THE DYNAMICS OF THE THERMAL SOLUBILIZATION OF ILLINOIS NO. 6 COAL.

Tetsuo Aida, Bogdan Slomka, Julianna C. Shei,
Yu-Ying Chen, and Thomas G. Squires

Ames Laboratory,
Iowa State University
Ames, Iowa 50011

INTRODUCTION

The role of retrogressive reactions in limiting the rate and extent of coal liquefaction has long been recognized (1). While the negative impact of these phenomena on the overall conversion is clear, their chemical nature and the extent of their impact have yet to be elucidated. This is due, in part, to the complexity of the problem and, more importantly, to technical difficulties in resolving and investigating consecutive dynamic processes at high temperatures and pressures.

Almost forty years ago, Neuworth (2) and Glenn and his co-workers (3) addressed this problem by equipping an autoclave with a cold head receiver. In this way, they hoped to suppress retrogressive reactions by removing distillable products from the hot reaction zone as soon as they were formed. More recently, two other approaches have been utilized. Short contact time (SCT) experiments have been employed as a means of controlling secondary reactions in hopes that primary processes will dominate the conversion (4). In this approach, tubing bombs containing the coal liquefaction mixture are rapidly heated to an appropriate temperature, maintained at these conditions for a short time, and quickly cooled to room temperature. Other investigators (5,6,7) have placed liquefaction products (e.g. SRC) in an autoclave under liquefaction conditions in order to explore secondary retrogressive phenomena.

However, it should be quite obvious that experimental approaches which **confine starting materials, intermediates, and products to the same reaction space** throughout the course of the conversion are simply incapable of resolving productive and counter-productive processes. From this perspective, autoclaves and tubing bombs promote (rather than inhibit) secondary interactions between unreacted coal and primary products, thus obscuring primary pathways in the conversion process. Consequently, dynamic analysis of conversion rates and products is not only difficult in batch systems, but interpretations of the results from these experiments **in terms of fundamental processes** are tenuous.

In contrast, fixed bed flow mode reactors are capable of rapid removal and quenching of conversion products and, when appropriately designed, also provide temperature and pressure programing flexibility. As a means of isolating and investigating the fundamental phenomena which comprise coal conversion, we have developed a unique, rapid heating, flow mode microreactor system and have used it to investigate the dynamics of the thermal solubilization of coal. Important features of our apparatus include:

- programable solvent residence times (1 to 30 seconds)
- programable heating rates (up to 150°C/minute)
- temperature and pressure programability
- rapid quenching of reactor effluent
- continous, "on-line" optical density monitoring of same
- data acquisition and manipulation capability
- time resolved product collection (up to 2 samples/minute).

The soundness of this approach to resolving fundamental processes which comprise coal liquefaction was examined in a series of experiments. In the first set of experiments, this apparatus was used in a temperature programing mode to generate benzene solubilization rate profiles for five coals of varying rank. Another set of experiments focused on our continuing investigation of supercritical water as a medium for coal solubilization (8). Here, conversion rate profiles and liquid chromatographic product analysis were used to compare water and benzene as solvents for the thermal solubilization of Illinois No. 6 coal.

EXPERIMENTAL

General

Coals from the Ames Laboratory Coal Library were used for these studies; analytical data for the coals is given in Table 1. Prior to use, coals were ground, sized to 200 x 400 mesh, riffled to insure uniformity, and dried at 110°C overnight under vacuum. All solvents were HPLC grade or better; samples and solvents were stored under nitrogen.

Solubilization Procedure

Flow mode solubilization experiments using benzene and water were carried out in an improved version of our flow mode reactor (9). New features include continuous, "on-line" optical density monitoring of the reactor effluent; real time data acquisition of optical density, temperature, and pressure; and an improved time resolved product collection system. In a typical experiment, a preweighed amount (25-200 mg) of 200-400 mesh coal was placed in the tubular reactor and fixed in place by 2 stainless steel frits. After connecting the reactor and purging the apparatus with nitrogen, the entire system was

Table 1 Analysis of Ames Laboratory Coals

	Ultimate analysis, %[a]					Volatile
COAL	C	H	N	S_{org}	O(diff)	Matter[a]
Dietz No.1 & 2	74.35	5.26	1.09	0.44	18.86	38.6
Illinois No.6	80.60	5.63	1.56	2.35	9.81	40.4
Kentucky No.9	82.48	5.89	1.91	2.36	7.34	44.2
Pittsburg No.8	85.08	6.53	1.54	2.72	4.09	44.8
Lower Kittanning	90.04	4.82	1.66	0.68	2.69	18.4

a. Dmmf basis; wt % mineral matter = 1.13(wt % Ash) + 0.47(wt % S_{pyr}) + 0.5(wt % Cl).

filled with solvent and pressurized at room temperature before adjusting the solvent flow to 1.0 ml/minute. The reactor was then inserted into the preheated furnace at the same time that the reactor booster heater was turned on. The targeted initial temperature was always attained and stabilized within the first 3 to 5 minutes; and temperature and pressure were controlled during the conversion according to a predetermined program. Temperature and pressure profiles in the coal bed, as well as the optical density profile of the product stream, were recorded throughout the conversion. At the end of the experiment, the reactor was quickly cooled to ambient temperature while purging with nitrogen; and the residue was removed from the reactor and (in some cases) weighed. Solubilization yields in Table 2 are reported on a dry, mineral matter free basis.

Liquid Chromatographic Analysis of Products

Products of coal solubilization were analyzed by reverse phase high-performance liquid chromatography on a 4.1 mm x 300 mm - Bondapak (phenyl/corasil) column supplied by Alltech Associates, Inc. Samples were prepared for analysis by first stripping the solvent from the solubilization product: benzene was removed under a slow stream of nitrogen at room temperature while samples containing water were heated in a water bath (60°C) under reduced pressure.

The dry samples were then dissolved in 1 ml of tetrahydrofuran and 10 l was injected onto the column. Excellent (and reproducible) separation was achieved at a flow rate of 1 ml/minute using gradient elution techniques. The initial solvent composition was 38.1% methanol, 27.6% water, 23.9% acetonitrile, and 10.4% tetrahydrofuran. Chromatograms were recorded using a variable wavelength uv detector set at 254 nm.

RESULTS & DISCUSSION

Conversion Rate Profiles for Representative Coals

For an Illinois No.6 coal, we have previously found a linear correlation between gravimetrically determined conversions and effluent absorbance integrated with respect to time (integrated absorbance, IntA)(10); and this provides a basis for interpreting the integrated absorbance curve as the conversion rate profile. We have also shown that, at 260°C, benzene solubilization has no detectable thermal chemical component while, above 350°C, the conversion is dominated by pyrolytic processes(9).

In the first series of experiments with "on-line" optical density monitoring, five coals of varying rank were extracted with benzene in constant pressure, staged temperature experiments. The physical extraction stage, conducted for 20 minutes at 260°C, was followed by a pyrolysis stage at 390°C for the final 25 minutes. Figures 1 and 2 show the relative absorbance traces recorded at 500 nm for 26±1mg samples of these coals. In view of the relationship between conversion and absorbance, these curves actually represent conversion rate profiles in which extraction and thermal chemical solubilization have been resolved through temperature programing. Furthermore, the peak areas offer a measure of the extent of conversion at each stage of the experiment.

Figure 1 illustrates the distinct dynamic behavior of three coals (Dietz No. 1&2, %C = 74.4; Illinois No. 6, %C = 80.6; L. Kittanning, %C = 90.0) of different rank under identical conversion conditions. As expected, widely different amounts of material were extracted from these coals at 260°C; but the time required for complete physical extraction was approximately the same. We interpret this to mean that extraction sites within the coal particles were accessed at approximately the same rate for all three coals. From this perspective, extraction rate data generated with this apparatus can be used to estimate reaction site accessibility under various conditions.

The pyrolysis portions of the curves (t > 20 minutes) are even more characteristic. Again, the extents of conversion differ widely but are roughly the same as those determined using batch methods. However, in contrast to the 260°C results, the rates of solubilization, especially for Lower Kittanning coal, also vary widely. The thermal chemical solubilization of this higher rank coal is practically complete within 1 to 2 minutes while most of the Illinois No.6 coal is converted a 5 to 10 minute period. From these conversion rate profiles, it is apparent that there is a small but critical "time window" for effectively redirecting chemical pathways under these pyrolysis conditions. The former profile also demonstrates that the reactor system can resolve events with a time constant of less than a minute. The lower limit of this resolution has not yet been experimentally established.

Figure 2 shows similar temperature programed solubilization rate profiles for three more nearly equivalent coals: Illinois No. 6, %C = 80.6; W. Kentucky No. 9, %C = 82.5; Pittsburgh No. 8, %C = 85.1. As expected, the two lower rank coals exhibit nearly equivalent behavior in both the extraction and pyrolysis stages. At this point, it is not clear whether the small difference in the second stage patterns is significant. The most striking comparison is between the dynamic behavior of Pittsburgh No.8 and that of the two lower rank coals. While a substantially higher conversion was expected for the 85% carbon coal, it is quite interesting that the entire difference reported to the extraction stage. We are continuing to investigate this phenomenon.

Aqueous vs. Benzene Solubilization of Illinois No. 6 Coal

Total weight loss determinations, "on-line" optical density monitoring, and staged pressure programing were used to compare benzene and water as solvents for the thermal solubilization of Illinois No.6 coal; the results are summarized in Table 2. On the basis of both weight loss and, more clearly, integrated absorbance, conversion in benzene at 360°C is greater for single stage solubilization (Exp. No.1) than for staged pressure conversion (Exp.No.2). These results are consistent with the general observation that, in the supercritical phase, the solubility of a substance increases with fluid density. During the low pressure (low density) stage, extraction of liquefaction products is inefficient; and, consequently, a portion of the unextracted products undergoes secondary "fixing" (retrogressive) reactions to form a more refractory material. This "fixed" material is no longer recoverable and cannot be extracted when the fluid phase density is increased to that of the one stage experiment (3180 psi).

In contrast, such retrogressive behavior is not observed when

Table 2. Thermal Solubilization of Illinois No. 6 Coal

Exp No	Solvent	First stage Temp (°C)	First stage Press (psi)	First stage Time (min)	First stage Int Abs[a]	Second stage Temp (°C)	Second stage Press (psi)	Second stage Time (min)	Second stage Int Abs[a]	Total Int Abs[a]	Weight Loss[b] (%)
8	C_6H_6	360	3180	60	709	-	-	-	-	709	35.6
6	C_6H_6	360	1280	20	153	360	3180	40	314	467	33.2
17	H_2O	370	2950	60	-	-	-	-	-	-	36.1
68	H_2O	370	1925	60	-	370	2950	60	-	-	35.9
2	C_6H_6	390	3180	60	644	-	-	-	-	644	38.5
4	C_6H_6	390	1500	20	210	390	3180	40	175	385	35.0
3	H_2O	390	3700	60	135	-	-	-	-	135	-
7	H_2O	390	1950	20	19	390	3700	40	114	133	45.0

a. Integrated Absorbance: area under the 500 nm absorbance trace; normalized to 25.0 mg of starting coal.
b. Dmmf basis.

water is used as the solvent for thermal solubilization of Illinois No. 6 coal. At 370°C, the total conversion of Illinois No. 6 coal in a two stage experiment (Exp. No. 68) is comparable to the conversion obtained in a single stage experiment (Exp. No. 17). Either water is acting to inhibit retrogressive reactions or the products of these "fixing" reactions are reactive in (with?) water but not in benzene.

The last four experiments, conducted at 390°C, were designed to further explore solvent induced differences in solubilization behavior. We reasoned that, at higher temperatures, retrogressive pathways should be more important and, thus, differences attributable to these phenomena might be more clearly discernable. The relative absorbance traces for benzene and water solubilization of Illinois No.6 coal are presented in Figures 3 and 4, respectively; and integrated absorbance values for the various stages of these experiments are included in Table 2. Distinct differences in the dynamic solubilization behavior in benzene (Figure 3) and water (Figure 4) suggests that the conversion is proceeding via different chemical pathways in the two solvents. A comparison of the single stage and two stage integrated absorbance values for benzene (Exp. Nos. 2 & 4) and water (Exp. Nos. 3 & 7) further supports this notion.

This hypothesis, that the thermal solubilization of Illinois No. 6 coal proceeds differently in benzene than it does in water, was tested by analyzing the solubilization products with high performance liquid chromatography. Using a reverse phase method, the first and second stage products from the pressure programed benzene solubilization (Exp. No. 4) were compared to their water derived counterparts (Exp. No. 7). The resulting chromatograms for the low pressure products are overlaid in Figure 5 and the high pressure overlay is shown in Figure 6. Unquestionably, the products produced in both stages of the benzene conversion are different from those obtained in the corresponding stages of aqueous solubilization. The nature of these differences will be the focus of further investigation.

These experiments illustrate rather clearly the usefulness of the flow mode approach as a means of **isolating particular conversion phenomena** and **investigating dynamic behavior** during coal liquefaction.

ACKNOWLEDGEMENT

Portions of this research were supported by 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.

REFERENCES

1. van Krevelen, D.W. in "Coal"; Elsevier: New York, 1961; pp. 201-216.

2. Neuworth, M.B. J. Am. Chem. Soc. **1947**, 69, 1653.

3. Glenn, R.A.; De Walt, C.W. Fuel **1953**, 32, 157.

4a. Neavel, R.C. Fuel **1976**, 55, 273.

4b. Mitchell, T.O.; Whitehurst, D.D. Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. **1976**, 21(2), 127.

5. Burke, F.P.; Winschel, R.A.; Jones, D.C. Fuel **1985**, 64, 15.

6. Painter, P.C., et. al. Fuel **1979**, 58, 233.

7. Ouchi, k.; Makabe, M.; Yoshimoto, I.; Itoh, H. Fuel **1984**, 63, 449.

8. Slomka, B.; Aida, T.; Squires, T.G. Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. **1985**, 30(2), 368.

9. Squires, T.G.; Aida, T; Chen, Y.Y.; Smith, B.F. Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem. **1983**, 28(4), 228.

10. Unpublished results from this laboratory.

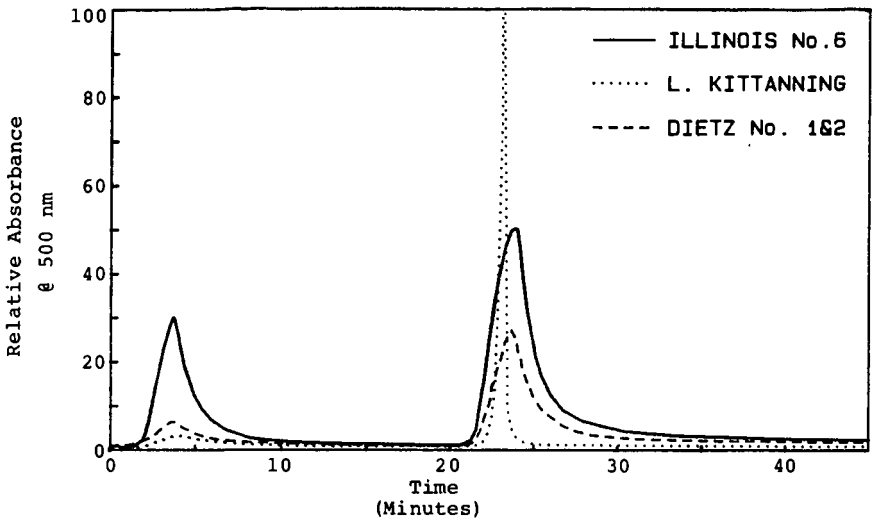

Figure 1. Staged Temperature Benzene Solubilization of Different Rank Coals. First Stage: 260°C/3180 psi; Second Stage: 390°C/ 3180 psi.

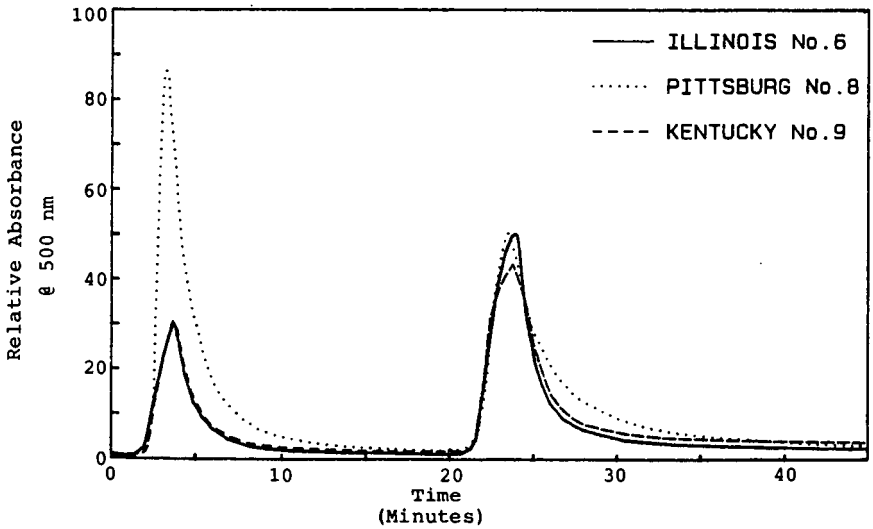

Figure 2. Staged Temperature Benzene Solubilization of Similar Rank Coals. First Stage: 260°C/3180 psi; Second Stage: 390°C/ 3180 psi.

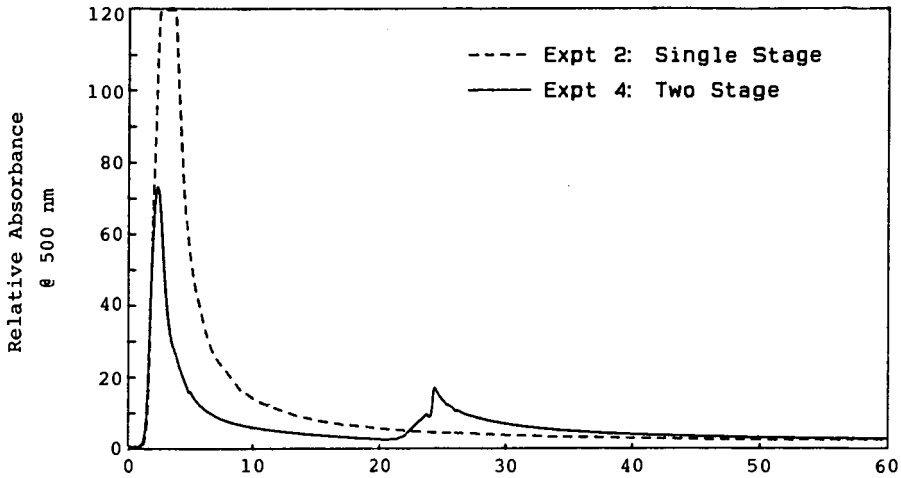

Figure 3. Effect of Pressure on Benzene Solubilization of Illinois No6 Coal at 390°C. Single Stage: 3180 psi; Two Stage: 1500/3180 psi.

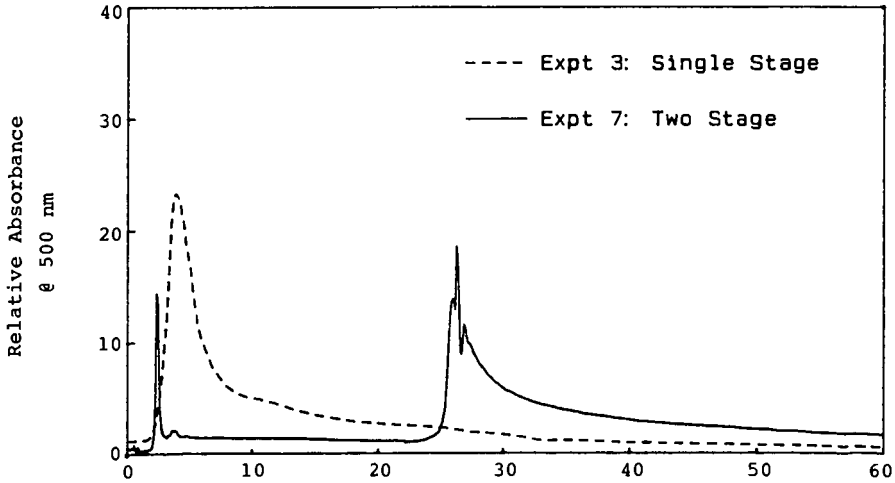

Figure 4. Effect of Pressure on Aqueous Solubilization of Illinois No6 Coal at 390°C. Single Stage: 3700 psi; Two Stage: 1950/3700 psi.

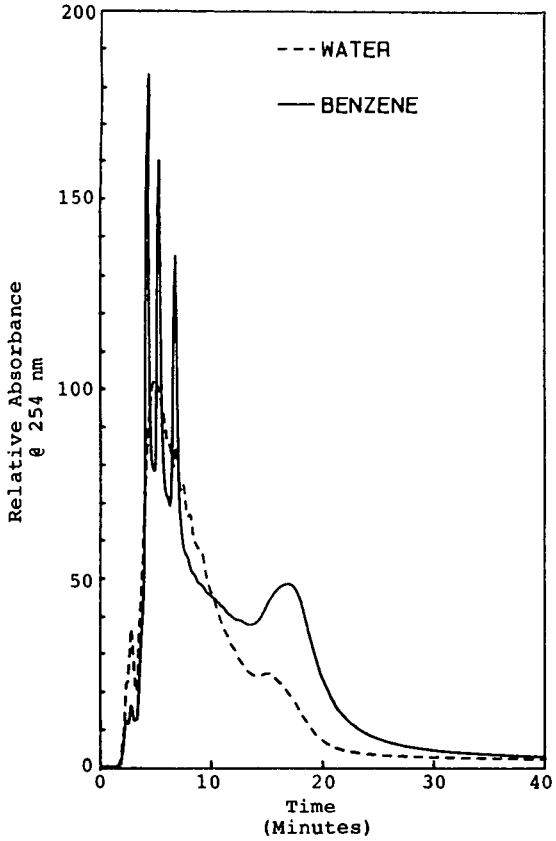

Figure 5. Chromatograms of Low Pressure Products from Staged Pressure Solubilization of Illinois No.6 Coal.

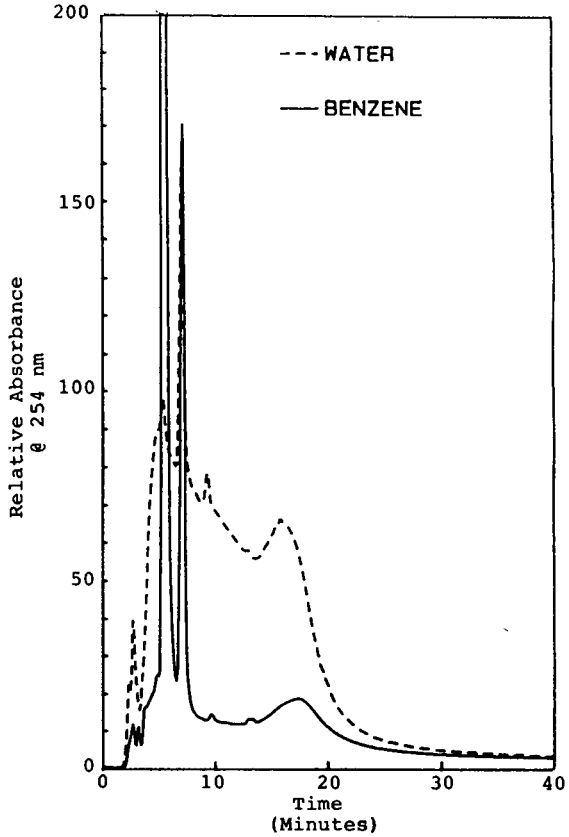

Figure 6. Chromatograms of High Pressure Products from Staged Pressure Solubilization of Illinois No.6 Coal.