

THE ROLE OF THERMAL CHEMICAL PROCESSES IN SUPERCRITICAL GAS EXTRACTION OF COAL

Thomas G. Squires*, Tetsuo Aida, Yu-Ying Chen, and Barbara F. Smith

Energy & Mineral Resources Research Institute
Iowa State University, Ames, Iowa 50011

INTRODUCTION

Many factors which limit the chemical conversion of insoluble, solid coal to soluble, smaller fragments are due to phenomena which are not routinely encountered in the chemical laboratory or in the chemical processing industry. In the first place, it often appears that the rate and extent of coal conversion is controlled by accessibility to reaction sites rather than by reaction energetics¹. Secondly, the chemical objective, depolymerization, is exactly the reverse of that of a major segment of the present chemical processing industry. While these observations are obvious, the implications for coal conversion are far reaching; and much of our recent research effort has focused on understanding the effects of these phenomena. Problems which limit the efficiency of current coal conversion processes are not necessarily amenable to solution using conventional solvents, standard reactor configurations, or other established chemical conversion concepts.

Currently, we are investigating supercritical fluids (SCF's) as solvents for extracting and chemically converting coal. The advantages of SCF's as solvents for coal extraction have been recognized for some time². Near the critical temperature, the solvent power, viscosity, and diffusion rates can be manipulated over wide ranges by relatively small changes in pressure or temperature³. Thus, SCF's have been touted as solvents which, by suitable manipulation of temperature and pressure, enhance both reagent access to interior reaction sites in coal and product removal from the microporous coal residuum. One of the primary objectives of the present research is to compare the efficacy of subcritical and supercritical solvents in this mass transport function.

In practice, most supercritical gas extractions (SGE's) of coal have been conducted at temperatures above 325°C⁴. While some investigators have acknowledged a thermal chemical contribution to these extractions⁵, others have reasoned that thermal processes are unimportant at 350°C⁶. Still others have sought to elucidate the thermal behavior of coal by investigating model compounds⁷. In any case, the thermal chemical component in SGE of coal has not been experimentally defined, and this is another important objective of our investigations.

Thermal conversion of coal to smaller fragments is best interpreted on the basis of three types of chemical processes. Primary reactions involving thermolysis of weak bonds generate smaller reactive fragments in conjunction with reactive sites within the coal residua. These reactive intermediates can then undergo two kinds of secondary reactions: stabilization to produce tar and light gases; and retrogressive recombination of the fragments and residua to produce refractory char. Obviously maximum liquid yields are obtained under conditions which promote stabilization reactions and inhibit retrogressive char-forming reactions.

In some liquefaction processes, the former objective has been accomplished by introducing a hydrogen donor stabilizing reagent into the conversion mixture^{8,9}. Other processes have sought to achieve the latter objective by heating the reaction mixture rapidly and limiting the reaction time⁹. While this approach has been partially effective, it does not address the root of the problem: intimate contact between reactive fragments and residua at elevated temperature for long periods.

Rapid vacuum pyrolysis of a thin bed of coal effectively minimizes retrogressive char-forming reactions by continuous removal of volatile tar fragments as they are generated¹⁰. Given the effectiveness of this approach to inhibiting char forming reactions, it is surprising that the concept has not been applied to other thermal liquefaction processes. Yet virtually all of these processes operate in the batch mode. Even those processes which purport to operate in a flow mode are not designed to quickly separate reactive coal fragments from reactive coal residua. Moreover, researchers in this area have directed little or no effort to exploring such ideas. Most investigators continue to employ batch mode techniques in which coal fragments and residua are mixed at elevated temperatures for substantial periods. Under such conditions, it is impossible to distinguish between primary and secondary products in a system as complex as coal. Therefore, a third important objective of this research is to develop a flow mode reactor system capable of rapidly separating coal fragments from residua and to investigate primary and secondary reactions in the chemical conversions of coal.

EXPERIMENTAL

General

Illinois #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. Weight loss, extent of devolatilization, and extraction yields are reported on a raw coal basis.

Vacuum Pyrolysis

Vacuum pyrolysis experiments were conducted with a constant voltage heated grid apparatus¹¹ surrounded by a water jacketed condenser for collecting the tar and equipped with a liquid nitrogen cold finger condenser for collecting the light gases. In a typical experiment, 200 mg of Illinois #6 coal and a Chromel-Alumel microthermocouple were placed in the grid, and the system pressure was adjusted to 0.25 mm by bleeding He into the system. This slow He purge was maintained throughout the run, and the pressure and temperature were continuously monitored. The grid was then heated at an initial rate of approximately 200°C/min. to the programmed final temperature where it was maintained for 60 minutes. The extent of devolatilization was determined by measuring the weight of char remaining in the grid.

Coal Extraction with Methanol

Flow mode extraction of coal with methanol was carried out in the an apparatus described previously¹². A booster heating tape was wrapped around the reactor to provide rapid heat up capability. Coal (ca. 500 mg.) was placed in the tubular reactor, and the ends were sealed with 2 micron stainless steel frits. The free volume in the loaded reactor was found to be 0.70 ml. After connecting the reactor and purging the entire system with nitrogen, the apparatus was filled with methanol and pressurized. In rapid sequence, the reactor was inserted into the preheated furnace; and, as flow through the reactor was initiated, the reactor booster heater

was switched on. The heating profile for this reactor was approximately equivalent to that of the heated grid. A stable final temperature was attained in less than 5 minutes, and the booster heater was switched off. Throughout the extraction constant temperature, pressure, and flow rate (0.8-1.0 ml/min.) were maintained. After extracting for two hours, the system was purged with N_2 and cooled to room temperature. The reactor residuum was removed, dried in a vacuum oven at 110°C overnight, and weighed to determine the extent of extraction.

Solvent Extraction of Coals and Residua

Coal (ca. 500 mg) or residuum (ca. 100 mg) was mixed with 10 ml of pyridine and ultrasonically irradiated under ambient conditions for 30 minutes. The resulting mixture was filtered with suction through a 3 micron Millipore filter, and the solid was washed with an additional 10 ml of solvent. After drying overnight at 110°C under vacuum, the solid was weighed to determine the extent of extraction.

RESULTS AND DISCUSSIONS

The primary objectives of our investigations of the SGE of coal are the following:

- (1) To differentiate the extractive and pyrolytic components of this process;
- (2) To explore flow mode concepts as a mean of inhibiting secondary reactions by rapidly removing products from the reaction zone;
- (3) To compare the effectiveness of subcritical and supercritical solvents in the extraction of coal.

Progress toward the first two objectives has been achieved through two parallel series of experiments.

Extractive and Pyrolytic Phenomena

In the first series of experiments, weight loss of an Illinois #6 coal was determined as a function of the final coal bed temperature using a heated grid vacuum pyrolyzer. The recorded bed temperature was up to 50°C less than the blank grid temperature measured under the same conditions. While the experimental difficulty of measuring the actual bed temperature is recognized¹⁰, we have reported the bed temperature because the grid temperature is assuredly attenuated by heat transfer inefficiencies and because it is the bed temperature that actually effects the coal pyrolysis. The room temperature pyridine solubility of each of the grid residua was also determined. Results from these experiments are reported in Table 1 and plotted in Figure 1.

The occurrence of two types of thermal processes are revealed by Figure 1. The first process, which occurs at a final temperature of approximately 200°C, apparently alters the solid coal structure in a way that reduces its pyridine extractibility. While this may be a physical alteration, one chemical change which would explain this is the formation of crosslinks. Whatever the cause, heating and maintaining the coal at 200°C decreases its ambient solubility in pyridine and, presumably, other solvents as well.

The onset of the second process, devolatilization, is clearly evident at 300 to 350°C. Such behavior has consistently been interpreted as resulting from thermalolysis of weak bonds in coal^{10,13}. An acceleration of these pyrolytic processes, as manifested by more extensive devolatilization, is evident at higher temperatures, e.g. 32% weight loss at 528°C. It is important to note that residua which derive from final temperatures above 350°C are minimally soluble in pyridine.

A parallel series of experiments were conducted using a short residence time flow mode reactor. Flow rates were adjusted so that methanol residence times in

the reactor were less than one minute, and experiments were conducted to determine the effect of extraction time on SGE yields at 320°C and 3000 psi. These results, which are included in Table 2 (Runs 8 and 9), establish that over 90% of the ultimate extraction has been accomplished within 30 minutes under these conditions. On this basis, extraction times of two hours (corresponding to a total extraction volume of 100 to 120 ml) were used for the remainder of the extractions. The two hour extraction yields (at 3000 psi) were then determined as a function of temperature; and these results and the pyridine extractibility of the residua are included in Table 2 and plotted in Figure 2.

The weight loss-temperature profile from these experiments, shown in Figure 2, is remarkably similar to the profile generated by the heated grid experiments. By 200°C a chemical or physical change has occurred which depresses the total extractibility of the coal, and the onset of extensive pyrolysis is again evident above 325°C. The coincidence of these thermal phenomena in the heated grid pyrolyses and the methanol flow mode extraction of Illinois #6 coal is clear evidence that thermal decomposition processes cannot be ignored in SGE experiments conducted above 325°C. These results are in substantial agreement with those of Slomka and Rutkowski in their investigations of toluene ($T_c=320^\circ\text{C}$) flow mode extractibility of an equivalent Polish coal¹⁴. By determining the extraction yield as a function of time and temperature, they found these extractions to be controlled by two distinct energies of activation. Between 200 and 320°C, E_a was about 3kJ/mole which is consistent with the operation of diffusion controlled, physical dissolution process. At higher temperatures (350-410°C), E_a was found to be 101 kJ/mole, and this can be taken as clear evidence for the operation of chemical processes.

In fact when considered in conjunction with the investigations of Slomak and Rutkowski, our experiments provide compelling evidence that, above 350°C, the SGE of coal is controlled by thermal decomposition processes rather than physical extraction processes. In light of this finding, it is surprising to discover a correlation between conversion yields and Hildebrand solubility parameters (δ) for the SGE of coal above 325°C^{4,5}. Yields should be influenced by the chemical nature of the solvent in this temperature range, and any correlation with δ must be coincidental or due to secondary effects.

Flow Mode vs. Batch Mode Extraction

In the flow mode extraction of coal with methanol utilized for these studies, the coal extract, once generated, is in contact with the residua for less than a minute. Although this time is long by molecular standards, it is short compared to contact times (45-100 minutes) in batch extraction of coal. While these considerations are not important below 325°C, they can certainly determine the efficiency and extent of SGE at higher temperatures. At 400°C, one can hardly expect a coal-like fragment to be chemically inert under conditions which cause coal to react or during various encounters with other fragments, residua, and reactive intermediates derived from these species.

The efficacy of flow mode extraction in minimizing secondary, char-forming reactions is demonstrated by the experiments reported here. Previous investigators⁴ have reported maximum methanol extraction yields of 19% at 450°C. In the present investigation a yield of 31% was obtained, indicating that, in the batch mode, at least one-third of the liquid product is lost to char.

Finally, other investigators⁵, using batch mode extraction, have been able to extract up to 12% of the extraction residua with pyridine. Presumably, this is due to extraction inefficiencies and to redeposition of solubilized material. Our results clearly show that this residual pyridine soluble material can be removed using flow mode extraction.

ACKNOWLEDGEMENT

This material was prepared with the support of the U. S. Department of Energy, Grant No. DE-FG22-82PC50786. 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. Larsen, J. W.; Green, T. K.; Choudhury, P.; Kuemmerle, E. W. In "Coal Structure"; Am. Chem. Soc. Adv. Chem. Ser. 1981, 192, 277.
2. Paul, P. F. M.; Wise, W. S. "The Principles of Gas Extraction;" Mills and Boon: London, 1971.
3. Schneider, G. M. Angew. Chem., Int. Ed. Engl. 1978, 17, 716.
4. Jezko, J.; Gray, D.; Kershaw, J. R. Fuel Processing Tech. 1982, 5, 229 and references cited therein.
5. Blessing, J. E.; Ross, D. S. In "The Organic Chemistry of Coal"; Am. Chem. Soc. Symp. Ser. 1978, 71, 171.
6. Larsen, J. W.; Yurum, Y.; Sams, T. L. Fuel 1983, 62, 476.
7. a. Poutsma, M. L. Fuel 1980, 59, 335.
b. Hung, M.-H.; Stock, L. M. Fuel 1982, 61, 1161.
c. Brucker, R.; Kolling, G. Brennstoff-Chemie 1965, 46, 41.
d. Schlosberg, R. H.; Ashe, T. R.; Pancirov, R. J.; Donaldson, M. Fuel 1981, 60, 155.
8. Gorin, E. In "Chemistry of Coal Utilization. Second Supplementary Volume"; Elliott, M. A., Ed., Wiley-Interscience: New York, 1981; Chapter 27.
9. Whitehurst, D. D. "Coal Liquefaction Fundamentals"; Symp. Ser. No. 139, Am. Chem. Soc.: Washington, DC, 1980.
10. Freihaut, J. D.; Zabielski, M. F.; Seery, D. J. Nineteenth Symposium (International) on Combustion, The Combustion Institute 1982, p. 1159 and references cited therein.
11. Anthony, D. B.; Howard, J. B.; Meissner, H. P.; Hottel, H. C. Rev. Sci. Instrum. 1974, 45, 992.
12. Koll, P.; Metzger, J. Angew. Chem., Int. Ed. Engl. 1978, 17, 754.
13. Solomon, P. R.; et. al. Fuel 1981, 60, 342.
14. Slomka, B.; Rutkowski, A. Fuel Processing Tech. 1982, 5, 247.

TABLE 1. THERMAL CONVERSION OF ILLINOIS #6 COAL BY HEATED GRID VACUUM PYROLYSIS

Run No.	Final Bed Temperature °C	Weight Loss: ^a RVP ^b %	Weight Loss: ^a PyE ^c %	Weight Loss: ^a Total %
Coal	-	-	10.2	-
1	191	0.2	8.6	8.8
2	248	0.8	6.0	6.8
3	326	6.1	-	-
4	337	5.7	2.3	8.0
5	448	19.7	1.0	20.6
6	448	21.1	0.9	22.0
7	528	32.3	0.7	33.0

^aWeight loss based on raw coal.

^bRapid vacuum pyrolysis.

^cPyridine extractibles.

TABLE 2. FLOW MODE EXTRACTION OF ILLINOIS #6 COAL WITH METHANOL

Run No.	Extraction Temperature °C	Extraction Pressure psi	Weight Loss: ^a FME ^b %	Weight Loss: ^a PyE ^c %	Weight Loss: ^a Total %
1	25	3000	2.6	9.7	12.3
2	100	3000	4.0	7.8	11.8
3	220	3000	7.4	0.6	8.0
4	270	1325	5.6	-	-
5	270	2000	8.3	-	-
6	270	3000	12.0	(0.9) ^d	12.0
7	270	4000	12.3	-	-
8	320	3000	12.0 ^e	-	-
9	320	3000	13.0	1.1	14.1
10	370	3000	22.0	-	-
11	420	3000	31.0	0.9	31.9

^aWeight loss based on raw coal.

^bFlow mode extraction.

^cPyridine extractibles.

^dWeight increase due to pyridine retention by the residuum.

^eExtraction time 30 minutes.

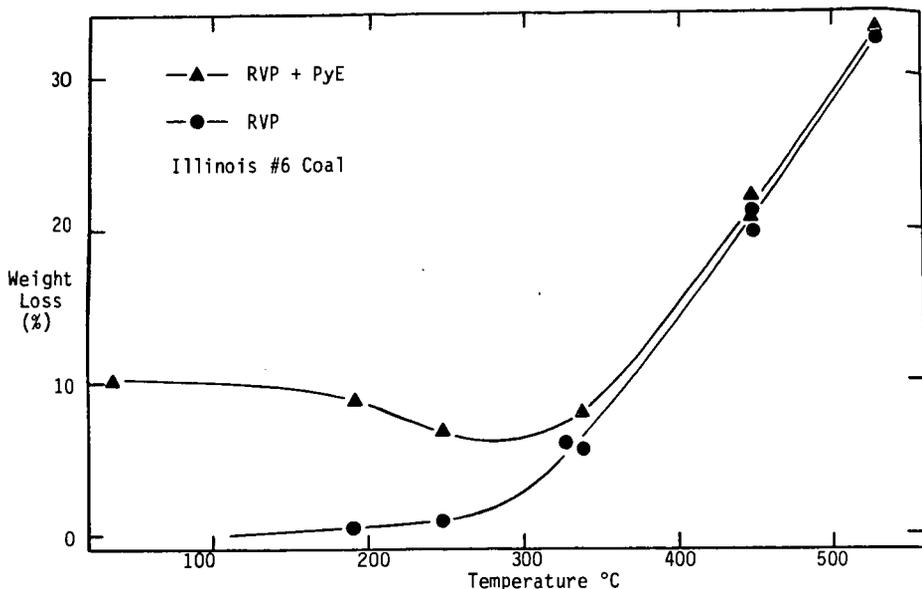


FIGURE 1. Effect of Final Temperature in Rapid Vacuum Pyrolysis

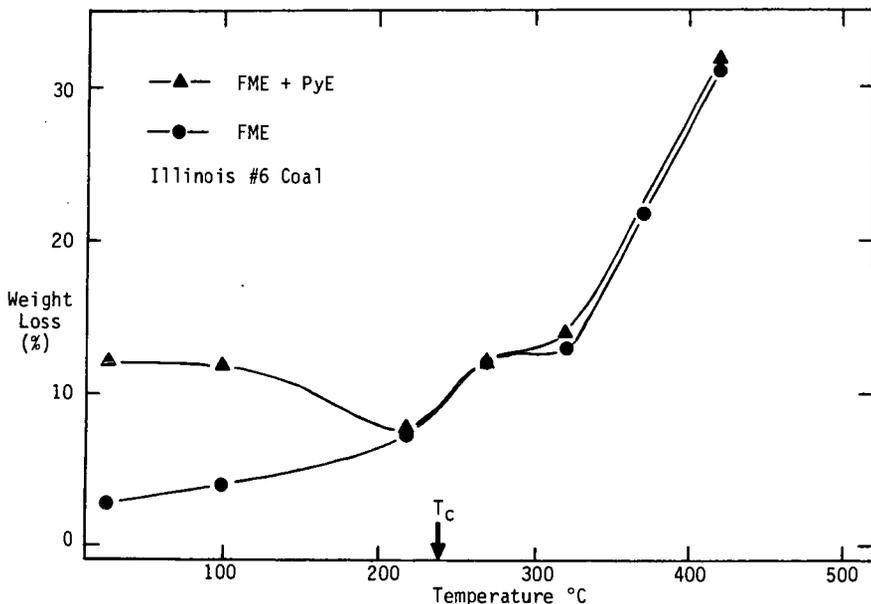


FIGURE 2. Effect of Final Temperature in Methanol Flow Mode Extraction