

AQUEOUS LIQUEFACTION OF ILLINOIS NO. 6 COAL

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INTRODUCTION

Near its critical point ($T_C = 374^\circ\text{C}$, $P_C = 218 \text{ atm.}$), water is a good solvent for organic (1) as well as inorganic materials while, at ambient conditions, most organics are insoluble in water. Water is also thermally stable, even at temperatures above 450°C , and has a large heat capacity. Finally, water is very cheap compared to other solvents.

By virtue of this combination of properties, water has great potential as a solvent for coal liquefaction and has drawn the attention of a number of investigators in recent years (2-6). These researchers have established a number of advantages for water including:

- i. Ease of separation of solvent and product;
- ii. Minimal char production (2);
- iii. Use of soluble catalysts (3,4); and
- iv. Relatively high liquefaction yields.

Recently, we developed a unique flow mode reactor (7) which has enabled us to isolate processes contributing to coal liquefaction and to investigate them dynamically. Using this reactor with a variety of solvents, we established 300°C as the threshold temperature for thermal chemical solubilization of Illinois No. 6 Coal; and in the $360\text{--}420^\circ\text{C}$ range, we obtained conversions ranging from 15% in hexane to 44% in toluene.

Our recent investigations have focused on two important components of coal conversion: thermal chemical reactions and dissolution of coaly material (including thermolysis products) in the solvent; and we are exploring the effects of temperature and pressure on these processes. Here, we report the initial results of our investigation of these effects in the aqueous liquefaction of coal and compare these results to those obtained with other solvents.

EXPERIMENTAL

General

Illinois No. 6 coal from the Ames Lab Coal Library was used in these studies. This coal has the following ultimate analysis (dmmf basis): 78.82% C; 5.50% H; 1.59% N; 2.29% S_{org} ; and 10.05% ash. Prior to use, this coal was ground, sized to 60 X 100 mesh, and dried at 110°C overnight under vacuum. Conversions were measured gravimetrically and are reported as % weight loss on a raw coal basis.

*Operated for the U.S. Department of Energy by Iowa State University under contract No. W-7405-Eng-82.

Flow Mode Extraction of Coal

The liquefaction experiments were carried out in the apparatus shown schematically in Figure 1. Typically, the reactor was loaded with 500 mg. of coal (leaving a free volume of 0.70 ml); and the system was filled with solvent and brought to operating pressure (usually 3000 psi). Heating (rate $\sim 150^{\circ}\text{C}/\text{min}$) and solvent flow (1.0 ml/min) were initiated simultaneously; and constant temperature and pressure were attained within three minutes. Extraction was continued for one or, in some cases, two hours. In some experiments, conditions were changed at predetermined points during the run. After cooling and flushing with nitrogen, the residue was removed from the reactor, dried at 110°C overnight under vacuum, and weighed.

RESULTS AND DISCUSSIONS

The advantages of the Flow Mode Extractor used in these experiments has been established in a previous report from this laboratory (7). These advantages are analogous to those reported for other rapid heating, continuous product removal techniques (e.g. heated grid vacuum pyrolysis (8)) and include suppression of retrogressive reactions and dynamic observation of changes which occur during the course of the conversion.

Flow Mode Extraction of Coal with Water

Our initial experiments were conducted for the purpose of comparing aqueous extraction yields to those which had been obtained using a series of nominally unreactive organic solvents (9). Figure 2 shows a comparison of the extraction yields for these solvents at 420°C and 3000 psi with that of water at 400°C and 3580 psi. Clearly, water is one of the best "nonreactive" solvents for the thermal liquefaction of coal. This conclusion also holds at 370 and 400°C , the other temperatures included in this investigation.

We can find only one basis for comparing batch and flow mode systems in the aqueous liquefaction of Illinois No. 6 Coal. At 400°C Vasilakos reports batch mode conversions of 34.0% (3580 psi) and 29.5% (3070 psi) (10). Under identical conditions in our reactor, we find extraction yields of 38.2% and 33.6%, respectively.

Temperature and Pressure Effects on Aqueous Liquefaction

Because of the unusually high critical pressure of water ($P_c = 3206$ psi; cf. benzene: $P_c = 716$ psi), interesting temperature/pressure/conversion relationships were expected for aqueous extraction of coal. The effects of temperature and pressure on conversion are reported in Table 1. Trends in this behavior are more apparent in Figure 3 which plots conversion vs. density for a series of isotherms.

At 370°C , conversion begins to decrease quite rapidly as the density approaches 0.15 g/ml, and we believe that there are similar "threshold" densities at the higher temperatures. However, pressures fluctuated wildly during the latter experiments, and we were unable to obtain meaningful data under these conditions. In the low density

Table 1. Effect of Temperature and Pressure on the Aqueous Extraction of Illinois No. 6 Coal

| Expt. No. | Temperature (°C) | Pressure (psi) | Density ^a (g/ml) | Weight Loss (%) |
|-----------|------------------|----------------|-----------------------------|-----------------|
| 16 | 370 | 1925 | 0.061 | 14.6 |
| 17 | 370 | 2950 | 0.151 | 31.8 |
| 18 | 370 | 3207 | 0.485 | 34.9 |
| 22 | 380 | 2950 | 0.128 | 34.3 |
| 11 | 380 | 3220 | 0.174 | 35.4 |
| 21 | 380 | 3750 | 0.482 | 35.6 |
| 19 | 400 | 3070 | 0.113 | 33.6 |
| 20 | 400 | 3580 | 0.163 | 38.2 |

a. For pure water (11).

region, it appears that conversion is limited by solubility since thermal processes should proceed at about the same rate under both high and low density conditions.

Our final series of experiments were designed to determine whether the "extract" remaining in the low density residue after extraction for one hour at 370°C and 1925 psi was recoverable by simply increasing the pressure to 2950 psi. We suspected that, at 370°C, much of this material would be fixed by retrogressive reactions during the period of low density extraction. Surprisingly, in a two stage experiment at 370°C (first stage 1925 psi, extraction time 1 hour; second stage 2950 psi, extraction time 1 hour), we obtained an extraction yield of 31.6% compared to 31.8% conversion for one stage extraction at 2950 psi. We are puzzled by this behavior and plan to continue our investigations by analyzing products at discrete intervals during the course of the conversion.

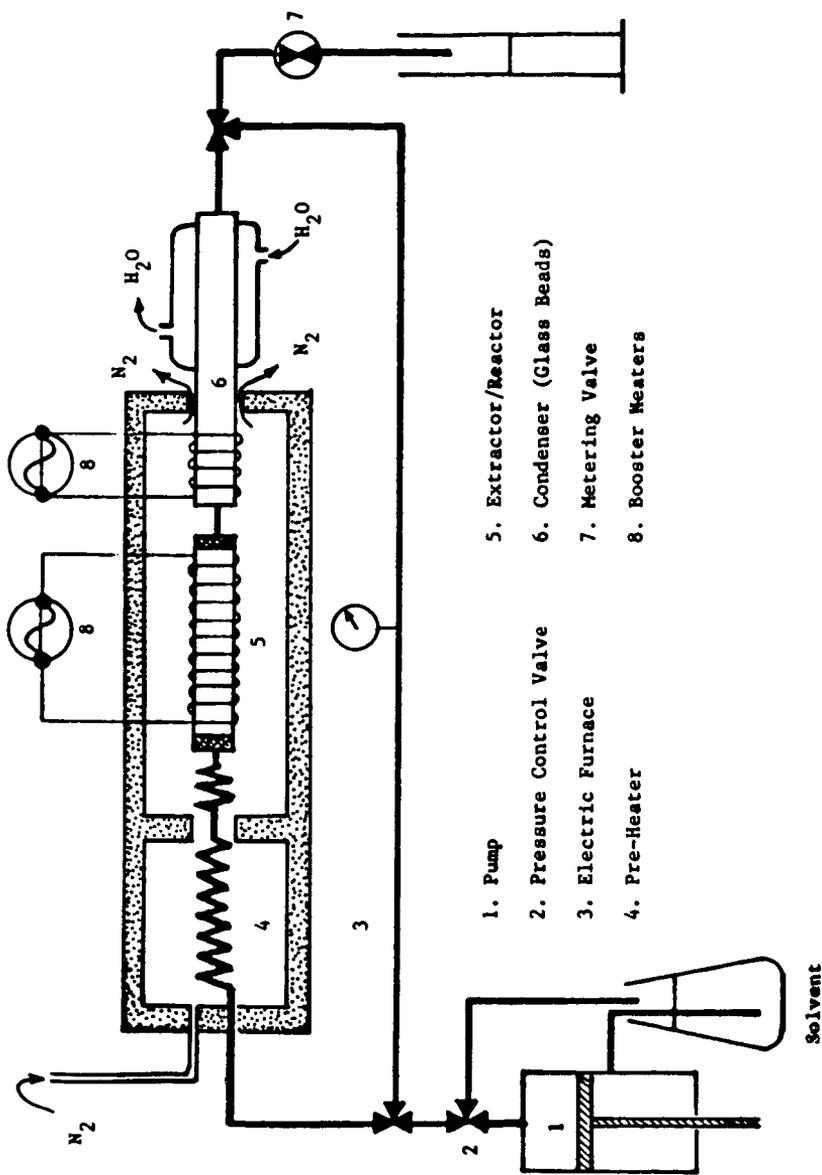
ACKNOWLEDGEMENT

This material was prepared with the support of the U. S. Department of Energy, Grant No. DE-FG22-82PC50786 for which we are grateful. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of DOE.

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- 1. Pump
- 2. Pressure Control Valve
- 3. Electric Furnace
- 4. Pre-Heater
- 5. Extractor/Reactor
- 6. Condenser (Glass Beads)
- 7. Metering Valve
- 8. Booster Heaters

FIGURE 1. Rapid Heating Flow Mode Reactor

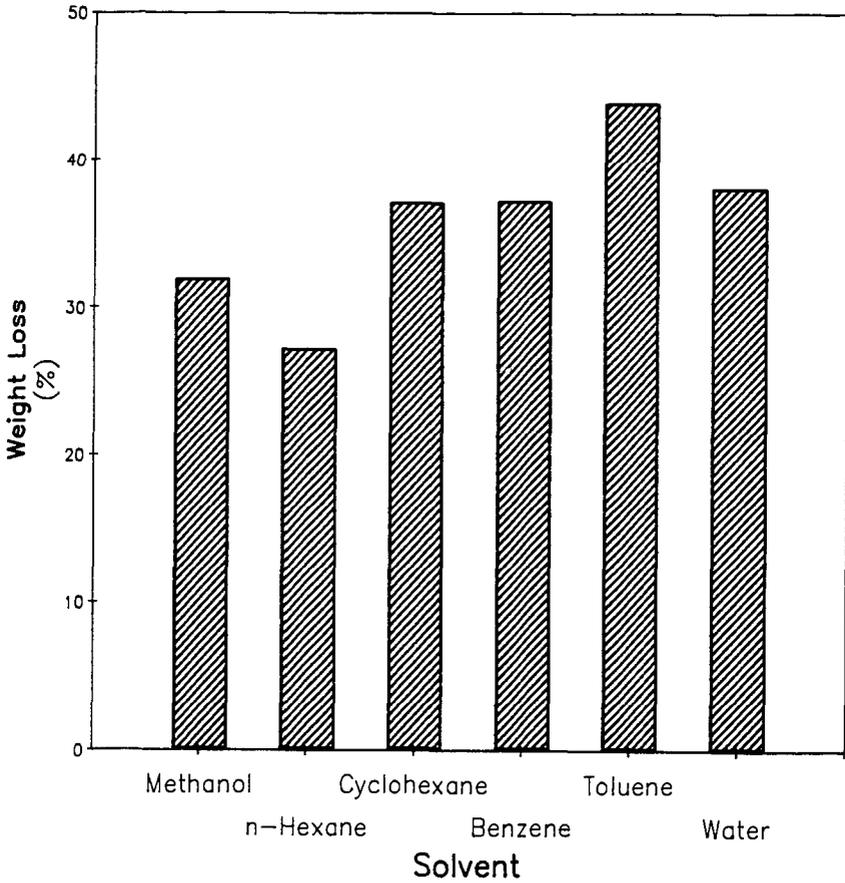


FIGURE 2. Solvent Extraction of Illinois No. 6 Coal at 420°C^a and 3000 psi^a (2 Hours^b)

a. Aqueous extraction conducted at 400°C, 3580 psi.

b. Benzene and water extractions reported for 1 hour.

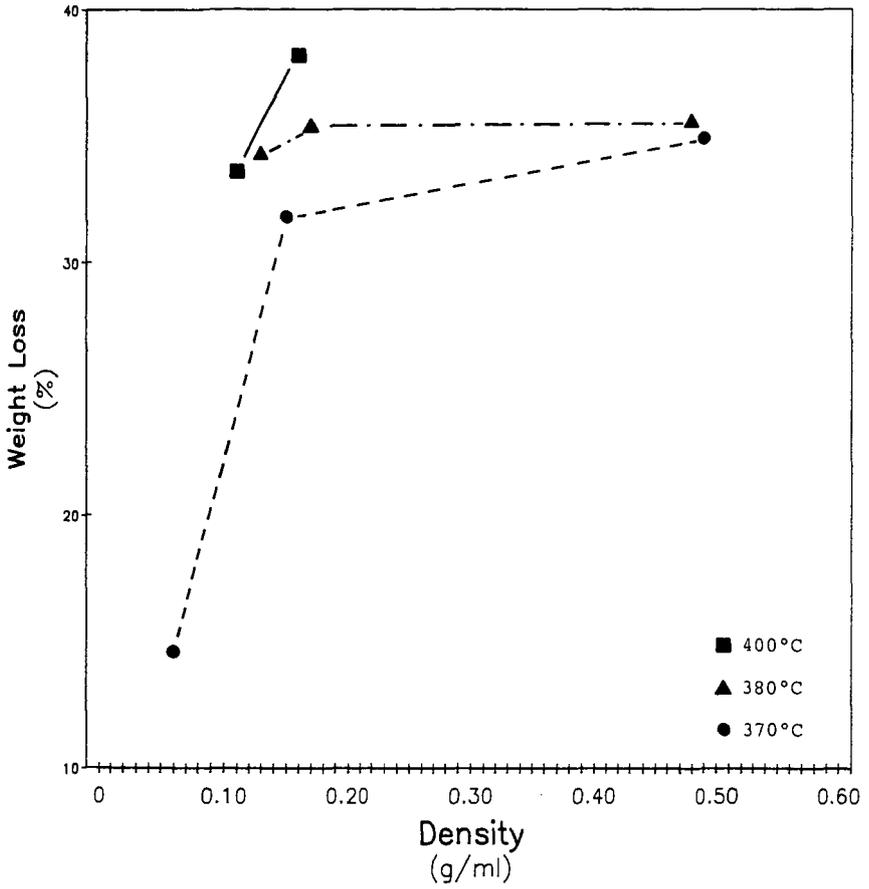


FIGURE 3. Density and Temperature Effects in the Aqueous Extraction of Illinois No. 6 Coal