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

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Introduction

Coal structure should be well understood for the effective development of liquefaction. A cross-linked three-dimensional macromolecular model has been widely accepted for the structure of coal. Current coal liquefaction technology are being developed based on this model. Recent studies, however, showed that significant portions (far more than generally believed) of coal molecules are physically associated¹. Therefore, care should be taken for the development.

One of the main goals in coal liquefaction is to decrease a gas yield in order to save the hydrogen consumption. Hydrogen is primarily lost with produced gas such as methane and ethane. It is expected that reactivity of dissolved coal is higher than that of undissolved coal. Higher reactivity will lead to lower severity in liquefaction, and this will result in decrease in a gas yield. High-temperature soaking in a coal liquid (recycle oil) produced from the same coal will be one method for effective dissolution in which any chemicals and hydrogen are not used.

Another important factor to decrease a gas yield is suggested on the basis of the associated molecular nature of coal. Hydrocarbons with lower molecular weight generally produce more gas by thermal pyrolysis compared to those with higher molecular weight. Severe conditions would be required for liquefaction of fractions with higher molecular weight. The associated structural model of coal can be regarded as material with a wide molecular weight distribution. Therefore, fractions with different molecular weight should be liquefied separately, if possible.

Based on these propositions, two issues were studied in the previous quarter: (1) maximizing dissolution of associated coal by high-temperature soaking and (2) step-wise conversion of associated coal with a wide molecular weight distribution. From the test results under various conditions, an improved liquefaction procedure was suggested. Tests for the suggested procedure showed 30% enhancement in oil and 15-20% reduction in gas yields. It is expected that the proposed procedure will lead to great cost down in coal liquefaction.

The proposed procedure was tested with an autoclave and microreactors. Low coal to liquid ratios were generally employed. For fractionation of coal after dissolution by

high-temperature soaking, cyclohexane extraction was used in stead of vacuum distillation. It was necessary to test under more realistic conditons to assess the proposed procedure. In this quarter, the proposed procedure was tested at high coal to liquid ratios in addition to vaccum distillation. The task for the second stage liquefaction was begun. Some of the results are also shown in this report.

Experimental

Illinois No. 6 coal was obtained from the DOE Coal Bank at Pennsylvania State University. A coal liquid derived from the Illinois No. 6 coal obtained from the Wilsonville pilot plant² was used. Their elemental analyses are shown in *Table 1*. All the reagents and solvents were obtained from Aldrich Chemical Co. (Milwaukee, WI) and Fisher Scientific (Pittsburgh, PA), and HPLC-grade solvents were used without further purification.

Two reactors, a 250 ml autoclave (Model 4576; Parr Instrument CO., Moline, IL) and 27 ml microreactors fabricated³, were used. For experiment, these reactors were evacuated and purged with nitrogen five times after charging a coal sample and a solvent. The autoclave was heated approximately at $8^{\circ}\text{C min}^{-1}$ to required temperature, and controlled to $\pm 3^{\circ}\text{C}$, while agitating with the autoclave stirrer (500 rev min^{-1}). Microreactors were heated in a fluidized sand bath (Model SBL-2; Techne Corp.,

Table 1 Elemental analyses of coal and a coal liquid used (wt%)

Symbol	Sample	H ₂ O	Ash	Element (daf)			
				C	H	N	S
DECS-2	Illinois no. 6 (hvb)	10.4	14.5	78.1	5.4	1.3	5.4
--	coal liquid	--	--	88.4	11.4	0.2	1.1

Princeton, NJ) which was controlled within $\pm 1.0^{\circ}\text{C}$ of the set point. The shaker (Model 75; the Burrell Corp., Pittsburgh, PA) was modified to shake the microreactor horizontally at 320 rev min^{-1} . Mixtures in the reactor attained the set point within 5 min, when the reactor was being immersed into the sand bath. Conditions for all runs are summarized in *Table 2*.

After reactions, the mixtures were filtered and Soxhlet-extracted with cyclohexane, toluene and tetrahydrofuran (THF) for 24 h, respectively, and then these samples were dried under vacuum at 95°C overnight. The amounts of THF solubles (TS), toluene solubles (ToS) and cyclohexane solubles (CyS) were determined from weights of the respective insolubles.

Table 2 Run numbers and experimental conditions

Run No.	Condition					
	Coal (g)	Temp. °C	Time h	Solvent (ml)	Atmosphere (MPa)	Cat. (mg)
90	15	350/400	1/1	45	N ₂ (0.7)	-
91	25	"	"	50	"	-
101	30	"	"	90	"	-
92	15	200/430	"	30	H ₂ (2.8)	MoS ₂ (100)
93	"	350/430	"	"	"	"
94	"	350/400/430	0.5/0.5/1	"	"	"
95	10 (CyI) ^a	430	1	20	"	MoS ₂ (60)
97 ^b	15	350/400/430	1/1/1	30	N ₂ /H ₂ ^c (0.7/2.8)	MoS ₂ ^c (100)
100	10	200/430 → 410 ^d	1/2 → 1	30	H ₂ → H ₂ (2.8 → 4.2)	MoS ₂ (200)
106	"	200/430 → 410 ^d	1/2 → 1	30	H ₂ → H ₂ (2.8 → 5.6)	MoS ₂ (200)
104	"	350/400/430 → 410 ^d	1/1/1 → 1	30	H ₂ → H ₂ (2.8 → 4.2)	MoS ₂ (200)
107	"	350/430 → 410 ^d	1/1 → 1	30	H ₂ → H ₂ (2.8 → 5.6)	MoS ₂ (200)
102	"	430 → 410 ^d	1 → 1 (2.8 → 4.2)	30 (200)	H ₂ → H ₂	MoS ₂

^aCyI: Cyclohexane insolubles^bThree runs were conducted under the same conditions (Runs 97-(1) to 97-(3)).^cHydrogen and MoS₂ were used only at 430°C.^dThe reactor was cooled down after reaction at 430°C.

Results and Discussion

Test at High Coal to Liquid Ratio (C/L)

A low weight ratio of coal to liquid ($C/L=1/10$) was used in the previous work. Since a high C/L value (generally $1/2$ to $1/3$) has been used in the conventional processes, the effect of the high C/L value on high temperature soaking and liquefaction was examined in this term. Two-step wise high-temperature soaking at 350°C and 400°C was carried out at the values of $C/L=1/2$ and $1/3$ (Runs 90, 91, and 101). The yields of cyclohexane solubles (CyS) were 40-60 wt%. The reproducibility was not good, because of difficulty with handling of highly sticky material. Since the CyS was average 50% under the condition of $C/L=1/10$, two-step wise high-temperature soaking was also effective to dissolve coal under the conditions of $C/L=1/2$ and $1/3$.

The effect of high C/L on liquefaction was next evaluated. For Runs 92 and 93, the mixtures were soaked at 200°C and 350°C , followed by liquefaction at 430°C under the same condition. The total conversions (TS) were approximately the same for both Runs, but CyS for Run 93 was higher than that for Run 92, as shown in *Figure 1*. For Run 94, the coal was liquefied under the same condition after two-step wise high-temperature soaking. The yield of CyS was not so high as that for Run 93. Two-step wise high-temperature soaking was more effective for dissolution than single-step high-temperature soaking, as shown in the previous report. However, when the soaked mixture was liquefied without separation of heavy fractions, two-step wise high-temperature soaking on liquefaction was not effective.

For Run 95, CyI was separated after two-step wise high-temperature soaking, and then liquefied under the same condition. This is the procedure proposed in the previous work, but conducted under $C/L=1/3$. *Figure 1* shows the total yield calculated for the original coal. Although the yields of CyS, ToS, and TS were 5-8% lower than those obtained under $C/L=1/10$, these yields were much higher than those for Run 92 (regarded as the base condition). Therefore, the procedure proposed in the previous report is proved to be quite useful even under the high C/L value.

Figure 1 Effect of high coal to liquid ratios on soaking and liquefaction (Conditions are listed in *Table 2*)

Liquefaction of Vacuum Distillated Residue

Vacuum distillation was proposed to isolate light fractions from two-step wise soaked coal. Cyclohexane extraction was simply used in stead of vacuum distillation in the previous quarter, because cyclohexane solubles approximately correspond to fractions distillable under vacuum. In this quarter, two-step wise soaked coal was distilled under vacuum, then the remaining fraction was liquefied at 430°C (Run 97).

The soaked coal was completely distilled up to 250°C under vacuum. Precise pressure was not measured at this time. The remaining fraction was hard solid material. THF was added to solve and remove it from a flask. The dissolved material was transferred to the autoclave, and THF was evaporated. The coal liquid was added to the evaporated fraction, but the fraction was not dispersed in the coal liquid at 100°C. Although a significant portion of the fraction was lump, the mixture was liquefied at 430°C (Run 97(1)). The TI yield was more than 100% due to the incorporation of the coal liqued into the product. For Run 92(2), coal liquid was added in the remaining residue to prevent the bottoms from forming hard material while the mixture was at $> 100^{\circ}\text{C}$, then the mixture was transferred to the autoclave. The bottom fraction was dispersed in the coal liquid to some extent, but a significant lump material was still seen. The conversion for this Run was better than that for Run 97(1), but still low (see *Figure 2*). The yield obtained in the previous quarter is shown in *Figure 2* for comparison.

Vacuum distillation was carried out approximately to half extent, and the coal liquid was added, followed by liquefaction (Run 97(3)). The dispersed mixture was obtained, and the conversion yield for this Run was better than that for Run 97(2). Therefore, the better dispersion is required for better conversion. It was not possible to get better dispersion using glasswares with this batch-wise operation. It is recommended to test the proposed procedure in a continuous and closed system with heating of fluid.

Figure 2 The yields of coal liquefaction after vacuum distillation (Conditions are listed in *Table 2*)

Second Stage Liquefaction

A study of second stage liquefaction was begun. The reactor was cooled down after liquefaction at 430°C to change the hydrogen pressure for second stage liquefaction. Then, the reactor was again heated to reaction temperature (410°C). For Runs 100 and 106, the coal was soaked at 200°C, followed by liquefaction at 430°C as the first stage. For Runs 104 and 107, the coal was soaked at 350°C and 350/400°C, followed by liquefaction under the same condition. Cyclohexane insolubles were also liquefied at 430°C, then at 410°C. These results are shown in *Figure 3*. The total conversion was calculated for Run 102 based on the original coal.

These are the initial results for the second stage liquefaction. Although any conclusion has not yet been made, the results suggest the followings: The effect of hydrogen pressure on the second stage liquefaction is larger for soaking at 200°C than at 350°C. High-temperature soaking provides the high overall conversion. Since the conversion was not so high as expected, the temperature and/or procedure (the mixture was cooled after the first stage) for the second stage need to be optimized.

Summary

The nearly equal conversions were obtained even with high coal/liquid ratio (1/3-1/2) for two-step wise high-temperature soaking and the first stage liquefaction. Expected conversions were not observed when vacuum distillation after soaking was used in stead of cyclohexane extraction. This is presumably due to the difficulty with redispersion of vacuum distilled bottoms in the coal liquid, because a batch wise procedure was taken by using glasswares. It is suggested that the proposed procedure in the previous quarter should be tested by a continuous procedure under enough heating conditions to keep low viscosity of the bottoms.

References

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- 2 Gollakota, S. V., Lee, J. M. and Davies, O. *Fuel Proc. Tech.* 1989, 22, 205
- 3 Bendale, P., Zeli, R. A. and Nishioka, M. *Fuel* in press

Figure 3 The yields of coal liquefaction after the second stage liquefaction (Conditions are listed in *Table 2*)

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