ANL/CEN/FE-79-1

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LABORATORY SUPPORT FOR IN SITU GASIFICATION--REACTION KINETICS

Annual Report
October 1976—September 1977

by

J. Fischer, J. E. Young, J. E. Johnson,
and A. A. Jonke

U of C-AUA-USDOE

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

Prepared for the U. S. DEPARTMENT OF ENERGY
under Contract W-31-109-Eng-38

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A03
Microfiche copy: A01

Distribution Category:
Coal Conversion and Utilization—
Coal Gasification (UC-90c)

ANL/CEN/FE-79-1

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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September 1979

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CHEMICAL ENGINEERING DIVISION

LABORATORY SUPPORT FOR *IN SITU* GASIFICATION--REACTION KINETICS ANNUAL REPORT

October 1976—September 1977

by

J. Fischer, J. E. Young, J. E. Johnson, and A. A. Jonke

ABSTRACT

This work, which is part of the ANL energy program for DOE, 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 being studied include steam-char, CO_2-char, H_2-char, and the water gas shift reaction.

In this report are presented additional kinetic data related to the reaction of steam with Hanna and Wyodak subbituminous coals. In addition, the catalytic effects of coal mineral matter on the water gas shift reaction and the effects of brackish water on the steam-char reaction rates are discussed.

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 kinetic data for gasification of chars under simulated *in situ* processing conditions. The coal samples studied are representative of coals 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. Studies carried out this year continue the investigation of the reaction of steam with chars prepared from Wyodak and Hanna western subbituminous coals.

At high temperatures (700-750°C), Wyodak char is 50-100% more reactive than is Hanna char, although at lower temperatures (600-650°C), the two have essentially equal reactivities with steam. The apparent activation energy (E_a) for the reaction of steam with the Wyodak char varies from 53 to 235 kJ/mol (12.8 to 56.3 kcal/mol) while for the Hanna char, E_a varies from 89 to 156 kJ/mol (21.2 to 37.2 kcal/mol), depending on the reaction temperature and the extent of carbon conversion. The lower apparent activation energy observed for the Hanna char indicates that its average pore size is smaller than that of the Wyodak char. The reaction order with respect to steam is greater for the Wyodak char than for the Hanna chars--undoubtedly also because of the differences in pore structure. The steam-char reaction is also severely inhibited by hydrogen, and this inhibition increases as a greater fraction of the carbon is gasified.

Mineral matter catalyzes the water gas shift reaction, and thermodynamic equilibrium is reached at approximately 550°C.

The alkali and alkaline earth cations present in brackish waters characteristic of western *in situ* gasification sites have been found to exert a minimal catalytic effect on the steam-char reaction.

I. INTRODUCTION

Current and predicted shortages of energy in this nation 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 expenditures for strip or deep shaft mining and aboveground 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 aboveground 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 chemical feedstock or can be converted to synthetic pipeline gas.

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

A number of different models of underground gasification have been described in recent literature.[1-6] 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 from different coals and at different pyrolysis conditions vary in reactivity. Little information on these reactions is available in the literature for chars prepared (1) from coals important in underground gasification and (2) under conditions similar to those encountered underground.

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 being 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. As stated above, 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:

$$H_2O + C \rightarrow H_2 + CO$$

$$CO_2 + C \rightarrow 2\ CO$$

$$2H_2 + C \rightarrow CH_4$$

$$H_2O + CO \rightarrow H_2 + CO_2$$

$$3H_2 + CO \rightarrow CH_4 + H_2O$$

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.

In this annual report, kinetic data are given for the reaction of steam with chars prepared from Wyodak and Hanna subbituminous western coals. In addition, the degree to which the water gas shift reaction is catalyzed by the coal mineral matter is discussed, as well as the effects on the steam-char reaction rates of using as the source of steam the highly brackish waters indigenous to the western subbituminous coal seams being considered for underground coal gasification.

II. EXPERIMENTAL

The kinetics studies are carried out in a packed-bed differential reactor system in which steam, carbon dioxide, and/or other reactants are blended with nitrogen to obtain the desired total pressure and partial pressures of reactants. The experimental apparatus and detailed operating procedures have been described in detail.[7]

Pyrolysis to form char is carried out immediately prior to gasification in the gasification reactor under conditions of pressure, heating rate, and sweeping gas composition similar to those encountered in underground gasification. The heating rate currently being used is 3°C/min up to the reaction temperature, the system pressure is 0.79 MPa (100 psig), and the sweeping gas consists of a blend of approximately 20 mol % hydrogen in nitrogen (the reason for selecting this gas composition is discussed below).

III. RESULTS AND DISCUSSION

The product gas in an underground gasifier consists primarily of hydrogen, carbon monoxide, carbon dioxide, methane and higher hydrocarbons, and nitrogen. This mixture constitutes a reducing atmosphere which sweeps through the coal bed during pyrolysis, immediately prior to gasification. It was our intention to reproduce underground processing conditions during the pyrolysis phase of our experiments and therefore to use in our studies a sweeping gas that contains each of these constituents.

However, at temperatures below approximately 700°C, the equilibrium constant for the reaction:

$$2CO \rightleftarrows C + CO_2$$

is greater than one; hence, at lower temperatures there is danger of producing carbon by the disproportionation of carbon monoxide. We have observed that this disproportionation reaction is indeed catalyzed by the coal ash and the α-alumina packing used in our reactor system. Hence, if we were to include carbon monoxide in the sweeping gas during the pyrolysis phase of our gasification kinetics experiments, we would be adding additional carbon to the system. This deposited carbon would not be quantitatively determinable and would have to be eliminated or made negligible in order to obtain carbon balances for our kinetics studies. Therefore, our pyrolysis reactions have been carried out in a reducing atmosphere consisting of only hydrogen and nitrogen. Our experiments have indicated that in the case of Wyodak coal, pyrolysis in a reducing atmosphere (20% H_2, 80% N_2) results in approximately ten percent less char being recovered following pyrolysis than when pure nitrogen is used as the sweeping gas. However, the reactivity of char produced in the nitrogen-hydrogen mixture is the same as that for char produced in pure nitrogen.

A. Temperature Dependence of Rate of Reaction of Steam with Wyodak Char

The rate of reaction of steam with chars prepared from Wyodak coal has been measured in the temperature range, 600 to 775°C, with a partial pressure of steam of about 250 kPa (2.5 atm) and a total pressure of about 900 kPa (9 atm). In all of these experiments, the coal was pyrolyzed immediately prior to gasification by heating to gasification temperature, using a heating rate of 3°C/min in an atmosphere of 20% H_2/80% N_2 at a pressure of 700 kPa (7 atm).

Plots of the reaction rates *vs.* fraction of carbon converted at 600, 650, 700, and 750°C and a steam partial pressure of 250 kPa (2.5 atm) are shown in Figs. 1-4. The reaction rate unit of measurement is grams of carbon gasified per hour per gram of ash-free carbon remaining, simplified to h^{-1}. At 600°C (Fig. 1), it is apparent that the fresh char is quite reactive, but this reactivity decreases to an approximate plateau in the conversion range from 10 to 35%; the reactivity of the residual carbon then decreases quite rapidly. At 650°C (Fig. 2), the overall reaction rate is, as expected, appreciably greater than at 600°C. However, the very high initial reactivity observed at 600°C is no longer apparent and the reaction rate remains fairly constant until approximately 40% of the carbon is gasified.

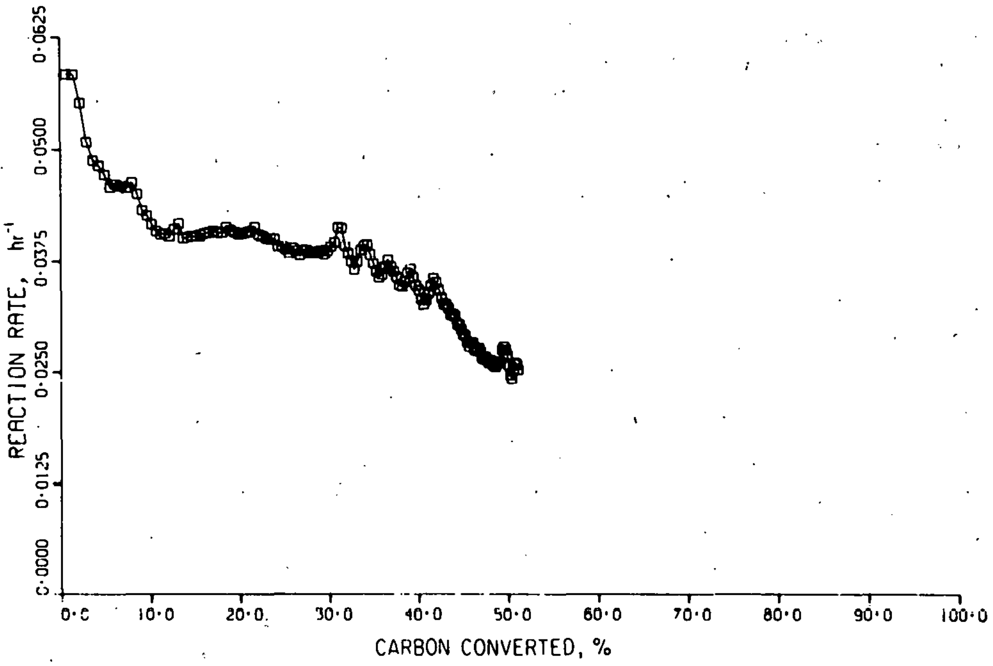

Fig. 1. Reaction Rate *vs.* Percent Conversion for Wyodak Char at 600°C and 270 kPa (2.66 atm) Steam

At higher temperatures (Figs. 3 and 4), the reaction rate for the fresh carbon is actually less than that for carbon which has been partially gasified. The most probable cause for this decreased reaction rate for fresh char at the higher temperatures is restricted diffusion of the steam reactant and the product gases through the pore structure of the char. (At 750°C, however, the first two data points are of questionable validity because the reaction rate was so high that, during the time necessary for the product gases to flush the reactor, the product-gas concentrations were excessively diluted by nitrogen.) At high temperatures, the reactivity of the carbon is great

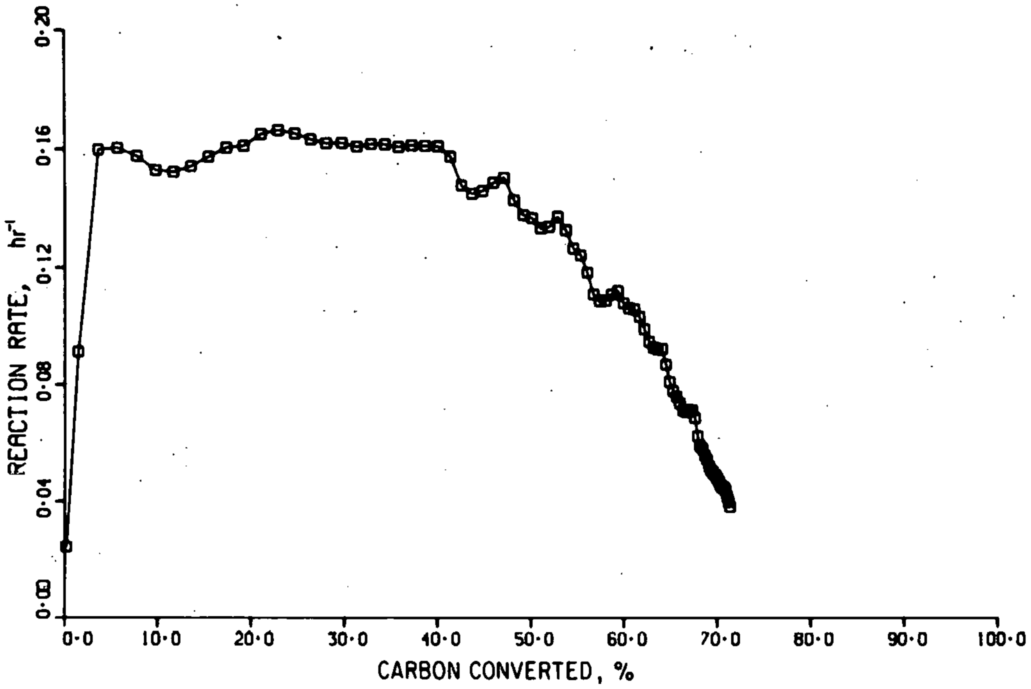

Fig. 2. Reaction Rate *vs.* Percent Conversion for Wyodak Char at 650°C and 262 kPa (2.62 atm) Steam

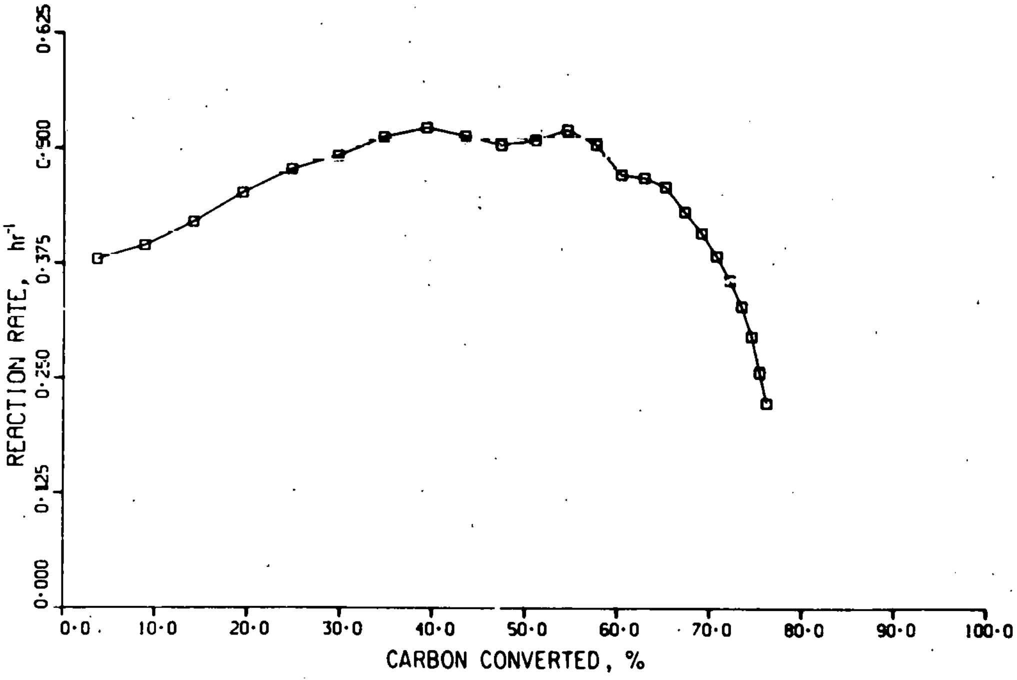

Fig. 3. Reaction Rate *vs.* Percent Conversion for Wyodak Char at 700°C and 247 kPa (2.47 atm) Steam

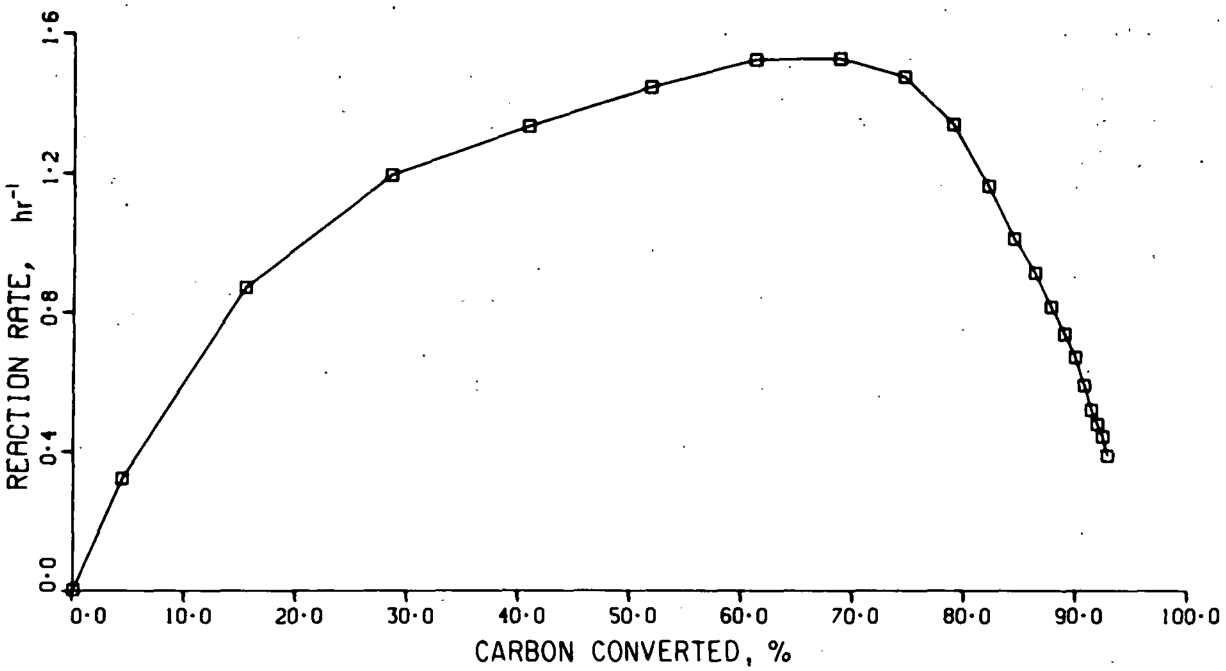

Fig. 4. Reaction Rate *vs.* Percent Conversion for Wyodak Char at 750°C and 235 kPa (2.35 atm) Steam

enough that the pore structure must be opened before the reaction can proceed at its full rate. At 750°C, the reaction rate does not reach its maximum until approximately 65% of the carbon has been consumed, indicating a very severe diffusion limitation at this high temperature.

The high initial reaction rate observed at 600°C is probably due to the presence of residual hydrocarbons in the coal, resulting from the low temperature at which pyrolysis is terminated for this run. These hydrocarbons would undoubtedly be steam-gasified more readily than would the residual char. However, these residual hydrocarbons account for a very small percentage of the overall carbon inventory and can essentially be ignored when determining a reaction model. The physical and chemical characteristics of the char obtained by pyrolyzing to 600°C will be quite different from those of a char pyrolyzed to 800°C. The hydrogen content of the low-temperature char will be higher than that of the high-temperature char. The carbon in the high-temperature char will have had greater opportunity to recrystallize, becoming more refractory and potentially less reactive than the low-temperature char, although this potentially lower reactivity is more than offset by the exponential temperature effect on the steam-carbon reaction.

During normal operation of an underground gasifier, the coal would not encounter temperature cycling, *i.e.*, would not encounter temperatures during the pyrolysis stage higher than those at which the reaction with steam would occur. Although pyrolyzing our coal samples to a uniformly high temperature would ensure that we were studying chars having uniform reactivities, this would not be a realistic condition for use in modeling an underground gasifier. The reaction model derived for use in *in situ* gasification must include the effects of differing char properties, and so the experimental data must be obtained by utilizing realistic pyrolysis conditions.

The rate of reaction is plotted as a function of reciprocal temperature (Arrhenius plot) in Fig. 5 for the temperature range from 600 to 775°C. At each temperature, reaction rates given are those following gasification of 10% of the carbon and of 50% of the carbon. The rate at 10% carbon conversion corresponds to the rate for fresh char, while the rate at 50% conversion corresponds to the rate for the more refractory residual char.

The effect of diffusion limitation on the reaction rate appears in this plot as a flattening of the curves at higher temperatures. The decrease in slope at high temperatures is much more apparent at 10% conversion than at 50% conversion, suggesting continual opening of the pore structure during gasification and consequent enhancement of the reaction rate.

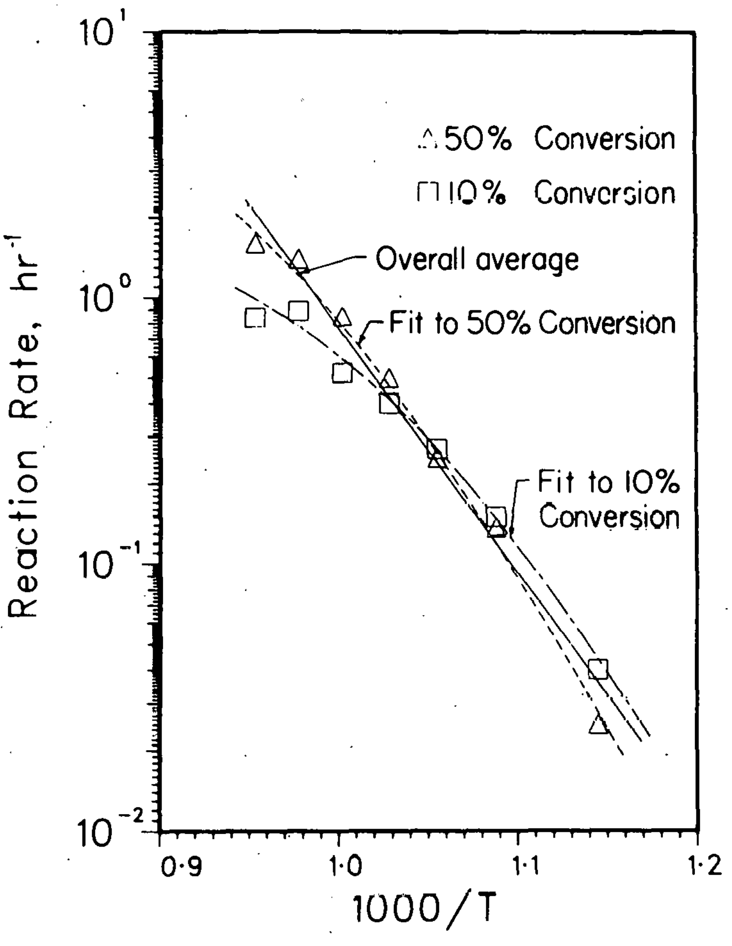

Fig. 5. Temperature Dependence of Reaction Rate of Wyodak Char with Steam at 250-kPa (2.5-atm) Partial Pressure

A straight line fit to most of the data points gives the solid curve in Fig. 5, which curve corresponds to an average apparent activation energy of 184 kJ/mol (44 kcal/mol). Taylor and Bowen[7] investigated the reaction of steam and carbon dioxide with Roland seam char at atmospheric pressure. (The Roland seam char is very similar in reactivity to Wyodak char.) Their study indicated no curvature of the Arrhenius plot; however, they included temperatures only as high as 675°C. They also obtained a value of 184 kJ/mol (44 kcal/mol) for the temperature range of their study. Their study was carried out at a lower partial pressure of steam, so that restricted diffusion would be expected to be a less serious problem. Earlier experiments in our own study[8] indicated that, at a steam partial pressure of 700 kPa (7 atm), the curvature of the Arrhenius plot resulting from diffusion limitations is even greater than that observed at 250 kPa (2.5 atm).

B. Reaction Order of Wyodak Char with Respect to Steam Partial Pressure

Wyodak chars prepared by pyrolysis at 3°C/min in either nitrogen or 20% H_2 in nitrogen were gasified at 700°C with steam at partial pressures of 120 to 650 kPa (1.2 to 6.5 atm). The reaction rates are plotted as a function of steam partial pressure in Fig. 6. At low partial pressures of steam [$\leq$300 kPa ($\leq$3 atm)], the curve is nearly linear, with a slope of approximately 0.85, which corresponds to a reaction order of 0.85. At higher steam partial pressures, the reaction order decreases. Since underground gasification of coal would generally involve partial pressures of steam at the lower end of this range of steam partial pressures, the value of 0.85 is probably more applicable for use in mathematical models than the lower reaction-order values.

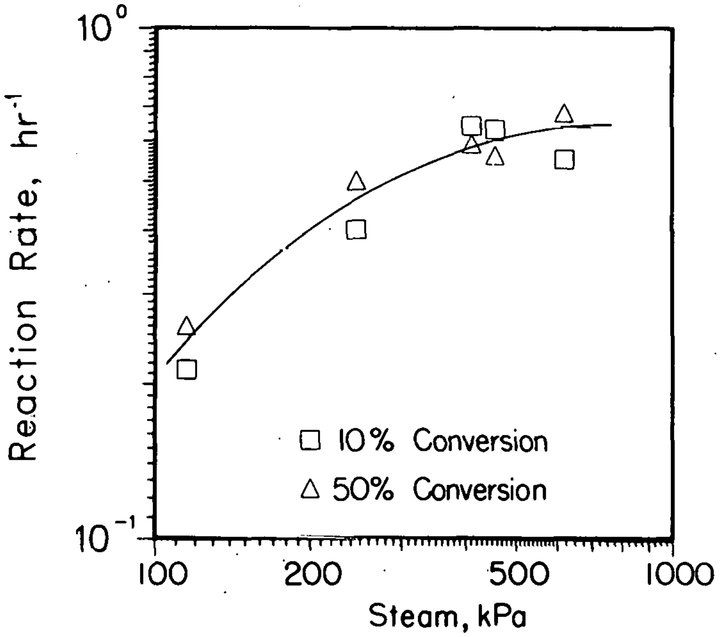

Fig. 6. Dependence of Reaction Rate of Wyodak Char on Partial Pressure of Steam at 700°C

C. Inhibition of the Steam-Wyodak Char Reaction by Hydrogen

All experimental runs made in the past have been designed to maintain the partial pressures of product gases at values as low as possible. Runs in which the gasification rate was extremely high (*e.g.*, at high temperatures or high partial pressures of steam) gave product gases with hydrogen contents of 2-4 mol %, but the majority of the runs resulted in product gases with hydrogen contents of considerably less than 1 mol %. Inhibition of the steam-char reaction by product hydrogen was investigated in a series of experiments in which hydrogen was added to the reactant steam. The range of hydrogen partial pressures investigated included hydrogen pressures expected to be encountered in the current low-pressure underground field tests--*i.e.*, up to approximately 100 kPa (1 atm). Four temperatures were investigated--600, 650, 700, and 750°C.

The results of these experiments are shown in Figs. 7-10. At 600°C (Fig. 7), hydrogen inhibition offsets the effects of the very reactive fresh char, resulting in quite a rapid decline in reaction rate as the char is consumed. At 700°C (Fig. 9), the hydrogen inhibition of the steam-char reaction is sufficient to obscure the effects of diffusion limitations during the early stages of the reaction. At 750°C (Fig. 10), the diffusion limitations are severe enough that they are apparent even at a hydrogen partial pressure of 75 kPa (0.75 atm). At each temperature, higher partial pressure of hydrogen causes the final decrease in the reactivity of the char to occur at a lower extent of conversion. The inhibitory effect of hydrogen is greater at higher temperatures and as the extent of conversion increases.

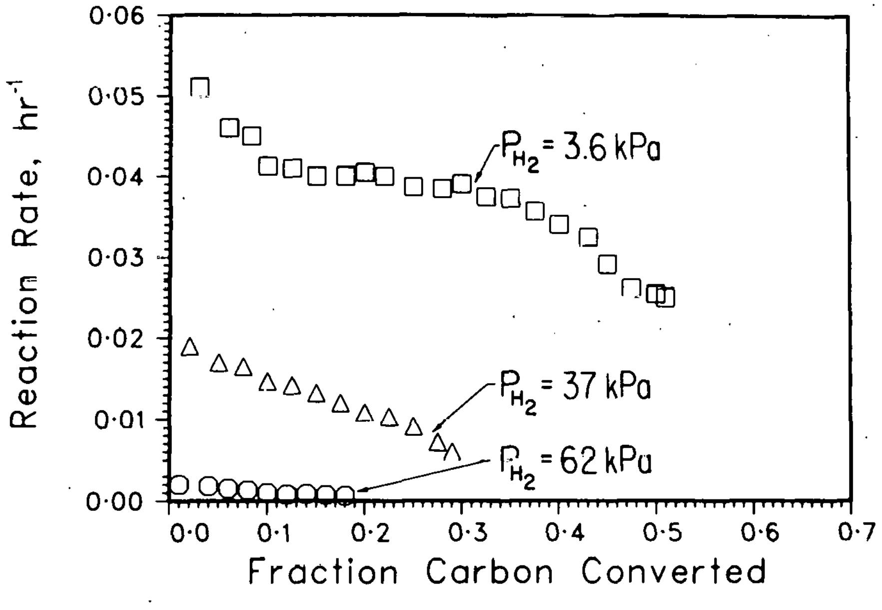

Fig. 7. Effect of Hydrogen Inhibition on Reaction of Wyodak Char at 600°C and P_{H_2O} = 250 kPa (2.5 atm)

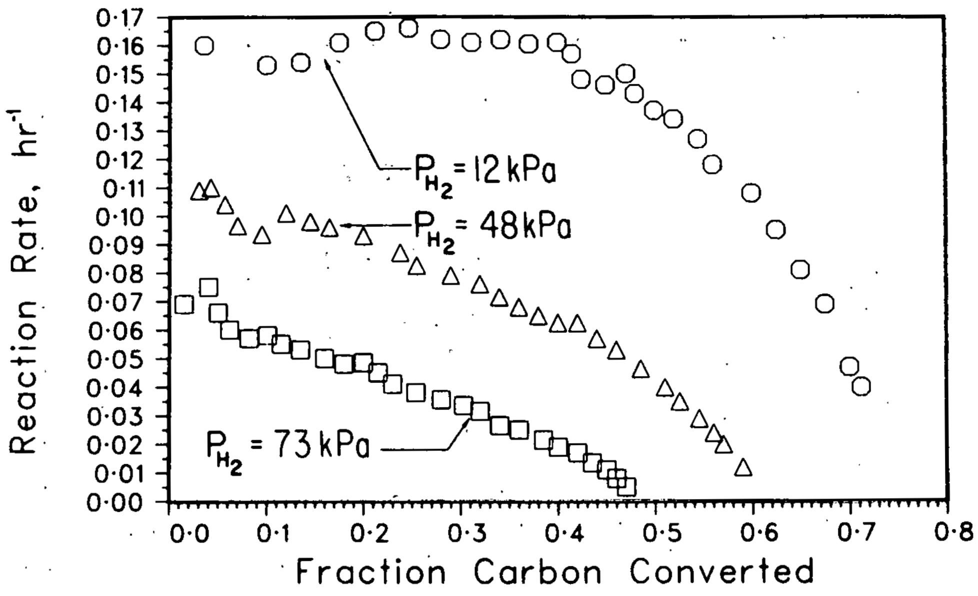

Fig. 8. Effect of Hydrogen Inhibition on Reaction of Wyodak Char at 650°C and P_{H_2O} = 250 kPa (2.5 atm)

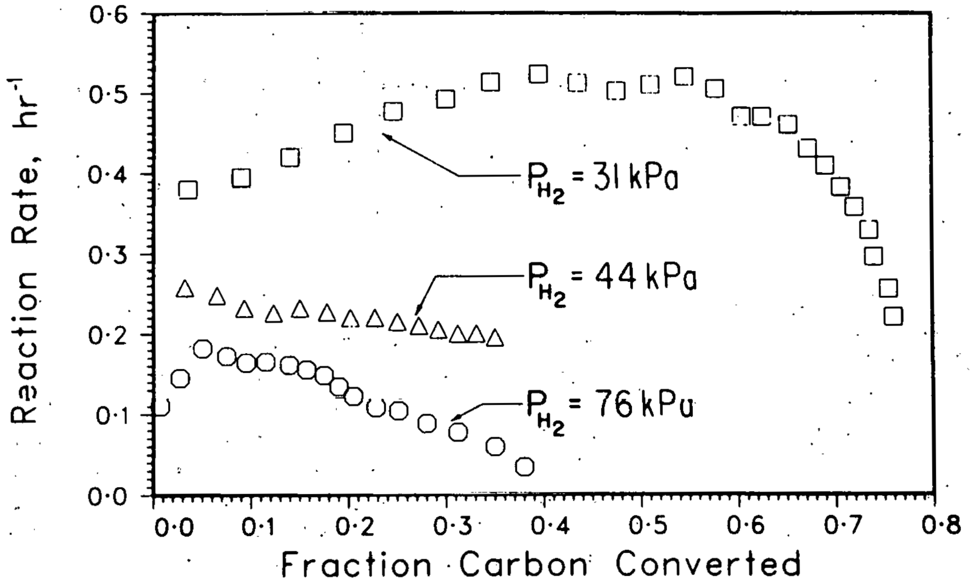

Fig. 9. Effect of Hydrogen Inhibition on Reaction of Wyodak Char at 700°C and P_{H_2O} = 250 kPa (2.5 atm)

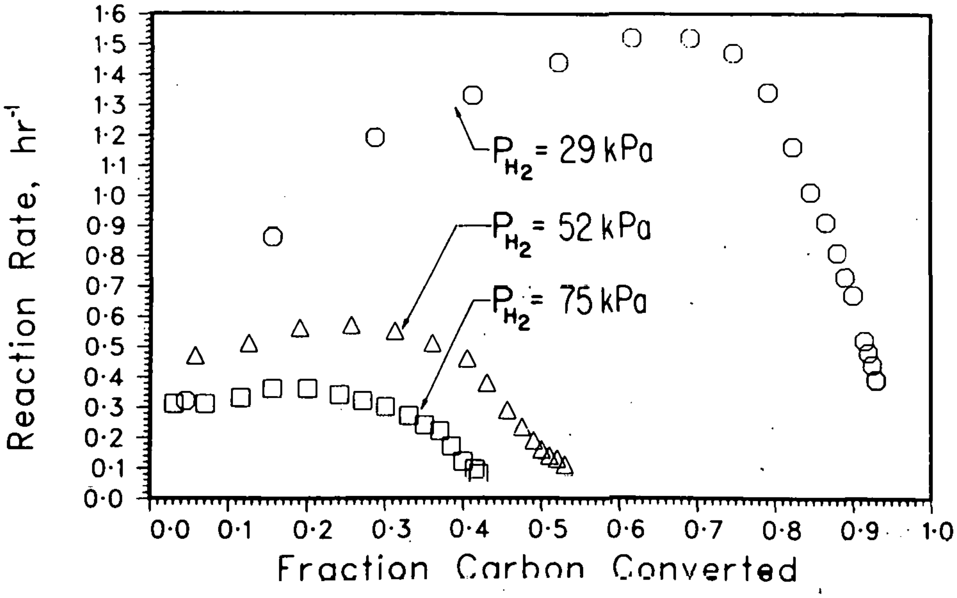

Fig. 10. Effect of Hydrogen Inhibition on Reaction of Wyodak Char at 750°C and P_{H_2O} = 250 kPa (2.5 atm)

D. Temperature Dependence of the Reaction Rate--Hanna Char

In seven experiments, Hanna coal was pyrolyzed to char immediately prior to gasification by heating to gasification temperature, using a heating rate of 3°C/min in an atmosphere of 20% H_2/80% N_2 at a pressure of 700 kPa (7.0 atm). Following pyrolysis, the char was gasified at the appropriate temperature, a partial pressure of steam of about 260 kPa (2.6 atm), and a total pressure of about 900 kPa (9 atm).

Plots of the reaction rate *vs.* percent carbon converted at 600, 650, 700, and 750°C and a steam partial pressure 260-275 kPa (2.6-2.75 atm) are shown in Figs. 11-14, respectively. At 600°C, a small fraction (<5%) of the char was observed to be highly reactive (Fig. 11). The reaction rate then decreased rapidly. During gasification of the next 50% of the char, diffusion was limited due to the micropore structure of the char, and the maximum reaction rate was not attained until approximately fifty percent of the char had been gasified. The reaction characteristics of the Hanna char are quite different from those observed for Wyodak char under similar operating conditions. A larger fraction of the Wyodak char exhibits high initial reactivity, and, in the case of the Wyodak char, limitation of reaction by diffusion is not apparent at all at 600°C (Fig. 1). For the higher temperature reactions of the Hanna char (Figs. 12-14), the delay before reaching the maximum reaction rate (due to the time necessary to open the pore structure) increased and is even more apparent, as expected.

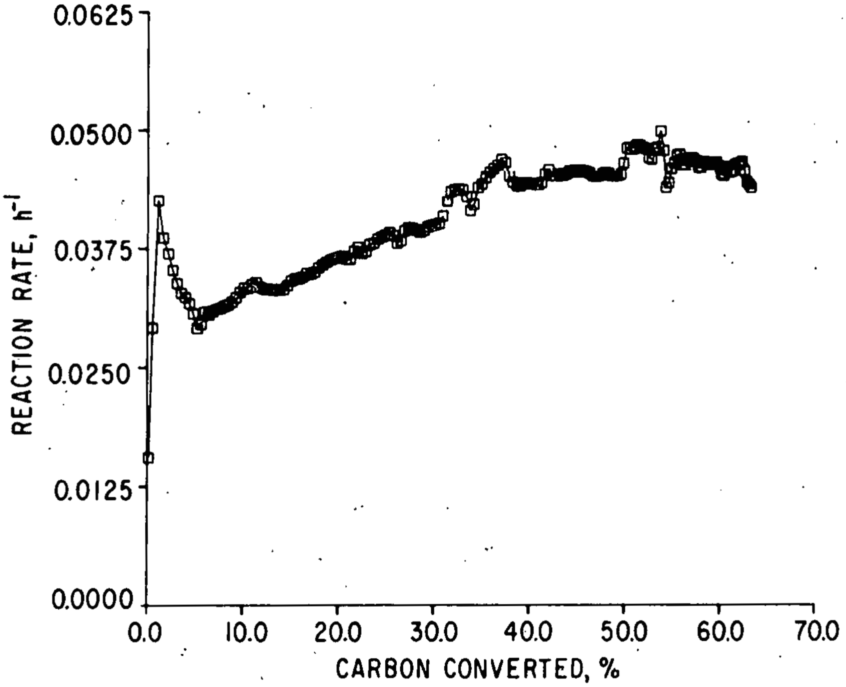

Fig. 11. Reaction Rate *vs.* Percent Conversion for Hanna No. 1 Char at 600°C, 271 kPa Steam

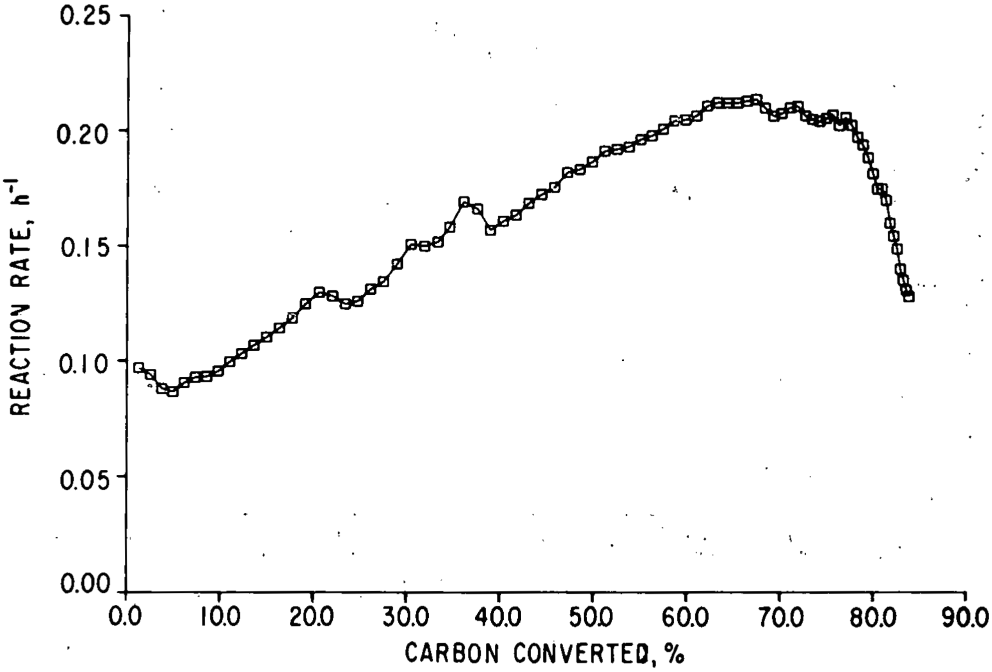

Fig. 12. Reaction Rate *vs.* Percent Conversion for Hanna No. 1 Char at 650°C, 277 kPa Steam

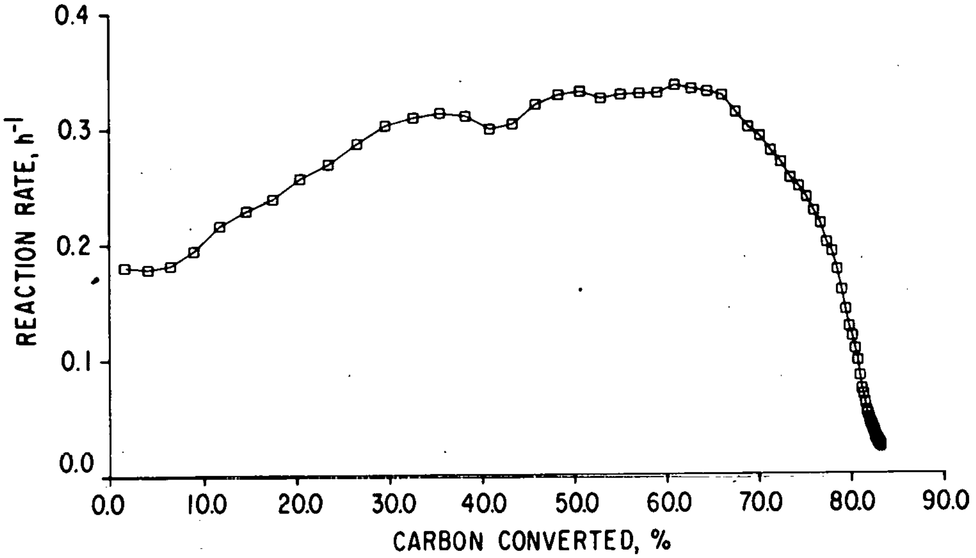

Fig. 13. Reaction Rate *vs*. Percent Conversion for Hanna No. 1 Char at 700°C, 263 kPa Steam

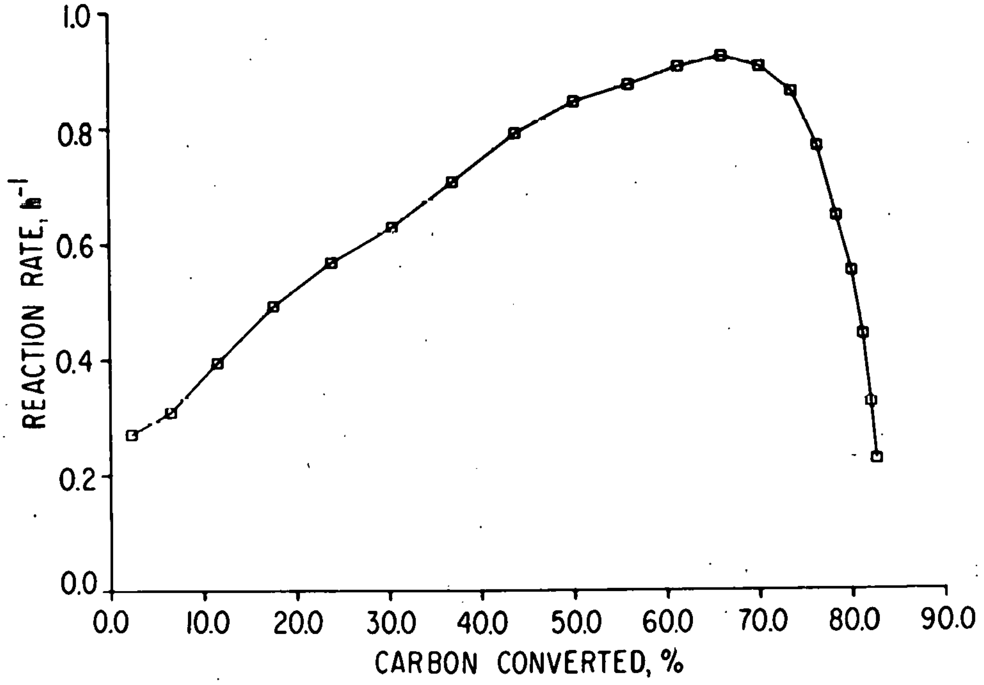

Fig. 14. Reaction Rate *vs*. Percent Conversion for Hanna No. 1 Char at 750°C, 274 kPa Steam

The rate of reaction of Hanna char with steam is plotted as a function of reciprocal temperature (Arrhenius plot) in Fig. 15 for the temperature range, 600 to 775°C. Shown for each temperature, are the reaction rates after gasification of 10% of the carbon and after gasification of 50% of the carbon. The rate at 10% carbon conversion corresponds to the rate for fresh char, while the rate at 50% conversion corresponds to that for the more refractory residual char.

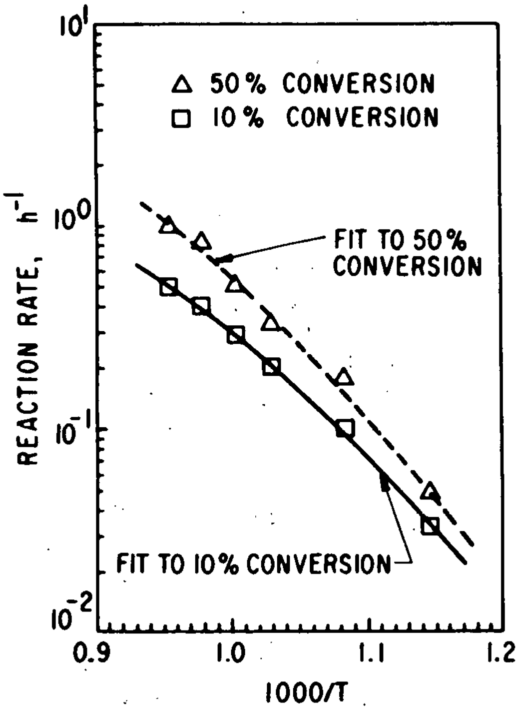

Fig. 15.

Temperature Dependence of Steam-Char Reaction Rate. Hanna No. 1. 260 kPa Steam.

The apparent activation energies (E_a) for reaction of both the Wyodak and Hanna chars are summarized in Table 1. For both chars, the decrease in E_a as the temperature increases is indicative of the micropore diffusion limitation observed for this reaction. The temperature dependence of E_a is more severe for the fresh char (10% carbon conversion) than for the char at 50% conversion. This suggests that by the time 50% of the carbon has been gasified, the pore structure of the carbon has been opened appreciably, reducing the effects of pore diffusion on the overall reaction rate. At the lower temperature, the micropore structure (*i.e.*, smaller average pore diameters) of the Hanna char has a greater limiting effect than that of the Wyodak char. However, at the higher temperature, the intrinsic reactivity of the Wyodak char is sufficiently greater than that of the Hanna char so that reaction is more severely limited by the pore structure of the Wyodak char than by the pore structure of the Hanna char.

Table 1. Apparent Activation Energies for Steam-Char Reaction

	E_a at 10% Conversion	E_a at 50% Conversion
Wyodak		
600°C	182 kJ/mol (43.6 kcal/mol)	235 kJ/mol (56.3 kcal/mol)
775°C	53 kJ/mol (12.8 kcal/mol)	109 kJ/mol (26.1 kcal/mol)
Hanna No. 1		
600°C	143 kJ/mol (34.1 kcal/mol)	156 kJ/mol 37.2 kcal/mol)
775°C	89 kJ/mol (21.2 kcal/mol)	110 kJ/mol (26.2 kcal/mol)

E. Reaction Order of Hanna Char with Respect to Steam Partial Pressure

Hanna chars prepared by pyrolysis at 3°C/min in 20% H_2 in nitrogen were gasified at 700°C in steam at partial pressures of 107 to 270 kPa (1.07 to 2.7 atm). The measured reaction rates in five experiments are plotted as a function of steam partial pressure in Fig. 16. The reaction rates for conversion of 10, 30, and 50% of the carbon are plotted. In the case of the Hanna char, a series of parallel straight lines can be fit through the points for the three extents of carbon conversion. The slope of these straight lines corresponds to a reaction order of 0.56 with respect to steam. This value is considerably lower than that obtained for the Wyodak char (0.85 for the same range of steam partial pressures, (Fig. 6)--undoubtedly, this is due to diffusion of steam being limited by the finer pore structure of the Hanna char.

F. Inhibition of the Steam-Hanna Char Reaction by Hydrogen

Inhibition of the steam-Hanna char reaction by product hydrogen has been investigated in a series of experiments in which hydrogen was added to the reactant steam. The range of hydrogen partial pressures investigated included those expected to be encountered in the present low-pressure underground field tests, *i.e.*, up to approximately 100 kPa (1 atm). In the case of chars prepared from the Hanna coal, four temperatures were investigated--650, 700, 750, and 800°C.

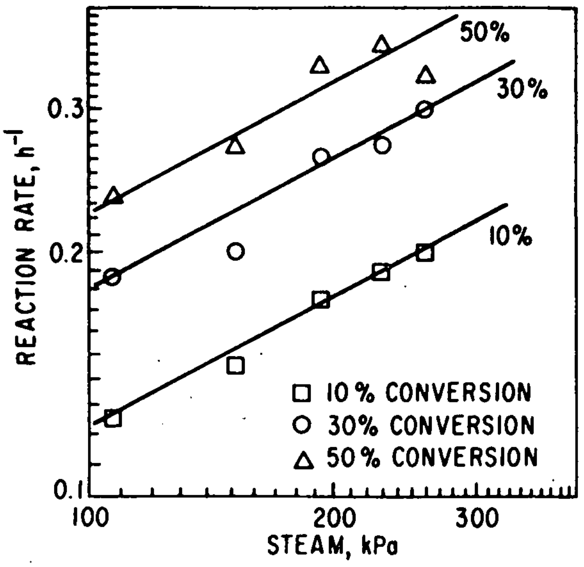

Fig. 16.

Dependence of Reaction Rate of Hanna No. 1 Char on Partial Pressure of Steam at 700°C.

The results of sixteen experiments are shown in Figs. 17-20. For Hanna chars, hydrogen exerts the greatest inhibitory effect at low temperatures (Fig. 17, 650°C), and inhibition of the steam-char reaction by hydrogen decreases markedly at high temperatures (Figs. 19 and 20 for 750 and 800°C, respectively). This is in contrast to the effects of hydrogen on the reaction of steam with the Wyodak char (Figs. 7-10), in which even at high

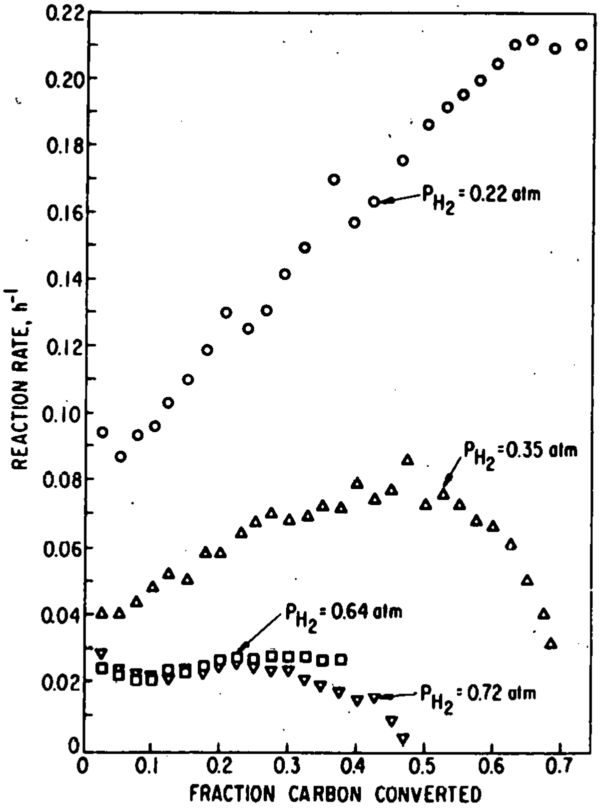

Fig. 17.

Effect of Hydrogen Inhibition on Reaction of Hanna No. 1 Char at 650°C. Partial pressure of steam: 250-270 kPa

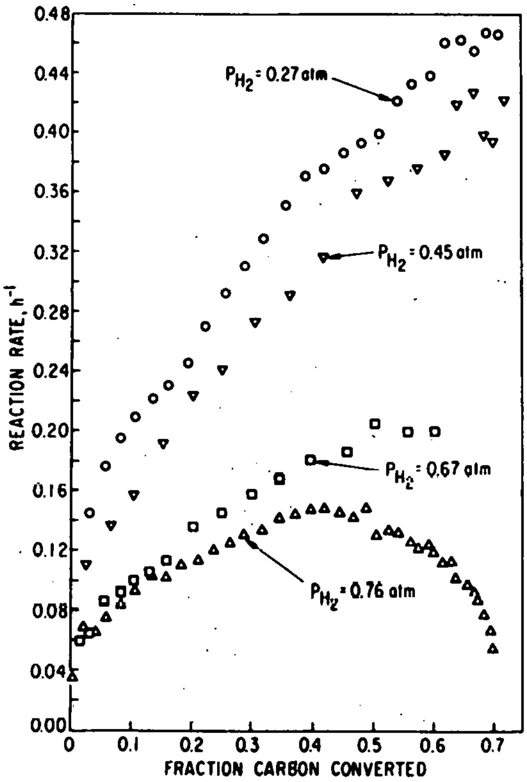

Fig. 18.

Effect of Hydrogen Inhibition on Reaction of Hanna No. 1 Char at 700°C. Partial pressure of steam: 240-260 kPa.

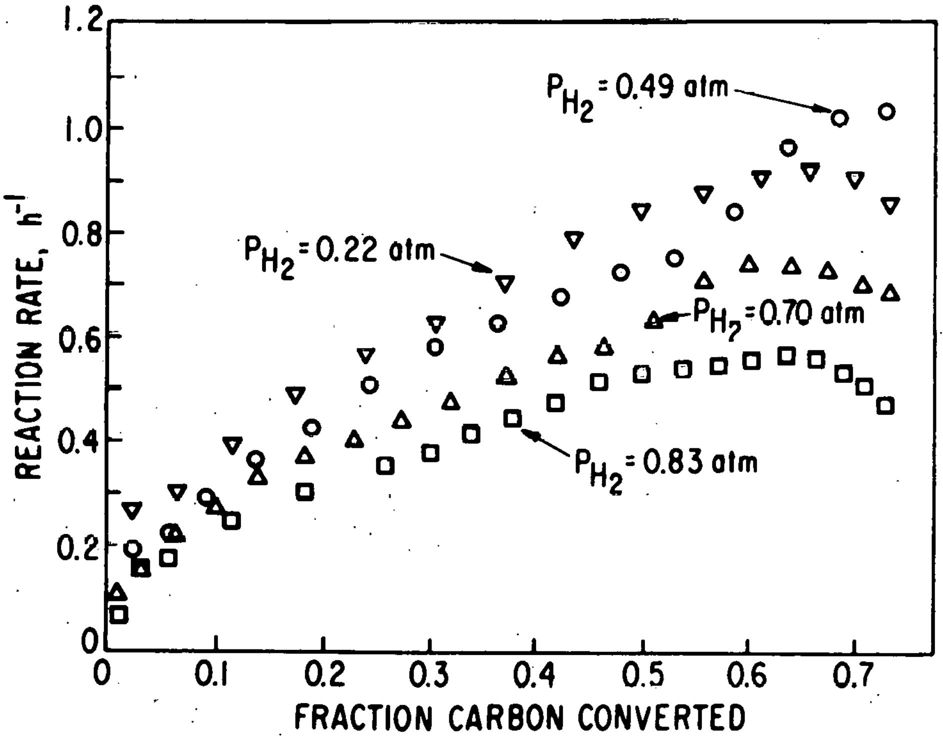

Fig. 19. Effect of Hydrogen Inhibition on Reaction of Hanna No. 1 Char at 750°C. Partial pressure of steam: 240-250 kPa.

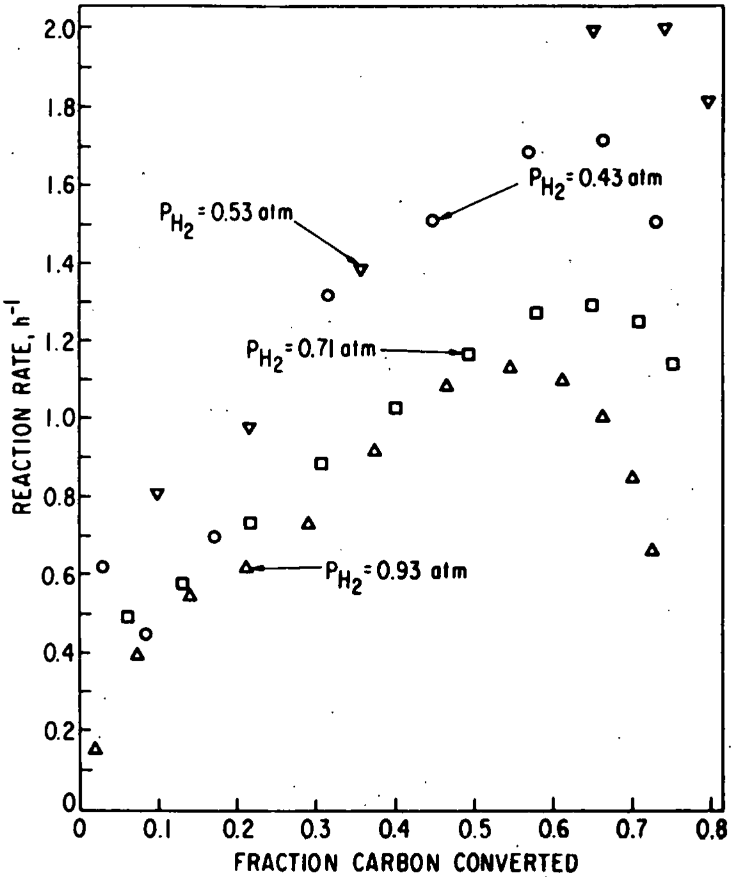

Fig. 20. Effect of Hydrogen Inhibition on Reaction of Hanna No. 1 Char at 800°C. Partial pressure of steam: 240-250 kPa.

temperatures the inhibition is great. At all temperatures except the lowest studied, partial pressures of hydrogen approaching 1 atm were insufficient to reduce the reaction rate to a level at which diffusion through the pore structure was no longer the limiting factor in the reaction of steam with the char. At 650°C, when a high hydrogen concentration reduced the reaction rate to approximately 0.03 h^{-1}, the reaction became chemically controlled rather than diffusion-controlled. In the Wyodak char, this transition from diffusion control to chemical control of the steam-char reaction occurred at a reaction rate of 0.3 h^{-1} (Figs. 9 and 10), indicating that the pore structure of the Wyodak char is considerably more open than that of the Hanna char.

G. Catalysis by Coal Ash

Many coals which would be good candidates for underground coal gasification have too high an ash content for economical aboveground utilization. Ash in such coals, would be expected to have a catalytic effect on gasification reactions occurring underground. The data presented below show that the ash in Hanna coal catalyzes the water gas shift reaction under the conditions expected in underground coal gasification.

To investigate this reaction, a series of experiments in which carbon monoxide and steam were reacted at various temperatures (250-650°C) over a bed of char prepared from Hanna coal was carried out in the following manner: The char was prepared by heating to a temperature of 600°C at a heating rate of 3°C/min. This pyrolysis was carried out in a reducing gas mixture condidting of 20% H_2 in nitrogen. The overall pressure was 0.76 MPa (100 psig). The temperature was limited to 600°C during pyrolysis in order to minimize chemical changes that might occur in the mineral matter of the coal. On the other hand, at 600°C, most of the hydrocarbon decomposition would have occurred, so that a clean, relatively hydrocarbon-free char would be exposed to the steam utilized for the reaction study.

Following pyrolysis, the temperature was reduced to the desired value, and 0.13 MPa (1.33 atm) steam was introduced into the reactor along with 60 kPa (0.6 atm) carbon monoxide. The balance of the gas was nitrogen, and the total system pressure was 0.76 MPa (7.6 atm). The contact time of the gas mixture in the char bed ranged from 1.1 s at 500°C to 1.6 s at 250°C. After utilization of the fresh char, 15% of the carbon was steam-gasified away at 600°C, and then the shift reaction was studied at lower temperatures (400-250°C). The purpose of the gasification step was to expose more of the mineral matter at the surface of the char particles. After the shift reaction rates were measured for the char from which 15% of the carbon had been removed, an additional 6% of the char was steam-gasified and the shift rates were measured again.

The results of these studies are shown in Fig. 21. The k_p values for the shift reaction over fresh char are appreciably lower than those for the partially gasified char, but the k_p differs little after 15 and 21% carbon removal. In Fig. 21, the extent of the shift reaction as a function of temperature is compared with the thermodynamic equilibrium curve. Once an appreciable amount of the carbon has been gasified from the char, the reaction approaches thermodynamic equilibrium in the temperature range of 500 to 600°C. The point plotted for Wyodak char at 650°C was calculated from data obtained in an earlier gasification run in which carbon monoxide was observed in the product gas, permitting calculation of an equilibrium value. This point confirms that the reaction is indeed at equilibrium at 650°C, for a contact time of the gas with the char on the order of 1 s.

H. Effects of Brackish Water on Gasification Kinetics

The water in the aquifers in the area of the Hanna underground coal gasification field test is quite brackish. A typical chemical analysis of water obtained from the Hanna No. 2 coal seam is as follows:[9]

Na	600 mg/L
K	7 mg/L
Ca + Mg	22 mg/L
$HCO_3^- + CO_3^{2-}$	1100 mg/L
SO_4^{2-}	400 mg/L
Cl^-	40 mg/L
pH	8.5
Total Dissolved Solids	1750 mg/L

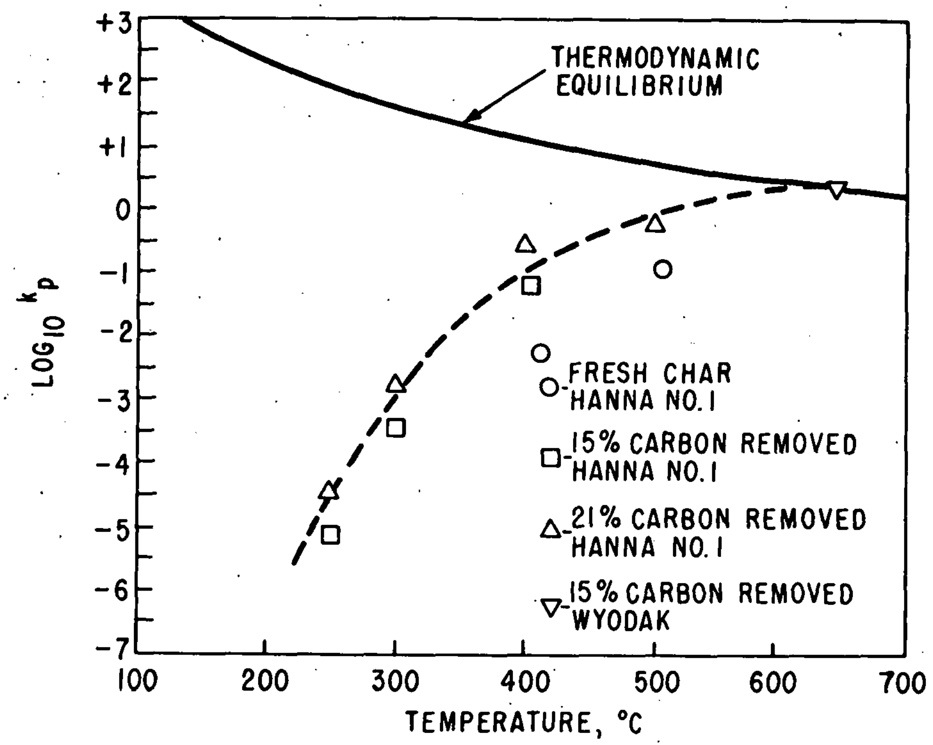

Fig. 21. Catalysis of the Water Gas Shift Reaction by Coal Mineral Matter (Hanna No. 1 Char). 1.0-1.5 s Contact Time.

$$k_p = \frac{\left[P_{H_2}\right]\left[P_{CO_2}\right]}{\left[P_{CO}\right]\left[P_{H_2O}\right]}$$

There are numerous reports in the literature that impregnation of coal with alkali or alkaline earth cations sometimes enhances the rates of gasification reactions with the coal. Hence, the unavoidable use of brackish water for underground coal gasification may in fact enhance the kinetics of the gasification reactions.

Two solutions were prepared simulating the brackish water. One solution contained approximately the above listed concentrations of impurities, and the other contained about five times the above concentrations. Calcium chloride ($CaCl_2$), sodium sulfate (Na_2SO_4), potassium carbonate (K_2CO_3), and sodium bicarbonate ($NaHCO_3$) were dissolved in distilled water to obtain the following concentrations:

Na	600.4 mg/L
K	7.3 mg/L
Ca	21.7 mg/L
$HCO_3^- + CO_3^{2-}$	1187.8 mg/L
SO_4^{2-}	402.2 mg/L
Cl^-	38.3 mg/L

A small amount of precipitate was observed in the prepared solution. This precipitate was resuspended prior to impregnation into the coal. The solution pH was 8.3. No adjustment of the pH was made. The pH of the more concentrated solution was 8.2.

A sample of Hanna No. 1 coal was crushed and washed in boiling distilled water several times to remove any soluble salts already in the coal. A portion of this washed coal was gasified to obtain a base line reaction rate. Ten grams of this washed coal was oven-dried, then impregnated with 1.0 mL of the simulated brackish water solution. The coal completely absorbed this solution; no excess liquid drained off. Likewise, a sample of the washed coal was dried and then impregnated with the five-fold-concentrated solution. Each of these impregnated coal samples was then gasified.

Pyrolysis was carried out in 20% H_2/80% N_2 with a heating rate of 3°C/min up to gasification temperature, and our standard gasification reaction conditions were used, *i.e.*, 700°C, and 2.5-atm steam. The results of these runs are summarized in Fig. 22. Impregnation of the washed coal with the simulated brackish water appears to enhance the rate of reaction of steam with the char by ten to fifteen percent. This small enhancement of the reaction rate may not be significant because very small samples of the coal were gasified in each run and normal variations in the coal composition can give this much variance in the measured reaction rate. The effects of single-fold and five-fold concentrations differed little, also suggesting that the observed enhancement may not be significant.

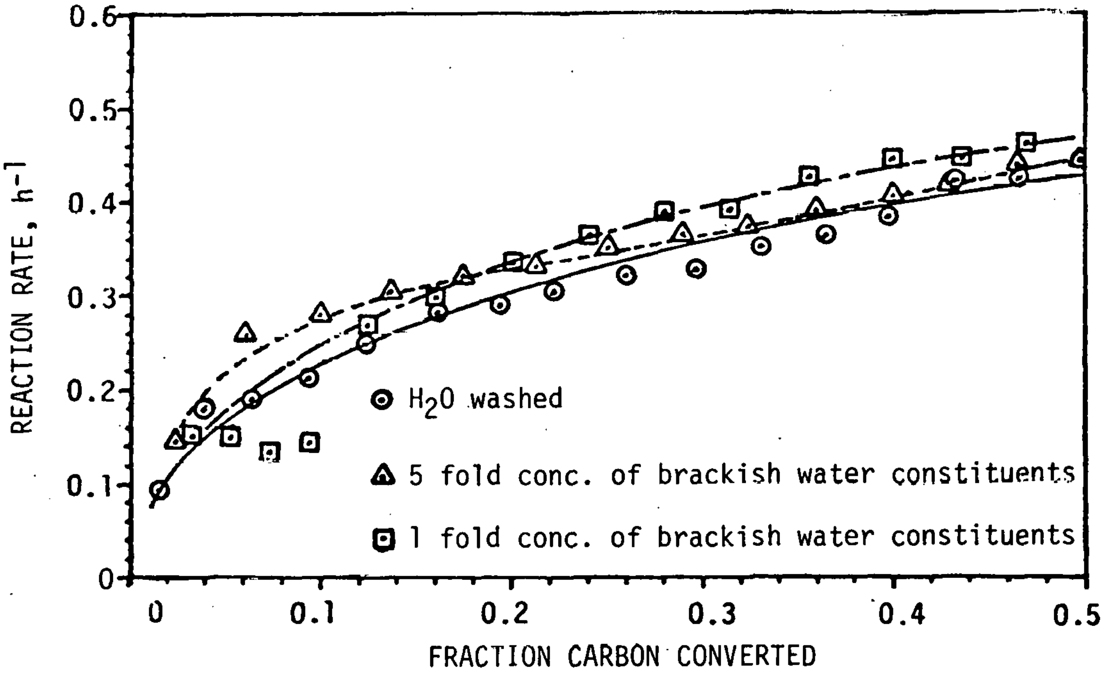

Fig. 22. Effect of Brackish Water on Steam/Char Gasification Rate. Hanna No. 1 Char, 700°C, 0.25-MPa (2.5-atm) Steam.

It is not unreasonable to expect minimal effects of brackish water on the reaction rate for a coal having the characteristics of Hanna No. 1. The core sample of Hanna coal that we are studying contains 17% ash on an as-received basis. Thus, the char remaining after pyrolysis contains 32% ash. When even five-fold concentrated simulated brackish water is added to this coal, the amount of inorganic material added is a rather small percentage of the total inorganic matter in this coal.

The possibility still exists that for chars that have a lower ash content than Hanna char, the brackish water may affect the rate of reaction of steam. We will obtain a sample of such a coal (a subbituminous coal) and repeat these experiments with it.

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