

**GASIFICATION OF CHARS PRODUCED UNDER  
SIMULATED in situ PROCESSING CONDITIONS**

**Annual Report for the Period  
October 1975—September 1976**

**by**

**J. Fischer, J. E. Young, R. N. Lo,  
D. C. Bowyer, J. E. Johnson,  
and A. A. Jonke**

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9700 South Cass Avenue  
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GASIFICATION OF CHARS PRODUCED UNDER  
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ABSTRACT

This work, which is part of the ANL energy program for ERDA, is directed toward support studies for the national endeavor on *in situ* coal gasification. The objective of this work is to determine the reaction-controlling variables and reaction kinetics for gasification of chars resulting when coal is pyrolyzed in underground gasification. The reactions to be studied include steam-char, CO<sub>2</sub>-char, H<sub>2</sub>-char, and the water gas shift reaction.

The chars studied were prepared from subbituminous coals from the Wyodak-Anderson and Hanna seams in Wyoming. Physical characteristics defined by surface area measurements and scanning electron microscopy are discussed. The characteristics of char prepared by pyrolyzing coal under simulated underground gasification conditions were appreciably different from those of a char prepared in some other way. The effects of these differences on the reactivity of the resulting char are discussed.

Kinetic data are reported for the reaction of steam with these chars. Rate expressions are derived describing the char reaction rate as a function of steam partial pressure, carbon consumption, and temperature. Also discussed are the effects on the kinetics of the reactions studied of catalysis of the water gas shift reaction by mineral matter present in the coal. In addition, some aspects of the hydrogen-char reaction in the range of temperatures and partial pressures of hydrogen and steam expected in *in situ* gasification are described.

SUMMARY

This work has the objectives of providing engineering data for process control and resource evaluation for underground coal gasification. This is to be accomplished by providing data for gasification of chars under simulated *in situ* processing conditions. The coal samples studied are representative of coal at sites where field tests either are currently being conducted or are under consideration. Chars for gasification are prepared by pyrolyzing the coal under conditions characteristic of the *in situ* gasification processes.

Kinetics studies of char gasification are carried out in a differential packed-bed reactor. The product gases are analyzed for hydrogen, methane, CO, and CO<sub>2</sub> by gas chromatography. The coals are pyrolyzed in the reactor immediately prior to gasification in order to simulate the conditions occurring underground.

The reactions of steam with chars prepared from Wyodak and Hanna coals have been studied in the temperature range of 600–750°C, and at steam partial pressures of 0.26 MPa (2.6 atm) to 0.7 MPa (7.0 atm). The data indicates that the reaction is first order with respect to carbon and 1.2–1.3 order with respect to steam. The apparent activation energies for the reactions indicate that the micropore structure of the char imposes limitation on the reactions due to restricted mobility of the reactants. The Wyodak char was found to be approximately twice as reactive as the Hanna char.

Surface area measurements and scanning electron microscopy of the chars indicate that the lower reactivity of the Hanna char is at least partially due to reduced surface area and a finer micropore structure than is found for Wyodak char.

The product gas composition indicates that the water gas shift reaction approaches thermodynamic equilibrium under these conditions and is probably catalyzed by the mineral matter present in the char. In addition, the product gases contain methane throughout the char-steam reaction, indicating that hydrogen is reacting with the carbon in the char. Preliminary results suggest that the presence of steam enhances the formation of methane.

## INTRODUCTION

Current and predicted future shortages of energy in this country have led to increased effort to develop processes for the underground conversion of coal to cleaner fuels or petrochemical feedstocks. The concept of *in situ* coal gasification has been investigated intermittently in the U.S.A. and European countries since the early part of this century. Extensive testing of the concept has been carried out in the U.S.S.R. However, underground gasification development has been interrupted in the past either by war or by alleviation of the need for gasification as a result of the discovery of extensive reserves of natural gas as in the case of the Soviet Union. The increased interest in underground gasification in this country can be attributed to the shortage of gaseous fuels and to a number of potential advantages:

1. Recent cost evaluations indicate that capital expenditure would be lower for underground gasification than the combined cost of strip or deep shaft mining and above-ground conversion to comparable gaseous fuels by Lurgi gasifiers.
2. Less disruption of the environment is caused by *in situ* gasification than by above-ground processing.
3. Coal that cannot be economically mined and utilized above ground could be gasified underground.

4. Personnel would not be subjected to hazards associated with underground mining.
5. Gas produced *in situ* can be used for local power production or as chemical feedstock or can be converted to synthetic pipeline gas.

During gasification of coal underground, three distinct reaction zones can be identified. The first zone involves drying and pyrolysis (devolatilization) of the coal. Following pyrolysis, a portion of the char is gasified by reaction with steam and carbon dioxide. The carbon dioxide is produced in the third zone, which involves combustion of the remaining char by air or oxygen injected into the coal seam. The combustion zone generates the heat for the process, which is carried into the other zones by flow of the hot gaseous products of combustion.

It is very important to develop mathematical models of *in situ* gasification processes. For a model to be useful, it should be capable of describing, with mathematical formulas, the time and spatial dependence of the gasification processes as they occur underground. This understanding is necessary if *in situ* gasification is to be employed to produce a variety of products and is to utilize a variety of coal sources. Petrochemical feedstocks, combined cycle power generation, and pipeline gas production will require product gases of different composition, and each application could make good use of the products of *in situ* gasification. An effective mathematical model can be used to determine how variables such as air rate injection, water infusion and steam partial pressure can be adjusted to tailor the product to the needs of the consumer.

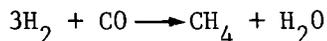
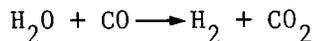
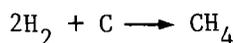
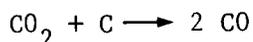
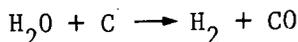
In addition to the prediction of product gas compositions, models permit calculation of efficiencies of the process, prediction of rates of movement of the various reaction zones during *in situ* gasification, specification of optimum process configurations and parameters, and prediction of the effects of processing upsets, e.g., massive subsidence into the reaction zone. Not all of those capabilities have yet been included in current models for *in situ* gasification, but refinements will be made to permit use of the models to meet these goals as well as other goals.

A number of different models of underground gasification have been described in recent literature.<sup>1-6</sup> All of the models are currently limited in utility because of a lack of kinetic data for the primary reactions involving coals of interest for *in situ* gasification. The reaction of carbon with oxygen is very rapid, and differences in the physical and chemical nature of the chars and coals have minor effects on the rates of this reaction. However, chars obtained by *in situ* coal pyrolysis with steam, carbon dioxide, or hydrogen vary in reactivity for different coals and pyrolysis conditions. Little information is available in the literature on these reactions for chars prepared (1) from coals important in underground gasification and (2) under conditions similar to those encountered underground.

Kinetic information used in current mathematical models have been obtained from studies with material and operating conditions unlike those encountered in underground gasification. In their model, Gunn and Whitman<sup>5</sup> used data for pitch coke,<sup>7,8</sup> data which they admit "are probably very inaccurate." Thorsness and Rosza<sup>4</sup> used kinetic data from work on high-pressure hydrogasification of coals and lignites.<sup>9</sup>

The purpose of our work at ANL is to obtain kinetic information that is directly applicable to mathematical models for *in situ* gasification. These studies will allow the important processing variables in underground gasification to be identified. The coals utilized are similar to those used in current field tests or proposed for use in commercial underground gasification. The processing conditions surveyed include those expected to be encountered in *in situ* gasification.

The kinetics of the reaction of oxygen with carbon is not included in our work. This reaction is rapid, and the results obtained in the mathematical models are quite insensitive to errors in the rate constants for this reaction. The reactions being studied in this program include:



Only the first three of the above reactions contribute directly to conversion of char to gaseous products. The final two reactions affect the composition of the product gases and are of considerable economic importance in relation to tailoring the product gas to the needs of various industries which would make use of the end products of *in situ* gasification.

Variables being investigated in this study include total pressure, reaction temperature, coal devolatilization conditions, and partial pressure of steam. Kinetic data to be obtained include rate constants, reaction orders with respect to each of the reactants, and apparent activation energies. These parameters are to be determined for bituminous coal from the Pittsburgh seam and are being determined for subbituminous coals from Wyodak and Hanna seams of Wyoming.

This annual report includes a detailed description of the experimental procedures and analytical techniques as well as still-incomplete data regarding the reaction of steam with chars prepared from the Hanna and Wyodak coals. In addition, some interesting aspects of the reaction of hydrogen with these chars are discussed.

#### EXPERIMENTAL APPARATUS AND PROCEDURES

The kinetic experiments are being carried out in a differential packed-bed reactor system. This reactor design ensures uniform temperatures and partial pressures of reactants throughout the reaction bed and minimizes interference of the reaction with product gases.

A schematic of the reactor system is shown in Fig. 1. Water for steam generation is supplied by a high-pressure, positive displacement, variable rate metering pump. The water supply reservoir consists of a calibrated buret, which is used to measure the quantity of water pumped during a given period of time. The water is pumped through a coiled-tube high-pressure steam generator, which is encased in a split-type furnace. The steam is then blended with additional reactant or carrier gases ( $N_2$ , CO,  $CO_2$ ,  $H_2$ ) prior to entering the reactor. The flow of gas to the reactor is monitored by means of a capillary tube and electronic differential pressure transducer, whose signal is fed to a process controller located on the remote-control console. The process controller drives a pneumatically activated high-pressure throttle valve, which controls the flow of gas. The combined steam and reactor gas flow can be remotely switched to bypass the reactor, either for flow calibration purposes or for standby conditions. An auxiliary nitrogen supply, which serves to rapidly flush the reactor of reactant and product gases, in the event a safety-related shutdown is required, is included in the system.

The reactor vessel (1.6 cm ID x 91 cm long) is constructed of Type 316 stainless steel. The lower half of the reactor is filled with 120-mesh high-purity alumina, above which the char or coal bed (2 to 5 cm in thickness), is placed. Above the char, the balance of the reactor is filled with 8-mesh alumina, which serves as a steam preheater section. The reactor is heated using a three-zone split-type tube furnace with heater sections 15.25, 30.5, and 15.25 cm long. Reactor temperatures are monitored by means of a cluster of three thermocouples situated at the central axis of the reactor.

After leaving the reactor, the product stream is cooled in a high-pressure, water-cooled condenser, and the steam and hydrocarbon (if any) condensates are collected in a separator vessel. A portion of the product gas is then reduced in pressure to 172 kPa (25 psig) and flows to the analytical system. The pressure of the balance of the product gas is lowered to atmospheric by means of a remotely controlled back-pressure regulator. The return gas from the analytical system is combined with the effluent from the back-pressure regulator, and the total gas flow is measured with a wet-test meter.

The product gas from the reactor is analyzed for  $H_2$ , CO,  $CH_4$ , and  $CO_2$  using a Hewlett Packard Model 5830A gas chromatograph equipped with both thermal conductivity detectors and flame ionization detectors. This unit is programmed for (1) automatic operation of the gas sampling valves, (2) automatic switching of the detector signals, and (3) integration of the areas under the peaks resulting from the various gas constituents.

Two chromatographic columns are used. A 91.4-cm (3-ft) long by 3.18-mm (1/8-in.) OD by 2.16-mm (0.085-in.) ID stainless steel column containing 80/100 mesh type 13X Molecular Sieve is used for separating  $H_2$ ,  $CH_4$ , and CO. Carbon dioxide is separated and measured in the second column--a 91.4-cm (3-ft) long by 3.18-mm (1/8-in.) OD by 2.16-mm (0.085-in.) ID stainless steel column containing 80/100 mesh Porapak Q-S. A separate gas sample is injected into each column.

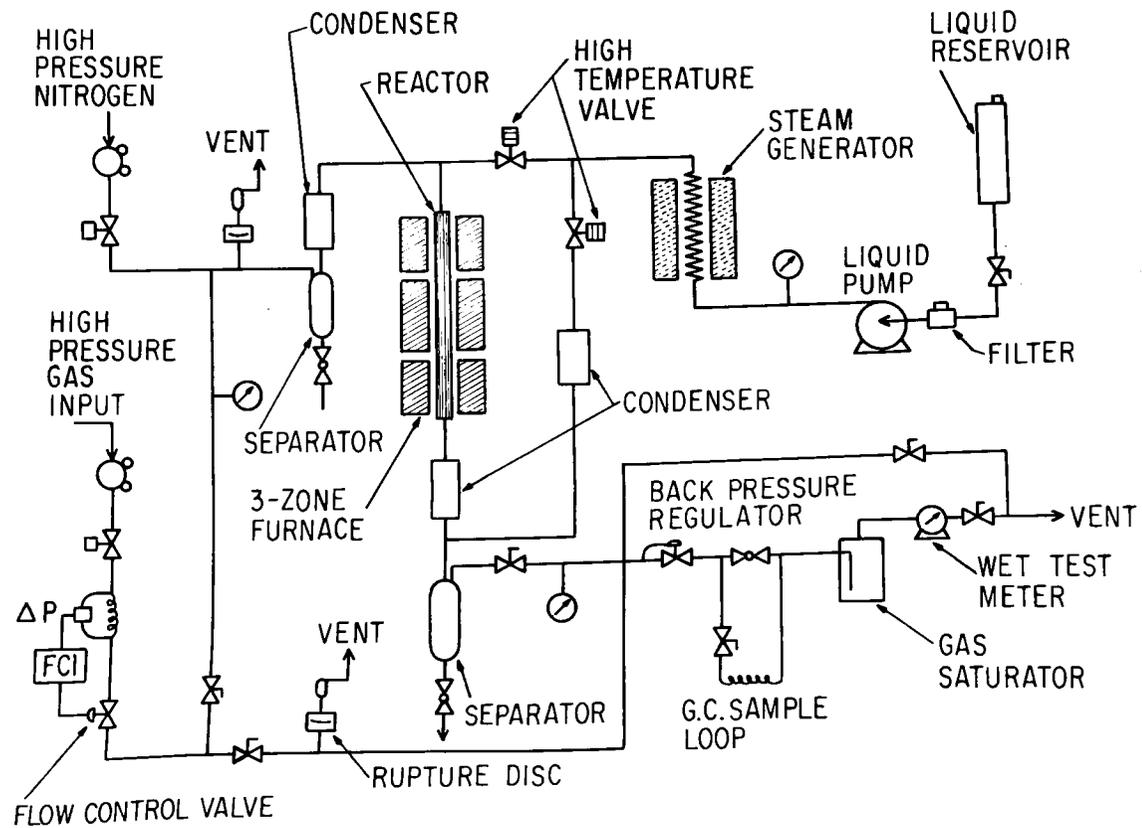


Figure 1. Schematic of Char Gasification System

Contamination of the Molecular Sieve column by  $\text{CO}_2$  is prevented by inserting, upstream from it, an absorber consisting of a 30.5-mm (1-ft) by 4.76-mm (3/16-in.) OD by 3.17 mm (1/8 in.) ID stainless steel tube containing Ascarite. The Ascarite consists of sodium hydroxide on an inert support, and permanently absorbs any acid gases ( $\text{CO}_2$  or  $\text{H}_2\text{S}$ ).

The effluent from the Molecular Sieve column is monitored by means of a thermal conductivity detector (TCD) and a flame ionization detector (FID) placed in series. The TCD is used for detecting hydrogen and  $\text{CO}$ ; the FID is used for detection of methane. The  $\text{CO}_2$  is detected by means of a TCD used in conjunction with the Porapak Q-S column.

Neon, the carrier gas, gives good sensitivity for all components in the product gas stream. A  $0.5\text{-cm}^3$  sample is injected into each column for analysis. The column temperature is  $35^\circ\text{C}$ , detectors are operated at  $100^\circ\text{C}$ , and carrier gas flow through each column is  $30\text{ cm}^3/\text{min}$ . The total time necessary for a complete analysis and data output for the four components is approximately 7.5 min.

All operating temperatures, pressures, and gas flows for the gasification reactor system are monitored by means of a data logging system and are recorded on punched paper tape. In addition, the data output from the gas chromatograph is recorded on punched tape. This permits rapid computer processing of the large amount of data produced.

For a typical gasification experiment, the coal is crushed to  $-4 +12$  mesh and approximately 5 g is placed in the reactor. The coal is then pyrolyzed in nitrogen at a pressure of 0.162 MPa (225 psig) with a flow rate of 1.0–2.5 liters(STP)/min. The coal is pyrolyzed at a heating rate of  $3^\circ\text{C}/\text{min}$ ; the final temperature is that at which the gasification experiment is to be carried out. When the final pyrolysis temperature is reached, the nitrogen flow is maintained until pyrolysis is complete (indicated by the absence of methane in the reaction effluent). This waiting period is generally approximately 30 min. After completion of pyrolysis, steam is injected. The experiment is then continued until 50 to 75% of the char has been consumed.

## RESULTS AND DISCUSSION

A number of experiments have been carried out in order to characterize the chars formed from the Wyodak-Anderson and the Hanna coals and to elucidate some of the differences between the two chars. It was anticipated that the conditions during pyrolysis and between the pyrolysis and gasification stages of the process would affect the reactivity of the resulting chars toward steam. Therefore, experiments were carried out to confirm such an effect.

Samples of the Wyodak and Hanna coals were pyrolyzed in our reactor system by the following procedure. The coals were crushed to  $-4 +12$  mesh and then pyrolyzed at  $3^\circ\text{C}/\text{min}$  to a maximum temperature of  $700^\circ\text{C}$ . The system pressure was 0.162 MPa (225 psig or 16 atm) with 2.5 liters (STP)/min nitrogen flowing through the reactor. Under these conditions, the average linear velocity of gas through the coal bed was 3 cm/sec. After the char was cooled in a nitrogen flow, it was removed from the reactor for characterization prior to gasification. The ash content was measured and the percent carbon recovered

was determined. For the Wyodak coal, 44% of the carbon on an as-received basis was recovered as char, which had an ash content of 16%. For the Hanna coal, 60% of the carbon (as received) was recovered as char. The ash content of the Hanna char was 6.1%.

Surface areas of these chars have been measured by nitrogen adsorption (BET method) and carbon dioxide adsorption. The results of these measurements are shown in Table 1. The surface areas of both the Wyodak and Hanna chars as determined by nitrogen adsorption are low, while the areas determined by CO<sub>2</sub> adsorption are high. This indicates that most of the surface is in the micropore structure of the char.

Table 1. Char Surface Area (m<sup>2</sup>/g)

Pyrolysis Conditions		Wyodak		Hanna	
		BET	CO <sub>2</sub>	BET	CO <sub>2</sub>
3°C/min, 16 atm (ANL)	700°C	1.2	455	0.2	549
3°C/min, 1 atm	650°C	4	320		
3°C/min, 1 atm (ORNL)	900°C	190	350		
1 atm	675°C	211			
1 atm (LLL)	800°C	124			

A char prepared at ANL at high pressure was compared with a char prepared at ORNL under similar heating conditions but at lower pressure. We measured the surface area of a sample of Wyodak char obtained from Oak Ridge National Laboratory. This char was the product of a pyrolysis experiment in which a large block of coal was heated at 3°C/min average heating rate to a maximum temperature of 650°C under an atmosphere of argon at ambient pressure. In addition, the BET and CO<sub>2</sub> surface areas were measured for a sample of char that had been pyrolyzed at ORNL to a maximum temperature of 900°C. The high-pressure char (ANL) has a BET surface area somewhat lower than that of either of the ORNL chars prepared at low pressures. However, the surface area of the high-pressure char as measured by CO<sub>2</sub> adsorption is greater than that of the low-pressure chars. This indicates that pyrolysis under high pressures produces a char in which the pores are smaller in size, but much greater in number. A greater proportion of the surface of the high-pressure chars is concentrated in the micropores.

Our surface area values for these chars differ from the values obtained by Taylor and Bowen at Lawrence Livermore Laboratory (LLL)<sup>10</sup> for a Wyodak char. The values obtained at LLL were from char pyrolyzed in 0.1 MPa (1 atm) pressure of argon at an unknown heating rate. The BET surface areas of the chars pyrolyzed to both 675°C and 800°C at LLL are considerably

higher than those obtained in our studies. Also, the char prepared at the higher temperature has a smaller area than did that prepared at lower temperature, which is an effect opposite to that observed in the case of the ORNL-prepared char. The reason for these anomalies is not known.

### Electron Microscopy of Chars

Scanning electron micrographs have been taken of the Wyodak and Hanna chars\* prepared in our reactor. Figure 2a is a low-magnification view of the Wyodak char, showing the macrofissures formed during pyrolysis. This view shows two surfaces of a char particle that are perpendicular to each other. These two surfaces differ greatly in structure, as seen in Fig. 2b and 2c. Figure 2b shows a more detailed structure of the edge surface of the particle shown in Fig. 2a. This surface contains a relatively small number of large fissures. However, there is also a great number of nearly round pores in this surface of the char, very closely spaced with diameters of 2-10  $\mu\text{m}$ . In Fig. 2c, we see the detailed structure of the flat surface of this same particle. Instead of rounded pores, there are many submicron-size cracks in addition to large macrofissures.

The Hanna and the Wyodak chars differ considerably in physical appearance. The Hanna char has a glassy appearance after pyrolysis and the particle edges and fissures are randomly oriented. The Wyodak char has a matte, porous appearance, with many fissures occurring parallel or perpendicular to each other. The surface character of a particle of the Hanna char is shown in Fig. 3a. Figure 3b shows a higher magnification view of one particle of the Hanna char. The microfissures observed in the Wyodak char do not appear in the Hanna char. With few exceptions, only submicron-size pores were observed in the Wyodak char, as seen in Fig. 2b. There appears to be a considerably smaller number of these pores in the Hanna char, although their sizes are roughly equal to the sizes of those observed in the Wyodak char. The bright specks in Fig. 3b are due to mineral matter in the char. X-ray analysis of the specks on the sample indicates the presence of iron, sulfur, aluminum, and silicon.

From these micrographs and from the surface area determinations, it appears that the macro-porosity of the Hanna char is considerably less than that of the Wyodak char, imposing mass transfer limitations on the reactant accessibility to the char surface.

### Pyrolysis of Coals and Gasification of Chars

In underground gasification, three reaction zones are evident. The pyrolysis of the coal occurs as a reaction immediately preceding gasification with steam. The third zone involves combustion of char with oxygen.

In order to demonstrate the importance of accurately simulating the pyrolysis step in our kinetics experiments, the reaction rate for the steam-char reaction was determined, utilizing a char prepared in a separate reactor, and was then compared with that for a char pyrolyzed immediately prior to gasification in our experimental reactor.

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\*Electron microscopy of chars was carried out by G. T. Chubb of the Biological and Medical Research Division, ANL.

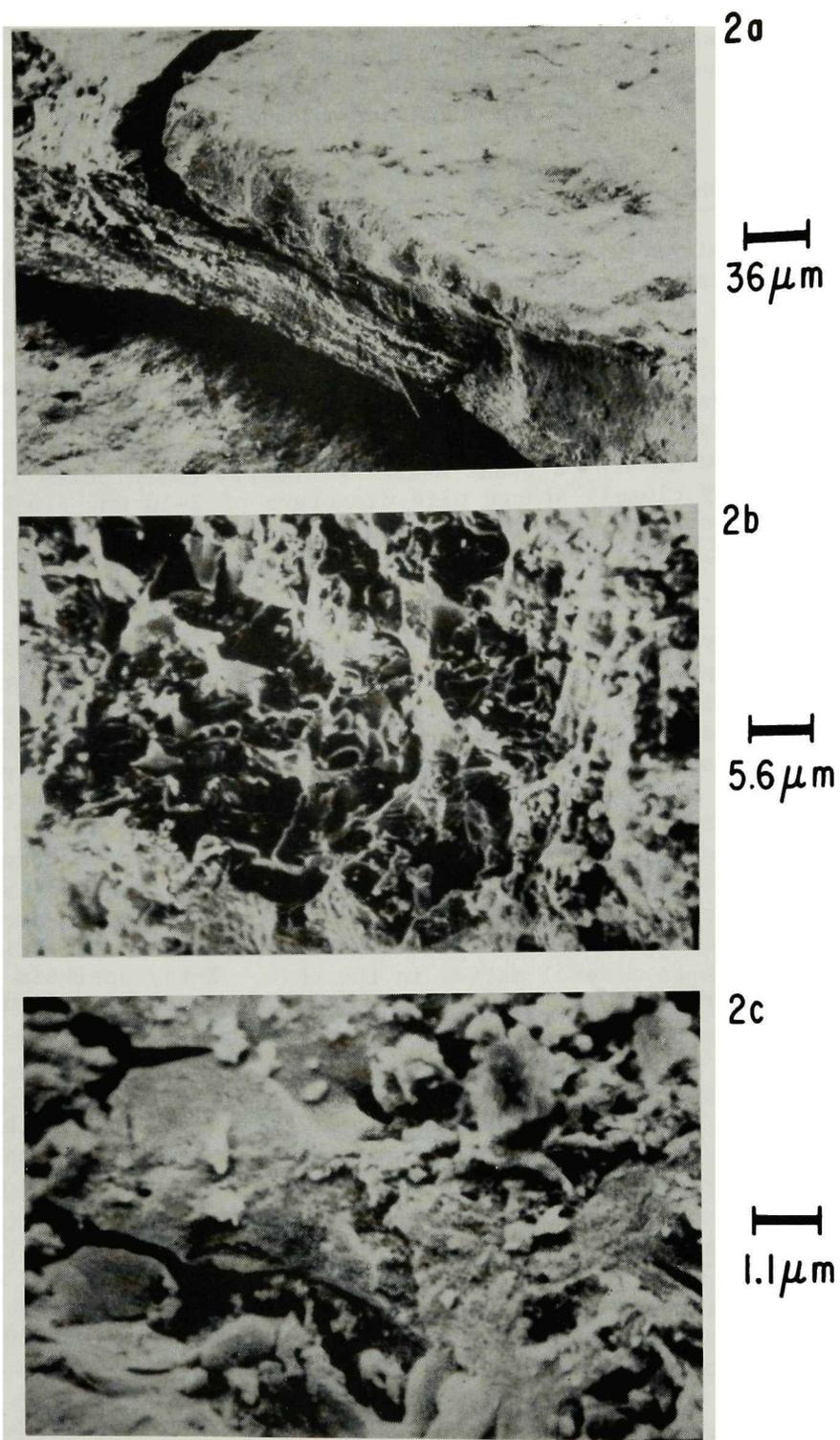
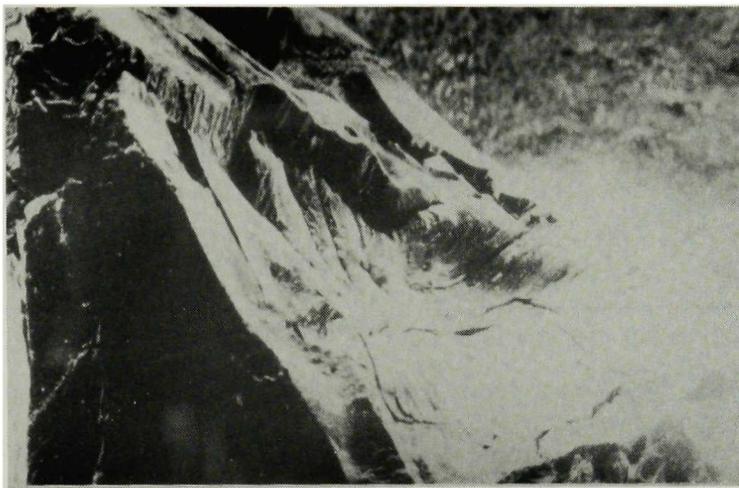


Fig. 2. Scanning Electron Micrographs of Wyodak Char



3a



105  $\mu\text{m}$



3b



5.1  $\mu\text{m}$

Fig. 3. Scanning Electron Micrographs of Hanna Char

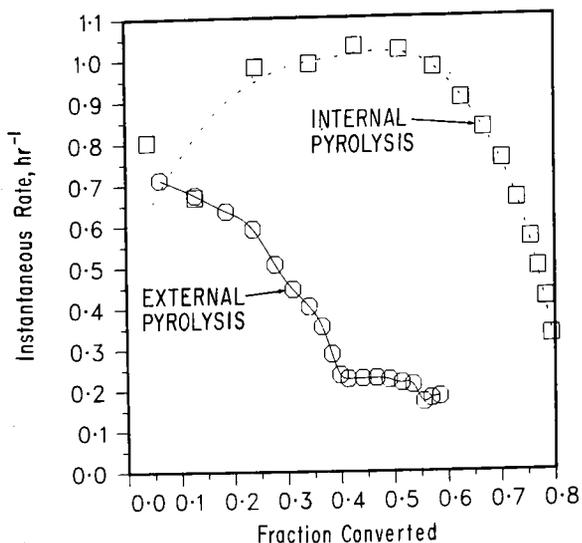


Fig. 4. Effect of Pyrolysis Conditions on Gasification Rates

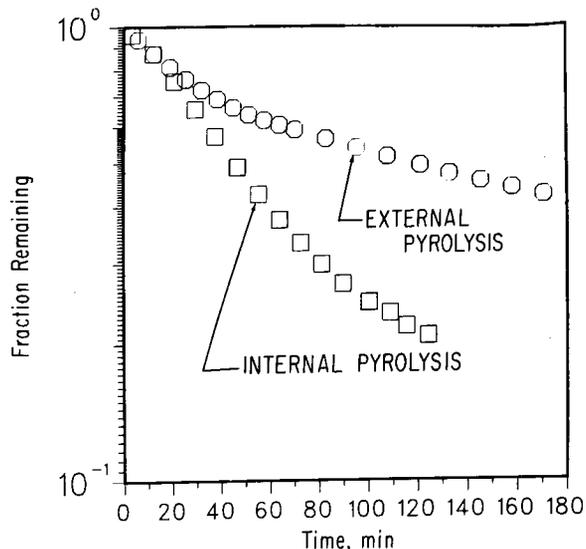


Fig. 5. Effect of Pyrolysis Conditions on Gasification Reaction Order

A sample of char prepared from Wyodak subbituminous coal was obtained from Oak Ridge National Laboratory. This char is a sample taken from a large block of coal pyrolyzed at a nominal heating rate of  $3^{\circ}\text{C}/\text{min}$  and with a maximum pyrolysis temperature of  $800^{\circ}\text{C}$ . The pressure of argon sweeping the coal during this pyrolysis was 100 kPa (1 atm). Since this char had been exposed to air during shipment to ANL, no precautions were taken to prevent its exposure to air during transfer to our gasification reactor. In the remainder of this report, this char is referred to as the externally prepared char or external pyrolysis. The char prepared in our gasification reactors was pyrolyzed at a heating rate of  $3^{\circ}\text{C}/\text{min}$  to  $700^{\circ}\text{C}$  in 1.6 MPa (16 atm) absolute pressure of nitrogen, with a flow rate of 2.5 liters (STP)/min. Gasification of both samples was carried out at  $700^{\circ}\text{C}$ , with a partial pressure of 0.64 MPa (6.3 atm) steam, and at a total system pressure of 1.6 MPa (16 atm).

In Fig. 4, the instantaneous reaction rate is expressed as grams carbon gasified/(hr) (g ash-free carbon remaining). On the abscissa, the fraction converted is plotted on an ash-free basis. The two chars initially have very similar reactivities, but as the carbon is consumed, the reactivity of the externally prepared char decreases rapidly, eventually leveling off at a value equal to approximately 30% of the original reactivity. The reactivity of the char prepared in the ANL reactor immediately before gasification increased and then held a high value of reactivity until at least 50% of the char was consumed.

An expression that has been used to describe the kinetics of the steam-char reaction is given in Equation 1.

$$\frac{dc}{dt} = A(X_c)^n (P_{H_2O})^m \exp\left(\frac{-E_a}{kT}\right) \quad (1)$$

where  $dc/dt$  = the instantaneous rate of gasification of the carbon

$X_c$  = fraction of carbon remaining

$P_{H_2O}$  = partial pressure of steam

$E_a$  = activation energy, kcal/g-mol

$T$  = reaction temperature, K

$k$  = gas constant, kcal(g-mol)<sup>-1</sup> (K)<sup>-1</sup>

$A$  = experimentally determined proportionality constant

$n$  = reaction order in carbon

$m$  = reaction order in steam

The value of  $n$  is generally considered to equal 1 for the steam-carbon reaction. If this is true, rearrangement and integration of Equation 1 would yield:

$$\frac{dc}{X_c} = A (P_{H_2O})^m \exp\left(\frac{-E_a}{kT}\right) dt$$

$$\ln X_c = A (P_{H_2O})^m \exp\left(\frac{-E_a}{kT}\right) t + B$$

where  $t$  is time and  $B$  is the integration constant. If this reaction is first order in carbon, then  $\ln X_c$  or  $\log X_c$  should be a linear function of time.

A plot of  $\log X_c$  versus time is shown in Fig. 5 for both the internally and the externally prepared chars. In the case of the internally pyrolyzed char, the reaction is very nearly first order with respect to carbon until more than sixty percent of the char is gasified. For the char prepared externally, the reaction appears to remain first order in carbon through the fifty percent conversion point, but the curve changes slope at approximately the thirty percent conversion point.

As a result of the above-described observations, in all subsequent studies reported here, pyrolysis was performed in the gasification reactor immediately before gasification.

The effect of  $P_{H_2O}$  on the gasification rate is indicated in Fig. 6. Wyodak char was used, and the reaction temperature was  $700^\circ\text{C}$ . Up to this time, only three partial pressures of steam have been studied: 0.26, 0.46, and 0.57 MPa (2.6, 4.5, and 5.6 atm, respectively). As defined in Equation 1, the value of  $m$  appears to be 1.3 for conversion of the first twenty percent of the carbon and then decreases to 1.2 for conversion of the balance. However, it will be necessary to investigate a wider range of steam partial pressures to better define a value for the constant  $m$  in Equation 1.

There is no consensus in the literature regarding the reaction order with respect to steam. Goring *et al.*<sup>11</sup> measured a reaction order of 1.5 for a range of steam partial pressures from 0.1 to 2.5 MPa (1 to 25 atm). This reaction order was roughly independent of both the fraction of carbon converted and the partial pressure of hydrogen present. However, other investigators have reported a fractional order between 0 and 0.5 with respect to steam.<sup>12</sup> Those who have correlated their data with Langmuir-type rate expressions imply that the maximum possible order is unity.

Possible inhibiting effects of product gases (hydrogen and CO) have not yet been investigated. Goring *et al.*<sup>11</sup> reported a strong inhibiting effect of hydrogen on the rate of formation of carbon oxides. This question will be studied in future experiments.

The reactivities towards steam for the Wyodak and the Hanna chars under similar pyrolysis and gasification conditions are compared in Fig. 7. The reaction temperature for these experiments was  $650^\circ\text{C}$ , the steam partial pressure was 0.71 MPa (7.0 atm), and the total system pressure was 1.6 MPa (16 atm). The reaction rate for the Wyodak char is approximately twice that

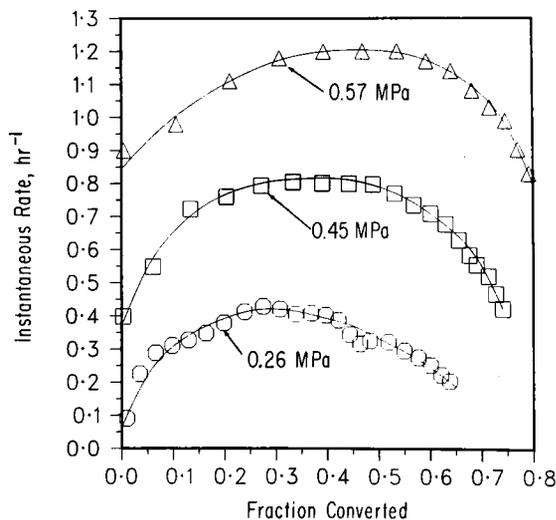


Fig. 6. Effect of Steam Partial Pressure on Gasification Rate (Wyodak Char)

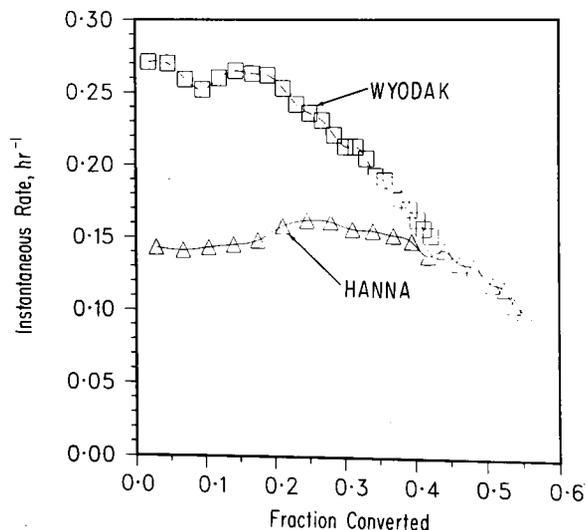


Fig. 7. Comparison of Reactivities of Hanna and Wyodak Chars

for the Hanna char. A partial explanation for this difference in reactivity is the differences in their surface area and porosities. The Hanna char has a much smaller number of macropores, as can be observed in the photomicrographs (Fig. 2 and 3). This limits accessibility of the reacting steam to the interior of the carbon particle. In addition, the BET-determined surface area of the Hanna char was less, although the  $\text{CO}_2$ -determined surface area was approximately 20% greater. Specific reaction sites are required for the reaction. Not all of the microporosity of the carbon indicated by  $\text{CO}_2$  adsorption is available to steam (the reactant).

The temperature dependence of the conversion rate for the Wyodak char is shown in Fig. 8. Four temperatures have been investigated--600, 650, 700, and 750°C. Lower temperatures will be studied in the future. At each temperature, the multiple points plotted on the graph correspond to the conversion rates at the various states of conversion--10%, 20%, 30%, etc. In most cases, the points are grouped closely enough that an average apparent activation energy can be determined throughout the range of conversion up to approximately 50% conversion. At 600°C, the reaction rate was so low that only the rate at 10% conversion was obtained. The partial pressure of steam for all of these determinations was 0.71 MPa (7.0 atm). Between 600 and 700°C, the apparent activation energy is 318 kJ/mol (76 kcal/mol); at higher temperatures, it decreases considerably. Between 700 and 750°C, the apparent activation energy is approximately 63 kJ/mol (15 kcal/mol). The radical decrease in  $E_a$  at higher temperatures points to rather severe diffusion limitations at these temperatures. The kinetics are no longer limited by the kinetics of the reaction, but the reaction rate is now high enough that diffusion of reactants and products through the pore structure is the limiting factor.

In Reference 10, an apparent activation energy of 184 kJ/mol (44 kcal/mol) was calculated for the reaction of steam with Wyodak char in the temperature range, 500 to 675°C. The partial pressure of steam in this study was 1 atm. Quite possibly, at this lower partial pressure of steam, diffusion limitations exert an effect, even at the lower temperatures.

In the case of the Hanna char, only three gasification temperatures have been studied at this time--650, 700, and 750°C. Their effect on conversion rate is plotted in Fig. 9. It should be noted that at 750°C, the variation in conversion rate as a function of extent of conversion is much greater at lower temperatures. The conversion rate at 50% conversion is more than a factor of two greater than the rate at 10% conversion. The apparent activation energy at 10% conversion is less than the  $E_a$  at 50% conversion in the 700-750°C temperature range. This change in apparent activation energy would be expected if micropore diffusion limitations were occurring. At the beginning of conversion, the pore structure has not yet been opened by partial consumption of the carbon; hence, the diffusion limitations would be greater at the earlier stages of conversion. At the maximum conversion rate observed, the apparent activation energy is 113 kJ/mol (27 kcal/mol) between 700 and 750°C, but it appears to be approximately 222 kJ/mol (53 kcal/mol) between 650 and 700°C. Obviously, a wider temperature range must be investigated to better define the range of activation energies encountered for this reaction. It also appears that for these chars, the apparent activation energy and the partial pressure of steam may be related. If this dependence is real, the reason for it is undoubtedly the limitations due to micropore diffusion.

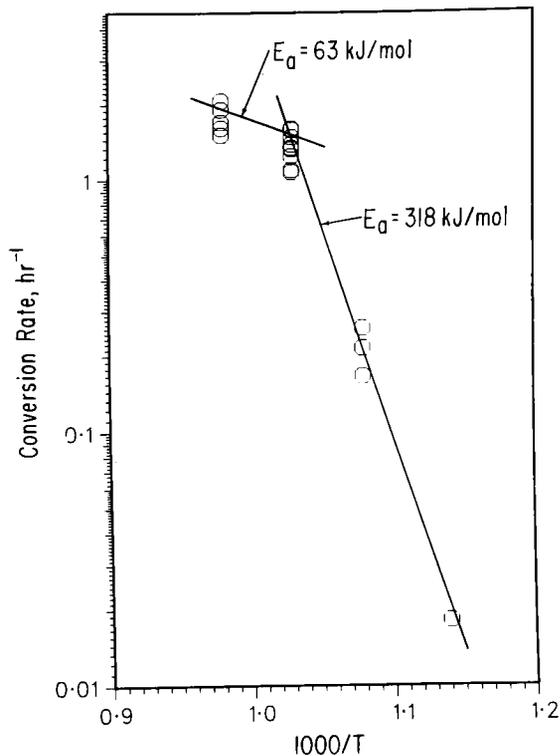


Fig. 8. Temperature Dependence of Gasification Rate, Wyodak Char

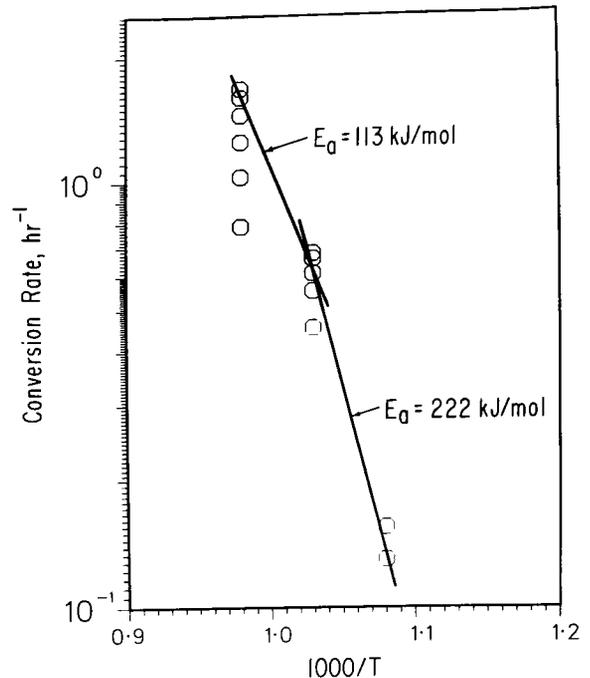


Fig. 9. Temperature Dependence of Gasification Rate, Hanna Char

The distribution of product gases for a typical steam-char gasification run is shown in Fig. 10. No carbon monoxide was detected; only in the case of very low partial pressures of steam is carbon monoxide observed in the product stream. The ratio of  $H_2$  to  $CO_2$  is almost exactly 2:1, indication that the water gas shift reaction ( $CO + H_2O \rightarrow CO_2 + H_2$ ) was occurring to a great extent. In fact, the observed  $H_2$  and  $CO_2$  concentrations indicate that thermodynamic equilibrium for the water gas shift reaction is reached for our reactor conditions and is most likely catalyzed by the ash content in the char. In the case of the Hanna chars, the hydrogen to carbon dioxide ratio is always somewhat less than 2:1, indicating that with this char the catalytic effect on the shift reaction is probably less.

There is also a surprising amount of methane observed in the product gas stream. This methane persists for the duration of an experiment, indicating that it is not the result of continuing pyrolysis reactions occurring after introduction of the steam to the char.

An experiment has been carried out in which the partial pressure of hydrogen was set equal to that expected in actual underground gasification. The results of this experiment are shown in Fig. 11. The Hanna coal was pyrolyzed in nitrogen at a heating rate of  $3^\circ C/min$  up to a final temperature

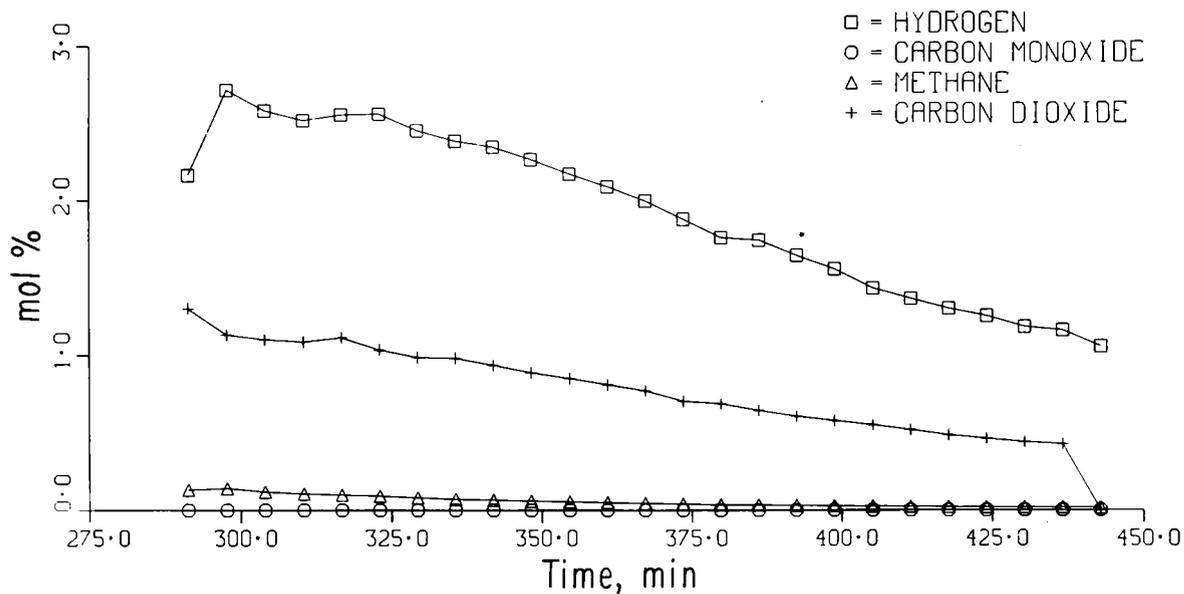


Fig. 10 Product Gas Composition, Wyodak Char. Temp. 650°C, 7.36-atm Steam, 16.31-atm Total Pressure

of 700°C. At this point, no methane was detected in the gas stream. After the final temperature was reached, a blend of hydrogen and helium was introduced giving a hydrogen partial pressure of 138 kPa (20 psia) (at time = 0 in Fig. 11). The average concentration of methane after introduction of the hydrogen was 0.015 mol %. After 60 min had elapsed, steam was introduced at a partial pressure of 0.33 MPa (3.3 atm). Upon introduction of the steam, the rate of production of methane doubled and the production rate of methane was 20% that of carbon oxides. Since this experiment was carried out under differential conditions, the increase in partial pressure of hydrogen due to the steam-char reaction was insignificant; hence, the hydrogen partial pressure remained constant throughout the experiment.

In a similar experiment in which the steam partial pressure was 0.5 MPa (5 atm), the rate of methane production after steam injection was four to five times greater than the rate before injection of steam. Too few experiments have been carried out to determine a kinetic model for this reaction, but it is apparent that there is a synergistic effect between hydrogen and steam on the production of methane. This phenomenon has been observed with both Wyodak and Hanna chars.

Pyrcioch *et al.*<sup>9</sup> considered the question of injection of steam with hydrogen in studies related to the hydrogasification of chars in above-ground gasifiers. They came to the conclusion that there was no activating effect of steam addition on the rate of formation of methane. Their studies were made with Pittsburgh seam bituminous coal and a North Dakota lignite. However, most of their experiments were carried out in a manner such that injection of steam to the reactor was accompanied by a decrease in the

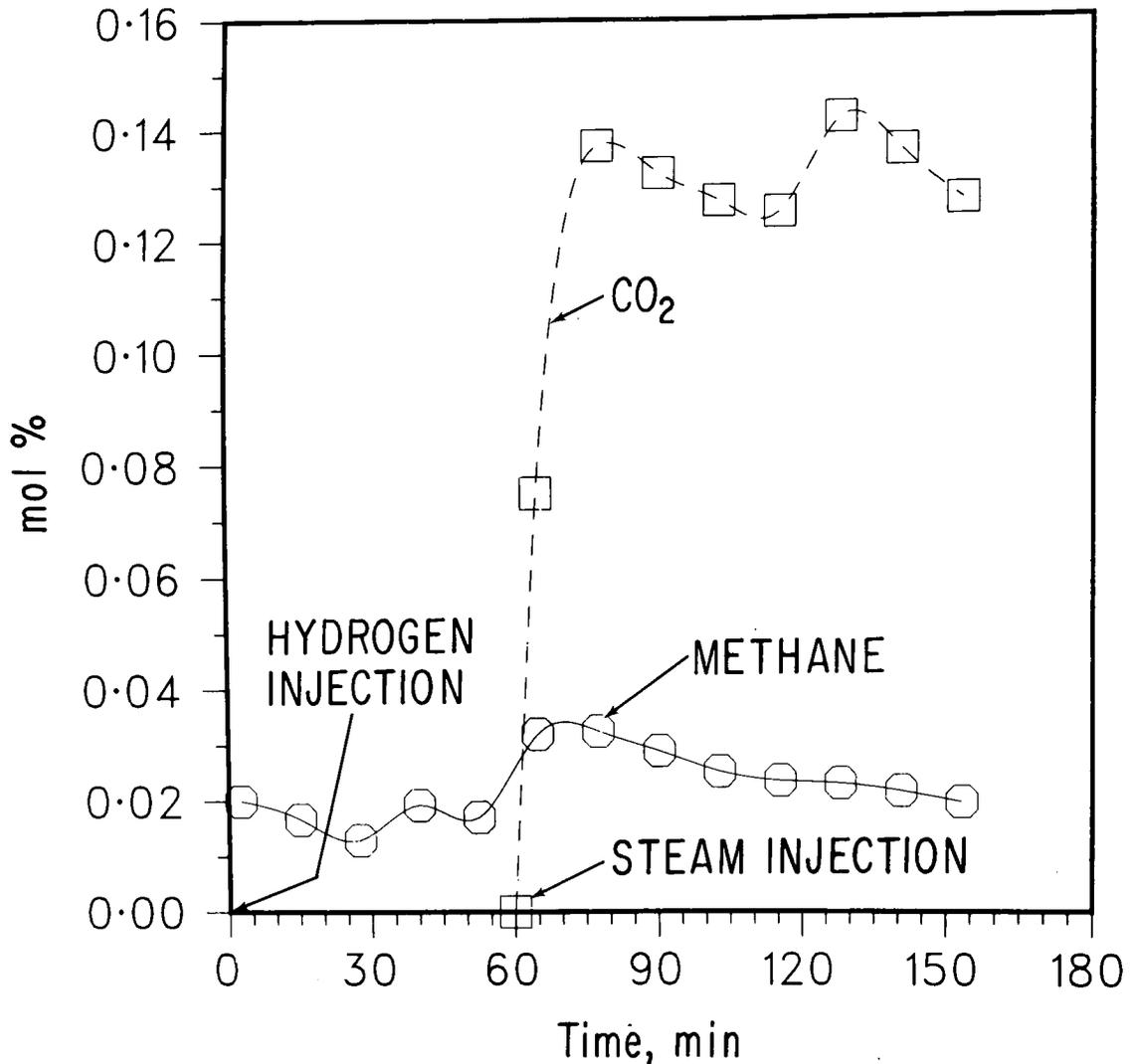


Fig. 11. Effect of Steam on Rate of Methane Formation, Hanna Char

partial pressure of hydrogen due to a major decrease in the rate of hydrogen injection. In a few experiments carried out by Pyrcioch *et al.*<sup>9</sup> the inlet hydrogen partial pressure was maintained at original values. In these cases an increase in the rate of methane formation was observed. These experiments were carried out at 7.0 MPa (1000 psig) pressure. Other investigators<sup>11,13-15</sup> found that at hydrogen partial pressures below 3.0 MPa (30 atm) and at 700-925°C, the addition of steam did indeed increase the rate of methane formation. Goring *et al.*<sup>11</sup> has postulated a model for this reaction, involving the direct interaction of carbon and steam. An alternative model is one involving methanation of the CO produced by the steam-char reaction.

Since the steam-char reaction produces both CO and hydrogen (albeit in the wrong proportion for stoichiometric production of methane), the methanation reaction could be catalyzed by the mineral matter in the char. The mechanism of this reaction will be studied in detail in the future, since this reaction has great economic importance to the *in situ* gasification process, where it is generally advantageous to maximize the methane content in the product gas if the products are to be used as fuel.

Our studies regarding the reaction of steam with chars prepared from subbituminous coals have progressed to the point where comparisons can be made with information previously published for these chars. Taylor and Bowman<sup>10</sup> studied the rate of reaction of steam and carbon dioxide with chars produced from Wyodak and other subbituminous coals. The results of microbalance studies of the reaction of steam and chars produced from Wyodak, as well as eastern bituminous coals, have been published by Fischer *et al.*<sup>16</sup> The microbalance studies (described in Ref. 16) were carried out in this laboratory as a preliminary investigation prior to construction of the differential reactor system currently in use.

Taylor's studies<sup>10</sup> were carried out utilizing a partial pressure of steam of 0.1 MPa (1 atm) in the temperature range of 500 to 675°C. Since only a single steam partial pressure was used, it was not possible to determine a reaction order with respect to steam. In this temperature range, the apparent activation energy for the Wyodak char was calculated to be 44 kcal/mol.

The microbalance studies also utilized a single partial pressure of steam--2.3 kPa (17.5 Torr). The temperature range of these studies was 800 to 900°C. For these conditions, the apparent activation energy for the Wyodak char was calculated to be 27 kcal/mol.

The studies described in this report involve a range of partial pressures of steam from 0.26 MPa (2.6 atm) to 0.71 MPa (7.0 atm) with a temperature range of 600 to 750°C in the case of the Wyodak char. At the higher temperatures, an apparent activation energy of 15 kcal/mol has been measured.

If the data from these previous studies are extrapolated to the range of those currently being carried out, the following comparison can be made: Assuming a first order reaction with respect to steam, extrapolation of Taylor's data to 700°C and  $P_{\text{H}_2\text{O}}$  of 0.26 MPa (2.6 atm) would give an expected reaction rate of 2.0 hr<sup>-1</sup> for the Wyodak char. Extrapolation of the microbalance data to this same point would give an expected reaction rate of 9.7 hr<sup>-1</sup>. The maximum reaction rate for Wyodak char at 700°C and a  $P_{\text{H}_2\text{O}}$  of 0.26 MPa (2.6 atm) was measured to be 0.4 hr<sup>-1</sup>. The discrepancies among these values are quite large. Pyrolysis conditions used during the earlier studies were quite different from those expected in underground gasification. In addition, our studies indicate the existence of severe mass transfer limitations at high reaction rates. It is probably this latter fact that most adequately explains the lower observed reaction rates for the high partial pressures of steam encountered in our current studies.

The problems described above demonstrate the importance of carrying out the kinetics studies under conditions simulating as closely as possible those encountered in underground gasification. Extrapolation of data obtained in the past from operating conditions differing from those of *in situ* gasification is proving to be questionable utility.

### CONCLUSIONS

1. A close simulation of the actual pyrolysis conditions is necessary, since variations in the pyrolysis conditions have a significant effect on the reactivity of the chars toward steam.

2. The chars obtained from the Wyodak and the Hanna coals are quite different with respect to both physical structure and chemical reactivity. The Wyodak char is about twice as reactive toward steam as is the Hanna char. The steam-char reaction is first order in carbon, while the order in steam appears to range from 1.3 to 1.2, depending on the extent of conversion of the carbon. The apparent activation energy for this reaction ranges from 63 to 318 kJ/mol (15 to 75 kcal/mol); the observed temperature dependence of the activation energy indicates that the reaction is limited by diffusion of the reactants and products through the micropore structure of char.

The above described variations in reactivity of the two chars, as well as the observed differences in activation energies for the reaction, interact in a complex manner to affect the rates at which product gases are formed under a given set of operating conditions. The total extent of this interaction can be predicted with a degree of certainty only by utilizing the mathematical models of the process as a whole.

Use of more reactive chars such as the Wyodak would probably result in more rapid motion of the gasification and combustion fronts through a coal bed. In addition, with greater reactivity, a greater fraction of the fixed carbon may be utilized by the gasification reaction prior to exposure to the oxygen and initiation of the combustion reaction in a given area of the coal bed. A more porous coal and char bed would also contribute to higher reaction rates and subsequent faster motion of the gasification and combustion zones.

3. The presence of steam promotes the reaction of hydrogen with the char, resulting in the formation of more methane than is formed with only an equivalent partial pressure of hydrogen. The economic significance of this finding is great for applications in which the product gas from *in situ* gasification would be used as fuel. An increase of only 1% methane in the product gas will increase the heating value of that product gas by 9.5 Btu/scf. This may warrant serious consideration of the question of operating the process at higher pressures, which would stimulate production of methane in the product gas.

## FUTURE WORK

These kinetics studies are being continued and will include the following aspects of char gasification:

1. Determination of how the reactivity of chars is affected by pyrolysis of the coal in the presence of reducing (gasification product) gases and variation of the pyrolysis heating rate.
2. Measurement of reaction rate constants and apparent activation energies for gasification of eastern Pittsburgh seam bituminous coal.
3. Determination of kinetic data for the reaction of  $\text{CO}_2$  with Wyodak, Hanna, and Pittsburgh chars.
4. Investigation of the promotion of the hydrogen-char reaction by steam.
5. Determination of the effects of brackish water on the kinetics.

These studies will continue to be coordinated with other working groups through direct contact with: personnel of major field test programs, groups doing laboratory work, and those doing the mathematical modeling.

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