Short Contact Time Direct Coal Liquefaction Using a Novel Batch Reactor

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INTRODUCTION

The primary objective of this research is to optimize the design and operation of the bench scale batch reactor (SCTBR) for studying direct coal liquefaction at short contact times (.01 to 10 minutes or longer). Additional objectives are to study the kinetics of direct coal liquefaction particularly at short reaction times and to investigate the role of organic oxygen components of coal and their reaction pathways during coal liquefaction. Many of those objectives have already been achieved.

This quarterly report discusses further kinetic studies of the liquefaction in tetralin of a Montana Lignite, Wyodak-Anderson subbituminous coal, Illinois #6 hv bituminous coal, Pittsburgh #8 hv bituminous coals, and Pocohontas lv bituminous coal at short contact times. All of these coals showed a distinct extraction stage. Further work has also been done to attempt to clarify the role of the liquefaction solvent in the direct liquefaction process.

EXPERIMENTAL

Coals Studied. The kinetics of liquefaction of a Montana Lignite, Pittsburgh 8 bituminous coal, and Pocohontas lv bituminous coal from the Penn State Coal Sample Bank, and Wyodak-Anderson subbituminous coal and Illinois #6 from the Argonne Coal Sample program were investigated.

Solvents Used. Tetrahydroquinoline (98%), decahydroquinoline, quinoline (98%), 1-methylnaphthalene(98%), dihydrophenanthrene (98%) and tetralin (99%) all from Aldrich Chemicals have been used in coal liquefaction experiments.

Coal Liquefaction. All liquefactions were run as mixtures of processing solvent and coal in varying proportions and in some cases with added catalyst.

Workup Procedures of the Reaction Products. The product mixtures were filtered and the solid residues washed with cold fresh tetralin thoroughly and dried in a vacuum oven with a nitrogen purge at 105°C for 48 hours. The filter cake was then rinsed with methylene chloride and dried in a vacuum oven with a nitrogen purge at 105°C for 12 hours. The solid residue and the liquid filtrate were analyzed separately by various procedures.

Thermogravimetric Analysis (TGA). As reported previously, thermogravimetric analyses were performed on both solid residues and liquid filtrates. On the basis of the ash content (by TGA) of the residue (compared to an unreacted coal), a conversion to soluble material was determined for the coals as a function of time and temperature.

RESULTS AND DISCUSSION

Liquefaction Kinetics. Detailed conversion vs time and temperature curves for Illinois #6 coal were included in the previous quarterly report. This also included a kinetic analysis of the process and calculation of reaction rate constants and activation energies. Conversion vs time curves for Wyodak-Anderson

subbituminous coal, Illinois #6, Pittsburgh #8 and Pocahontas bituminous coals in tetralin (8 to 1 tetralin to coal wt ratio) at 390°C have now been run and are included in this report (Figure 1). All these coals show the same stages of conversion, i.e., an extraction stage, a transition interval in which the extraction is levelling off, and a coal structure breakdown stage.

After the extraction stage, the slope of the conversion curve is a function of the breakdown of the coal structure itself. Examination of Figure 1 shows that there is a great deal of difference in the coal structure breakdown rates among the four coals investigated. The Pittsburgh 8 and the Illinois #6 show similar rates, but the low volatile bituminous coal (Pocahontas) shows very slow conversion rate.

All these runs were made without added catalyst under nitrogen pressure. Although conversions under these conditions are lower than those in a catalyzed system, these experiments allow us to differentiate the effect of solvent from catalyst.

A list of liquefaction runs on a Montana Lignite (MT Pust lignite A from Penn State) is shown in Table 1. Analysis of the conversion results are in progress.

The Extraction Stage. In the previous report it was pointed out that the extraction stage was an approach to equilibrium under the liquefaction conditions (solvent to coal ratio, temperature etc). The equilibrium at an additional temperature has now been measured which confirms and strengthens the previous data. This allowed us to measure the approximate equilibrium constant (K_s) at very low conversions (X), i.e.,

$$K_s = \frac{X}{1 - X} \quad (1)$$

and to plot $\ln(K_s)$ as a function of $1/T$ (Figure 2). The slope of that line allows the computation of the heat of extraction which turns out to be 44.4 kJ/mol (10.6 kcal/mol). This low value supports the view that that stage is really an extraction which does not involve cleavage of covalent bonds.

Liquefaction Solvents. Based on reports in the literature (1,2) and previous results obtained in this project tetrahydroquinoline (THQ) used as a liquefaction solvent gave very high and rapid liquefaction conversion compared to other solvents (tetralin, 1-methylnaphthalene, etc.). To determine whether this improvement is due to a greater hydrogen donor ability or a solvent effect or a combination of the two, some liquefaction runs have been made using quinoline, tetrahydroquinoline and decahydroquinoline as solvents. Preliminary results using these solvents and no catalyst are summarized in Table 2. The quinoline shows a rapid solvent extraction stage followed by no detectable breakdown of the coal structure itself. The equilibrium extraction with that solvent at 410°C is approximately 23.0 wt% daf. The tetrahydroquinoline, gave approximately 84% solubility of the coal. When decahydroquinoline was used as a solvent at the same

temperature, approximately 90% of the coal was dissolved at 410°C and 25 wt% was dissolved even at ambient temperature. While a mechanism for hydrogen donation can be postulated for tetrahydroquinoline, it appears to be less likely for decahydroquinoline. This suggests that the solvent effect of the decahydroquinoline is due to its strongly basic properties probably in the breaking of hydrogen bonds in the coal, and the breakup of the colloidal structure of the coal. The THQ might be expected to have similar basicity and solvating power to the DHQ, suggesting that it may not be primarily the hydrogen donor ability of the THQ that is giving its high conversion to liquids. If that is the case, the THQ may be solubilizing but not breaking down the coal structure significantly. This question is being explored further.

Thermogravimetric analyses of the solid residues from liquefactions using these three nitrogen containing solvents reveal more details of the chemistry involved. Compared to the original coal, DTG (the differential curves) of coal treated at ambient conditions show no change in the coal itself. However, when liquefactions are run in these nitrogen containing solvents both THQ and DHQ show additional peaks at about 725±3 °C of similar peak heights. Comparison with DTG curves of unreacted coal suggest they may consist of "solubilized" coal which has not been broken down. Residues from liquefaction in quinoline do not show these peaks. The TGA curves are provided in the attached appendix.

PUBLICATIONS (since the last report)

1. "Coal Liquefaction Kinetics" S. Wang, K. Wang, H. Huang, M.T. Klein, and W.H. Calkins *ACS Fuel Chem Div Preprints* **41** (3) 935-940 (1996).
2. "Effect of Solvent Characteristics on Coal Liquefaction" H. Huang, S. Wang, K. Wang, M.T. Klein and W.H. Calkins *ACS Fuel Chem Div Preprints* **41** (3) 961-966 (1996)

SUMMARY AND CONCLUSIONS

1) Further data on the extraction stage in the liquefaction of Illinois #6 has been extended to additional temperatures. This has increased our confidence that extraction is an equilibrium process not involving the cleaving of strong bonds. (heat of extraction is approximately 10.6 kcal).

2) Conversion vs time data have been extended to 5 coals of ranks from lignite to low volatile bituminous coal. A broad range of reaction rates have been observed with a maximum in the high volatile bituminous range.

3) The very high liquefaction conversion of Illinois #6 in tetrahydroquinoline may be primarily a solvent effect. Liquefaction in quinoline itself showed only low conversion which was entirely due to solvent extraction whereas liquefaction in decahydroquinoline as well as tetrahydroquinoline gave very high conversion to liquid products.

PROGRAM

The affect of solvent characteristics on direct coal liquefaction will continue to be investigated at low conversions, and the interaction between solvent and catalyst during liquefaction will also be studied.

The so called "shuttling effect " during coal liquefaction will continue to be studied by addition of aromatic compounds to liquefactions using various solvents and coals.

The oxygen species in coal will continue to be examined as a function of liquefaction conversion.

REFERENCES

1. Derbyshire, F.J; Odoerfer, G.A.; and Whitehurst, D.D. Fuel 63, 56 (1984)
2. Kaufman, M.; Jamison, W.C.L.; Gandi, S; and Liotta, D. Fuel 66, 1621 (1987)

Table 1 Liquefaction of MT-Pust ligA coal (Penn State DECS-25)

Run No.	t, min	T, C
DOE349	5.00	20
DOE350	0.17	388
DOE351	0.50	391
DOE352	1.00	390
DOE353	2.00	391
DOE354	5.00	389
DOE355	10.00	390
DOE356	30.00	393
DOE357	60.00	392

Liquefaction Run Conditions: Tetralin:Coal = 8:1; 1000 psig N₂

Table 2 Liquefaction of Illinois #6 coal in 1000 psig N₂ (Solvent:Coal = 8:1)

Solvent	T, C	t, min	X, wt% (daf)
Quinoline	25	-	6.3%
	410	10	23.9%
1,2,3,4-Tetrahydroquinoline	25	-	6.3%
	410	10	83.9%
Decahydroquinoline	25	-	25.1%
	410	10	89.8%

Figure 1 Conversion (X) vs time for uncatalyzed direct coal liquefaction (390 °C; Tetralin:Coal = 8:1 wt. ratio; 1000 psig N₂)

Figure 2 $\ln(K_s)$ vs $1/T$ for the extraction stage of Illinois #6 coal liquefaction in tetralin

Appendix

TGA curves for the original Illinois #6 coal and its liquefaction
solid residues using nitrogen-containing solvents

A TG scan on the Illinois #6 bituminous coal at 10 °C/min

Sample: Control: 25 °C, Quinoline
Size: 40.3930 mg
Method: DOE Coal Liquifaction
Comment: DOE Coal Liquifaction, 10 °C/min
File: C:\DOE323S1.002
Operator: Keyu Wang
Run Date: 26-Nov-96 13:48

Sample: Liquefaction: 410 °C, 10 min, 1000 psig N₂, Quinoline
Size: 40.4090 mg
Method: DOE Coal Liquefaction
Comment: DOE Coal Liquefaction, 10 °C/min

File: C:\DOE319S1.002
Operator: Keyu Wang
Run Date: 23-Nov-96 20:49

File: A: DOE259S1.001
Operator: Keyu Wang
Run Date: 9-May-96 23:57

Sample: Control: 25 °C, 1,2,3,4-Tetrahydroquinoline
Size: 52.2270 mg
Method: DOE Coal Liquefaction
Comment: 10 °C/min to 950 °C; Gas 2

Sample: Liquefaction: 410 °C, 10 min, 1000 psig N₂, 1,2,3,4-Tetrahydroquinoline **File:** A: DOE199S1.001
Size: 44.5000 mg **Operator:** Keyu Wang
Method: DOE Coal Liquefaction **Run Date:** 17-Apr-96 09:04
Comment: 10 °C/min 950 °C

Sample: Control: 25 °C, Decahydroquinoline

Size: 47.1870 mg

Method: DOE Coal Liquifaction

Comment: 5 °C/min to 150 °C Iso. 30 min. 10 °C/min to 850 °C

File: C:\DOE374S1.001

Operator: Keyu Wang

Run Date: 27-Jan-97 11:46

Sample: Liquefaction: 410 °C, 10 min, 1000 psig N₂, Decahydroquinoline
Size: 42.4880 mg
Method: DOE Coal Liquefaction
Comment: 10 °C/min to 850 °C DOE

File: C:\DOE369S1.002
Operator: Keyu Wang
Run Date: 26-Jan-97 15:11