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KINETICS OF CHAR GASIFICATION REACTIONS UNDER CONDITIONS OF UNDERGROUND COAL GASIFICATION

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Kinetics of Char Gasification Reactions Under Conditions of Underground Coal Gasification

by

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ABSTRACT

This project, which is part of the Argonne National Laboratory 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 the gasification of chars resulting from pyrolysis of coal in underground gasification. The data obtained from these studies are used in the mathematical modeling of in situ gasification systems, in order to understand and interpret field experimental data and to design future field studies. The reactions being studied include steam-char, CO_2-char, and water gas shift reactions, as well as methane-producing reactions such as the methanation of CO or the hydrogen-char reaction.

The kinetics studies are carried out in a packed bed differential reactor in which steam, hydrogen, carbon dioxide, and/or other reactants are blended with nitrogen to obtain the desired total pressure and partial pressures of reactants. The preparation of the char is carried out immediately prior to gasification in the reactor under conditions of pressure, heating rate, and sweeping gas composition similar to those encountered in underground gasification. The coals studied include Wyodak and Hanna subbituminous coals and Pittsburgh seam high volatile bituminous coal.

Kinetic data are reported for the reaction of steam with chars prepared from the Wyodak and Hanna coals. The dependence of the reaction rate on the partial pressures of reactant steam and product hydrogen is described. The temperature dependence of the reaction rates indicates that diffusion of the reactants and products through the pore structure of the Hanna char limits the reaction more severely than in the case of the Wyodak char. The rate of reaction of steam with Wyodak char is approximately fifty percent greater than the rate observed with the Hanna char. The reaction order with respect to steam at low partial pressures of steam varies from 0.5 to approximately 1.

Preliminary information is also reported for the reaction of steam with chars prepared from Pittsburgh seam coal.

INTRODUCTION

The purpose of our work at Argonne National Laboratory 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:

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

$$CO_2 + C \rightleftarrows 2\ CO$$

$$2H_2 + C \rightarrow CH_4$$

$$H_2O + CO \rightleftarrows H_2 + CO_2$$

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

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 reactants.

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.

EXPERIMENTAL

The kinetics studies are carried out in a packed bed differential reactor 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 Ref. 1.

Pyrolysis of the char is carried out immediately prior to gasification in the 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, the system pressure is 0.79MPa (100 psig), and the sweeping gas consists of a blend of approximately 20 mol % hydrogen in nitrogen.

RESULTS AND DISCUSSION

The product gas from the underground gasification process consists primarily of hydrogen, carbon monoxide, carbon dioxide, methane, and nitrogen. This mixture constitutes a reducing atmosphere which sweeps through the coal during pyrolysis. In order to obtain a true simulation of these conditions during the pyrolysis prior to our gasification kinetics studies, our sweeping gas mixture should contain all of these components.

However, addition of carbon monoxide to the pyrolysis sweeping gas results in deposition of carbon, which is added to the char in the gasification reactor. This additional carbon is a result of the reverse Boudart reaction catalyzed by the coal ash and the alumina packing materials in the reactor:

$$2CO \rightleftarrows C + CO_2$$

The deposited carbon is not quantitatively determinable and must be eliminated or made negligible in order to obtain carbon balances. Therefore, our pyrolysis reactions have been carried out in a reducing atmosphere consisting of only hydrogen and nitrogen. Our experiments indicate that in the case of Wyodak coal, pyrolysis in a reducing atmosphere (20% H_2, balance N_2) results in recovery of approximately ten percent less char following pyrolysis than when pure nitrogen is used as the sweeping gas. However, the reactivity of this char produced in hydrogen is the same as that for char produced in pure nitrogen.

The rate of reaction of steam with chars prepared from Wyodak coal has been measured in the temperature range of 600-775°C, with a partial pressure of steam of 2.5-2.6 atmospheres and a total pressure of approximately nine atmospheres.

Plots of the reaction rate vs. fraction of carbon converted at 600, 650, 700, and 750°C are shown in Figs. 1-4, respectively. The reaction rate is expressed as g carbon gasified/hr/g ash-free carbon remaining. At 600°C (Fig. 1), it is apparent that the char initially gasified is quite reactive, but this reactivity decreases to an approximate constant value while the next 10-35% of the carbon is gasified. The reactivity of the residual carbon then decreases rapidly. At 650°C (Fig. 2), the very high initial reactivity 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 which has been partially gasified. (At 750°C, the first two data points are of questionable validity because the reaction rate was so rapid 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 would be restricted diffusion of the steam reactant and the product gases through the pore structure of the char. At high temperatures, the reactivity of the carbon is great enough that the pore structure must be opened up to provide more reactant surface 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 these high temperatures.

The rate of reaction for the Wyodak char with steam is plotted as a function of reciprocal temperature (Arrhenius plot) in Fig. 5. The range of temperatures is 600 to 775°C. At each temperature, the reaction rates following gasification of 10% of the carbon and also following gasification of 50% of the carbon are shown. The rate for 10% carbon conversion would correspond to the rate for fresh char; the rate for 50% conversion would correspond to that for the more refractory residual char.

The effect of the reaction rate being limited by diffusion 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 that the pore structure must open at high temperatures, to give the enhanced reaction rate.

If a straight line is fitted to the majority of the data points, the solid line in Fig. 5 is obtained, which corresponds to an average apparent activation energy of 44 kcal/mole. Taylor and Bowen[2] investigated the reaction of steam and carbon dioxide with Roland seam char at atmospheric pressure. The reactivity of Roland seam char is very similar to that of Wyodak char. Their study indicated no curvature of the Arrhenius plot (they included temperatures only as high as 675°C). They also obtained a value of 44 kcal/mole for the temperature range of their study. Since their study was carried out utilizing a lower partial pressure of steam, it would be expected that the diffusion limitation would be a less serious problem. Our earlier experiments[3] indicated that at a steam partial pressure of 7.0 atm, the curvature of the Arrhenius plot caused by diffusion limitations is even greater than that observed at 2.5 atm.

In Figs. 6-9, rates of reaction of steam with chars prepared from Hanna No. 1 coal are shown. This coal is a portion of the core sample obtained from Well No. 4 at the Hanna IV test site. The sample was supplied to us by the Laramie Energy Research Center. The temperatures, which are shown in Figs. 6-9, are 600, 650, 700, and 750°C, respectively. The reaction of Hanna char exhibits the limitations caused by diffusion through the pore structure of the char throughout the temperature range studied; the shape of all of the reaction rate curves is in general the same as the shape of the high temperature curve for the Wyodak char. At the lower temperatures (600°, 650°C), there are indications that a very small proportion of higher reactivity char is present during the very early stages of the reaction, although it appears that this makes an insignificant contribution to the overall reaction.

The Arrhenius plot for the Hanna char is shown in Fig. 10. At conversion of ten percent of the carbon, the apparent activation energy varies from 34.1 kcal/mole at low temperatures to 21.2 kcal/mole in the higher temperature region.

For 50% carbon conversion, the apparent activation energy varies from 37.2 kcal/mole to 26.2 kcal/mole. This dependence of the apparent activation energy on both temperature and extent of carbon conversion is consistent with different reaction mechanisms predominating at different temperatures. At higher temperature, the reaction occurs largely on the more available outer surface, and there is insufficient time for diffusion of gases through the fine pore structure.

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 1.2 to 6.5 atm. Reaction rate is plotted as a function of steam partial pressure in Fig. 11. At lower partial pressures of steam, the curve is nearly linear, with a slope of approximately 0.85. This corresponds to a reaction order of 0.85 with respect to steam, i.e., the dependence of the reaction rate on the partial pressure of steam. 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, the reaction order of 0.85 is probably applicable for use in the mathematical models proposed for this process.

Figure 12 shows the dependence of the reaction rate on the partial pressure of steam for Hanna char. The reaction rate is plotted for conversion of 10, 30, and 50% of the carbon, in the range of 1.07 to 2.7 atm steam. 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--undoubtedly due to diffusion of steam being limited by the finer pore structure of the Hanna char.

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 with very high gasification rates (e.g., at high temperatures or high partial pressures of steam) resulted in hydrogen levels of 2-4 mol %. However, in the majority of the runs, hydrogen content of the product was considerably less than 1 mol %. In order to investigate inhibition of the steam-char reaction by product hydrogen, a series of experiments was carried out in which hydrogen was added to the reactant steam. The range of hydrogen partial pressures investigated includes those expected to be encountered in the current low-pressure underground field tests (i.e., up to approximately 1 atm). Four temperatures have been investigated--600, 650, 700, and 750°C.

The results of these experiments are shown in Fig. 13-16. At 600°C (Fig. 13), inhibition of the reaction by hydrogen results in a rapid decline in reaction rate as the char is consumed. At 700°C (Fig. 15), inhibition of the steam-char reaction by hydrogen is sufficient to eliminate the effects of diffusion limitations during the early stages of the reaction. At 750°C (Fig. 16), the diffusion limitations are severe enough that they are apparent even in the presence of 0.75 atm. hydrogen. At all temperatures, the rapid decrease in the reactivity of the char (at the later stages of the reaction) occurs earlier in the reaction as the partial pressure of hydrogen increases. Hydrogen exerts a greater inhibitory effect at higher temperatures and as the extent of gasification increases.

We have not yet obtained data showing the effects of hydrogen on the reaction rate of steam with Hanna char. Such studies are currently under way.

Because of the severe hydrogen inhibition of the steam-char reaction, we cannot use a simple Arrhenius expression to describe the kinetics:

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

where

$\frac{dC}{dt}$ = differential rate of conversion of carbons to gas

X_c = fraction of carbon remaining

P_{H_2O} = partial pressure of steam

m = reaction order with respect to carbon

n = reaction order with respect to steam

E_a = apparent activation energy

T = reaction temperature, K

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

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

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 includes no term describing the opening of the pore structure and the resulting change in apparent activation energy at higher temperatures. This equation also fails to account for the dependence of the inhibition term on temperature and the extent of carbon conversion (X_c). When additional data are obtained for Hanna and Pittsburgh seam coals, a mathematical expression will be derived which will improve the correlation of the data obtained with the variables being studied. These data will then have maximum utility for use in the mathematical models of the underground gasification process.

CONCLUSIONS

At high temperatures (700-750°C), the Wyodak char is 50-100% more reactive with steam than is Hanna char, although at lower temperatures (600-650°C), the two have essentially equal reactivities with steam. 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 the pore structure.

Hydrogen severely inhibits the reaction of steam with Wyodak char; this inhibition is greater in magnitude as temperature increases and as a greater fraction of the carbon is gasified.

A conventional Arrhenius kinetic expression modified by the Langmiur adsorption term (for hydrogen inhibition) has been found to be unsuitable for adequately describing the dependence of the reaction rate on the variables: partial pressure of steam, temperature of reaction, extent of gasification, and partial pressure of hydrogen.

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

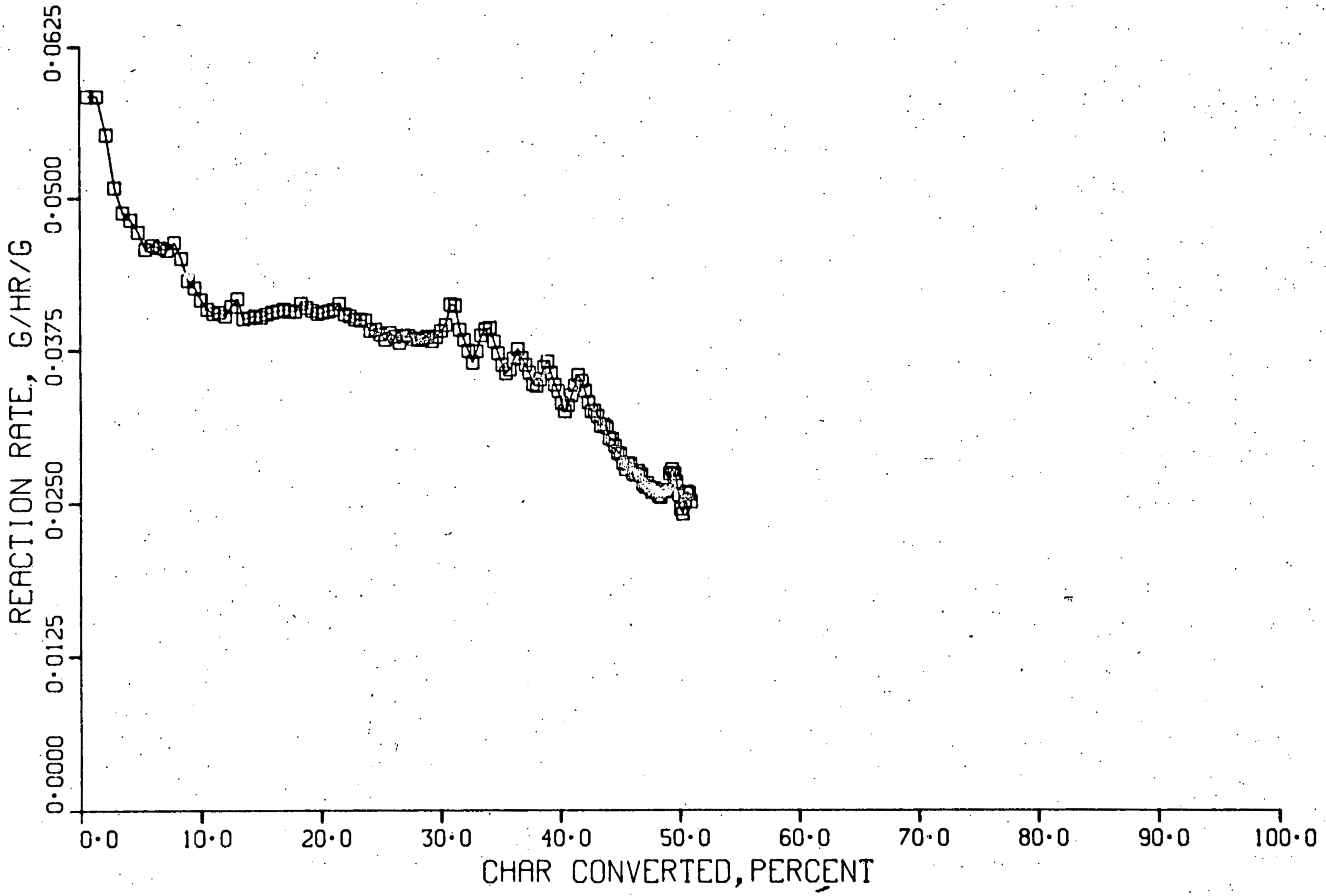

Fig. 1

INSTANTANEOUS CARBON CONVERSION RATE
WYODAK
600°C, 2.66 atm Steam
Run Number 70

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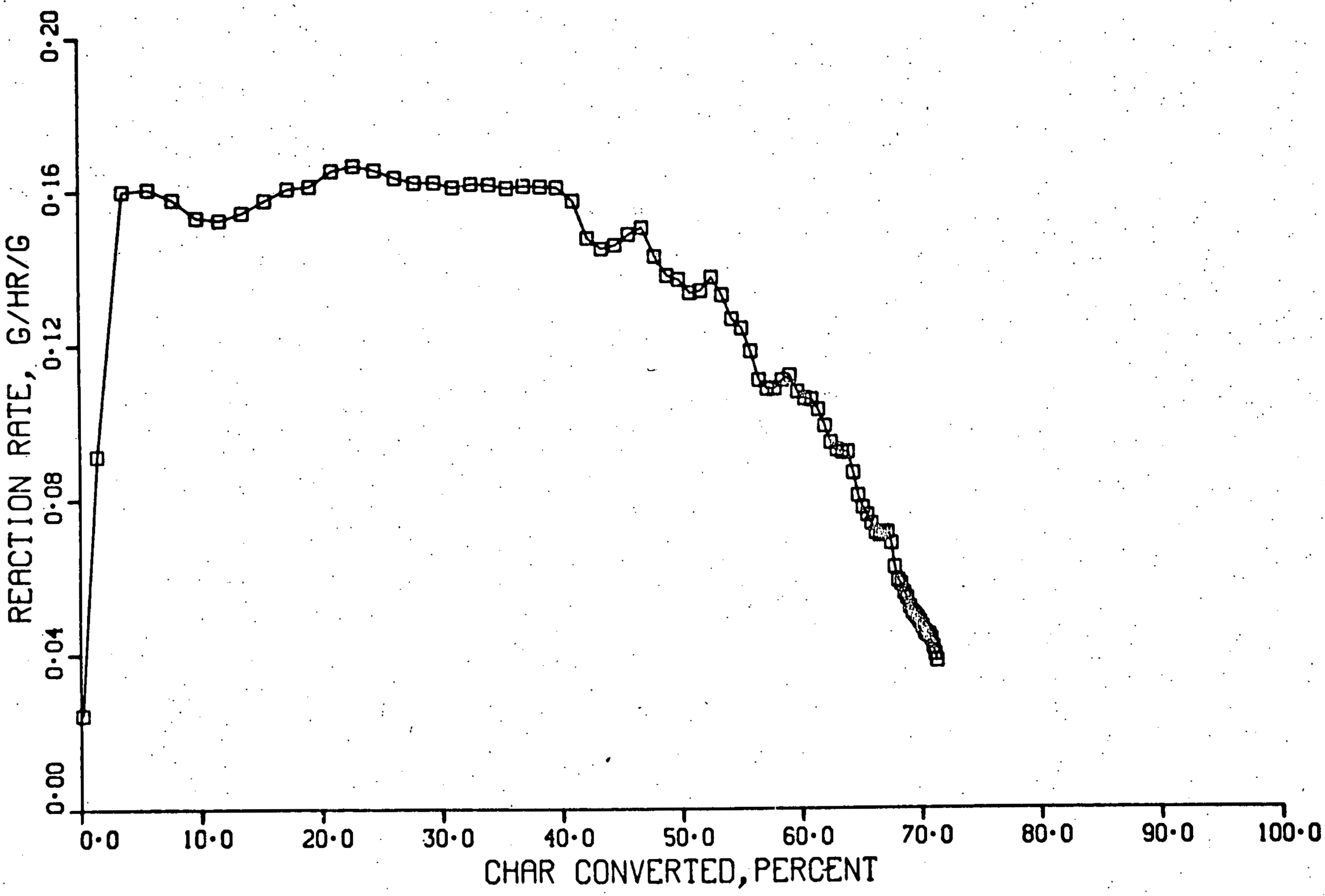


Fig. 2

INSTANTANEOUS CARBON CONVERSION RATE
WYODAK 9
650°C, 2.62 atm Steam
Run Number 69

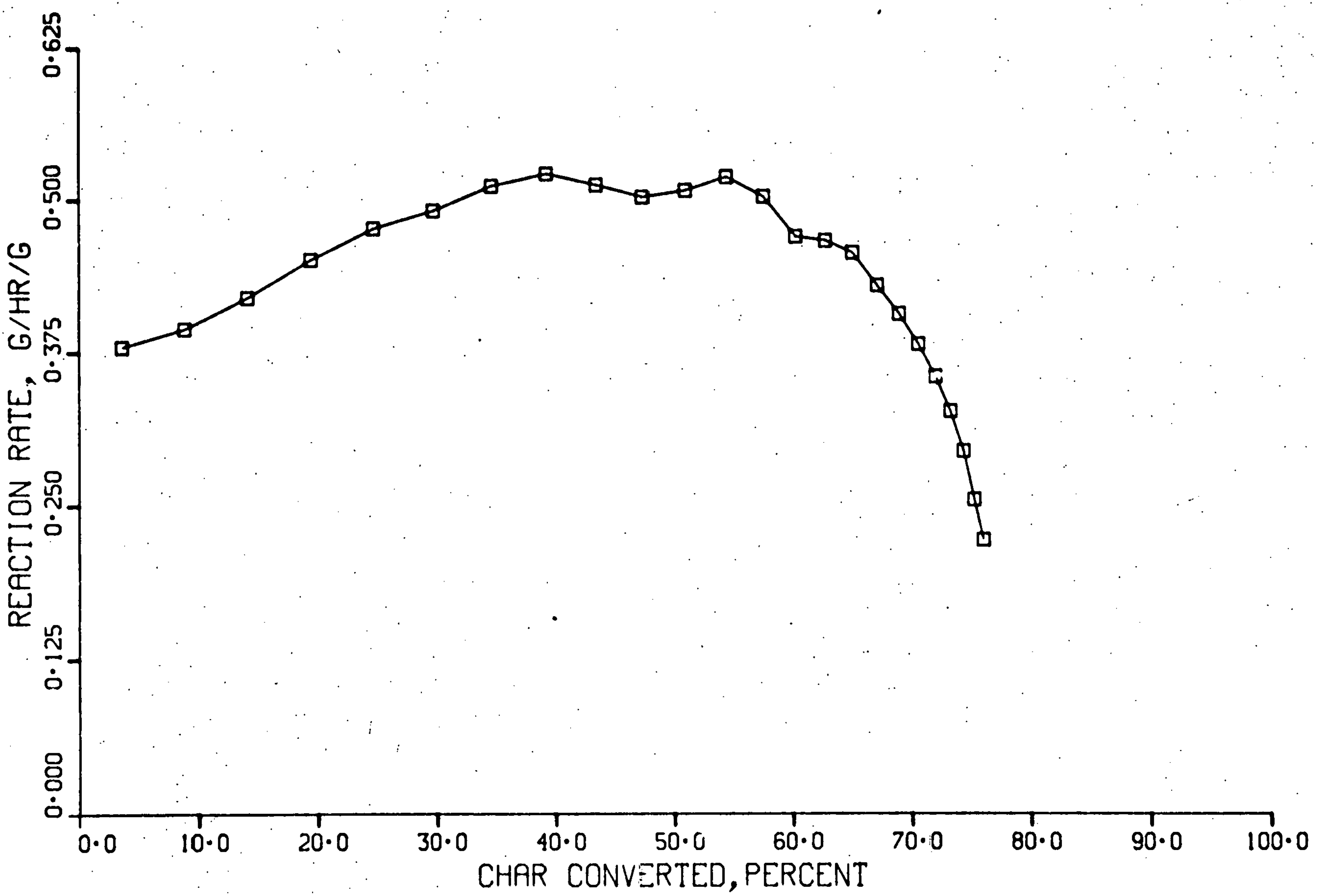


Fig. 3

INSTANTANEOUS CARBON CONVERSION RATE
WYODAK
700°C, 2.47 atm Steam
Run Number 63

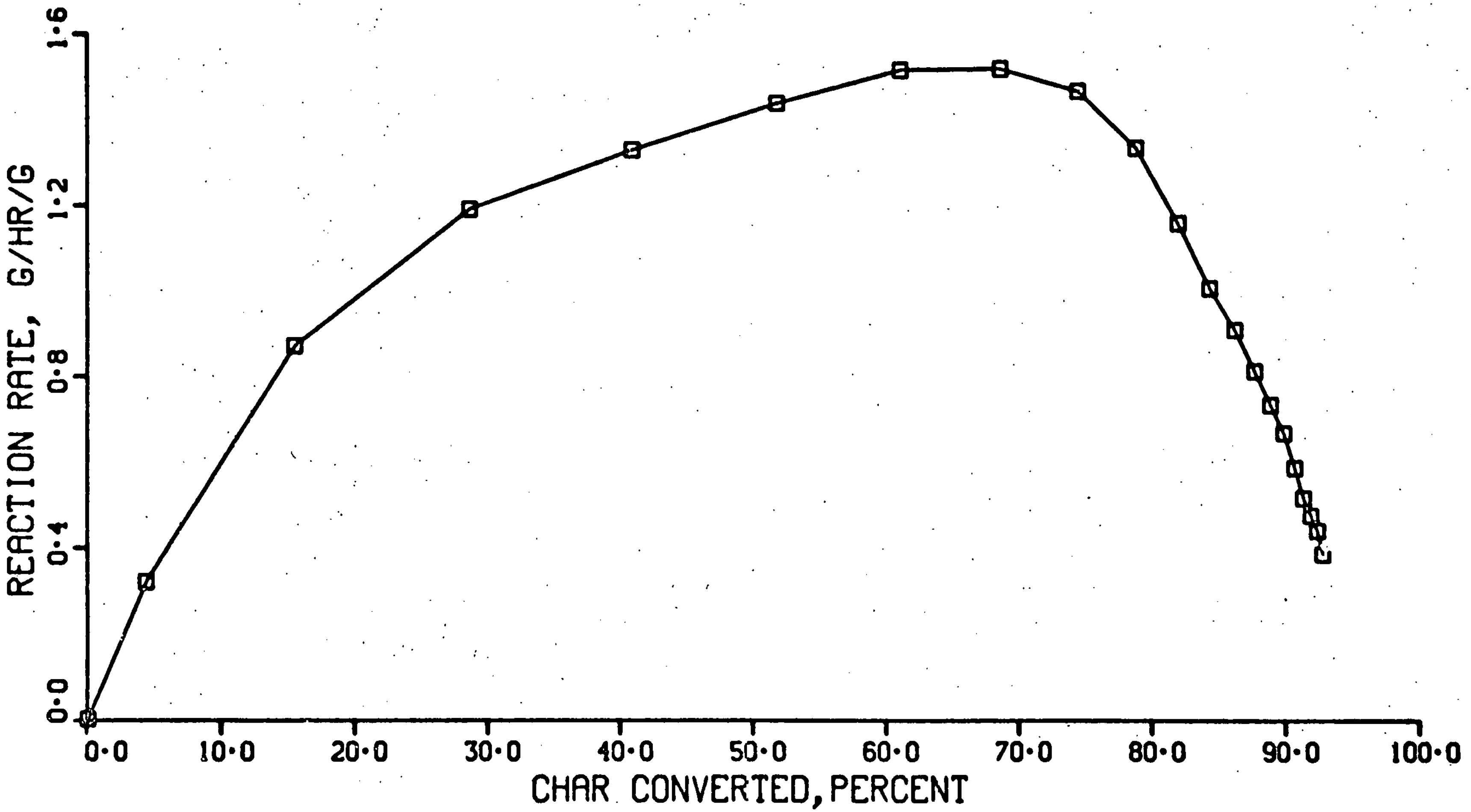
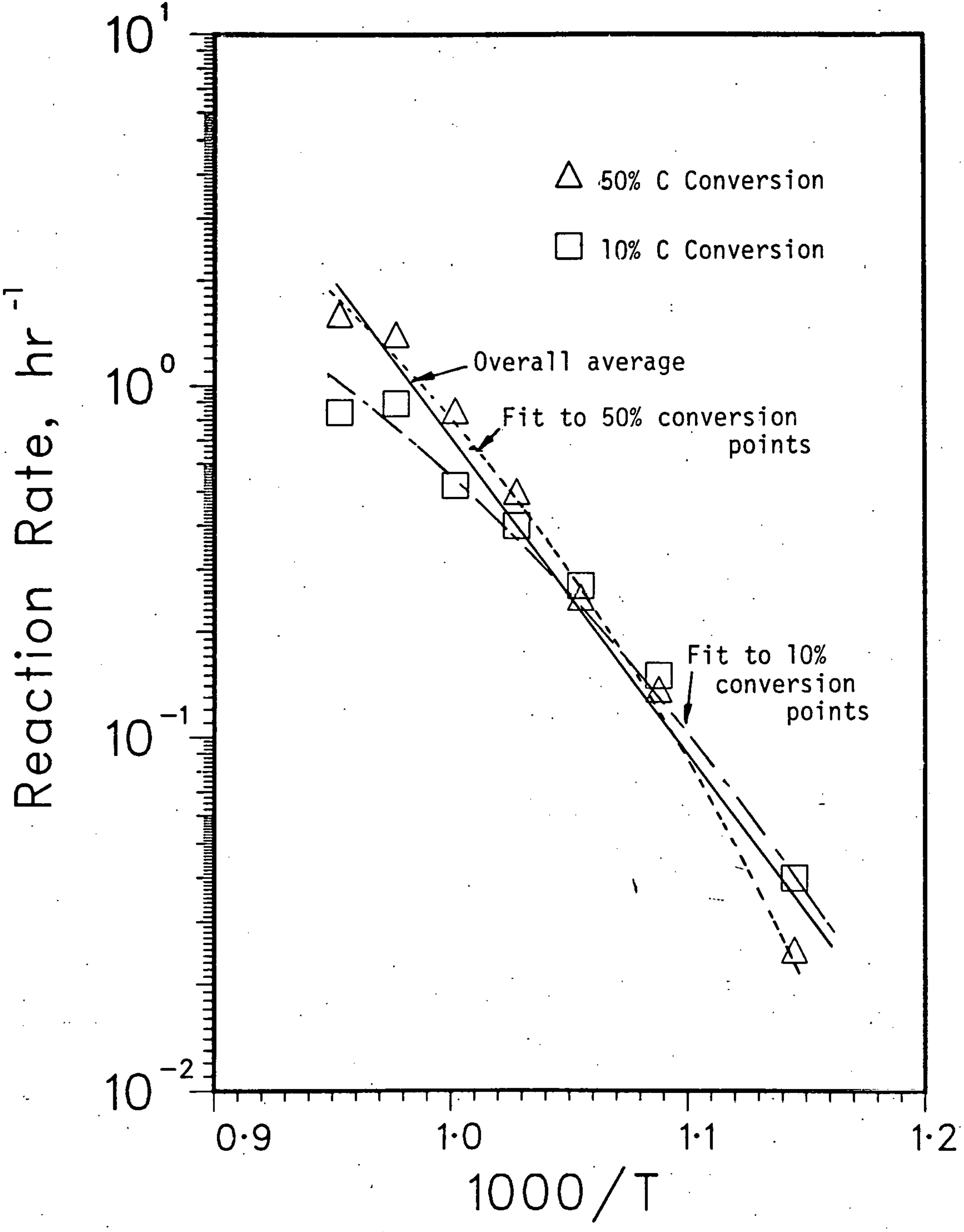


Fig. 4

INSTANTANEOUS CARBON CONVERSION RATE
WYODAK
750°C, 2.35 atm Steam
Run Number 66

Fig. 5
TEMPERATURE DEPENDENCE OF
STEAM-CHAR REACTION RATE

Wyodak Char
2.5 atm Steam



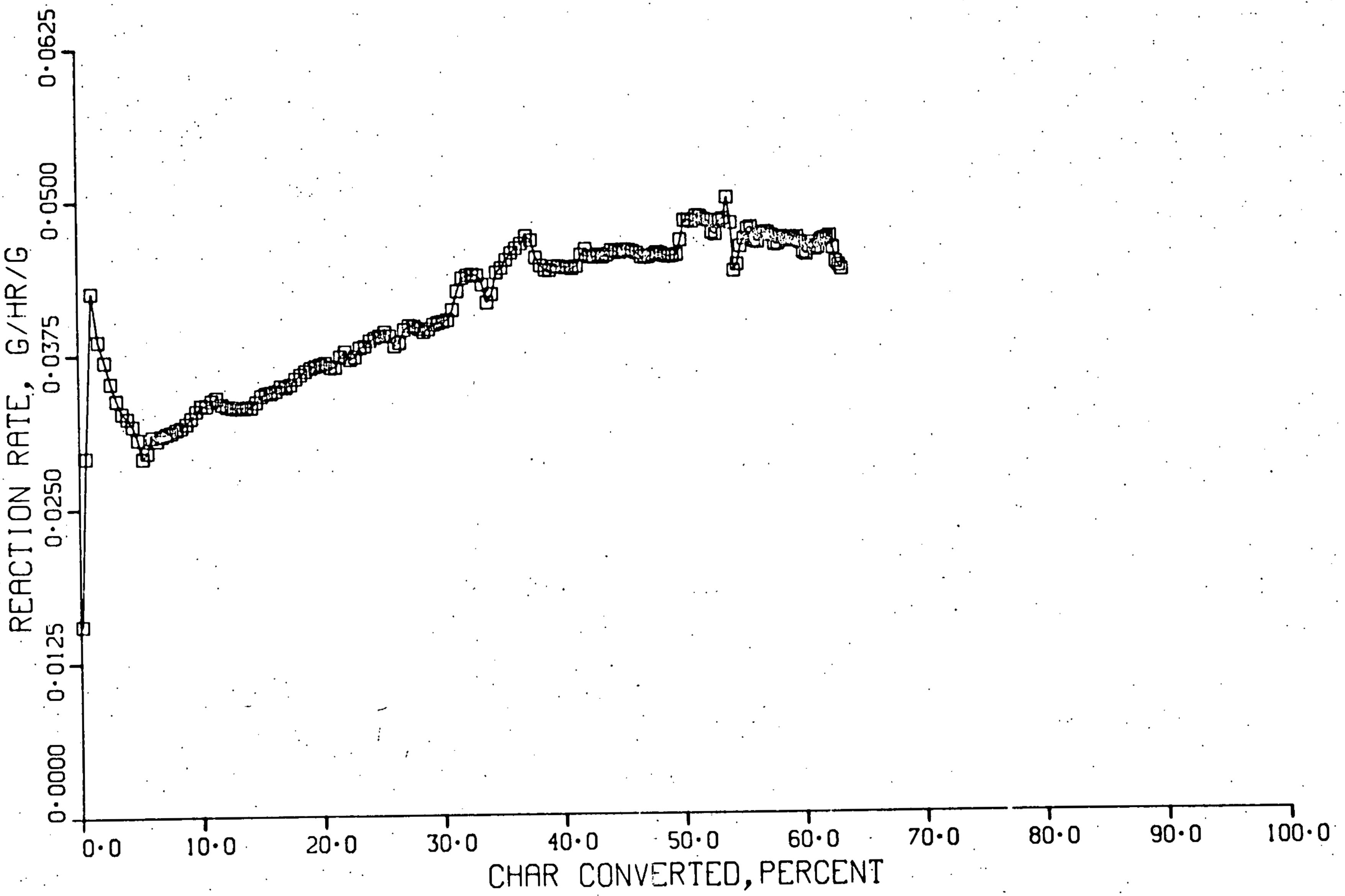


Fig. 6
INSTANTANEOUS CARBON CONVERSION RATE
HANNA NO. 1
600°C, 2.68 atm Steam
Run Number 86

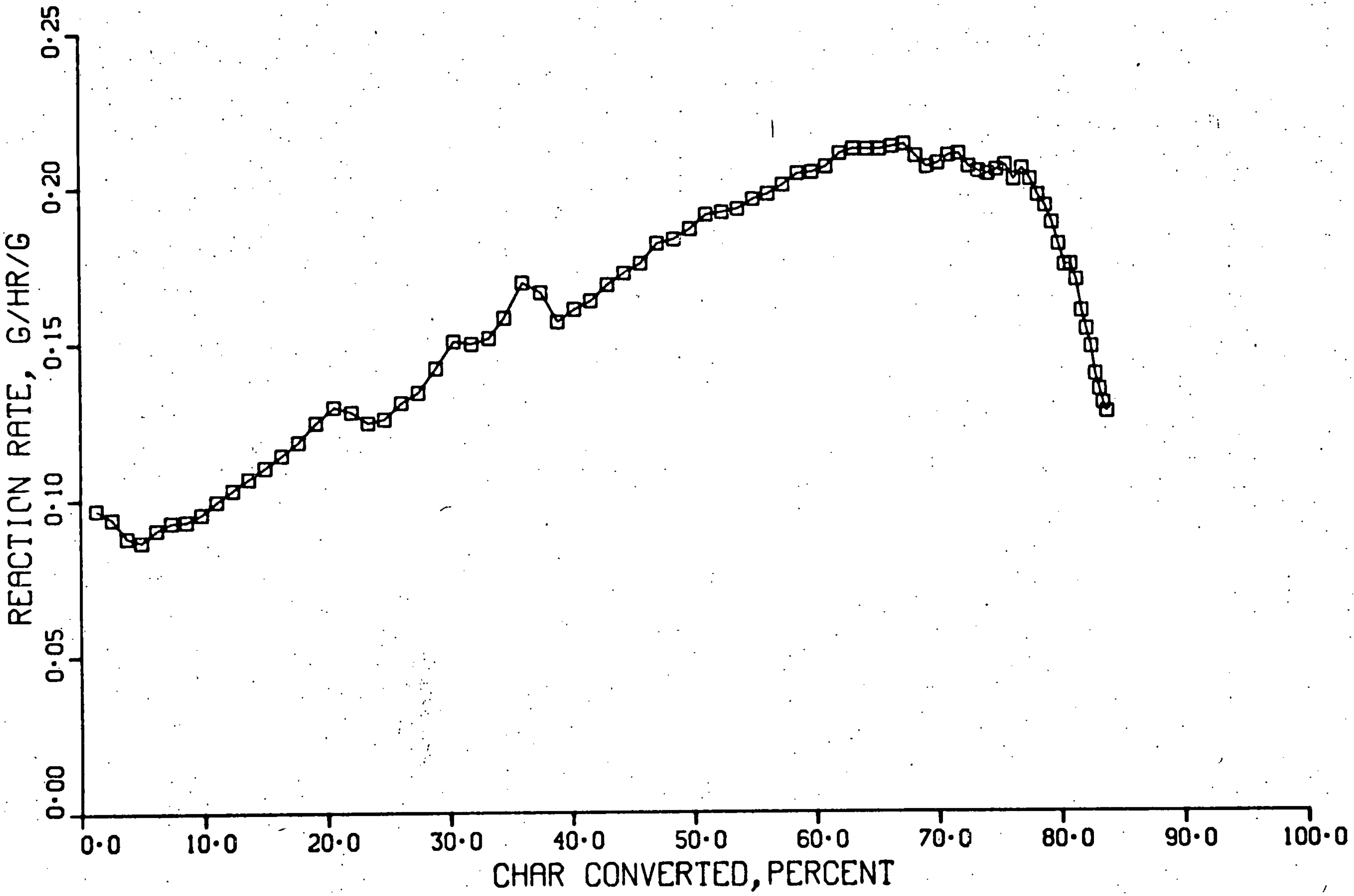


Fig. 7
INSTANTANEOUS CARBON CONVERSION RATE
HANNA NO. 1
650°C, 2.73 atm Steam
Run Number 85

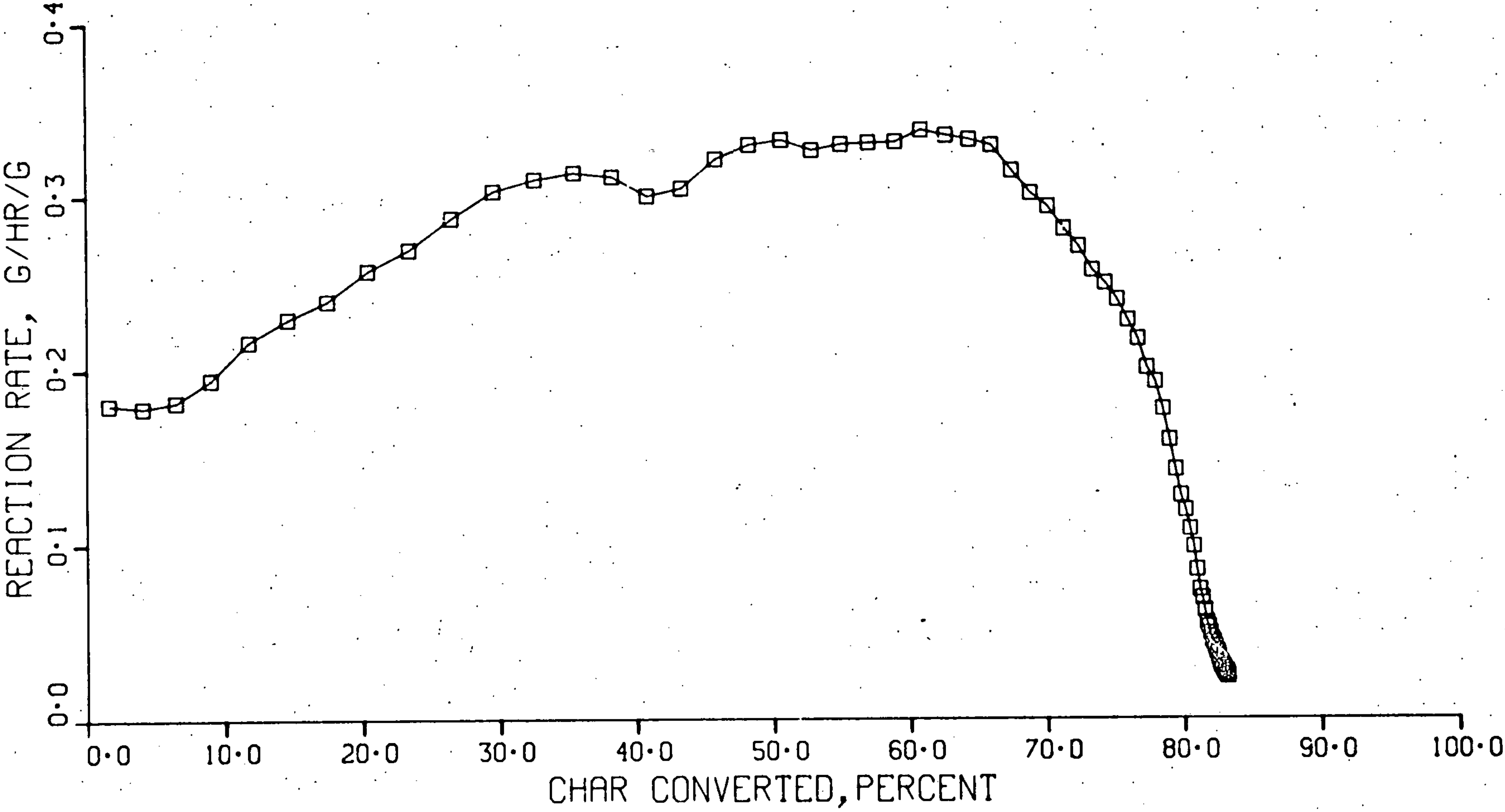


Fig. 8
INSTANTANEOUS CARBON CONVERSION RATE
HANNA NO. 1
700°C, 2.60 atm Steam
Run Number 84

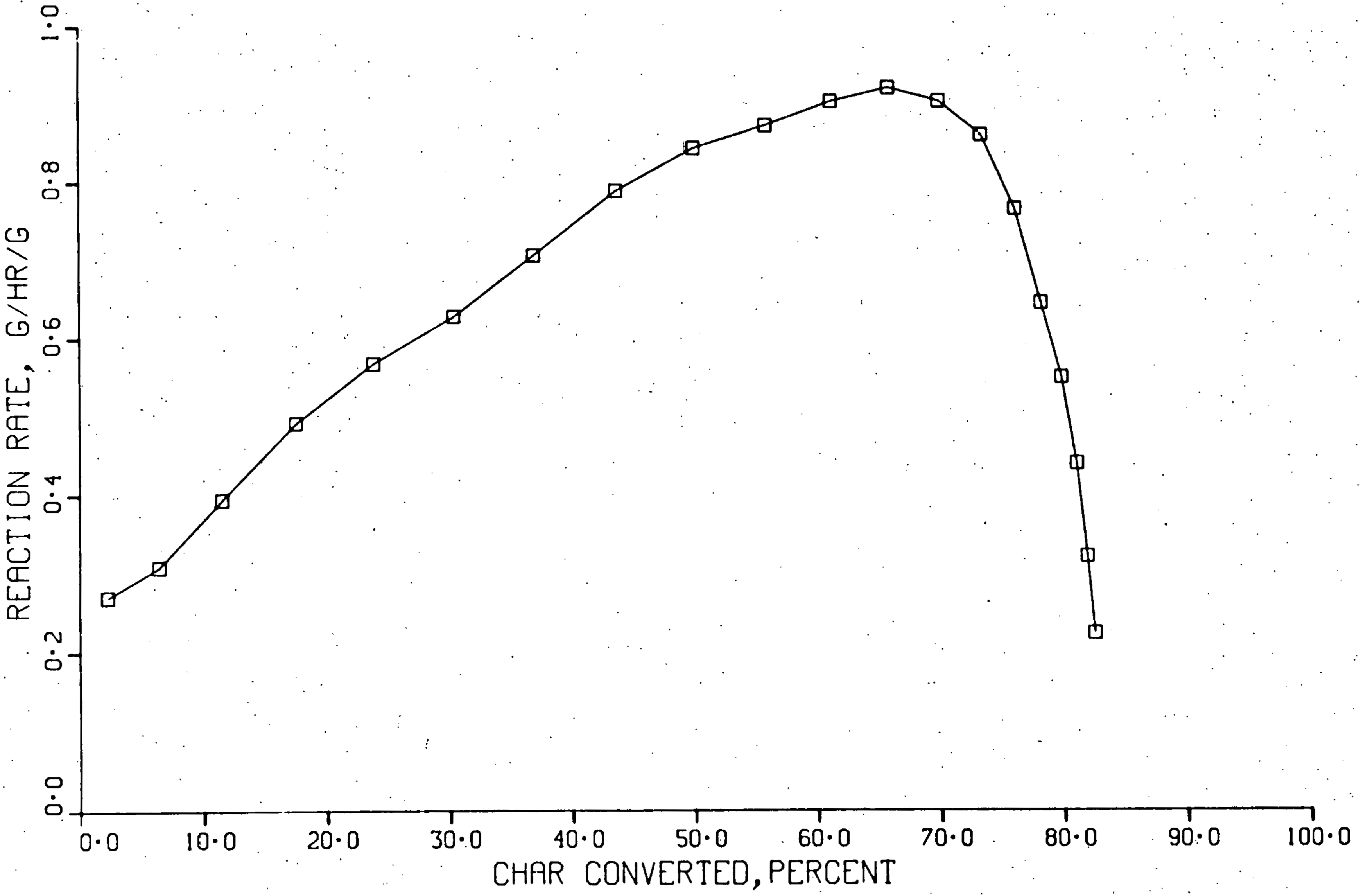
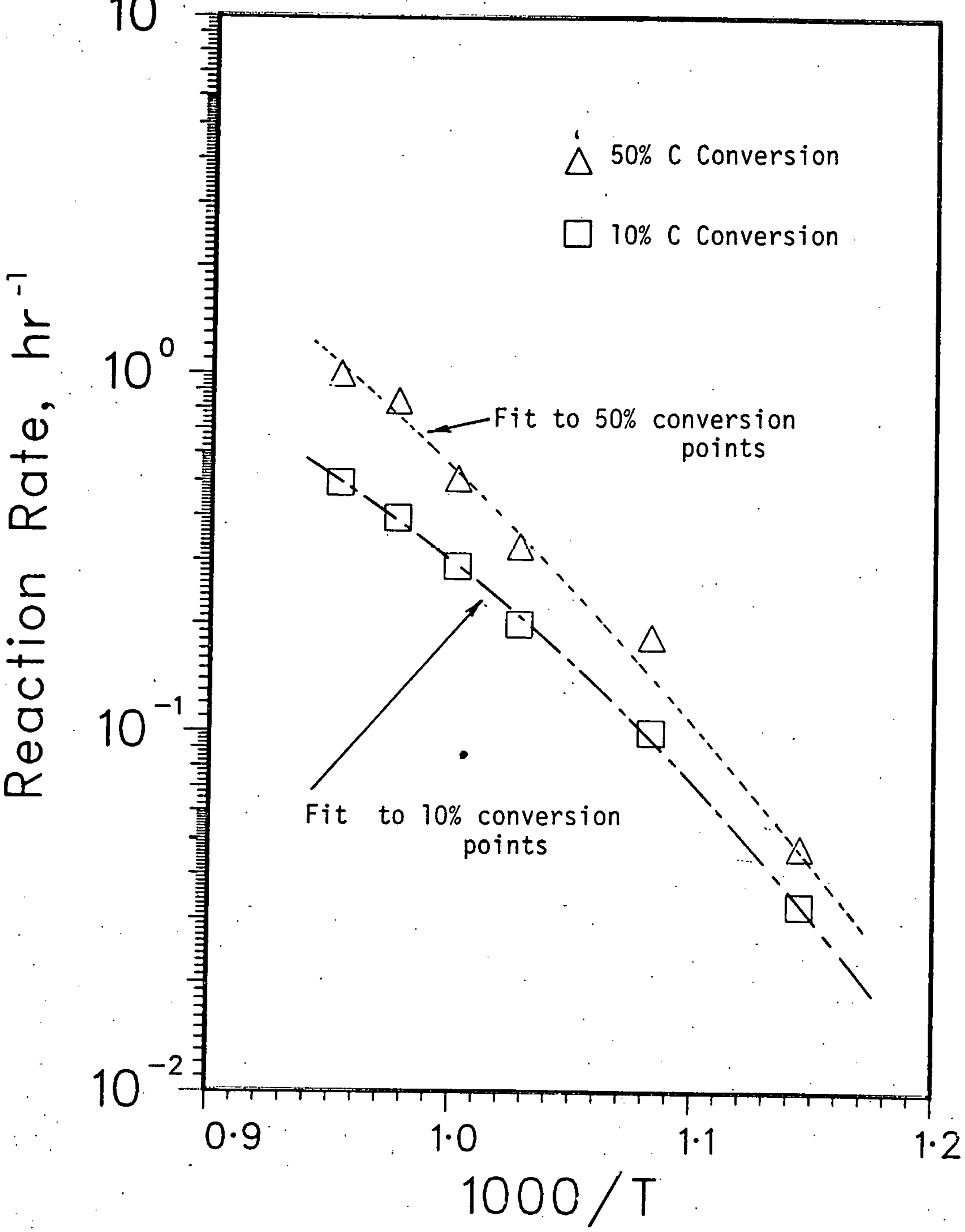


Fig. 9
INSTANTANEOUS CARBON CONVERSION RATE
HANNA NO.1
750°C, 2.71 atm Steam
Run Number 81

Fig. 10
TEMPERATURE DEPENDENCE OF
STEAM-CHAR REACTION RATE

Hanna No.1
2.6 atm. Steam



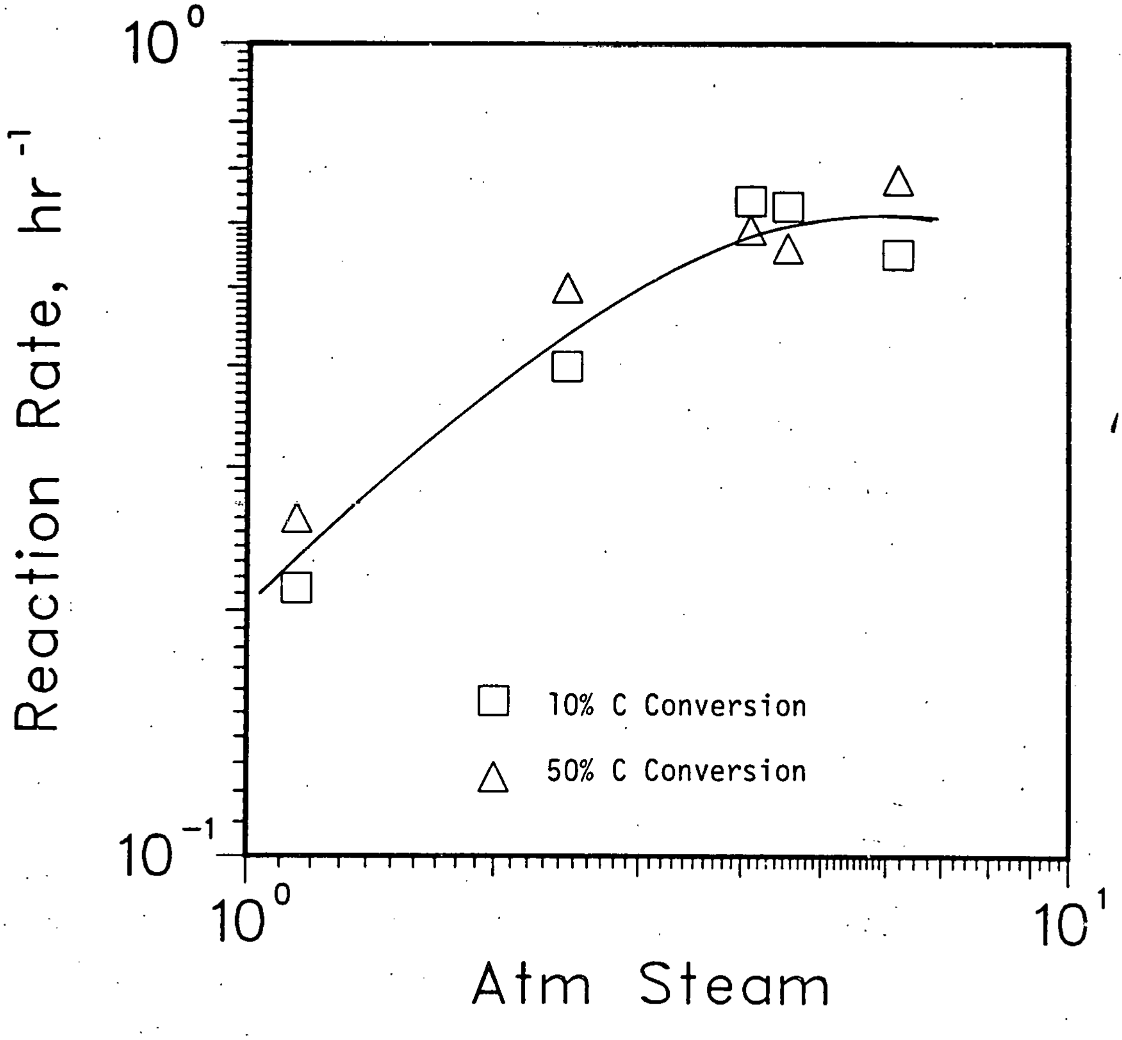


Fig. 11
Dependence of The Steam-Char Reaction Rate on Partial Pressure of Steam

Wyodak Char, 700°C

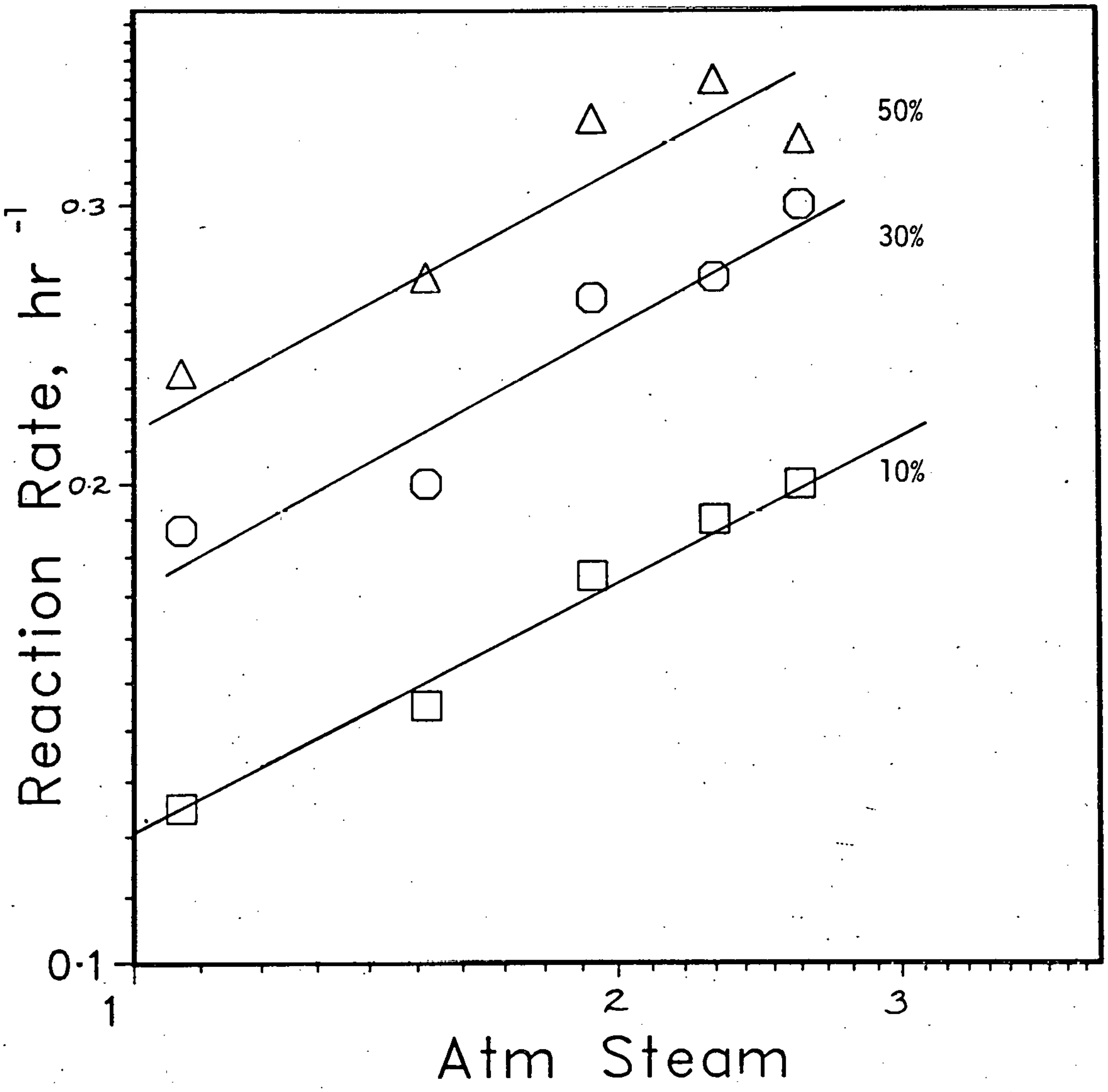


Fig. 12
Dependence of The Steam-Char Reaction Rate on The Partial Pressure of Steam

Hanna No. 1 Char, 700°C

Fig. 13
Hydrogen Inhibition of The Steam-Char Reaction

Wyodak Char
600°C, 2.5 atm Steam

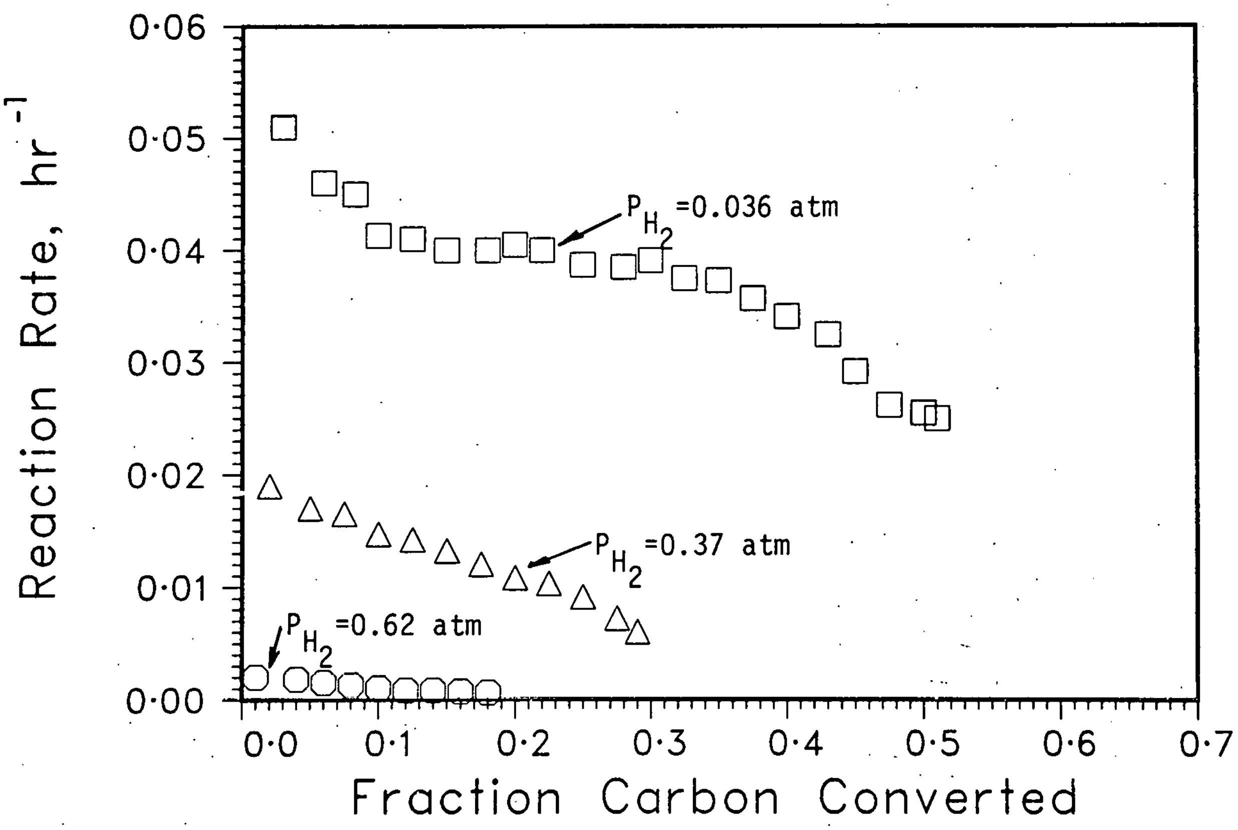


Fig. 14
Hydrogen Inhibition of The Steam-Char Reaction

Wyodak Char
650°C, 2.5 atm Steam

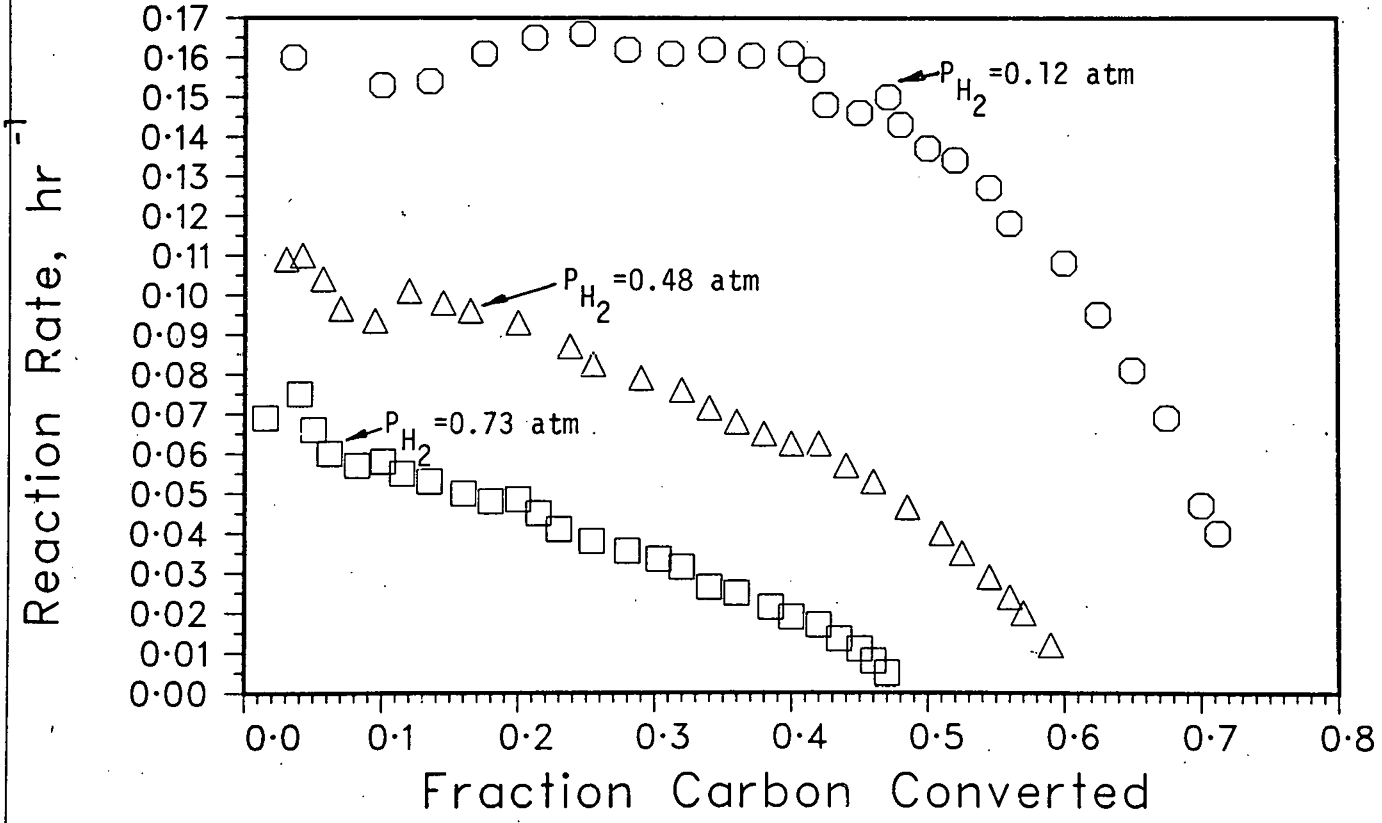


Fig. 15
Hydrogen Inhibition of The Steam-Char Reaction

Wyodak Char
700°C, 2.5 atm Steam

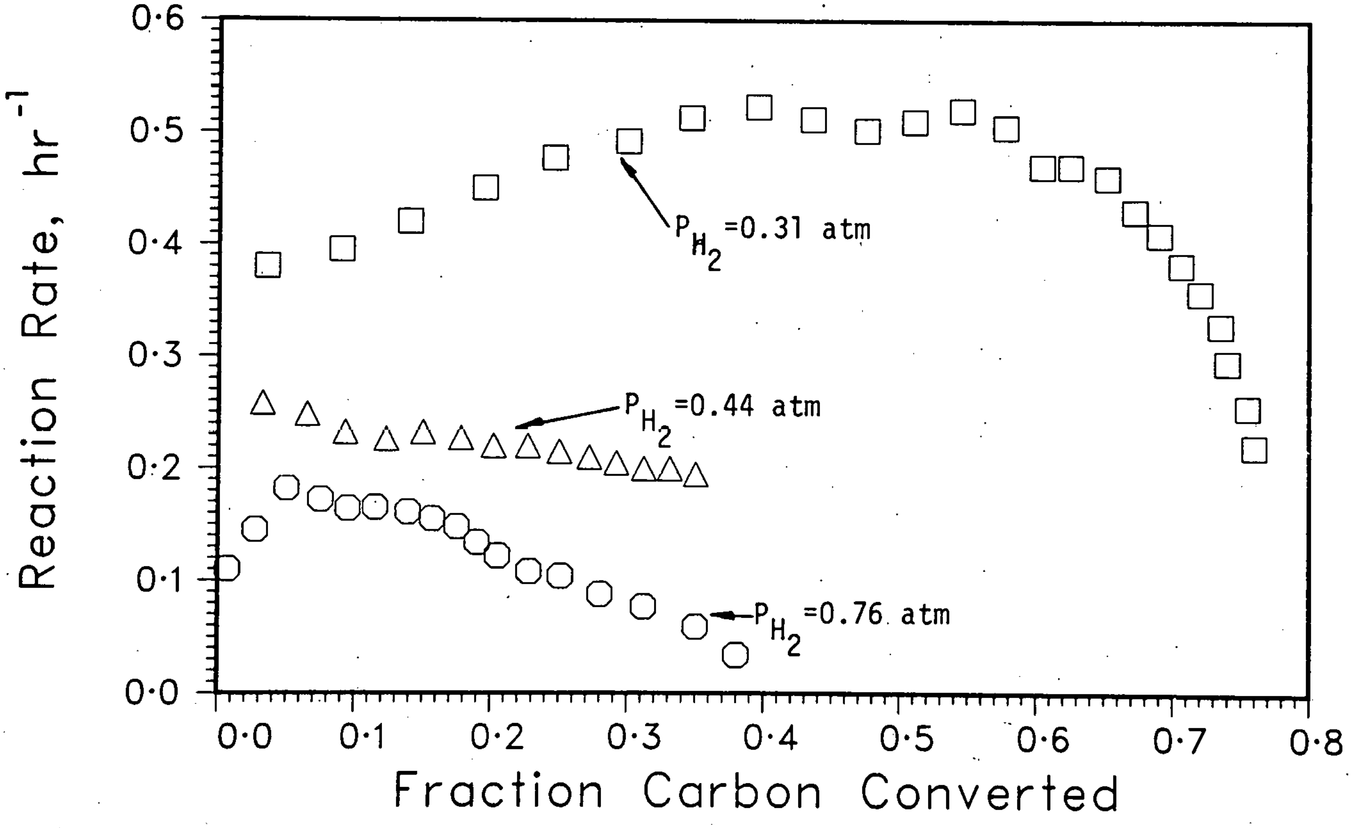


Fig. 16
Hydrogen Inhibition of The Steam-Char Reaction

Wyodak Char
750°C, 2.5 atm Steam