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Short Contact Time Direct Coal Liquefaction Using a Novel Batch Reactor

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INTRODUCTION

The 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 of Illinois #6 bituminous coal, Wyodak-Anderson subbituminous coal, and Pittsburgh #8 bituminous coal. The thermodynamic characteristics of the extraction stage at the start of the liquefaction process in the liquefaction of Illinois #6 coal is also discussed. 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 Illinois #6 bituminous coal from the Argonne Coal Sample program, Pittsburgh 8 bituminous coal from the Penn State Coal Sample Bank, Wyodak-Anderson subbituminous coal from the Argonne Coal Sample program were investigated.

Solvents Used. Tetrahydroquinoline (98%), quinoline (98%), methylnaphthalene(98%), dihydrophenanthrene (98%) and tetralin (99%) all from Aldrich 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 tetralin 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 and Pittsburgh #8 bituminous coal in tetralin (8 to 1 tetralin to coal wt ratio) at 390°C have also been run and are included in this report. Conversion vs time curves for the three coals for which we have completed data are shown in 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.

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). 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 43.8 KJ/mol. This low value supports the view that that stage is really an extraction which does not involve cleavage of covalent bonds.

Liquefaction Solvents. In the previous report, a range of liquefaction solvents were tested and the substantial increase in liquefaction conversion using tetrahydroquinoline over other solvents of poorer hydrogen donor ability was graphically illustrated. To determine whether this great 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 as the solvent. Conversion in quinoline alone has now been determined. The conversion vs time curve is shown in Figure 3. This curve shows a rapid solvent extraction stage and no detectable breakdown of the coal structure itself. The equilibrium extraction with that solvent at 410°C is approximately 18 daf wt%.

Dihydrophenanthrene has been reported to be a strong donor solvent (1,2). For this reason, a series of runs was made to liquefy Illinois #6 coal in 1-methylnaphthalene (a very poor hydrogen donor) with various amounts of added 9,10 dihydrophenanthrene (up to approximately 18 wt%). A conversion vs dihydrophenanthrene concentration in methylnaphthalene is shown in Figure 4. It is interesting to note that the initial addition of dihydrophenanthrene increases the conversion significantly. However, the effect of added dihydrophenanthrene diminishes rapidly over 10 wt%. The reason for this phenomenon is not yet clear.

PUBLICATIONS (since the last report)

1. "Kinetics of Coal Liquefaction at Very Short Reaction Times" He Huang, Keyu Wang, Shaojie Wang, Michael T.Klein, and William H. Calkins *Energy and Fuels* 10, (3) 641-648 (1996).
2. "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).
3. "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) The extraction stage in the liquefaction of Illinois #6 has been shown to be an equilibrium process not involving the cleaving of strong bonds.

2) The three stage liquefaction behavior has been shown to be applicable to at least three coals studied thus far, including Pittsburgh 8, a med. volatile bituminous coal.

3) The very high liquefaction conversion of Illinois #6 in tetrahydroquinoline does not appear to be a solely solvent extraction effect, since liquefaction in quinoline itself showed only low conversion which was entirely due to solvent extraction.

4) Liquefaction with added dihydrophenanthrene up to 10 wt% in a poor donor solvent (methyl naphthalene) showed increased conversion. Over that concentration, conversion levels off. The explanation for this behavior of a strong hydrogen donor in this system is being investigated.

PROGRAM

The conversion vs time curves for other Argonne coals will be investigated.

The effect of solvent characteristics on direct coal liquefaction will continue to be investigated at low conversions.

The so called "shuttling effect " during coal liquefaction will also be studied.

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

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1. Raaen, V.F. and Roark, W.H. *Fuel* 57, 650 (1978).
2. Bockrath, B.C. and Noceti, R.P. *ACS Fuel Chem. Div. Preprints* 26 (1),94 (1981).

**Conversion vs time for uncatalyzed direct liquefactions
(390 °C; Tetralin:Coal = 8:1; 1000 psig N₂)**

Figure 1

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

Figure 2

Conversion vs time for Illinois #6 coal liquefaction in quinoline (410 °C; 1000 psig N₂)

Figure 3

Liquefaction conversions of Illinois #6 coal in various concentrations of dihydrophenanthrene in 1-methylnaphthalene (412 °C; 5 min; 1000 psig N₂)

Figure 4