

A KINETIC STUDY OF COAL HYDROGASIFICATION— THE RAPID INITIAL REACTION

C. Y. Wen

Institute of Gas Technology
Chicago 16, Illinois

INTRODUCTION

The production of synthetic methane from coal by hydrogasification has considerable economic potentiality. A number of experimental studies of coal hydrogasification have been reported during the last few years. Only a few studies were concerned with reaction kinetics. A thorough literature survey has been presented elsewhere. (3)

There are many problems associated with coal hydrogasification which must be solved before the process can become economically feasible. One of the important problems is concerned with the properties of coal which affect hydrogasification. From a reaction-kinetic point of view, carbon in coal consists roughly of two types differing greatly in reactivity — the portion associated with the volatile matter and the remainder corresponding to the residual carbonaceous matter, coke.

Under the high temperatures and pressures required for hydrogasification, coals tend to soften and agglomerate, thus preventing free flow through the reactor. Pretreatment of coal, therefore, has been required in moving-bed or fluidized-bed reactor operation. Roughly, 30 percent of the carbon in coal is in the form of volatile matter which reacts rapidly with hydrogen to form methane at temperatures ranging from 1300° to 1800°F. and pressures ranging from 50 to 200 atmospheres. The remainder of the carbon reacts very slowly and the reaction rate is subject to more severe equilibrium hindrance. (3) During the pretreatment of coal, which usually involves oxidation or charring of the coal surface by air or other gases to produce a protective film, a great portion of the reactive volatile matter is lost. In most cases, approximately one half of the volatile matter carbon content is lost in pretreatment.

It is quite appropriate, therefore, to search for means of utilizing unpretreated coals in order to fully utilize the highly reactive portion of coal. One such process is to conduct the hydrogasification of coal in a so called "free-fall" reactor. Coal particles pass through the top of the reactor in a dilute suspension and hydrogen gas is passed either counter-currently or co-currently. In such a process the contact time between the coal particle and the gas must be, by necessity, much shorter than in a moving-bed or fluid-bed operation. It is the purpose of this paper to present a kinetic study of the rapid reaction during the initial contacting of coal and hydrogen.

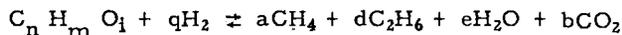
RESULTS

Mechanism of the Hydrogasification Reaction

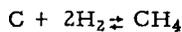
It has been postulated that, in the initial period of hydrogasification, pyrolysis of the char occurs, involving devolatilization of light components which is then followed by their hydrogenolysis. The devolatilization produces reaction intermediates that are derived from aliphatic hydrocarbon side chains and oxygenated functional groups. (2) The remainder of the organic matter in the coal is converted more slowly to methane, apparently almost according to the carbon-hydrogen reaction. The rate-controlling steps of this reaction in moving and fluid beds have been studied. (3)

For convenience, the following two abbreviated simultaneous reactions will be employed to represent the mechanism of hydrogasification of different reactive coal components.

First-Phase Reaction:



Second-Phase Reaction:



Of course, the actual reactions are much more complex than indicated by the above simple schemes. However, these two reactions are believed to be sufficient to characterize the two greatly different rate periods observed in coal hydrogasification.

If X , x_1 , and x_2 are respectively the total carbon gasified, the fraction of reactive carbon gasified in the first-phase reaction and the residual carbon gasified in the second-phase reaction, then:

$$X = fx_1 + (1 - f) x_2 \quad (1)$$

where f is the fraction of carbon in coal which reacts according to the first phase reaction. For short reaction times, θ , the first phase reaction prevails, and:

$$X \cong fx_1$$

Coal char hydrogasification data, obtained in a semiflow system by Feldkirchner and Linden (1), indicate that the rate of carbon conversion in the first-phase reaction is proportional to the amount of unreacted carbon

and to the effective hydrogen partial pressure. Accordingly,

$$dx_1/d\theta = k_1 (1-x_1) (P_{H_2} - P_{H_2}^*) \quad (2)$$

where P_{H_2} and $P_{H_2}^*$ are the partial pressures of hydrogen in the system, and the partial pressure of hydrogen at equilibrium, respectively, and k_1 is the proportionality constant for the first-phase reaction expression. Combining Equations 1 and 2:

$$dX/d\theta = k_1 (f-X) (P_{H_2} - P_{H_2}^*) = k_1 P_t (f-X) (y - y^*) \quad (3)$$

where P_t is the total pressure of the system and y and y^* are the mole fractions of hydrogen in the system and at equilibrium, respectively. Integration of Equation 3 between the initial and final conditions for media of constant hydrogen concentration gives,

$$\ln (1-X/f) = -k_1 P_t (y - y^*)\theta \quad (4)$$

when $y \gg y^*$ (for pure hydrogen feed and small conversion),

$$\ln (1-X/f) = -k_1 P_t y \theta \quad (5)$$

A plot of $\ln (1-X/f)$ vs. $P_t y \theta$ can be made from the experimental data and the slope of the line, k_1 , may be evaluated.

Analysis of Semiflow Tests

Feldkirchner and Linden (1) measured coal char hydrogasification rates by dropping char particles into a heated reactor, with gas passing through it. Their semiflow study covers the pressure range up to 2500 p.s.i.g. and the temperature range up to 1700°F. They carried out their experiments in such a way that both char heatup and product gas residence times were very short. This enabled them to follow directly the course of the reactions during the initial high rate period. Their data were examined in light of the mechanism presented. Figure 1 is a plot of $\ln (1-X/f)$ vs. θ for Montour No. 10 char and North Dakota lignite. Since the feeds were nearly pure hydrogen and the change in composition of the gas was small, $P_t y$ was approximately constant throughout the run. As is seen in Figure 1, the initial portion of the data for lignite and bituminous coal char can be represented by straight lines. From the slopes of these lines, k_1 is calculated to be 2.0 (atmosphere-hour)⁻¹. The displacement of the intercept at $\theta = 0$ from unity is due to the initial heatup of the particle to the reaction temperature. The higher the volatile matter content, the larger the value of f (the fraction of carbon which reacts by the first-phase reaction) must become if a straight line is to be obtained.

Thus, the value of f for Montour No. 10 char is 0.25 at 1700° F. and that of lignite is 0.48 at 1700° F.

A slight effect of particle size may be seen in Figure 1, but the slope of the line is independent of the particle size, which indicates that a definite time is required to heat the particle which in turn, affects the position of the lines.

Figure 2 shows the linear relation of the data from two tests at different total gas pressures. The displacement at $\theta = 0$ is again due to particle heatup time. The slope of the lines is 2.0 (atmosphere-hour)⁻¹. A detailed comparison of results of tests with different feed gas compositions is given in Figure 3 and Figure 4.

Instead of θ , $P_t y \theta$ was plotted on semilogarithmic coordinates according to Equation 1 (Figure 3). Feeds include pure hydrogen, hydrogen-nitrogen mixtures, and hydrogen-methane mixtures. The data points indicate almost a linear relationship, but deviate somewhat from each other. However, if $P_t(y-y^*)\theta$ is used instead of $P_t y \theta$, a better agreement is obtained as is shown in Figure 4. y^* is the equilibrium composition of hydrogen obtained from Figure 5 and the temperature-correction equation:

$$(K_p)_T = [1/34713] (K_p)_{1300^\circ\text{F.}} \exp(18400/T). \quad (6)$$

T is the temperature, in °R.

Therefore, a slight equilibrium hindrance of the reaction exists even during the rapid, initial reactions, but the effect may be so small under most of the experimental conditions, particularly when pure hydrogen feed is employed, that this can be neglected.

Figure 6 shows the effect of temperature on the rate constant, k_1 , and f . For relatively small temperature changes, the value of k_1 may be kept constant with a small adjustment of the value of f . The increase of the value of f as temperature is increased may be explained as follows. As the temperature of reaction is increased, the rate of devolatilization of reactive carbon becomes larger; consequently, the recondensation of the reactive carbon during pyrolysis to form stable ring compounds (as residual carbon) becomes less. In terms of the amount of carbon available for the first-phase reaction, this means the value of f increases as temperature increases. This relation is shown in Figure 7. However, the rates of pyrolysis should also increase as the temperature is increased. Therefore, the extrapolation of Figure 7 to the higher temperature range beyond the experimental points should be avoided.

Analysis of Continuous Free-Fall Reactor Test Results

To apply the above analysis of semiflow test results to continuous flow reactors, a material balance between the carbon in the solid phase and carbon in the gaseous phase must be made:

F = pounds of coal fed per hour.

G = moles of inlet gas per hour.

ψ = fraction of carbon in coal fed.

y_0 = mole fraction of hydrogen in inlet gas.

a = q/n = stoichiometric ratio of hydrogen and carbon for first-phase reaction.

Accordingly, for plug-flow of both gas and solids:

$$-(a F \psi / 12) dX = d(Gy) \approx G dy \quad (7)$$

Integrating Equation 7 between the limits of the conditions at the reactor inlet and exit,

$$X(a F \psi / 12) = G (y_0 - y) \quad (8)$$

$$\text{or } y = y_0 - (a \psi / 12) (F/G) X = y_0 - mX$$

where $m = (a \psi / 12) (F/G)$

Substituting y into Equation 3,

$$dX/d\theta = k_1 P_t (f-X) (y_0 - mX - y^*) \quad (9)$$

Since y^* may be taken to be nearly constant for a small conversion taking place in the first-phase reaction, Equation 9 can be integrated between the inlet and exit of the reactor. Hence:

$$k_1 \theta P_t (y_0 - y^* - mf) = \ln[f (y_0 - y^* - mX) / (y_0 - y^*) (f-X)] \quad (10)$$

$$\text{or } k_1 = [1/P_t \theta (y_0 - y^* - a \psi F/12G)] \ln[f (y_0 - y^* - a \psi X F/12G) / (y_0 - y^*) (f-X)] \quad (11)$$

The results of several continuous pilot plant free-fall tests conducted at the Institute of Gas Technology were used to verify the above analysis.

The values of $a = q/n$, computed from inlet and exit gas analysis of the tests, seem to be affected only slightly by conversion as is shown in Figure 8. Since residence times could not be readily calculated from the data given in the report, experiments were conducted. Terminal velocities of Montour No. 10 particles char were found by dropping the char from a hopper through a 2-inch inside diameter pipe approximately 10 feet long. The gas medium was air at 70° F. and 1 atmosphere.

The holdup of particles in the pipe was measured by simultaneously closing plug valves at the inlet and exit. The terminal velocities of the particles were calculated from the solids holdups and solids flow rates. If W is the weight of solid particles trapped in the pipe and L is the length of

the pipe through which the particles fall, then the average solid terminal velocity, U_t , is:

$$U_t = FL/W \quad (12)$$

Terminal velocities of the solids at the reactor conditions were calculated from those at ambient conditions in air by use of Stokes Law. Both the terminal velocity in air and that calculated at reactor condition are shown as a function of solids feed rate in Figure 8. The residence time is,

$$\theta = \frac{L}{U_t - U_g} \quad (13)$$

where U_g is gas velocity. The results of three countercurrent free-fall reactor tests were used to compute the values of k_1 and are listed in Table 1.

Table 1.
Results of Countercurrent Free-Fall Reactor Runs

Run No.	T, °F.	P_t , atm.	F, lb./hr.	G, SCF/hr.	f, %	ψ	L, ft.	θ , sec.	k_1 , (atm.-hr.) ⁻¹
SD56	1270	139.8	4.53	46.53	21.7	0.78	9	8.57	3.10
SD57	1245	137.6	7.68	50.21	21.5	0.782	9	6.67	2.10
SD58	1240	137.0	11.75	105.24	21.4	0.783	7	4.12	1.8

In view of some uncertainties involved in calculating the values of particle residence times, the agreement of the k_1 values from continuous reactor tests with those obtained from semiflow tests [$k_1 = 2.0$ (atm./hr.)⁻¹] is good. Because of the high rate of the first-phase reaction, the particles must undergo deformation, reduction in size, and reduction in density during free-fall. The actual particle residence times must be affected by these changes, which did not exist in the residence-time measurement tests described previously.

Because of the assumptions and uncertainties introduced for such a complex system, instead of using Equation 11, simplified equations may be employed for practical application without introducing additional errors. This involves the use of some average driving force such as $(y - y^*)_{av}$. From Equation 4:

$$k_1 = -\ln(1 - X/f) / P_t (y - y^*)_{av} \theta \quad (14)$$

$$\text{and } X = f \left\{ 1 - \exp[-k_1 P_t (y - y^*)_{av} \theta] \right\} \quad (15)$$

CONCLUSION

It has been shown that the initial rate of coal hydrogasification can be assumed to be proportional to the amount of reactive carbon left in the particles and to the effective hydrogen partial pressure. The rate constant, k_1 , was found to be 2.0 (atmosphere-hour) $^{-1}$ and the reaction model, used in the analysis of semiflow tests was found to be applicable to continuous free-fall reactors. Product gas compositions for continuous reactors may be computed by the empirical relationships developed elsewhere for the partial pressures of CO , CO_2 , C_2H_6 and H_2O . (3)

ACKNOWLEDGMENT

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Notation:

- D_p = Particle diameter, ft. or in.
- F = Char feed rate, lb. per hr.
- f = Fraction of carbon that reacts according to the first-phase reaction.
- G = Gas feed rate, SCF per hr. or moles per hr.
- k_1 = Reaction rate constant in the first phase reaction (hr. -atm.) $^{-1}$
- K_p = Thermodynamic equilibrium constant = $P_{\text{CH}_4}^* / (P_{\text{H}_2}^*)^2$
- L = Length of the reactor, ft.
- P_t = Total pressure, atm.
- P = Partial pressure, atm.
- P^* = Equilibrium partial pressure, atm.
- T = Absolute temperature, °R.
- U_g = Gas velocity, ft. per sec.
- U_t = Terminal velocity of particles, ft. per sec.
- W = Weight of bed, lb.
- X = Overall fractional conversion of carbon.
- x_1 = Fraction of carbon converted in the first-phase reaction.
- x_2 = Fraction of carbon converted in the second-phase reaction.
- y = Mole fraction of hydrogen.
- y^* = Mole fraction of hydrogen at equilibrium
- θ = Time, sec. or hr.
- ψ = Fraction of carbon in coal
- α = q/n , ratio of the hydrogen to carbon stoichiometric coefficient for the first-phase reaction.

References Cited:

1. Feldkirchner, H. L.; Linden, H. R., Ind. Eng. Chem. Process Design and Develop. 2, 153-62 (1963).
2. Pycioch, E. J., Institute of Gas Technology Monthly Work Report PB-23a.
3. Wen, C. Y., Huebler, J., Paper presented at the 56th National Meeting American Institute of Chemical Engineers, Houston, Texas Dec. 1-5, 1963.

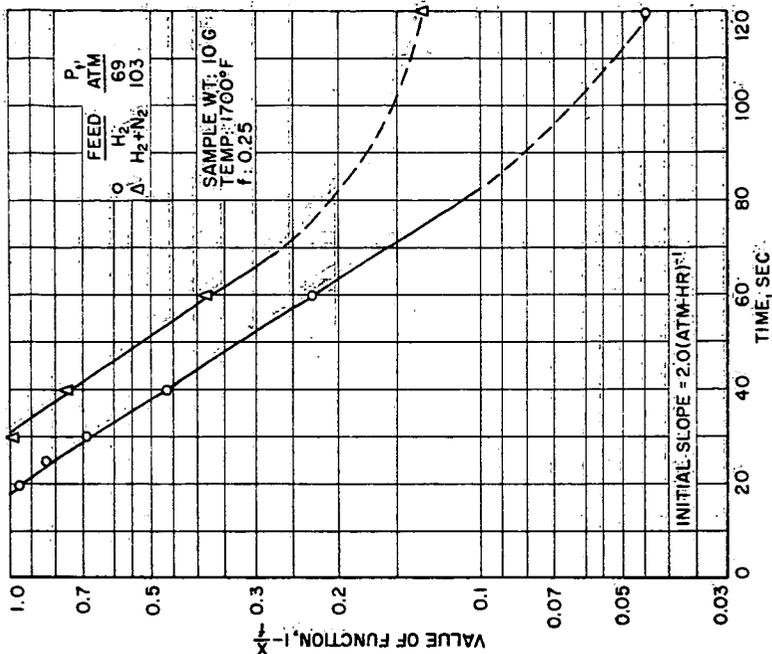


Fig. 2.-LINEAR RELATIONSHIP OF THE LOGARITHM OF THE FIRST-PHASE CONVERSION FUNCTION WITH TIME AT TWO DIFFERENT PRESSURES

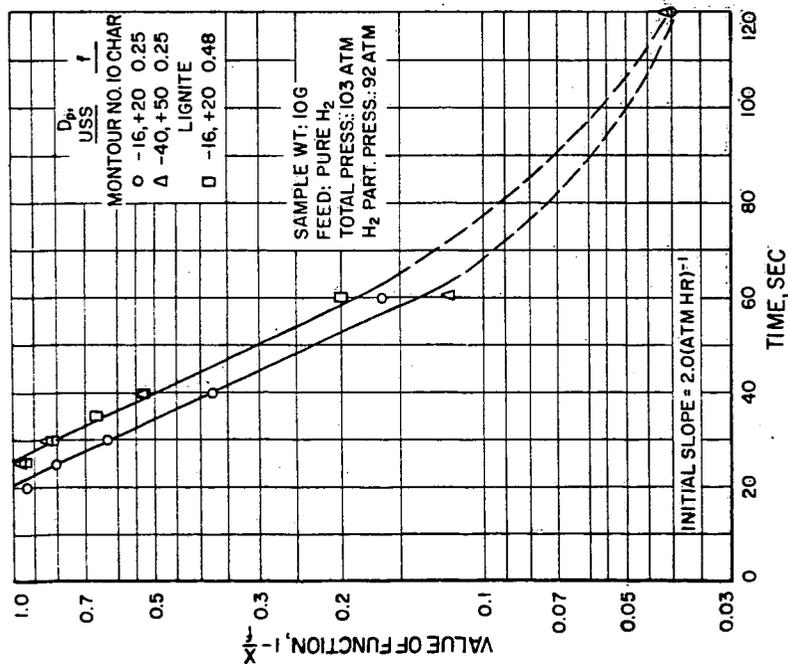


Fig. 1.-LINEAR RELATIONSHIP OF THE LOGARITHM OF THE FIRST-PHASE CONVERSION FUNCTION WITH TIME

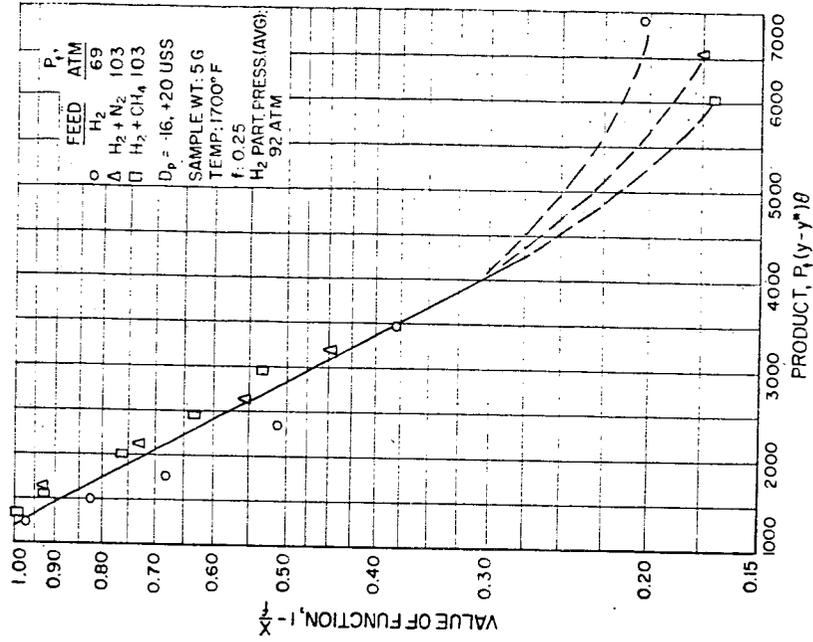


Fig. 4.- EFFECT OF HYDROGEN PARTIAL PRESSURE AND PRODUCT $P_t(y-y^*)^\theta$ ON THE LOGARITHM OF THE FIRST-PHASE FUNCTION

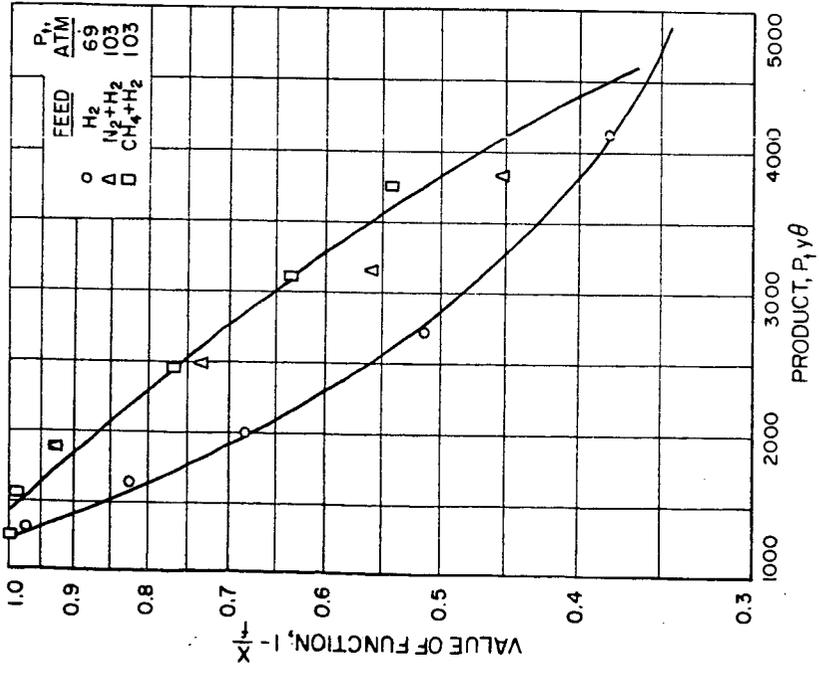


Fig. 3.- EFFECT OF HYDROGEN PARTIAL PRESSURE AND PRODUCT $P_t y^\theta$ ON THE LOGARITHM OF THE FIRST-PHASE CONVERSION FUNCTION

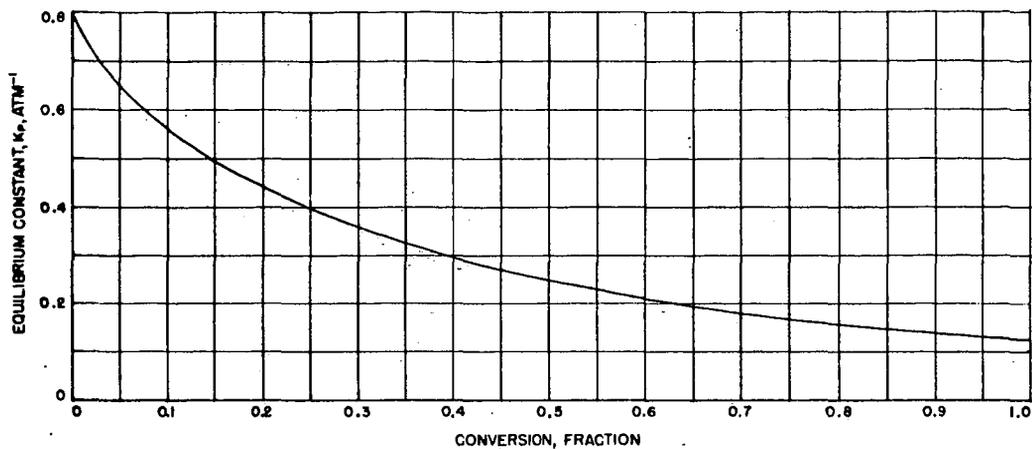


Fig. 5.- APPROXIMATE TREND OF THE EQUILIBRIUM CONSTANT AS A FUNCTION OF CONVERSION FOR THE HYDROGEN-CHAR REACTION AT 1300°F AND 2000 P.S.I.G. TOTAL PRESSURE

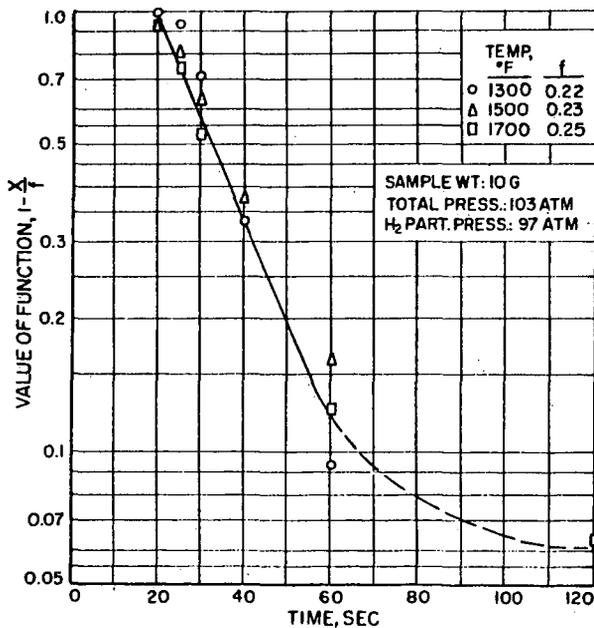


Fig. 6.- EFFECT OF TEMPERATURE AND TIME ON THE LOGARITHM OF THE FIRST-PHASE CONVERSION FUNCTION

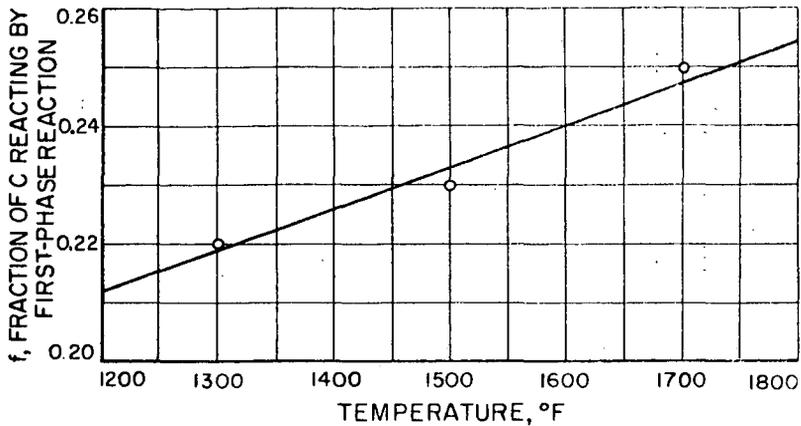


Fig. 7.-EFFECT OF TEMPERATURE ON THE FRACTION OF CARBON REACTING BY FIRST-PHASE REACTION

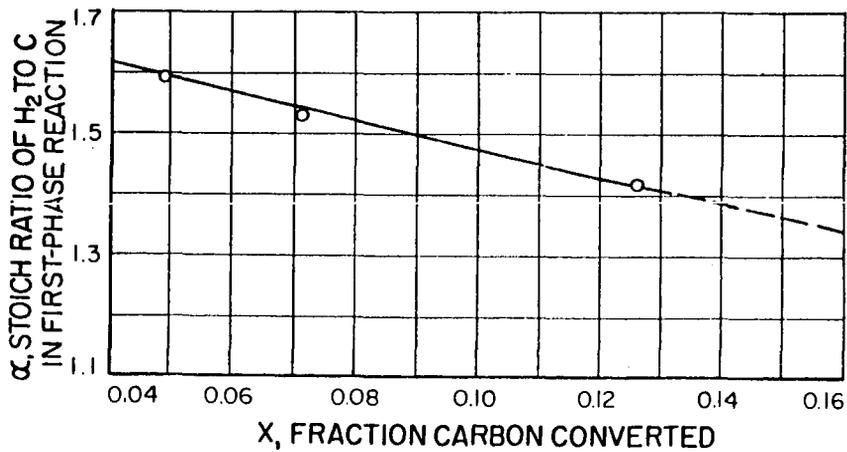


Fig. 8.-EFFECT OF CARBON CONVERSION ON α , THE STOICHIOMETRIC RATIO OF HYDROGEN TO CARBON IN THE FIRST-PHASE REACTION

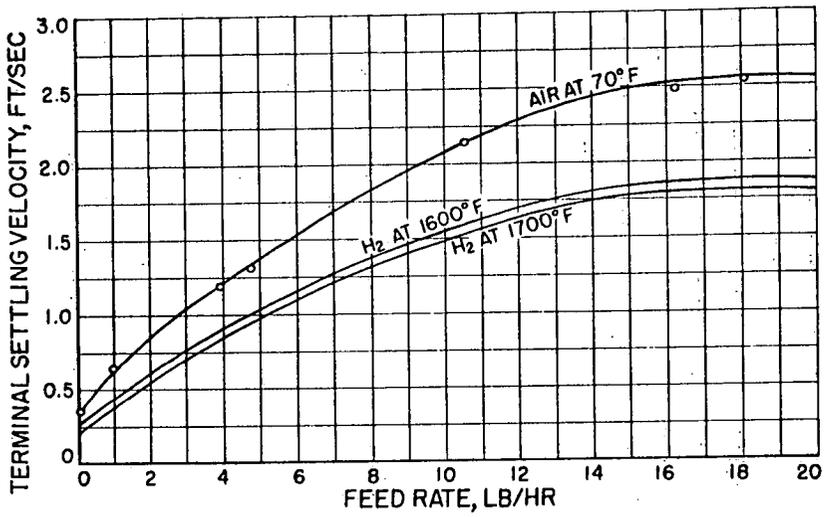


Fig. 9.-EFFECT OF CHAR FEED RATE OF
TERMINAL SETTLING VELOCITY OF MONTOUR NO. 10 CHAR
IN A TWO INCH I.D. TUBE