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

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Introduction

The overall objective of this project is to evaluate the role of the resid in co-processing. The primary purpose of the initial work was to establish under thermal and catalytic reaction conditions whether hydrogen transfer occurred between cycloalkane type structures that are present in resids and aromatics that are present in coal and liquefied coal. The goal of the research this quarter was to evaluate the reactivity of an anthracene (ANT) and perhydropyrene (PHP) system to determine if this system was the one desired for the parametric evaluation. ANT, an aromatic, was chosen to represent a hydrogen acceptor molecule, while PHP was chosen to represent cycloalkanes, a hydrogen-rich molecule.

The idea being explored was to determine if hydrogen could be transferred from the cycloalkane to the aromatic in a hydrogen atmosphere. The reason that the hydrogen atmosphere is important is because a hydrogen atmosphere is always present in coprocessing. In order to determine if the reactions probably occur during coprocessing, the conditions need to stimulate those of co-processing as much as possible. Hence, catalytic as well as thermal reactions need to be performed because it is most likely that co-processing will be performed under catalytic conditions.

The experiments performed this quarter were preliminary in nature. This quarter's work established a procedure for performing thermal and catalytic reactions without using a solvent. The procedure for analysis of the reaction products was also established. The individual thermal and catalytic reactions using ANT and PHP were the primary reactions performed this quarter.

Initial Reactions

The reaction system chosen for the initial reactions used PHP as the hydrogen-rich cycloalkane and ANT as the hydrogen-deficient aromatic species. These reactions were performed without a solvent in order to eliminate any interference that might occur from the solvent such as possible hydrogen transfer activity under thermal and catalytic conditions. A substantial change in the experimental procedures and handling of reaction products was encountered. New experimental techniques and a development of reproducibility in using these technique had to be established.

Reactions were performed in ~20 cm^3 stainless steel tubular microreactors at reaction temperatures of 380 and 440°C. Thermal reactions and catalytic reactions using Mo naphthenate as the catalyst were performed. In order to analyze the products by gas chromatography, gas chromatographic response factors were established for PHP and ANT using biphenyl as the internal standard. A Varian Model 3300 gas chromatograph with a flame ionization detector was used. Temperature programming of an initial column temperature of 60°C and a final temperature of 320°C and a program rate of 2.5°C/min were used to enhance the resolution of the products.

Thermal baseline experiments using ANT and PHP were performed first as shown in Tables 1 and 2. These initial experiments showed some difficulty in recovery as well as some unidentified peaks. The amount of the unidentified peaks in the PHP system was not large and could have been the result of cracking at these high reaction temperatures.

Substantial reactivity of ANT was observed at 440°C which was more than had been observed previously in our laboratory (Wang, 1992) but was in accordance with the results

Table 1. Preliminary Thermal Reactions of Anthracene at 440°C

Product Distribution (wt %)						Recovery (%)
ANT[a]	DHA	OHA	THA	OHA	Others[b]	
2.80	28.46	12.28	46.29	7.80	2.38	85.42
2.01	16.31	18.44	47.42	11.88	4.01	77.29
5.16	36.70	10.09	40.18	5.72	2.20	75.82

[a] ANT = anthracene; DHA = dihydroanthracene; OHA = octahydroanthracene; THA - tetrahydroanthracene

[b] Others are unidentified GC peaks.

Table 2. Preliminary Thermal Reactions of Perhydropyrene at 440°C

Product Distribution (wt %)			Recovery (%)
PHP[a]	PYR	Others[b]	
94.1	3.5	2.4	64.4
92.7	3.7	3.6	63.3
94.3	1.9	3.8	61.5
96.0	1.5	2.5	70.0

[a] PHP = perhydropyrene; PYR = pyrene

[b] Others are unidentified GC peaks.

presented in the literature (Song et al., 1988). The products, though, also showed some suspect peaks that were later shown not be part of the products obtained from the thermal hydrogenation of ANT. Experimental recovery for both ANT and PHP, but particularly for PHP, was low and further technique development to needed and planned for next quarter.

The initial catalytic reactions were performed at an extremely high concentration of active metal per gram of feed for a slurry-phase catalyst system. The reactions were performed at 380 and 440°C in ~20 cm^3 stainless steel tubular microreactors. The results are presented in Tables 3 and 4. The amount of ANT and PHP charged was 0.1 g but the catalyst charged at 500 and 1000 ppm of active metal was based on having 4 g of solvent present which was not actually present in the reaction. This amount of catalyst was chosen because it was equivalent to that of some successful experimenters in our group. The catalyst used was Mo naphthenate with excess sulfur present. The sulfur was added at a stoichiometric 3:1 ratio of S:Mo, presuming that the end product from the slurry-phase catalyst precursor was MoS_2.

The products produced from ANT yielded a substantial number of products at both 380 and 440°C. Some of the products were the expected hydrogenation products from ANT including dihydroanthracene (DHA), tetrahydroanthracene (THA), and octahydroanthracene (OHA). Many other products were obtained which were presumably cracked products because of the high concentration of catalysts. One of the peaks was an impurity that was present in the system. The total recovery was quite low which led to a wide variability in the results.

Table 3. Catalytic Reactions of Anthracene at 380°C with High Catalyst Loading

Catalyst Loading (g)	Catalyst Level[a] (ppm)	Product Distribution (wt %)										Recovery (%)
		ANT[b]	DHA	OHA	THA	A[c]	B	Un-known	OHA	OHA	Other[d]	
Catalysts Concentration = 500 ppm[a]												
0.0338	508	0.43	0.83	28.97	16.29	5.43	6.07	2.91	24.54	8.37	6.26	59.57
0.0370	550	2.17	1.23	34.40	21.36	1.83	3.01	0.19	24.77	8.78	1.57	71.03
0.0463	694	0.00	0.82	32.83	16.51	3.71	5.73	2.19	25.43	8.59	4.21	61.46
0.0421	631	0.00	0.40	30.87	19.00	3.83	6.44	2.81	23.46	8.10	5.12	59.69
0.0368	552	1.50	22.26	26.20	20.07	1.45	1.69	0.73	16.20	7.25	2.96	84.58
0.0361	541	0.79	6.11	34.71	11.68	2.02	3.03	1.44	22.49	8.65	9.08	68.58
Catalyst Concentration = 1000 ppm[a]												
0.0609	914	1.00	0.00	22.25	3.22	12.33	16.62	5.63	14.21	6.17	17.96	66.37
0.0675	1012	0.00	0.00	27.43	16.67	4.27	4.98	2.65	22.35	7.74	12.82	21.95
0.0707	1060	0.00	0.00	25.84	17.72	6.94	11.17	4.05	20.61	7.32	6.36	49.58
0.0751	1126	0.00	0.00	31.82	16.07	4.87	7.79	2.92	24.34	8.28	3.89	19.28
0.0762	1143	0.00	4.64	32.09	3.07	4.60	6.77	2.30	24.16	8.05	14.32	78.01
0.0662	993	1.73	6.59	34.32	12.14	2.51	3.14	1.26	23.45	9.63	5.12	68.07

[a] Catalyst level is based on 4 g of imaginary solvent.

[b] ANT = anthracene; DHA = dihydroanthracene; OHA = octahydroanthracene; THA = tetrahydroanthracene

[c] Identified as an impurity

[d] Others are unidentified GC peaks.

Table 4. Catalytic Reactions of Anthracene at 440°C With Low and High Catalyst Loading

Catalyst Loading (g)	Catalyst Level (ppm)	Product Distribution (wt %)										Recovery (%)
		ANT[c]	DHA	OHA	THA	A[d]	THA	Un-known	OHA	OHA	Others[e]	
0.0364	546[a]	0.71	0.47	29.25	29.72	2.12	3.30	6.13	16.75	7.78	3.77	41.61
0.0329	493[a]	1.22	2.44	35.24	37.56	0.00	0.61	2.32	13.90	6.22	0.49	81.92
0.0335	502[a]	0.83	16.67	21.94	25.56	1.94	2.50	6.67	12.78	6.11	5.00	34.32
0.0412	618[a]	0.97	0.48	26.32	34.70	1.95	2.53	6.63	14.62	6.82	4.68	49.66
0.0646	969[a]	4.04	0.00	24.94	27.79	3.80	5.23	8.55	14.49	7.36	3.80	42.78
0.0658	987[a]	11.69	0.00	23.38	26.46	2.77	4.62	7.38	13.85	6.46	3.38	31.93
mean				24.16	27.12							
0.0018	505[b]	2.38	31.00	14.78	39.57				6.26	3.38	2.63	73.12
0.0017	498[b]	2.94	35.99	12.00	40.76				4.59	2.63	1.10	79.86
0.0036	1008[b]	2.94	33.30	13.74	38.12				5.48	3.05	3.38	82.87
0.0033	986[b]	3.95	38.39	12.37	36.38				4.89	2.88	1.15	66.88

[a] Based on 4 g of imaginary solvent.
[b] Based on grams of reactant introduced.
[c] ANT = anthracene; DHA = dihydroanthracene; OHA = octahydroanthracene; THA = tetrahydroanthracene
[d] A identified as an impurity
[e] Others - unidentified GC peaks.

Catalytic Reactions with Lower Catalyst Contents

A second set of reactions were performed in which the catalyst content was lowered to 500 to 1000 ppm of active metal based on the reactants charged. This level of catalyst addition was much more realistic. The results from reactions performed at the lower catalyst level at 440°C are given in Table 4. The recovery from these reactions was much higher and more consistent than the higher catalyst loading levels also given in Table 4. The number of products produced was also less which supports the hypothesis that at least some of the peaks from the high catalyst loading experiments were caused by of the cracking of ANT caused by the high catalyst loading.

Catalytic Reactions of Perhydropyrene at High Catalyst Loading

Catalytic reactions of PHP were performed at high catalyst loading levels as shown in Table 5. These reactions were performed at both 380 and 440°C. At the high catalyst loading level substantial conversion of PHP occurred which resulted in the production of several different products including pyrene (PYR) and several unidentified peaks present in small amounts. These reactions will be performed again at lower catalyst loadings.

Future Work

The preliminary results obtained this quarter indicated that anthracene may not be a sensitive hydrogen acceptor in a hydrogen atmosphere. Anthracene may be too reactive in the presence of hydrogen to give a good indication of the amount of hydrogen donated from a cycloalkane such as perhydropyrene. However, anthracene will be tested further next quarter using new reactors which have not been contaminated by metals from high catalyst loadings; anthracene will be tested at lower catalyst

Table 5. Catalytic Reactions of Perhydropyrene at 380 and 440°C at High Catalyst Loadings

Catalyst Loading (g)	Catalyst Level[a] (ppm)	Reaction Temperature (°C)	Product Distribution (wt %)			Recovery (%)
			PHP[b]	PYR	Others[c]	
0.0694	1041	380	86.79	10.65	2.57	99.3
0.0596	894	380	89.23	8.98	1.80	107.6
0.0326	489	380	86.89	4.93	8.19	106.2
0.0390	585	380	85.50	8.08	6.42	112.2
0.0820	1230	440	79.35	16.30	4.36	65. 6
0.0750	1125	440	78.97	18.94	2.09	73.2
0.0382	575	440	85.73	12.64	1.62	64. 8
0.0353	529	440	85.55	12.18	2.27	64.5

[a] Based on 4 g of imaginary solvent.
[b] PHP = perhydropyrene; PYR = pyrene
[c] Others - unidentified GC peaks.

levels. Other possible hydrogen acceptor such as phenanthrene, dihydroanthracene and benzophenone will be evaluated as well.

References

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