

A KINETIC STUDY  
OF THE REACTION OF COAL CHAR  
WITH HYDROGEN-STEAM MIXTURES

C. Y. Wen  
O. C. Abraham  
A. T. Talwalkar

Institute of Gas Technology  
Chicago, Illinois

INTRODUCTION

The gasification of coal with hydrogen-steam mixtures for the production of a gaseous product of high heating value in a practical continuous reactor is of paramount importance to the gas industry. A number of research programs are now under way to develop an efficient and economically feasible process for the production of high-heating-value gas from coal. One of these, a study at the Institute of Gas Technology, has led to the work reported here.

The reaction of coal with a steam-hydrogen mixture represents a system of heterogeneous reactions in which solid and gas phases are present. The study and interpretation of two such phase reactions is inherently more complex than those of homogeneous reactions in which only a single phase is present. For a reaction to proceed between a fluid and a solid, a combination of diffusional and kinetic processes with adsorption and surface-reaction steps are considered to occur.

The literature contains a number of papers<sup>2, 4, 13, 14, 18, 19, 21, 23-25, 27, 30, 31, 33-36</sup> concerned with the kinetics of these reactions. The carbon studied in these papers ranges from coal to graphite.

Because it requires a large number of possible variables, such as temperature, pressure, the nature of chemical reaction, and the character of the solid surface, and because it incorporates a large number of constants which require experimental evaluation, the general mathematical model to estimate the product gas distribution for different levels of carbon conversion can become exceedingly complicated. Practical application of this model is particularly difficult when a choice has to be made between reaction mechanisms, each of which can generate complex functions with a sufficient number of arbitrary constants to fit any given experimental curve. The purpose of the work discussed in this paper was to study the influence of temperature and the partial pressure of hydrogen and steam on the rate of steam-hydrogen and coal char reactions and to develop a correlation to estimate the performance of a hydrogasification reactor in terms of its product gas distribution for different levels of carbon conversion.

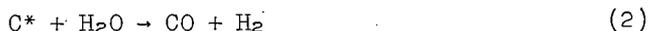
GENERAL CONSIDERATIONS

Most coals are made up of a number of macerals. Carbons derived from different macerals differ in reactivity. As gasification proceeds, a decline in rate is expected since carbon of progressively lower reactivity remains. Differences in the chemical reactivity of macerals have been reviewed by Brown<sup>3</sup> and Channabasappa and Linden,<sup>5</sup>

who found, in increasing order for hydrogenation, that fusain, durain, and vitrain have different reactivities.

In their study of coal pyrolysis, Chermin and Van Krevelen<sup>6</sup> showed that, upon heating, coal first becomes metaplastic and then gives off volatile matter, leaving a rather stable coke. Thus coal char consists of two portions which differ greatly in reactivity. The highly reactive portion is related to the amount of volatile matter characterized by the aliphatic hydrocarbon side chain and to the oxygenated functional groups present. The low reactivity portion is the residual carbonaceous stable coke. Thus the gasification of coal by simultaneous reactions with steam and hydrogen at elevated temperatures is divided into first- and second-phase reactions, each reaction representing one of the two distinctly different reactivities of carbon present in coal.

#### FIRST-PHASE REACTION



where  $C^*$  is the reactive carbon present in the first phase.

Of course, the actual reactions are much more complex than indicated by the above simple schemes. It has been demonstrated<sup>10</sup> that the gaseous products due to the first-phase reactions are predominantly methane, carbon monoxide, and hydrogen. The experimental data of the same investigations show that the hydrogen and steam reactions in the first phase are taking place independently of each other and are probably undergoing pyrolysis followed by the vapor-phase reaction of hydrogen and steam. The rates of the two first-phase reactions, therefore, are assumed to be additive. Let  $X_{H_2}$  and  $X_{H_2O}$  be the conversions of carbon due to hydrogen and steam respectively, then the overall conversion of carbon is simply:

$$X = X_{H_2} + X_{H_2O} \quad (3)$$

#### Hydrogen-Char Reaction

The hydrogen-char reaction in the first phase may be represented by:

$$\left[ \frac{dX_{H_2}}{d\theta} \right]_1 = k_1(f-X) (P_{H_2} - P_{H_2}^*) \quad (4)$$

or

$$\frac{[dX_{H_2}]_1}{(1-X)d\theta} = \frac{k_1(f-X)}{1-X} (P_{H_2} - P_{H_2}^*) \quad (5)$$

where  $k_1$  is the rate constant obtained, which has the unit of  $(\text{atm}\cdot\text{hr})^{-1}$ , and  $f$  is the fraction of carbon that reacts according to the first-phase reaction. This mechanism states that the first-phase reaction occurs in such a way that the rate of reaction at any time is proportional to the mass (or volume) of the unreacted portion of the volatile carbon still present in the particle and to the effective partial pressure of hydrogen. Figures 1, 2, and 3 compare the proposed rate equation with the experimental results obtained from a semiflow system<sup>10</sup> at three temperature levels.

### Equilibrium of Coal Char Hydrogen Reaction

The coal-hydrogen reaction has been shown to exceed the carbon-hydrogen-methane equilibrium at low conversion and to reach the carbon-hydrogen equilibrium at nearly complete conversion.<sup>35,36</sup> From the equilibrium composition of the hydrogen-char system, a pseudo-equilibrium constant,  $K_p$ , is defined as:

$$K_p = \frac{P_{CH_4}^*}{(P_{H_2}^*)^2} \quad (6)$$

which has been calculated as a function of the carbon conversion level.

Figure 4 indicates the general trend of the  $K_p$  values at 1300°F with respect to the fraction of carbon converted. An empirical relationship was developed to convert the equilibrium constant from one temperature to another. The relationship is:

$$(K_p)_T = \frac{(K_p)_{1300^\circ F}}{34,713} \exp\left(\frac{18,400}{T}\right) \quad (7)$$

where T is in degrees Rankine.

### Effect of Hydrogen Partial Pressure

Apart from the equilibrium hindrance, the rate of gasification is affected by the partial pressure of hydrogen. The rate of reaction of coal with hydrogen in the first phase is shown by Figures 1, 2, and 3 to be roughly proportional to the partial pressure of hydrogen. A similar type of reaction was proposed for hydrogen-char reactions.<sup>35,36</sup> This has been shown to agree with the majority of previous investigators who found that the reaction is approximately a first-order one with hydrogen. Gorin et al.,<sup>16</sup> showed that the methane formation rates with pure hydrogen and hydrogen-steam mixtures at the same partial pressure as hydrogen are a strong function of the partial pressure of hydrogen. Wen and Huebler<sup>35,36</sup> demonstrated that the rate of methane formation is roughly proportional to the difference between the partial pressure of hydrogen and the hydrogen partial pressure in equilibrium with the char. Von Fredersdorff<sup>32</sup> observed that an increase in hydrogen partial pressure would increase the rate of hydrogenolysis. This relationship is further confirmed by Moseley and Paterson,<sup>28</sup> who reported that the rate of hydrogenation of coal to methane is directly proportional to the hydrogen partial pressure even in the very early stages of the reaction.

### Effect of Temperature

Figures 1, 2, and 3 show that the fraction of the carbon that reacts according to the first phase,  $f$ , increases with the temperature. Moseley and Paterson<sup>28</sup> pointed out that the fraction of carbon that reacts according to the first phase is a function of both temperature and pressure. Since the total pressures employed in the present investigation were nearly constant at approximately 70 atm, total pressure had no significant effect on the value of  $f$ . Previous investigators<sup>11</sup> observed that an increase of pressure broadens the range of the initial high-rate period. But, for a small range of pressures, the fraction of carbon that goes into the first-phase reaction can be assumed to be a function of only the temperature.

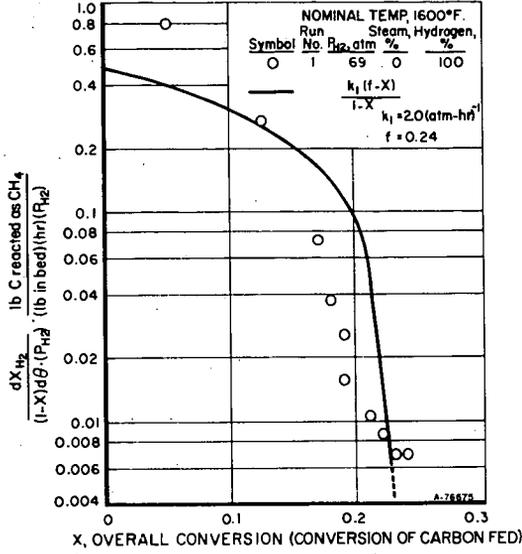


Figure 1. RATE OF HYDROGEN-CHAR REACTION DURING FIRST-PHASE REACTION AT 1600°F

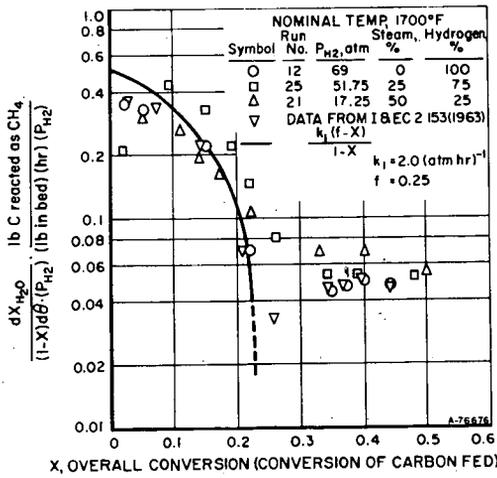


Figure 2. RATE OF HYDROGEN-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1700°F

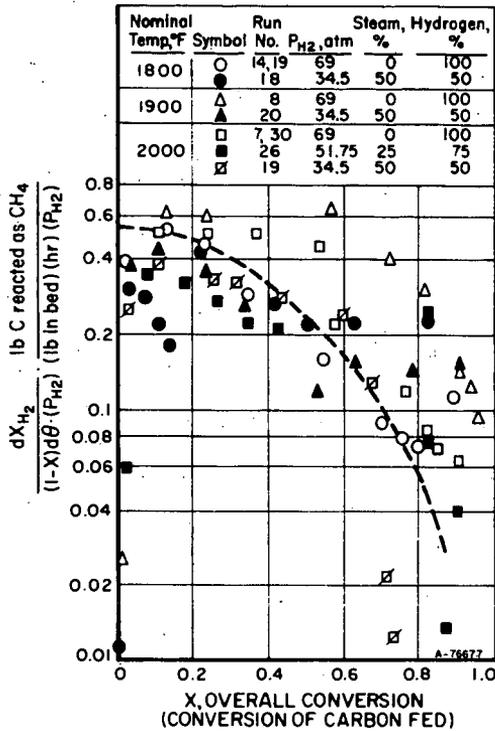


Figure 3. RATE OF HYDROGEN-CHAR REACTION DURING THE FIRST-PHASE REACTION ABOVE 1800°F

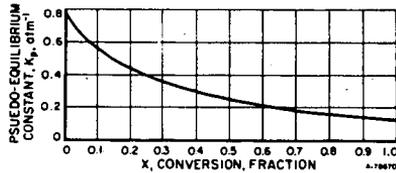


Figure 4. APPROXIMATE TREND OF THE EQUILIBRIUM CONSTANT AS A FUNCTION OF CONVERSION FOR THE HYDROGEN-CHAR REACTION AT 1300°F AND 2000 PSIG TOTAL PRESSURE

The values of  $f$  for various temperatures are tabulated as follows:

Temperature, °F	$f$
1300	0.22
1500	0.23
1700	0.25

Above 1800°F, the rate of the hydrogen reaction is not substantially affected by the temperature, as shown in Figure 3. This is probably because, at these high temperatures (1800°-2050°F), the chemical reaction is so rapid that the rate becomes controlled by diffusion. In addition, at such high temperatures, the reaction rate for the remainder of the relatively stable carbon is no longer small enough to be neglected. Thus differentiation of the first-phase reaction from the second-phase reaction becomes so difficult that an accurate value of  $f$  cannot be obtained.

### Steam-Char Reaction

The steam-char reaction in the first phase is represented by:

$$\left[ \frac{dX_{H_2O}}{d\theta} \right]_1 = k_2 (f-X) \quad (8)$$

and

$$\frac{[dX_{H_2O}]_1}{(1-X)d\theta} = \frac{k_2 (f-X)}{1-X} \quad (9)$$

where  $k_2$  is the rate constant having the unit of  $hr^{-1}$ , and  $f$  is the fraction of carbon that will react according to the first-phase reaction. As in the hydrogen-char reaction, the first-phase reaction of steam-char is a volume reaction, the rate of which is proportional to the amount of the unreacted portion of the volatile carbon still present in the particle.

### Effect of Partial Pressure of Steam

Contradictory conclusions have been reported in the literature regarding the effect of the partial pressure of steam. The reaction has been variously reported to be of the zero order,<sup>30</sup> fractional order, first order,<sup>12, 15, 17, 18, 20</sup> and between first and second order<sup>20, 30</sup> with respect to steam. As shown in Figures 5, 6, 7, and 8, the rate of the steam-char reaction is not affected by the partial pressure of steam, so far as detectable by the experiment. This is in agreement with the previous investigators.<sup>13, 25, 28, 29</sup>

### Effect of Temperature

The fraction of carbon that will react according to the first-phase mechanism for steam also increases with increasing temperature. As shown in Figures 5, 6, 7, and 8, the temperature dependency of  $f$  and  $k_2$  can be evaluated by the proposed mechanism. However, these correlations must be treated with caution since the second-phase reaction may become so rapid at temperatures above 1900°F that the isolation of the first-phase reaction from the second-phase reaction would become difficult; thus the evaluation of  $f$  might no longer be accurate.

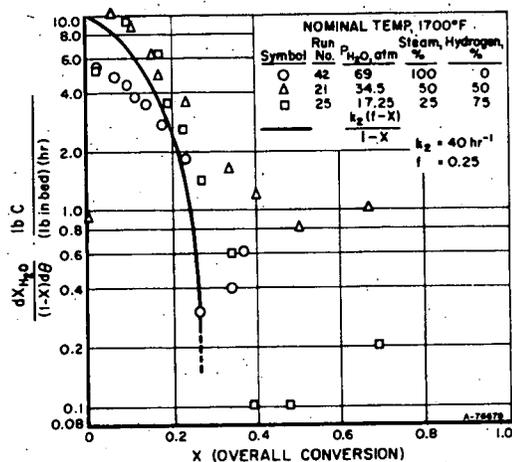


Figure 5. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1700°F

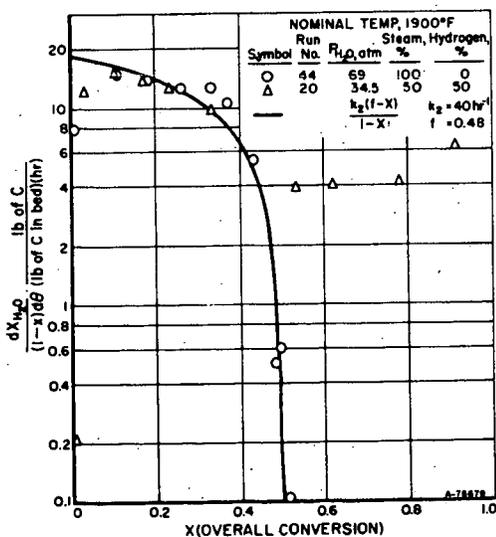


Figure 6. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 1900°F

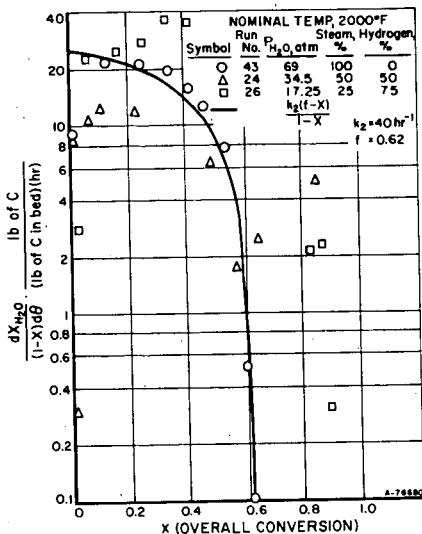


Figure 7. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 2000°F

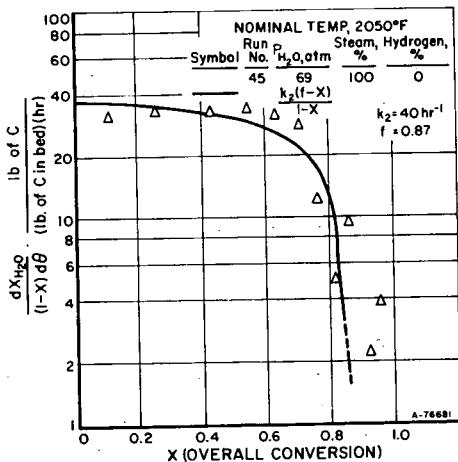


Figure 8. RATE OF STEAM-CHAR REACTION DURING THE FIRST-PHASE REACTION AT 2050°F

## SECOND-PHASE REACTION

The second-phase reaction is a heterogeneous reaction which occurs at the surface of the particle. The reaction causes the reacting surface to shrink and leaves an ash layer as the particle moves through the reactor. Unlike the first-phase reaction which is only slightly affected by temperature, the second-phase reaction is quite sensitive to variations in temperature. At temperatures below 1700°F, the first-phase reaction rate is an order or two larger than the second-phase reaction rate, but as the temperature approaches 2000°F, the two rates become comparable. This is, of course, true only when the reaction is controlled by the chemical step.

Hydrogen Reaction

As discussed previously,<sup>35, 36</sup> if this reaction under experimental conditions in the continuous flow reactor is controlled by gas diffusion, the reaction rate may be characterized by:

$$\left[ \frac{dX_{H_2}}{d\theta} \right]_2 = \frac{(K_g)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) \quad (11)$$

where  $(K_g)_{H_2}$ , the effective mass transfer coefficient for hydrogen, is defined as:<sup>22</sup>

$$(K_g)_{H_2} = \frac{3kg}{\rho_c} \quad (12)$$

and can be obtained from the moving-bed data by the relation:

$$(K_g)_{H_2} = \frac{x_{H_2} D_p}{\left(\frac{W}{F}\right) (\Delta P_{H_2})_{avg}} \quad (13)$$

In the above equation  $x_{H_2}$  differs from  $X_{H_2}$  and is the fractional conversion of carbon present in the second-phase reaction, i.e. based on  $(1-f)$ .  $(\Delta P_{H_2})_{avg}$  is the mean hydrogen partial pressure difference,  $(P_{H_2} - P_{H_2}^*)$ , at the gas inlet and at the point where  $X$  equals  $f$  in the moving-bed reactor.

Since in the flow reactor the reaction in the second phase has been proved to be controlled by the diffusion,<sup>35, 36</sup> the rate is less sensitive to the change in temperature than to the change in gas velocity.

The values of  $(K_g)_{H_2}$  from the moving-bed reactors using both pure hydrogen feed and hydrogen-steam mixture feed are calculated and are plotted in Figure 9 as a function of average particle Reynold's number, at the operating conditions listed. Two correlation lines are obtained: one at an average temperature of 1300°F and the other at temperatures above 1500°F. At the higher temperatures, coal particles may crack due to sudden and severe heating immediately after being fed to the reactor. This heating results in rather violent devolatilization and the subsequent first-phase reaction. However, the particle disintegration due to devolatilization can reach only a certain magnitude. Between 1500° and 1800°F,  $(K_g)_{H_2}$  is affected less by the temperature. The two correlations may be written as:

$$\begin{aligned}
 (K_g)_{H_2} &= \frac{D_p x_{H_2}}{W (\Delta P_{H_2})_{avg}} = 1.2 \times 10^{-5} (N_{Re})^{1.11} \text{ for } T > 1500^\circ F \\
 &= 0.35 \times 10^{-5} (N_{Re})_{IM}^{1.11} \text{ for } T = 1300^\circ F \quad (14)
 \end{aligned}$$

Figure 9 includes the data from the char feed that contains approximately 17% volatile matter and the spent char feed that contains less than 5% volatile matter. Because of the complexity of the process, the scattering of the data points may be attributed to many causes. Among them, the temperature uniformity and the particle size distribution can be considered significant. Because it was difficult to maintain a uniform temperature throughout the bed, an average temperature (nominal) is used in the correlation. In addition solid feed contains a fraction of particles that are so small that during their migration through the reactor they must be in a state of semifluidization. Since these factors can make the mass transfer characteristics extremely complex and since many variables are involved, the correlations obtained in Figure 9 must be regarded as satisfactory.

### Steam-Char Reactions



The steam-char reaction during the second phase is probably very similar to the carbon-steam reaction occurring at the char surface. Analogous to the hydrogen-char reaction in the second phase, the rate of the steam-char reaction in the continuous-flow moving-bed reactor is probably controlled by gas diffusion and may be characterized as:

$$\left[ \frac{dx_{H_2O}}{d\theta} \right]_2 = \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (16)$$

$$\text{where } (K_g)_{H_2O} = \frac{x_{H_2O} D_p}{W (\Delta P_{H_2O})_{avg}} \quad (17)$$

$x_{H_2O}$  and  $(\Delta P_{H_2O})_{avg}$  are defined as analogous to those for the hydrogen-char reaction.  $P_{H_2O}^*$  is calculated based on unit carbon activity.<sup>38,37</sup> The amount of carbon conversion due to steam is evaluated from the experimental product gas analysis based on carbon oxides. Figure 10 shows the relationship between  $(K_g)_{H_2O}$  and  $(N_{Re})_{IM}$ . As is evident from the figure, at temperatures above 1500°F, the effective mass transfer coefficients are functions of the particle Reynold's number and are insensitive to the temperature variations. At 1300°F, the steam-char reaction is very slow and probably controlled by the chemical step at the reaction surface of the char particles. Reasons similar to those given for the hydrogen-char reaction can be given here to account for the scattering of the data points. The correlation line for temperatures above 1500°F can be given as:

$$(K_g)_{H_2O} = \frac{D_p x_{H_2O}}{W (\Delta P_{H_2O})_{avg}} = 1.7 \times 10^{-5} (N_{Re})_{IM}^{1.20} \quad (18)$$

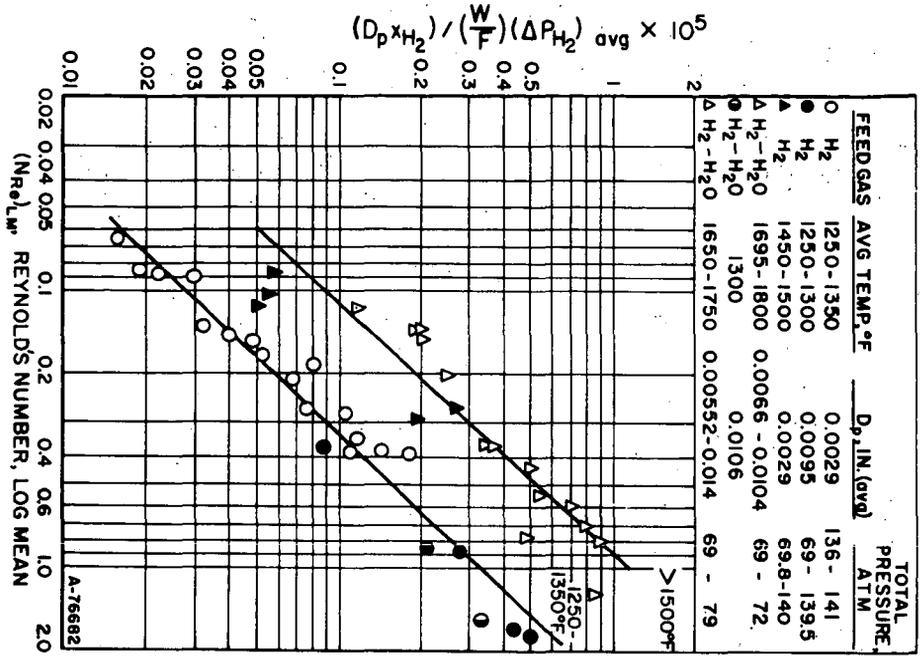


Figure 9. EFFECTIVE MASS TRANSFER COEFFICIENT FOR HYDROGEN-CHAR REACTION AND REYNOLD'S NUMBER RELATION INDICATING DIFFUSION CONTROL MECHANISM

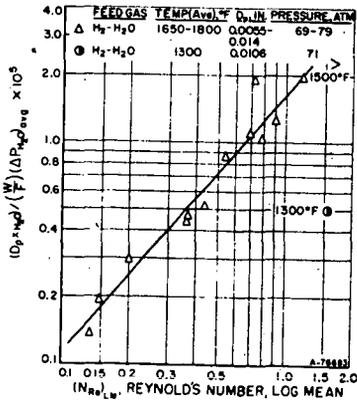


Figure 10. EFFECTIVE MASS TRANSFER COEFFICIENT FOR STEAM-CHAR REACTION IN SECOND PHASE INDICATING DIFFUSION CONTROL

The overall reaction, including both the first phase and the second phase, may now be written as:

Overall Reaction Rate:

$$\frac{dX}{d\theta} = \frac{dX_{H_2}}{d\theta} + \frac{dX_{H_2O}}{d\theta} \quad (19)$$

Hydrogen-Char Reaction Rate:

$$\frac{dX_{H_2}}{d\theta} = [k_1(f-X) + \frac{(K_g)_{H_2}}{D_p}(1-f)] (P_{H_2} - P_{H_2}^*) \quad (20)$$

for  $X < f$

$$\frac{dX_{H_2}}{d\theta} = \frac{(K_g)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) \quad (21)$$

for  $X > f$

Steam-Char Reaction Rate:

$$\frac{dX_{H_2O}}{d\theta} = k_2(f-X) + \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (22)$$

for  $X < f$

$$\frac{dX_{H_2O}}{d\theta} = \frac{(K_g)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*) \quad (23)$$

for  $X > f$

#### WATER-GAS SHIFT REACTION

$CO_2$  is assumed to be produced solely by the water-gas shift reaction:



This reaction, which occurs simultaneously with the gasification of carbon by steam and hydrogen, can proceed either heterogeneously on the char surface or homogeneously in the gas phase, or by a combination of both, depending upon the reaction and operation conditions. The water-gas shift reaction probably occurs predominantly on the char surface<sup>1, 7-9</sup> and is catalyzed by the inorganic ashes present in char.

The water-gas shift reaction may account for a substantial fraction of the steam produced. Opinions concerning the extent of this reaction differ greatly from investigator to investigator. Some<sup>19</sup> have pointed out that it appears to be fast enough to reach equilibrium in a reacting steam-carbon system. The data reported by others<sup>25, 31</sup> support the view that quasi-equilibrium is reached between char and product gas.

In calculating the product gas distribution for the moving-bed reactor in the present work, water-gas shift equilibrium at the exit is assumed.

## APPLICATION TO MOVING-BED REACTOR DESIGN

For a small-diameter, long-length shaft-type reactor, the assumption of plug flow for both solids and gases is valid. Below is a carbon balance for the differential volume,  $dV$ :

$$F dX = \left[ \frac{dX_{H_2}}{d\theta} + \frac{dX_{H_2O}}{d\theta} \right] \rho_B dV \quad (25)$$

Substituting Equations (20) through (23) in Equation (25) and integrating, we get:

$$\frac{V\rho_B}{F} = \int_0^f \frac{dX}{\left[ \left[ k_1(f-X) + \frac{(K_G)_{H_2}(1-f)}{D_p} \right] (P_{H_2} - P_{H_2}^*) + k_2(f-X) + \frac{(K_G)_{H_2O}(1-f)}{D_p} (P_{H_2O} - P_{H_2O}^*) \right]} + \int_f^X \frac{dX}{\frac{(K_G)_{H_2}}{D_p} (1-f) (P_{H_2} - P_{H_2}^*) + \frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)} \quad (26)$$

Numerical or graphical integration of Equation (26) may be performed to obtain the reactor volume necessary for a carbon conversion of  $X$ :

$$dX = \left[ 1 + \left( \frac{dX_{H_2O}}{dX_{H_2}} \right) \right] dX_{H_2} \quad (27)$$

The fraction of carbon converted by hydrogen can be found by:

$$\int_0^{X_{H_2}} dX_{H_2} = X_{H_2} = \int_0^f 1 + \frac{\frac{dX}{k_2(f-X) + \frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)}}{\left[ k_1(f-X) + \frac{(K_G)_{H_2}}{D_p} (1-f) \right] (P_{H_2} - P_{H_2}^*)} + \int_f^X 1 + \frac{\frac{dX}{\frac{(K_G)_{H_2O}}{D_p} (1-f) (P_{H_2O} - P_{H_2O}^*)}}{\frac{(K_G)_{H_2}/D_p (1-f) (P_{H_2} - P_{H_2}^*)}} \quad (28)$$

and the fraction of carbon converted by steam is given by:

$$X_{H_2O} = X - X_{H_2} \quad (29)$$

Then, knowing the fractions of carbon converted by hydrogen and steam and assuming water-gas shift equilibrium at the exit, product gas composition can be calculated. The evolution of gases from coal is neglected in making this calculation. However, this evolution can easily be accounted for by assuming that the gases  $H_2$ ,  $H_2O$ ,  $H_2S$ , and  $N_2$  are evolved instantaneously at  $X = f$  and by adding corresponding amounts to the gas stream at that point.

As an approximation, the second-phase reactions may be neglected for carbon conversions less than  $f$ . This will simplify Equations 26 and 28 considerably.

## CONCLUSION

The gasification of coal char with a hydrogen and steam mixture at high temperatures and high pressures can be satisfactorily represented by the proposed mechanism to estimate the product gas distribution for different levels of carbon conversion.

The coal char reaction with a hydrogen and steam mixture is represented by the first-phase and the second-phase reactions. The first-phase reaction is related to the amount of volatile matter and may be regarded as a volume (or mass) reaction. The second-phase reaction is characterized by the heterogeneous reaction at the carbon surface, a reaction which is controlled by gas diffusion for the range of operating conditions in the continuous moving-bed reactor.

The char-hydrogen reaction and the steam-char reaction are considered as taking place independently so that the rates of the reactions are additive.

## NOMENCLATURE

$D_p$  = average char particle diameter, ft

$f$  = fraction of carbon in the coal char which potentially can react with hydrogen and/or steam according to the first-phase reaction

$F$  = coal char feed rate, lb/hr

$G$  = mass velocity of the gas, lb/sq ft-hr

$k_1$  = hydrogen reaction rate constant in the first phase, (atm-hr)<sup>-1</sup>

$k_2$  = steam reaction rate constant in the first phase, hr<sup>-1</sup>

$k_g$  = mass transfer coefficient, lb/sq ft-hr

$(K_g)_{H_2}$  = effective mass transfer coefficient for hydrogen, ft/hr-atm

$(K_g)_{H_2O}$  = effective mass transfer coefficient for steam, ft/hr-atm

$N_{Re, LM}$  =  $\frac{DG}{\mu}$ , the particle Reynold's number log-mean

$P_{CH_4}^*$  = partial pressure of methane, atm

$P_{H_2}$  = partial pressure of hydrogen, atm

$P_{H_2}^*$  = partial pressure of hydrogen in equilibrium with coal char and methane, atm

$P_{H_2O}$  = partial pressure of steam, atm

$P_{H_2O}^*$  = partial pressure of steam in equilibrium with C, CO, CO<sub>2</sub>, and H<sub>2</sub>, atm

$T$  = temperature, °F

$V$  = volume of the reactor, CF

$W$  = weight of coal char in bed, lb

$X$  = fraction of carbon converted

$X_{H_2}$  = fraction of carbon converted by hydrogen

$X_{H_2O}$  = fraction of carbon converted by steam

$x_{H_2}$  = fraction of carbon converted in the second phase by hydrogen,

$x_{H_2O}$  = fraction of carbon converted in the second phase reaction by steam

$\rho_C$  = density of carbon in coal char, lb/CF

$\rho_B$  = bulk density of coal char in bed, lb/CF

$\theta$  = time, hr

$\mu$  = viscosity of the gas, lb/ft-hr

#### ACKNOWLEDGMENT

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