0.16
Oil			
HHA	19.90±0.01	19.87±0.04	19.98±0.08
Hexadecane	45.21±0.09	44.36±0.20	43.74±0.31
Coal	32.31±0.11	32.23±0.24	32.60±0.22
Catalyst		0.94±0.01	1.07±0.01

^aReaction Conditions: 350°C, 500 psi H₂, 60 min, 1.22 g HHA, 0.03 gS, 2.78 g hexadecane.

Table 7. Comparison of the Product Distributions from Hexahydroanthracene Reacted in the Presence of Illinois No. 6 Coal at Two Catalyst Loadings

Data	Catalyst Type	Catalyst Loading (ppm)	Reaction Time (min)	H ₂ Pressure (psi)	Wt of HHA (g)	Product Distribution (wt %)				HYD (%)
						ANT ^a	DHA	HHa	OHA	
New	None	0	60	500	0.61	14.9±2.3	26.1±0.5	48.6±1.7	10.4±0.3	-12.4
New	MoNaph+S ^b	500	60	500	0.61	10.0±1.0	33.6±1.2	46.3±1.0	10.1±1.2	-12.5
New	MoNaph+S	1000	60	500	0.61	8.0±1.3	35.9±1.9	45.3±2.1	10.8±0.9	-12.2
Old	None	0	60	500	0.61	29.1±2.6	17.9±1.7	44.3±1.4	8.7±0.9	-16.3
Old	MoNaph+S	500	60	500	0.61	17.9±0.7	22.6±0.9	50.1±0.3	9.5±0.4	-12.8
Old	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

^a ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene

^b MoNaph+S = molybdenum naphthenate plus sulfur

Table 8. Product Distribution of Hexahydroanthracene at Different Reaction Conditions 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	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
MoNaph+S	1000	60	1000	0.61	5.4±1.4	37.1±0.6	46.3±1.0	11.2±0.6	-11.3
None	0	60	1000	1.22	10.0±1.3	32.4±1.0	42.9±1.3	14.6±1.7	-11.5
MoNaph+S	500	60	1000	1.22	4.0±1.2	40.3±1.8	42.7±1.2	13.0±0.7	-11.4
MoNaph+S	1000	60	500	1.22	5.0±1.2	37.7±1.6	45.5±1.0	11.9±0.5	-11.2

^a ANT = anthracene; DHA = dihydroanthracene; HHA = hexahydroanthracene; OHA = octahydroanthracene

^b MoNaph+S = molybdenum naphthenate plus sulfur

PART II

MILD ACIDIC PRETREATMENT TO ENHANCE LOW SEVERITY LIQUEFACTION PROMOTED BY CYCLIC OLEFINS

Introduction

Cyclic olefins have been shown to be successful as hydrogen donors in low severity liquefaction (Curtis, 1993). Mild acidic pretreatment of the feed coals has also proven effective as a means of increasing reactivity (Shams et al., 1992). A process utilizing both cyclic olefins and this pretreatment should further promote coal solubilization. Investigation of the effect of these two means for improving reactivity of coal in low severity liquefaction is the purpose of this study.

1,4,5,8,9,10-Hexahydroanthracene (HHA) has been the most extensively used hydrogen-donating cyclic olefin in previous low severity studies (Curtis, 1993). In this study, 1,4,5,8-tetrahydronaphthalene, isotetralin (ISO), will be used. By using this alternate hydrogen donor to study how pretreatment increases reactivity, a secondary benefit is achieved. If the ISO proves reactive, it would suggest that the cyclic olefins are reactive because of their inherent reactivity. This finding would increase the likelihood that the success with HHA is caused by the ability of these compounds to release hydrogen at fairly low temperatures (Bedell and Curtis, 1991). Only a basic comparison will be possible. The work of An-Ping Huang (Curtis, 1993) with HHA involves use of catalysts, and the emphasis of this research will be the use of pretreatment to increase reactivity.

It was important this quarter to set some baselines for comparison. To be able to interpret the results of a thermal reaction of ISO with coal, the products of a thermal reaction of ISO, by itself, must be resolved. As seen in Figure 1, the dehydrogenation of ISO yields 1,4-

dihydronaphthalene (1,4-DHN); 1,2-dihydronaphthalene (1,2-DHN); 1,2,3,4-tetrahydronaphthalene (tetralin, TET) and naphthalene (NAP) (Bedell, 1991). Each of these products was individually reacted at conditions of 350 °C and 500 psig H₂ for 30 minutes. Decahydronaphthalene (decalin, DEC), the hydrogen-saturated double ring, was also reacted although it most likely would not be present, since hydrogenation to the saturated species is not favored under these conditions. These reaction conditions were suggested by the success of earlier work of cyclic olefins in low severity liquefaction (Curtis, 1993). These single component reactions also provided a familiarity with the apparatus and methods to be used in the more complex coal reactions. Response factor data with an internal standard, *p*-xylene, also had to be accumulated for the column in the gas chromatograph (GC). These data provide a quantitative method to analyze the products of the reaction by establishing correlations between GC peak area ratios and component weight ratios in the samples.

Experimental

Response factor data for each of the dehydrogenation products of ISO are required to be able to determine the amounts of each compound present in a product sample using peaks from a GC output. A response factor is the linear correlation between the ratio of peak area of a specific component to the peak area of a standard and the ratio of weight of the component to the weight of the standard. By injecting known weights of both sample and standard through the column, a linear relationship between weight ratio and area ratio can be plotted. A Varian 3700 GC containing a Durabond 5 wide bore column, a septumless injector and flame ionization detector was used in the GC analyses. Six solutions in hexadecane (99% purity from Aldrich)

of compositions between 0.25 and 2% of ISO (97% purity, recrystallized by M.W. Bedell), TET (99% purity from Aldrich), NAP (99+ % purity from Aldrich) and DEC (99+ % purity from Aldrich). Each of these had ~2% *p*-xylene as an internal standard. A response factor graph for each component was then made. The results of these experiments were checked by using a known sample where the weight of the components found using the response factor charts were compared with the actual weights. This quarter, 1,4-DHN and 1,2-DHN were not available. It is planned to make response factor plots for these compounds before work with coal begins.

The next step was observing the behavior of ISO and each of its possible dehydrogenation products under the reaction conditions. Solutions of 2% ISO, TET, NAP and DEC were each placed in ~20 ml stainless steel tubing bombs, charged with 500 psig H₂ and reacted at 350 °C for 30 minutes. Again, the 1,2-DHN and 1,4-DHN were not available at the time these reactions were run. The internal standard was added to the product recovered which in turn was subjected to a GC analysis. This information should provide a basis for understanding the thermal activity of each compound with a special interest in the results for ISO, since it will be used as a hydrogen donor in the coal reactions.

Results and Discussion

A large portion of time this quarter was spent in familiarization of methods used and ensuring that once reactions with coal were begun, analysis of the products would be timely and accurate. The overall process, from pretreatment to reaction to recovery to analysis, is rather arduous. By taking the necessary time to practice each step and perfect each method, time will be better spent later in the actual research.

Good response factor data was formulated for each of the components, but there was some difficulty experienced. Initially, there was a difficulty with reproducibility of data points. Because of this difficulty, a linear relationship between peak area ratios and weight ratios was almost impossible. This problem may have been partially caused by residue on the column that could be seen in the GC output. After attempting and failing to clean the column, it was decided that the best course of action was to purchase a new column. The new column worked much better. The placement of data points for each of the components in six different solutions was much tighter and much more linear (Figure 2). The difference between the actual weights of the components of the known sample and the weights found using the response factor graphs was around 5%. In Table 1, average values for three GC analyses of two known unknowns are listed. These graphs may have to be improved because of the lower concentrations of the dehydrogenation components in the reaction products compared to the concentrations used in the response factor samples. Altering the temperature program can also cause changes. Developing new response factor plots should not be difficult due to familiarity with the procedure.

Observation of the activity of ISO and the dehydrogenation products at the reaction conditions was done in order to understand the origins of the reaction products once coal is introduced into the system. This process also provided an opportunity for familiarization with reactions involving the stainless steel tubing bomb reactors. In order to maintain a seal at 350 °C and 500 psig cold pressure, care must be taken to prevent any damage to the stainless steel surfaces that cold weld to form the seal. The same phenomenon must be halted to prevent the threads on the cap from cold welding to the bomb. Only through experience were these problems solved.

There was no change after the reaction to TET, NAP, and DEC. Because of the stability of these compounds, no hydrogen atoms were lost. The ISO provided different results. ISO produced 1,2-DHN, 1,4-DHN, TET, and NAP. The peaks for these four dehydrogenation products were easily identified, but there were also four currently unidentifiable peaks in the GC output that have yet to be identified. A new problem also arose with the GC. With the current temperature program, the peaks for TET and 1,2-DHN were very close together. In order to ensure resolution of each of the peaks, the temperature program had to be changed. This could cause problems with the current response factor graphs. If so, these will have to be plotted again.

Summary

The best experimental results come from good preparation. It is much better to learn the process by concentrating on each individual step. An understanding of the best method for pretreatment and the reaction process will be followed by understanding of the best method for recovery of the solubilized coal and analysis of the coal liquids and spent ISO. An effective, repeatable routine for each of these steps must be developed to achieve good reproducibility.

The gas chromatograph is an important instrument in the analysis of the products, but it must be used properly. Again, use of the equipment leads to understanding and ease of operation. The response factor data provide a good quantitative method for interpreting GC output.

Early next quarter, a familiarity will be developed with reactions involving coal. Reproducibility and good recovery of products can be learned using inexpensive coals. Once

a routine has been established from start to finish, then reactions may be run using coals from the Argonne Premium Sample Bank. By this point, the procedure should go smoothly and quickly.

Comparison will then be made of the conversion of lower rank coals, subbituminous [Wyodak] and lignite [Beulah-Zap], when treated and untreated. Other parameters may be changed also. Different coals and different reaction conditions provide the most obvious options, but a special emphasis will be placed on finding new acids. The constant goal being the improved reactivity on low severity liquefaction and the increased feasibility of the process.

References

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

Figure 1: Dehydrogenation of Isotetralin

Figure 2: Response Factor Data for Isotetralin and Its Dehydrogenation Products.

Table 1: Response Factor Verification						
Component	Known Sample #1			Known Sample #2		
	Actual Weight (g)	Weight from RF Plot ^a (g)	% Error	Actual Weight (g)	Weight from RF Plot (g)	% Error
Isotetralin	0.1825	0.1831	+0.3	0.1467	0.1472	+0.3
Naphthalene	0.1380	0.1425	+3.2	0.1481	0.1518	+2.5
Tetralin	0.1311	0.1303	-0.6	0.0609	0.0594	-2.5
Decalin	0.0369	0.0391	+6.0	0.0593	0.0612	+3.2

^a RF = response factor

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