

LOW TEMPERATURE ISOTHERMAL PYROLYSIS OF ILLINOIS NO. 6 AND WYODAK COAL

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INTRODUCTION

Despite what appear to be sufficient supplies of petroleum and natural gas to meet current U.S. energy needs, it is almost certain that future U.S. energy demands will be met in part by synthetic fuels produced from solid fossil fuels. The vast U.S. reserves of coal, in particular, have and will continue to receive considerable attention as a source of synthetic fuels. There are, however, certain fundamental constraints that limit the efficient processing and conversion of coal to synthetic fuels. Besides their chemical and physical heterogeneity, coals have highly aromatic chemical compositions. The high carbon aromaticity means that coals are hydrogen-deficient and as such do not readily convert to liquid and gaseous products. Consequently, innovative approaches are required to efficiently convert these hydrogen deficient materials to useful synthetic fuels.

Most coal conversion processes require thermal processing; therefore, pyrolysis is an important initial step in all coal utilization and conversion processes. Although coal pyrolysis has been studied extensively for several decades (1-4) it continues to be an active area of coal research. In part, this is a result of coal researchers' awareness of the need to understand pyrolysis in relationship to the basic structure of coal.

As a first step towards a systematic approach to understanding the relationship between coal structure and its conversion during pyrolysis, isothermal decomposition studies in the temperature range of 375°C to 425°C have been conducted on Illinois No. 6 and Wyodak coals. While prevailing attitudes favor the use of nonisothermal techniques to study coal pyrolysis, these techniques do not easily allow direct measurement of all the reaction products. Consequently, detailed chemical analyses of the reaction products are usually absent in such studies. In particular, intermediate states such as the metaplast are seldom measured directly.

With isothermal methods, it is possible to measure all the products of thermal decomposition including soluble intermediates. In addition to obtaining the overall weight conversions to products, detailed chemical and spectroscopic analyses can be obtained for each product class. For example, elemental analyses of all the products provide detailed carbon, hydrogen, sulfur, nitrogen, and oxygen balances. Solid and liquid state ^{13}C NMR measurements can be used to determine the partitioning of aliphatic and aromatic carbon in the products.

EXPERIMENTAL

Coal Samples

Isothermal pyrolysis experiments were conducted on Illinois No. 6 high volatile bituminous and on Wyodak subbituminous coal samples. Both coals were crushed and screened to obtain a 20/45 mesh particle size distribution. The initial crushed sample was thoroughly mixed and successively riffled to obtain aliquots of approximately 22 grams. Pyrolysis studies were conducted on samples taken from these aliquots. Ultimate and proximate analyses and carbon aromaticities of the two coals are given in Table 1.

Table 1. Analyses of Coal Samples

	Illinois No. 6	Wyodak
Proximate (% mf)		
Ash	8.1	8.0
Volatile Matter	39.0	47.0
Fixed Carbon	52.9	45.0
Ultimate (% mf)		
Hydrogen	5.3	5.5
Carbon	74.0	67.5
Nitrogen	1.0	0.8
Sulfur	3.4	0.7
Oxygen (diff)	8.3	17.5
Ash	8.1	8.0
Carbon Aromaticity	0.673	0.657

Pyrolysis Reactor System

The isothermal pyrolysis studies were carried out in a heated sand-bath reactor system described in detail elsewhere (5). In this system, nominally 10- to 20-gram samples were heated to reaction temperature by quickly immersing a tube reactor containing the coal sample into a preheated fluidized sand-bath. Typically, the coal sample reached the predetermined reaction temperature in less than 2 minutes. The reaction was quenched by removing the reactor from the sand bath and spraying liquid CO₂ on its surface. A helium sweep gas flow rate of 30 cc/min was used to remove the products from the reaction zone. The liquid product was collected in a dry-ice trap. Gaseous products were analyzed by gas chromatography, either by collecting the total gaseous product in an evacuated vessel or by analyzing the product gas on-line.

Material balances were calculated by measuring the weight change of the coal sample, the weight of collected liquid, the volume of collected water, and the weight of each gas component. The gas evolution curves were integrated, taking into account analytical system delays and backmixing, to calculate the total amount of gas evolved during each experiment. The reactor material balance closures were typically 100.2 ± 0.7%.

Product Analyses

Elemental analyses (CHN and S) were obtained on the solid and liquid reaction products using standard instrumental techniques. Molecular weights were determined by vapor phase osmometry, using pyridine or methylene chloride as a solvent. Liquid state ¹³C NMR measurements were made on a Varian CFT-20 or a JEOL 270 MHz NMR spectrometer. Solid state ¹³C NMR measurements of the solid products were obtained at the NSF Regional NMR Center at Colorado State University. Gas analyses were obtained on a Hewlett Packard 5830 gas chromatograph modified to obtain complete gas analyses as frequently as every 3 minutes.

RESULTS AND DISCUSSION

Soluble Intermediate

One objective of this work was to investigate the transient nature of intermediate products that are formed during pyrolysis. Generally, global models of coal pyrolysis involve some form of intermediate (6-9). The simplest of these models can be written (9),



The intermediate is often referred to as "thermobitumen" (10) or "metaplast" (6). Thermobitumen is the primary tar or bitumen formed during the initial stages of pyrolysis and acts as a plasticizer for the coal. Metaplast refers to coal which has been transformed into a fluid mass via depolymerization reactions, i.e., a metastable, plastic state. Neither material is defined in terms of solubility in a given solvent as, for example, the term bitumen is in oil shale pyrolysis. In fact, van Krevelen et al. (11) preferred the term metaplast to avoid the connotation that thermobitumen is a completely soluble material in a common petroleum solvent. Nevertheless, the properties and kinetic behavior of the soluble portion of the intermediate are known to affect the plasticity and conversion behavior of coals (12,13).

In this work, the residue coal from each isothermal pyrolysis experiment was extracted with chloroform to obtain information about the chloroform soluble portion of the intermediate. Chloroform was chosen over other commonly used solvents, such as pyridine, because it does not appreciably dissolve the raw coal and gives fairly high yields of soluble products from pyrolyzed caking coals (12).

Only small amounts of material were extractable with chloroform at any stage of pyrolysis for either coal (Figures 1 and 2). In the context of the simple model (Equation 1), the data in Figures 1 and 2 illustrate that either 1) $k_2 \gg k_1$, and the soluble material is not retained long enough to plasticize the coal or 2) significant devolatilization occurs directly from the raw coal, without involving an intermediate state. The latter has been suggested to account for the increase in volatile matter with pyrolysis temperature, as well as development of fluidity in coal (9). We have observed a similar behavior of soluble intermediates during isothermal pyrolysis of New Albany shale from Kentucky, and have concluded that the greater the carbon aromaticity of the source material, the greater is the direct conversion of source material to products (primarily residue) (14).

Properties of Residue Products

Global models of coal pyrolysis, such as that depicted by Equation 1, do not incorporate any components of coal structure, although the ultimate yields of pyrolysis products are determined to a large degree by the carbon structure of the raw coal. With isothermal pyrolysis methods and solid state ^{13}C NMR techniques, it is now possible to measure changes that occur in the carbon structure of coal as a function of time and temperature. In addition, by obtaining the ultimate and proximate analyses of the residue coals, it is possible to monitor these changes quantitatively on a mass basis. These data were collected during the 425°C experiments for Wyodak and Illinois No. 6 coals (Figure 3).

The data in Figure 3 confirm that the aliphatic carbon weight loss behavior is similar to that of the total carbon. Conversely, the aromatic carbon remains relatively constant with time. Chou et al. (15) have observed a similar behavior of chars produced from flash pyrolysis of Illinois No. 5 coal at charring temperatures from 300°C to 800°C. These data support the theory that coal devolatilization

involves primarily the breaking of aliphatic carbon bonds and that the aromatic carbon tends to remain in the residue (16).

Total Aromatic Carbon in Products

During pyrolysis of fossil fuels, a net increase always occurs in the amount of aromatic carbon in the products (tar plus residue) over that in the starting material. This increase results from aromatization reactions of aliphatic moieties and the associated release of light, high hydrogen-content aliphatic species. Aromatization of hydroaromatic structures, such as tetralin, is a likely mechanism for contributing to the increase in aromatic carbon.

The extent of aromatization during pyrolysis can be determined by combining solid and liquid ^{13}C NMR measurements and the carbon mass balance data (Figures 4 and 5). For some experiments NMR carbon aromaticity and/or total organic carbon measurements were not obtained because insufficient quantities of tars were produced. In these cases the amount of aromatic carbon in the tar was estimated using the weight percent of produced tar and the average values of organic carbon and/or carbon aromaticities from other experiments at the same temperature. These data are denoted by the symbol θ (Figures 4 and 5). The increases in aromatic carbon content for the Illinois No. 6 and Wyodak coals are about 18% and 10%. The reason for the low values is that only about 10% of the raw coals was converted to tars at the longest time (480 min) and highest temperature (425°C) studied.

An interesting feature of the data is that the net production of aromatic carbon approaches its limiting value during the early stages of pyrolysis (Figures 4 and 5). For example, at 425°C the net production of aromatic carbon for the Illinois No. 6 coal has reached 95% of the limiting value within 2 minutes (Figure 4c). Similar behavior is noted for the Wyodak coal. Thus, aromatization of the aliphatic moieties appears to be a very facile chemical reaction; however, it is not possible from these data to determine to what extent these reactions occur directly in the solid coal or in the produced tars.

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DISCLAIMER

Mention of specific brand names or models of equipment is for information only and does not imply endorsement of any particular brand.

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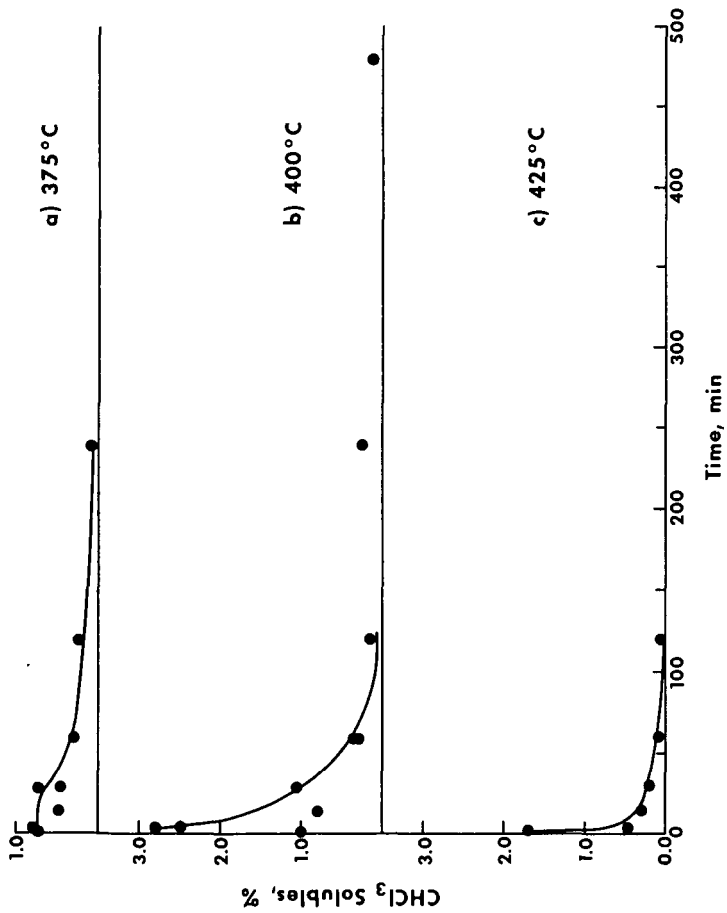


Figure 1. Chloroform-Extractable Material in Illinois No. 6 Coal vs. Time at a) 375°C, b) 400°C, and c) 425°C.

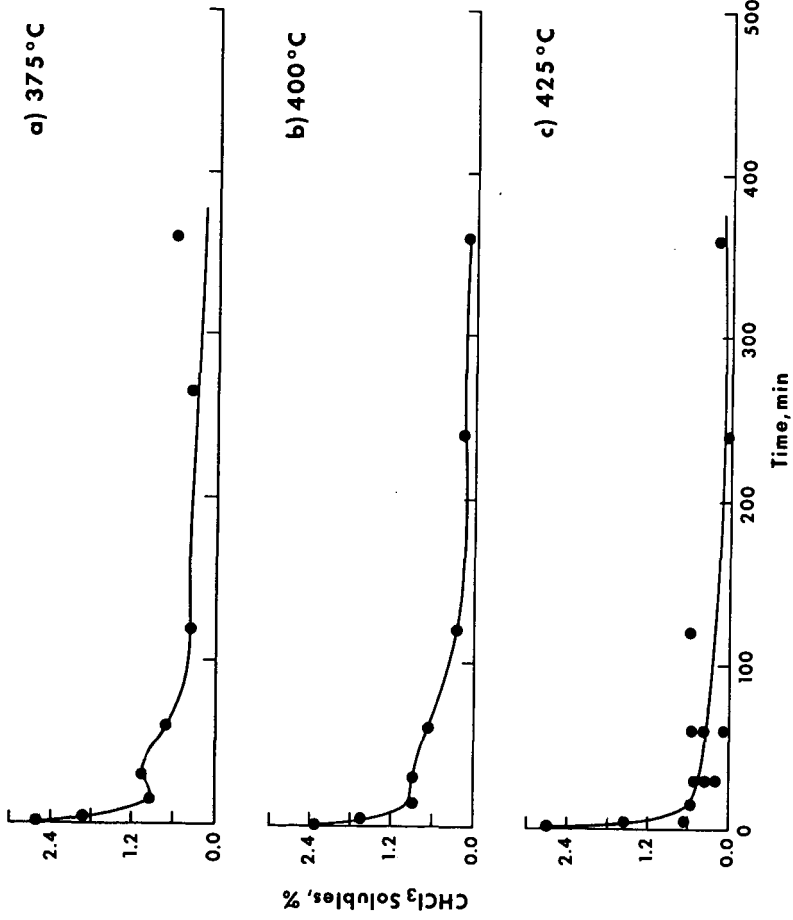


Figure 2. Chloroform-Extractable Material in Myodak Coal vs. Time at a) 375°C, b) 400°C, and c) 425°C.

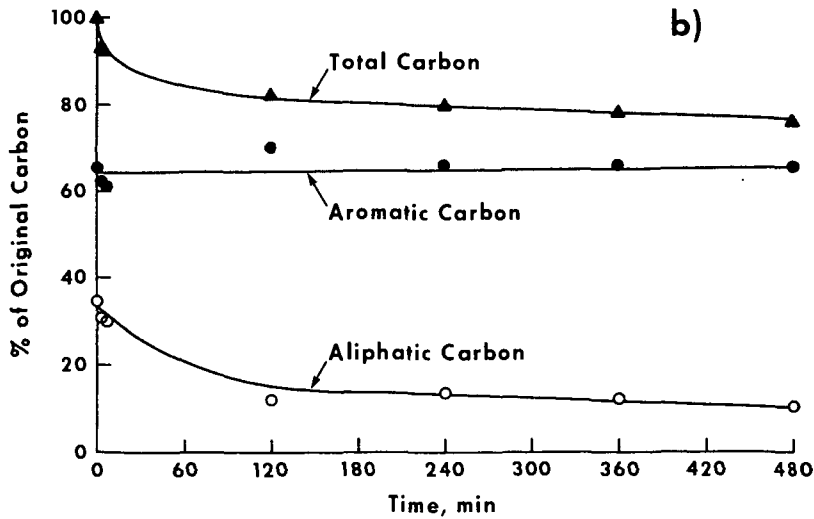
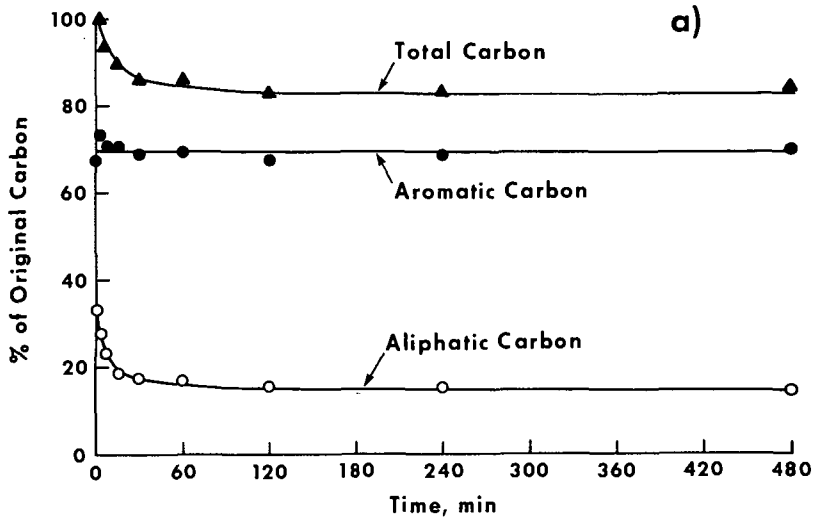


Figure 3. Distribution of Carbon Types vs. Time at 425°C for
 a) Illinois No. 6 and b) Wyodak Coal.

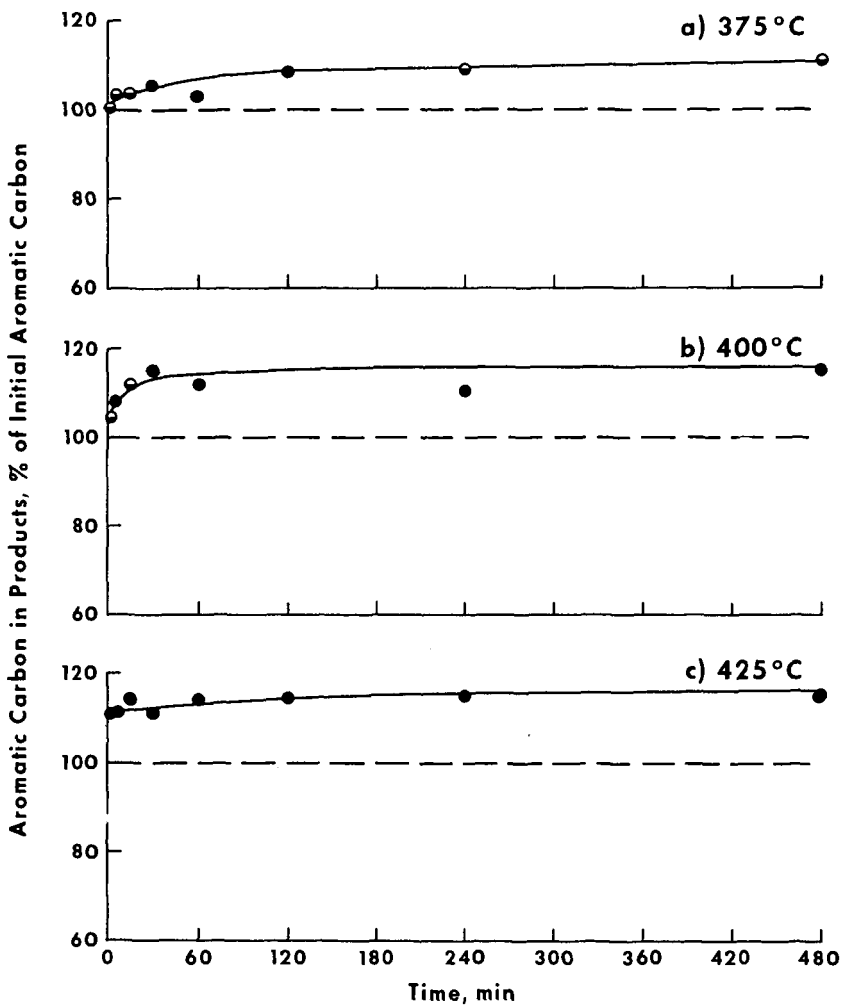


Figure 4. Total Aromatic Carbon in Products vs. Time for Illinois No. 6 Coal at a) 375°C, b) 400°C, and c) 425°C.

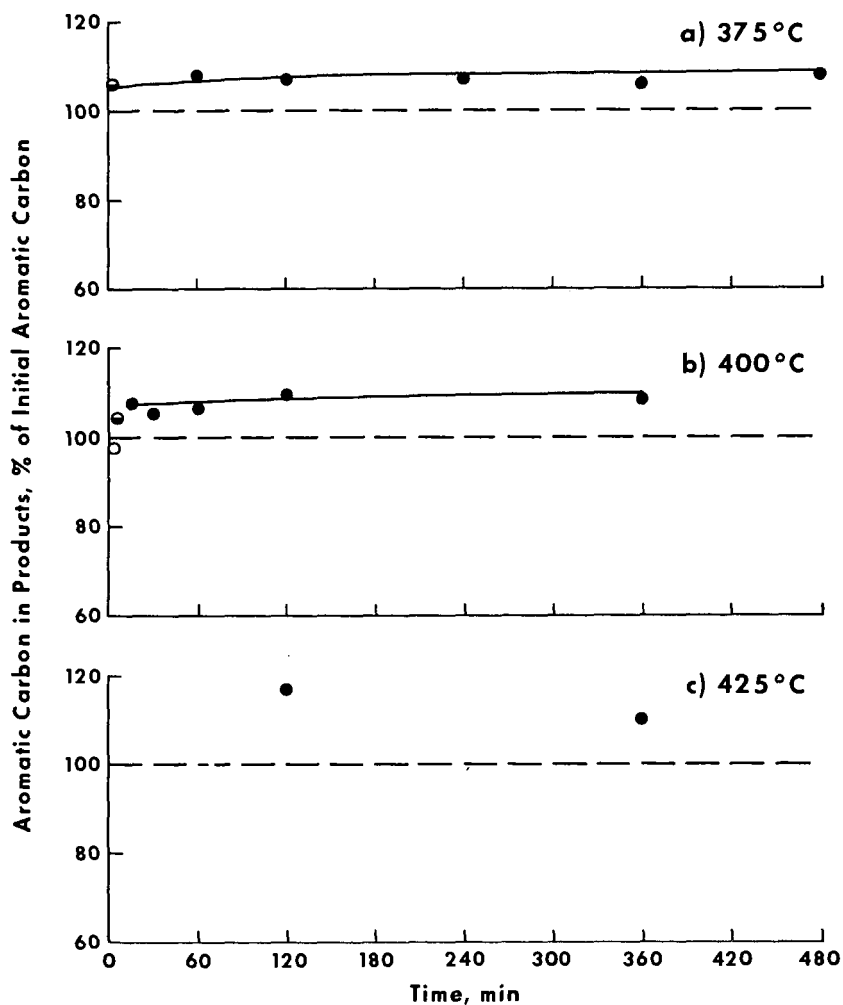


Figure 5. Total Aromatic Carbon in Products vs. Time for Myodak Coal at a) 375°C, b) 400°C, and c) 425°C.