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PRECONVERSION PROCESSING OF BITUMINOUS COALS
- NEW DIRECTIONS TO IMPROVED DIRECT CATALYTIC COAL LIQUEFACTION-
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Introduction

This project is focussed on the effective preconversion and liquefaction of coal. One of the main goals of this project was to reduce hydrogen consumption by decreasing the gas yield and increasing the oil yield based on a new structural model of coal. This new model proposes that significant portions of coal molecules are physically associated¹ in contrast with the widely accepted conventional model that projects coal as three-dimensionally cross-linked macromolecules. A physically associated model of coal has gained credibility from recent tasks conducted by this investigator²⁻⁵. Two factors were critically evaluated during these tasks: (1) maximizing dissolution of associated coal and (2) different reactivity of fractions with different molecular weight.

A summary of the results obtained from previous tasks showed:

- (1) High-temperature soaking at ~ 350°C in a coal liquid (recycle oil) was one method for effective dissolution not requiring additional chemicals and/or hydrogen.
- (2) Two-step soaking at 350°C and 400°C was more effective for maximum dissolution.
- (3) The addition of a relatively small amount of hydrogen peroxide during soaking slightly enhanced preconversion.
- (4) Separation of dissolved coal into light and heavy fractions, followed by liquefaction of the heavy fraction, was effective as a means to improve product selectivity.
- (5) Vacuum distillation was projected for the simple separation method.
- (6) Cyclohexane extraction was used instead of vacuum distillation since cyclohexane solubles closely resemble the distillable oil fraction.
- (7) Tests of the suggested procedure inferred a 30% increase in the oil yield and a 15-20% decrease in the gas yield.
- (8) The effectiveness of the suggested procedure was confirmed from coal/oil ratios (g/ml) of 1/10 - 1/2.
- (9) Batchwise vacuum distillation was tested, but was not successful due to inherent problem in resolubilizing pitch samples in coal liquid. A test by a continuous

operation is highly recommended.

Based on the above results, second stage liquefaction was initiated during the previous quarter. The effect of hydrogen pressure on second stage liquefaction was more pronounced for high-temperature soaking (350°C). Two-step soaking at high temperatures enhanced overall conversion; however, the conversion was not as high as expected. In the previous experiment, the reactor was cooled to room temperature after first stage liquefaction, then repressurized with hydrogen to the pressure desired for second stage liquefaction. The reactor was then reheated to the desired second stage liquefaction temperature. It was thought that the uniformity of the mixture could change after first stage liquefaction if the mixture was cooled, which would significantly affect conversion at the second stage. Therefore, second stage liquefaction was carried out continuously *without cooling* after first stage liquefaction. Catalysts and hydrogen were added before soaking and coal was continuously liquefied. Although radical initiators showed a positive effect on preconversion during high-temperature soaking, they showed a slightly negative effect at > 430°C. Therefore, radical initiators were not used because of the apparent complexity of the reaction.

Experimental

Illinois No. 6 coal was obtained from the DOE Coal Bank at Pennsylvania State University, with an elemental analysis (wt%, daf) of C 78.1, H 5.4, N 1.3, S 5.4. A coal liquid derived from the Illinois No. 6 coal obtained from the Wilsonville pilot plant⁶ was also used. Reagents and solvents were procured from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA) and HPLC-grade solvents were employed without further purification. Two catalysts were used including MoS₂ (Aldrich Chemical Co.) and AKZO AO-60 (obtained from Hydrocarbon Research Inc., Lawrenceville, NJ). The analysis of AKZO AO-60 is shown in *Table 1*.

A 250 ml autoclave (Model 4576; Parr Instrument CO., Moline, IL) was obtained for this work. For each experiment, the reactor was evacuated and purged with nitrogen five times after charging a coal sample and a solvent. The autoclave was heated at approximately 8°C min⁻¹ to the required temperature, then controlled to ± 3°C while

Table 2 Run numbers and experimental conditions for second stage liquefaction studies

Run No.	Condition											
	Coal (g)	Coal Liq. (ml)	Soaking		First Stage		Second Stage		Atmosphere ^a	Catalyst		
			Temp. Time (°C) (h)	Temp. Time (°C) (h)	Temp. Time (°C) (h)	Temp. Time (°C) (h)						
111	10	30	200	1	430	1	410	1	400	-	MoS ₂	200 ^b
112	10	30	350	1	430	1	410	1	400	-	MoS ₂	100
113	10	30	350	1	430	1	410	1	800	-	MoS ₂	200
114	10	30	350	1	430	1	420	1	400	-	MoS ₂	200
115	10	30	350	1	430	1	420	1	800	-	MoS ₂	200
116	10	30	350	1	430	1	420	1	1200	-	MoS ₂	200
117	10	30	350/400	0.5/0.5	430	1	420	1	400	-	MoS ₂	200
118	10	30	350	1	430	1	420	1	400	-	AKZO	200 ^c
119	30	90	350/400	1/1	-	-	-	-	-	100	-	-
120	CyI ^d /10	30	-	-	430	1	410	1	800	100	MoS ₂	200
121	10	30	200	1	430	2	410	1	800	100	MoS ₂	200
122	10	30	350/400	1/1	430	1	410	1	800	100	MoS ₂	200
123	-	30	350/400	1/1	430	1	410	1	800	100	MoS ₂	200
124	10	30	350/400	1/1	430	1	400	1	800	100	MoS ₂	200
125	10	30	350/400	1/1	430	1	410	1	800	100	AKZO	200
126	10	30	350/400	1/1	430	1	400	1	800	100	AKZO	200
129	CyI ^d /10	30	-	-	430	1	400	1	800	100	AKZO	200

^a@25°C

^b~ 3,500 ppm as Mo in the mixture

^c~ 600 ppm as Mo in the mixture

^dCyI: Cyclohexane insolubles

Results and Discussion

Effects of Hydrogen Pressure and Temperature at the Second Stage

A catalyst (200 mg), MoS₂ or AKZO AO-60, was used. The MoS₂ catalyst represented 3,500 ppm as the Mo base in the coal/coal liquid mixture while the AKZO catalyst represented 600 ppm as the Mo base in the mixture. Coal to coal liquid ratio was 1/3 (wt/vol), and residence time was 1 h for each step. For Run 117, the coal was soaked at 350 and 400°C for 0.5 h, respectively; therefore, the residence time remained constant (3 h) between these Runs. Hydrogen pressure was changed between 400 and 1200 psi (pressure: @25°C) at 420°C of the second stage temperature for Runs 114-116. As shown in Figure 1, incremental increases in the oil (CyS) and total (TS) yields paralleled this increase in hydrogen pressure. The same effects were obtained at 410°C of the second stage temperature (Runs 112 and 113) as a response to pressure differences. No significant effects of temperature, however, were evident between 410 and 420°C under these conditions. Effects related to high-temperature soaking were compared under 400 psi of hydrogen pressure (Runs 111, 112, and 117). The TS yield held steady or increased, but the CyS yield decreased as a function of soaking temperature. Therefore, the effect of high-temperature soaking at 350 and 400°C was small or slightly negative under 400 psi of hydrogen. This hydrogen pressure is presumably too low for second stage liquefaction.

Product Selectivity

Based on the previous results, 800 psi of hydrogen pressure and 410°C of second stage temperature were used for the study of product selectivity (Runs 120-122). As previously indicated in Table 2 for Run 121, the DECS-2 coal was soaked at 200°C, then liquefied at 430 and 410°C. The coal for Run 122 was soaked at 350 and 400° for 1 h each, then liquefied at 430 and 410°C for 1 h. (Total residence time was adjusted to 4 h for Runs 121-126). As shown in Figure 2, the gas yield between these Runs decreased ~ 5% while the CyS and total (TS) yields increased ~ 10%. The difference, therefore, can be considered a function of two-step high-temperature soaking. For Run 120, the mixture was extracted with cyclohexane after high-temperature soaking and the recovered cyclohexane insolubles (CyI) fraction was liquefied under the same condition. The gas yield (~ 1%) was

remarkably low. The total yield increased 2%, but an increase in the CyS yield was remarkable compared to Run 122. The oil (CyS) yield increased > 20% over Run 121 (the base condition). For Run 124, the coal was liquefied in a continuous operation mode as with Run 122, but at 400°C of the second stage temperature. Although CyI was not separated after high-temperature soaking, the gas yield was very low (< 2%), and the CyS yield was > 65%. From a comparison of the results from Runs 122 and 124, the optimum temperature of the second stage may be ~ 400°C. Therefore, milder conditions of the second stage are attainable by two-step high-temperature soaking which leads to low gas and high oil yields. If soaked coal is separated into light and heavy fractions with only the heavy fraction liquefied, much better product selectivity is attainable. The detailed gas composition and the approximate mass balance at each step are currently under investigation.

Effect of Catalyst

Although this project does not encompass develop of the optimum catalyst for coal conversion, the AKZO AO-60 catalyst was suggested by the DOE project manager. For Run 118 this catalyst was used under the same conditions used for Run 114. Hydrogen pressure effects were not seen under 400 psi for Run 114 (MoS₂), but were noted using the AKZO AO-60. As shown in *Figure 1*, the CyS yield increased ~ 10%. For Runs 125, 126, and 129, this catalyst was examined under 800 psi of hydrogen. The conditions for Run 125 were the same as those for Run 122. The gas yield decreased ~ 5% while the CyS yield increased ~ 5%. The temperature of the second stage was further lowered to 400°C. The catalyst effect was again significant at 400°C of the second stage (compare Runs 124 and 126) while the gas yield was the same as that for Run 120. Therefore, the effect of this catalyst is remarkable, particularly under mild conditions.

Figure 1 The product yields from second stage liquefaction (No.1) (Conditions are listed in *Table 2*, Key: CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

Figure 2 The product yield from second stage liquefaction (No.2) (Conditions are listed in *Table 2*, Key; CyS: cyclohexane solubles, ToS: toluene solubles, TS: tetrahydrofuran solubles, TI: tetrahydrofuran insolubles)

Characteristics of Products

The coal liquid and the CyS (oil) fraction converted from the coal cannot be separated because of the similar physico-chemical nature of these fractions. To obtain the oil fraction, it is necessary to replace the original coal liquid with the oil fraction produced from coal in a continuous operation mode. If it is assumed that all coal liquids are recovered in the CyS fraction, the weight % of the CyS fractions for Runs 120-122 ranges from 11 to 14%. Therefore, the detailed characterization of the CyS (oil) fraction is not required. In this work, elements of fractions from Runs 120-122 were analyzed for information only.

Run 121 was soaked at 200°C, followed by liquefaction. This can be regarded as the base operation. Run 122 was soaked at 350 and 400°C, followed by liquefaction. Run 120 was also conducted following the proposed procedure. Elemental analyses are shown in *Table 3*. The products (CyS, ToS•CyI, and TS•ToI) from Run 120 are less aliphatic than those from Run 121, as seen from H/C ratios in these fractions. Heteroatom contents in the fractions from Run 120 are approximately the same as those in fractions from Run 121, or slightly lower. Therefore, properties of products from the proposed procedure may be better than projected.

References

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Table 3 Elemental analyses of products from liquefied DECS-2 coal

Sample	Element (daf wt%)					H/C atom atom	Ash (wt%)
	C	H	N	S	O (dif.)		
IL Coal Liq.	88.4	11.4	0.2	neg.	neg.	1.55	-
Run-121 ^a CyS ^b	87.2	9.1	0.3	0.1	3.4	1.25	-
Run-122 CyS	87.1	9.4	0.3	0.1	3.2	1.30	-
Run-120 CyS	87.8	9.7	0.3	neg.	2.1	1.33	-
Run-121 ToS•CyI	87.4	5.2	2.1	0.4	4.9	0.71	-
Run-122 ToS•CyI	81.6	5.4	2.2	0.5	0.3	0.79	-
Run-120 ToS•CyI	90.8	5.6	2.7	0.4	0.5	0.74	-
Run-121 TS•ToI	88.6	5.0	2.2	0.5	3.7	0.68	-
Run-122 TS•ToI	87.3	5.1	2.2	0.5	4.9	0.70	-
Run-120 TS•ToI	90.2	5.2	2.3	0.4	2.0	0.69	-
Run-121 TI	81.8	3.5	1.6	14.5	neg.	0.51	57.2
Run-122 TI	66.9	3.0	1.5	17.9	10.7	0.54	59.8
Run-120 TI	83.1	3.6	1.7	10.3	1.3	0.52	52.2
DECS-16 CyI	87.3	5.5	1.9	5.0	0.3	0.76	25.4

^aConditions:

Run-121: 200/430/410°C (1/2/1 h)

Run-122: 350/400/430/410°C (1/1/1/1 h)

Run-120: 350/400 → 430/410°C (1/1 → 1/1 h)

CyI

^bKey:

CyS; Cyclohexane solubles

ToS•CyI; Toluene soluble/cyclohexane insolubles

TS•ToI; Tetrahydrofuran soluble/toluene insolubles

TI; Tetrahydrofuran insolubles

CyI; Cyclohexane insolubles

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