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ANL/CEN/FE-77-2

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois   60439

LABORATORY SUPPORT FOR *IN SITU*
GASIFICATION REACTION KINETICS

Quarterly Report for the Period
January—March 1977

by

J. Fischer, J. E. Young, J. E. Johnson,
D. C. Bowyer, and A. A. Jonke

Chemical Engineering Division

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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, $CO_2$-char, $H_2$-char, and the water-gas shift reaction.

In this report are presented kinetic data related to the reaction of steam with Wyodak subbituminous coal. The temperature dependence of the reaction, the apparent reaction order with respect to steam, and the inhibitory effects of hydrogen are discussed.

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Gasification
Coal gasification
*In-situ* gasification
Pyrolysis

Steam
Carbon dioxide
Carbon monoxide
Methane
Shift processes
Hydrogen

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Char

17c. COSATI Field/Group

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## TABLE OF CONTENTS

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# LIST OF FIGURES

# LIST OF TABLES

p

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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, $CO_2$-char, $H_2$-char, and the water-gas shift reaction.

In this report are presented kinetic data related to the reaction of steam with Wyodak subbituminous coal. The temperature dependence of the reaction, the apparent reaction order with respect to steam, and the inhibitory effects of hydrogen 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 quarter include determination of the temperature dependence of the reaction of steam with char prepared from Wyodak subbituminous coal. In addition, the dependence of the reaction on the partial pressure of steam as well as the inhibitive effect of hydrogen were investigated.

An average apparent activation energy of 184 kJ/mol (44 kcal/mol) was observed for the steam-char reaction in the temperature range from 600 to 775°C. Diffusion of reactants and products through the pore structure of the char limits the reaction rate at higher temperatures, causing a decrease in the apparent activation energy at these temperatures. A reaction order of 0.85 with respect to steam was determined for the range of steam partial pressures from 100 to 250 kPa (1 to 2.5 atm). Hydrogen severely inhibits the reaction of steam with char, with the inhibitory effect being greater at high temperatures and at greater extents of conversion of the carbon. The conventional Arrhenius expression with added Langmuir adsorption terms does not adequately

describe the kinetics of the reaction throughout the range of operating variables studied.

## PROJECT PLAN AND STATUS

The project plan is shown in Table 1. As a result of the complicated effects of the interaction of hydrogen and steam on the kinetics of the steam-char reaction, more experiments than expected had to be carried out to investigate the inhibition by hydrogen of the reaction of steam with Wyodak char. Similar studies are now being carried out with Hanna chars, and the work using Pittsburgh seam bituminous coal will begin within approximately two months.

Table 1. Laboratory Support for *In Situ* Gasification Reaction Kinetics

| | 1976 | | | 1977 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | OCT | NOV | DEC | JAN | FEB | MAR | APR | MAY | JUNE | JULY | AUG | SEPT |
| Steam/Char Reaction Western Coals | | | | | | | | | | | | |
| Steam/Char Reaction Pittsburgh Seam Coal | | | | | | | | | | | | |
| CO$_2$/Char Reaction Western Coals | | | | | | | | | | | | |
| CO$_2$/Char Reaction Pittsburgh Seam Coal | | | | | | | | | | | | |
| Water-Gas Shift Reaction | | | | | | | | | | | | |
| Brackish Water Effects | | | | | | | | | | | | |
| Final Report on Reaction Kinetics | | | | | | | | | | | | |

## INTRODUCTION

Current and predicted 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. Primary advantages of *in situ* gasification over above-ground coal conversion include decreased capital requirements and less disruption of the environment, as well as possible utilization of coal which cannot be economically utilized by other means.

The purpose of ANL's studies in support of the national ERDA *in situ* gasification effort is to obtain reaction kinetic data for use in mathematical models of *in situ* gasification. These models are necessary if *in situ* gasification is to be employed in an efficient and economic manner to produce a variety of products, utilizing a variety of coal sources. Petrochemical feedstocks, combined-cycle power generation, and pipeline gas production will require product gases of different compositions; each application could make good use of products of *in situ* gasification. An effective mathematical model

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can be used to determine how variables such as air injection rate, water infusion, and steam partial pressure can be adjusted to tailor the product to the needs of the consumer.

Kinetic information used in current mathematical models has been obtained from studies with coals and operating conditions unlike those encountered in underground gasification. 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 are 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:

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

$$CO_2 + C \rightleftharpoons 2\ CO$$

$$2H_2 + C \rightarrow CH_4$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

$$3H_2 + CO \rightleftharpoons CH_4 + H_2O$$
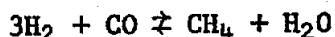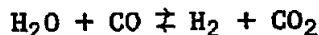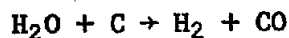
Only the first three of the above reactions contribute directly to conversion of char to gaseous products. The final two reactions affect the composition of the product gases and are of considerable economic importance in relation to tailoring the product gas to the needs of the various industries that 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 currently being determined for subbituminous coals from Wyodak and Hanna seams of Wyoming and are to be determined for bituminous coal from the Pittsburgh seam. In addition, the effects on the reaction kinetics of introducing various constituents of brackish water will be determined.

In this quarterly report are described results of three series of experimental runs with Wyodak char, which were carried out to determine: (1) the temperature dependence of the reaction of steam, (2) the dependence of the reaction rate on the partial pressure of steam, and (3) the inhibitory effect of hydrogen on the rate of reaction of steam.

## RESULTS AND DISCUSSION

The experimental apparatus and operating procedures were described in detail in Ref. 1.

### Temperature Dependence of Reaction Rate

The rate of reaction of steam with chars prepared from Wyodak coal has been measured in the temperature range from 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 rate *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, respectively. The reaction rate is expressed as grams of carbon gasified per hour per gram of ash-free carbon remaining. 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. At higher temperatures (Figs. 3 and 4), the reaction rate for the fresh carbon is actually less than that for carbon



Fig. 1. Reaction Rate *vs.* Percent Conversion for Wyodak
Char at 600°C and 266 kPa (2.66 atm) Steam

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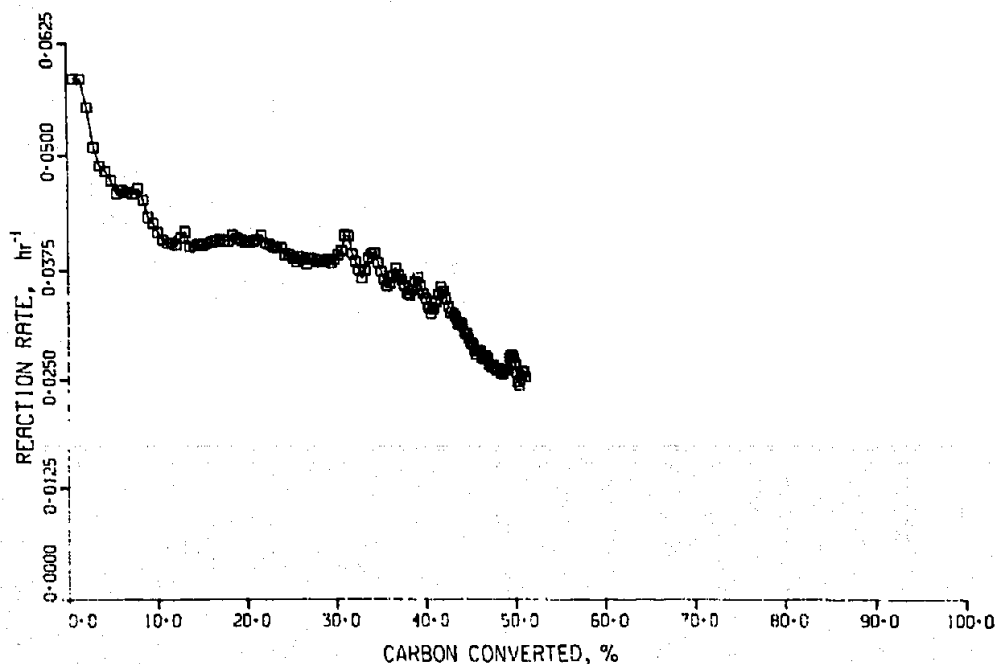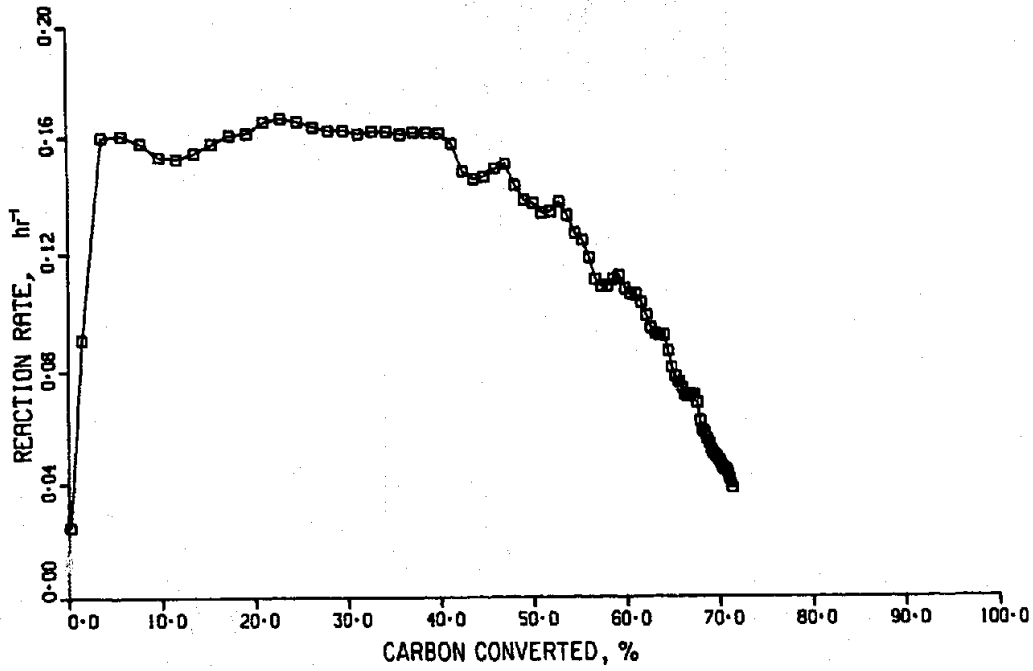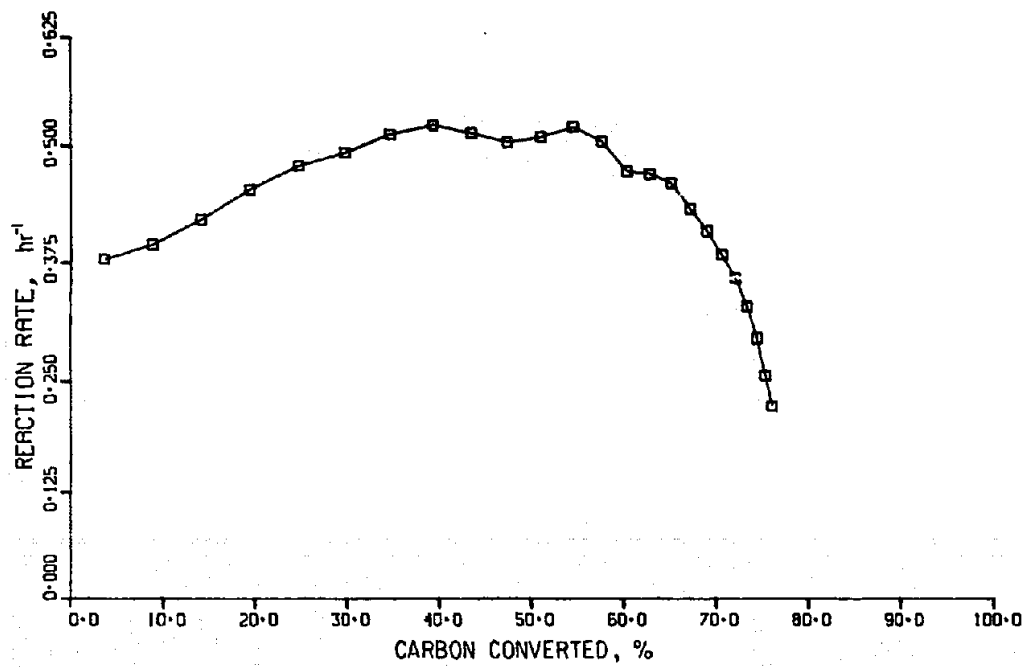Char at 650°C and 262 kPa (2.62 atm) Steam



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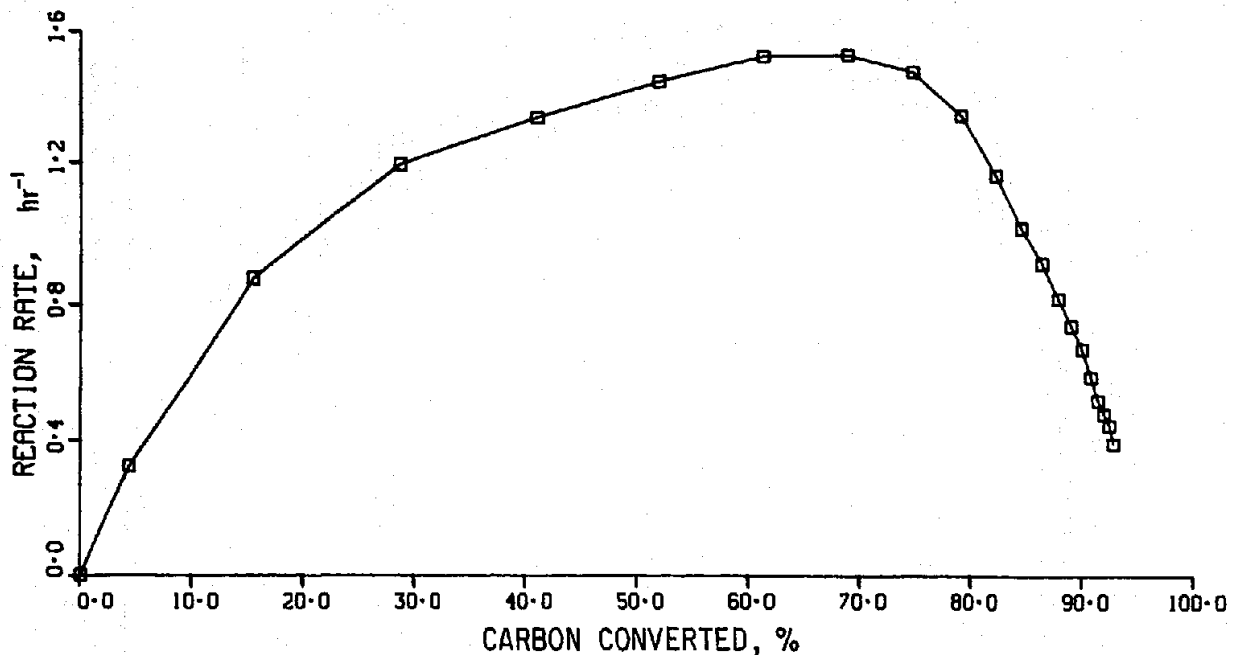Char at 700°C and 247 kPa (2.47 atm) Steam

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

which has been partially gasified.  (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.)  The
most likely 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 high temperatures, the reac-
tivity of the carbon is great 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 con-
sumed, indicating very severe diffusion limitation at these high temperatures.

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, the reaction rate is shown following gasification of 10% of
the carbon and also 50% of the carbon.  The rate at 10% carbon conversion
corresponds to the rate for fresh char, while the rate at 50% conversion cor-
responds to that for the more refractory residual char.

The effect of the 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, again suggesting the phenomenon of opening of the pore struc-
ture and consequent enhancement of the reaction rate.

A straight line fit to the majority of the data points gives the solid
line in Fig. 5, which corresponds to an average apparent activation energy of
184 kJ/mol (44 kcal/mol).  Taylor and Bowen[2] investigated the reaction of
steam and carbon dioxide with Roland seam char at atmospheric pressure.  The
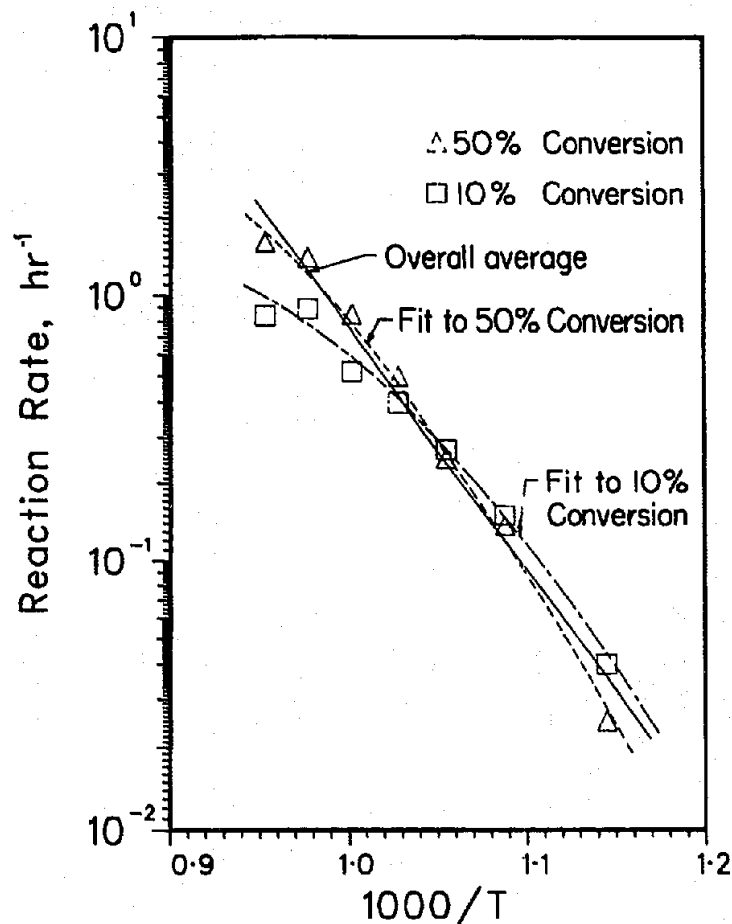
Fig. 5. Temperature Dependence of Reaction
Rate of Wyodak Char with Steam at
250 kPa (2.5 atm) Partial Pressure

Roland seam char is very similar in reactivity to Wyodak char. Their study
indicated no curvature of the Arrhenius plot; however, they included tempera-
tures 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. Since their study was
carried out at a lower partial pressure of steam, diffusion would be expected
to be a less serious problem. Earlier experiments in our own study[1] 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).

Reaction Order with Respect to Steam

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 lower partial pressures of steam
[≤300 kPa (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
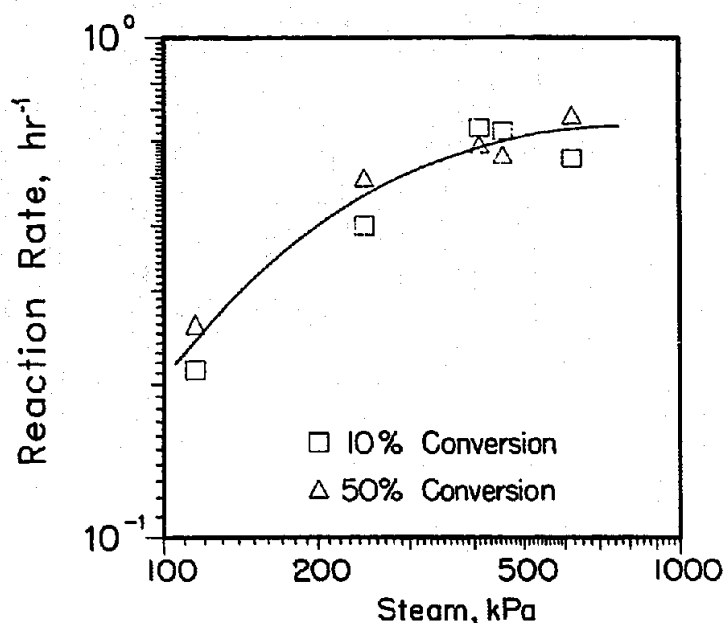
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8



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

range, the value of 0.85 is probably more applicable for use in mathematical
models than the lower reaction-order values.

## Inhibition of the Steam-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.*, 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 %.  The 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, the
hydrogen inhibition eliminates 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, 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, the diffusion limitations are severe enough that they
are apparent even at a hydrogen partial pressure of 75 kPa (0.75 atm).  At all
temperatures, high partial pressures of hydrogen cause the final decrease in
the reactivity of the char to occur at increasingly lower extents of conver-
sion.  The inhibitory effect of hydrogen is greater at higher temperatures
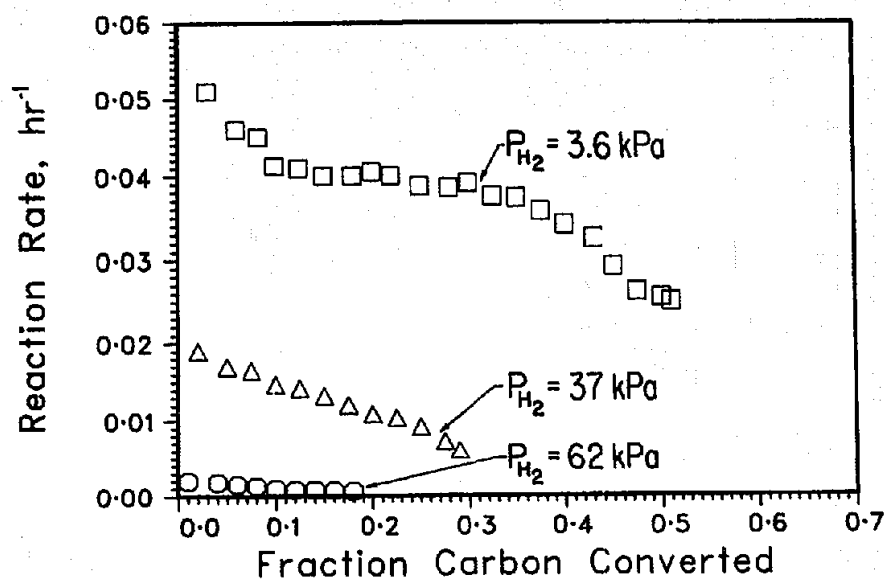and as the extent of conversion increases.

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9



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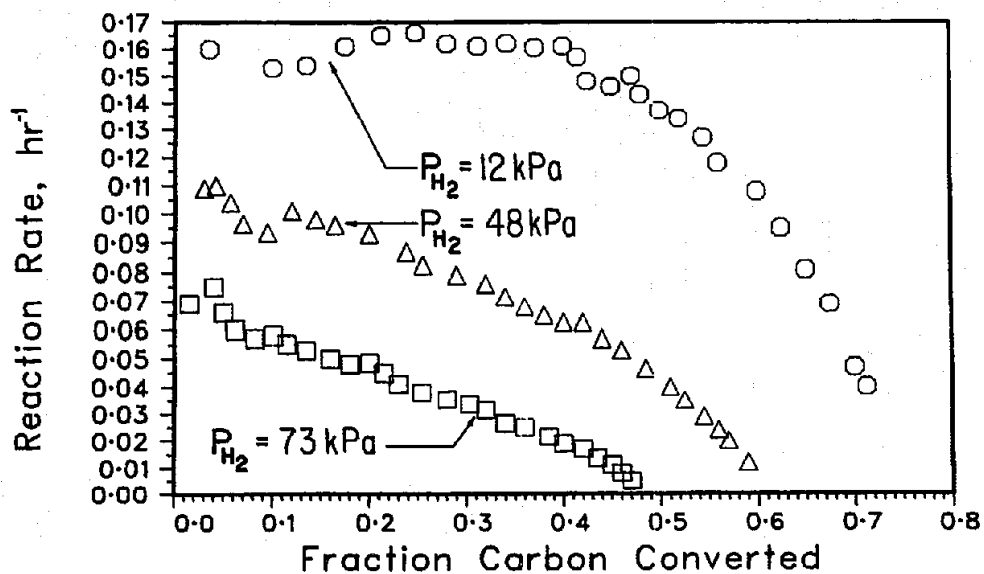Wyodak Char at 600°C and $P_{H_2O}$ = 250 kPa
(2.5 atm)



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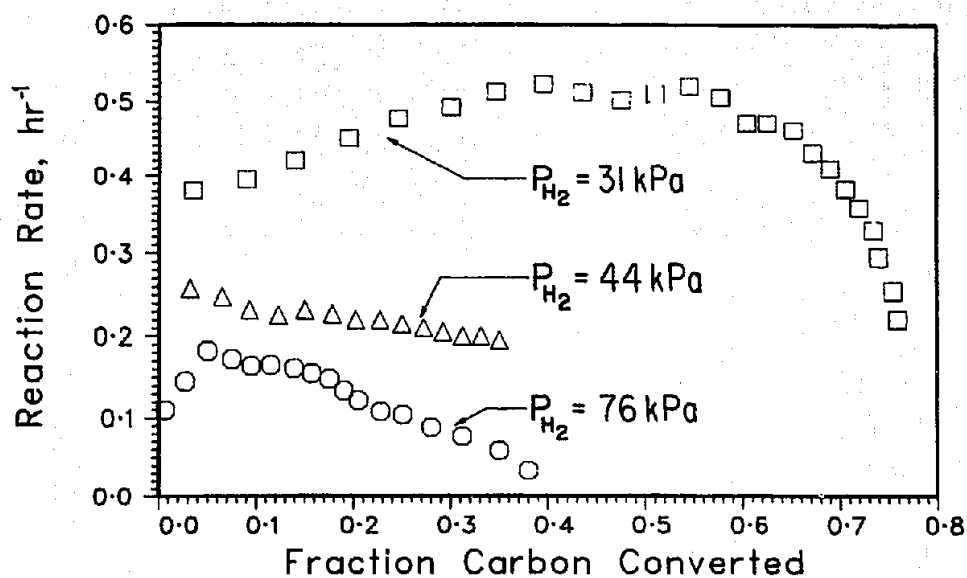Wyodak Char at 650°C and $P_{H_2O}$ = 250 kPa
(2.5 atm)

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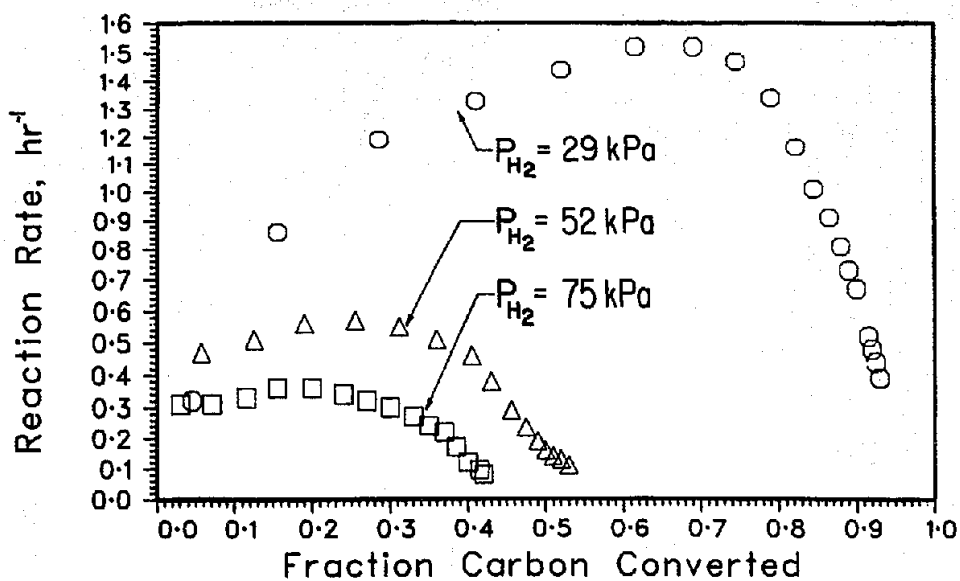Wyodak Char at 700°C and $P_{H_2O}$ = 250 kPa
(2.5 atm)



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

Because of the severe hydrogen inhibition of the steam-char reaction, the kinetics cannot be described by the simple Arrhenius expression:

$$\frac{dC}{dt} = k_o (X_c)^m (P_{H_2O})^n \exp\left(\frac{-E_a}{RT}\right) \tag{1}$$

where

$\dfrac{dC}{dt}$ = differential rate of conversion of carbon to gas

$X_c$ = fraction of carbon remaining

$m$ = reaction order with respect to carbon

$P_{H_2O}$ = partial pressure of steam

$n$ = reaction order with respect to steam

$E_a$ = apparent activation energy

$T$ = reaction temperature.

The simplest way to account for inhibition by the product hydrogen is to add a Langmuir adsorption term to Eq. 1, yielding:

$$\frac{dC}{dt} = \frac{k_o (X_c)^m (P_{H_2O})^n \exp\left(\frac{-E_a}{RT}\right)}{1 + k_1 P_{H_2}} \tag{2}$$

where

$P_{H_2}$ = partial pressure of product hydrogen.

Unfortunately, Eq. 2 still does not adequately describe the kinetics of the steam-char reaction, as determined by our experimental measurements. Equation 2 does not include a term describing the opening of the pore structure and the resulting change in apparent activation energy at higher temperatures. This expression also does not account for the dependence of the inhibition term on temperature and on the extent of conversion ($X_c$). When additional data are obtained for Hanna and Pittsburgh seam coals, a mathematical expression will be derived which will maximize the correlation of the data obtained with the variables being studied.

## FUTURE WORK

During the next quarter, studies will be completed on the reaction of steam with Hanna subbituminous and Pittsburgh seam bituminous coals. In addition, all the data obtained to date will be correlated to derive a mathematical expression relating the reaction rates with the various processing variables for the Hanna, Wyodak, and Pittsburgh coals.

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1.  J. Fischer, J. E. Young, R. N. Lo, D. C. Bowyer, J. E. Johnson, and
    A. A. Jonke, *Gasification of Chars Produced Under Simulated In Situ
    Processing Conditions, Annual Report for the Period October 1975-
    September 1976*, ANL-76-131 (December 1976).

2.  R. W. Taylor and D. W. Bowen, *Rate of Reaction of Steam and Carbon Dioxide
    with Chars Produced from Subbituminous Coals*, UCRL-52002 (Jan 16, 1976).