

DETERMINATION OF THE KINETICS OF  
HYDROGASIFICATION OF CHAR USING  
A THERMOBALANCE

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INTRODUCTION

The gasification of coal with fairly pure hydrogen, referred to as "direct hydrogasification", is considered to be an attractive approach for the production of substitute natural gas (1,2). Conceptually, direct hydrogasification processes involve two stages of gasification, one for hydrogasification of the coal and another for steam-oxygen gasification of the char from the first stage as shown in Figure 1. The hydrogen required by the hydrogasification stage is produced in the steam-oxygen gasification stage. About 85-95 percent of the methane in the final product gas is formed directly in the gasifier (3,4). Thus, the requirement for catalytic methanation is greatly reduced compared to single-stage steam-oxygen processes. Process analyses indicate several technical advantages, which add up to a significant economic advantage, of direct hydrogasification processes over single-stage steam-oxygen processes (1-6). Some examples of the direct hydrogasification processes under development are: (a) the Hydrane process (1,3) being developed by the Pittsburgh Energy Research Center (PERC), (b) the Rocketdyne Process (7), and (c) a catalytic hydrogasification process being developed by Battelle's Columbus Laboratories (4,8,9).

In support of the hydrogasification processes under development, it is necessary to obtain accurate kinetic and yield data for design and scale up. These data should properly take into account the suppressing effect of the primary product of reaction, namely,  $\text{CH}_4$ , on the rate of conversion of coal. Unfortunately, however, there is only a limited amount of data presented in literature (10,11) on the kinetics of hydrogasification in the presence of  $\text{CH}_4$  present at levels representing commercial design. The bulk of the available data are for gasification with essentially 100 percent hydrogen. Another problem with available data is that most if it have been obtained using preoxidized coal while all the direct hydrogasification processes under development do not employ preoxidation.

In this paper we provide kinetic data on the hydrogasification of coal char, produced by partial hydrogasification of raw, caking bituminous coal, with mixtures of  $\text{H}_2$  and  $\text{CH}_4$ . The data are correlated employing a combination of kinetic models proposed by Johnson (11) and Gardner, et al (12). Although the data were obtained for the Hydrane process, general applicability to other direct hydrogasification processes is suggested. In the Hydrane process, which operates at a total pressure of about 1000 psig, the required carbon conversion for the hydrogasification stage is about 50 percent for achieving balanced operation, i.e., to avoid excess  $\text{H}_2$  or char from the steam-oxygen step. The hydrogasification stage itself consists of two countercurrent stages as shown in Figure 2. In the first hydrogasification stage, raw coal is contacted in a free fall, dilute phase with a mixture of primarily  $\text{H}_2$  and  $\text{CH}_4$  (greater than about 40 percent of each) to hydrogasify about 25 percent of the carbon. The char from the first hydrogasification step is further hydrogasified in a fluid bed with essentially pure  $\text{H}_2$ , and the resulting product gas is fed to the first hydrogasification stage (3). It is this second stage of hydrogasification for which the kinetic data reported in this paper were obtained (13).

### EXPERIMENTAL DETAILS

The hydrogasification experiments were carried out in a thermobalance reactor described elsewhere (8,13). By continuously recording the mass of a sample held in a wire-mesh basket the progress of a reaction can be easily monitored in such a system. The operation is essentially isothermal and the gas conversion is limited to a few percent. A typical experiment in the thermobalance involves bringing the reactor to operating conditions first and then lowering the sample basket, measuring 0.63 inch O.D. and containing a 0.5 to 1.0 gram sample of char, at the rate of about one inch per second until it reaches the desired position in the reactor (I.D. = 0.75 inch). Thus, there is no weight trace for about the first 0.15 minute during which the sample is exposed to the reactive atmosphere. An additional minute or so is required for the sample to reach operating temperature. The temperature is measured by a thermocouple placed 1/4-inch below the sample basket.

The eight char samples employed in this study were produced at PERC in a dilute phase hydrogasifier operated at a nominal feed rate of 10 lb/hr of coal. The chars were derived from a Pittsburgh No. 8 hvAb and an Illinois No. 6 hvCb coal each processed in the dilute phase reactor at four temperatures: 725 C, 800 C, 850 C, and 900 C. Typical analyses of chars from the two types of coal are shown in Table 1. The raw coal

TABLE 1. TYPICAL ANALYSES OF CHARS FROM DILUTE PHASE HYDROGASIFIER

Analysis, wt %	Coal Source	
	Pittsburgh No. 8 hvAb	Illinois No. 6 hvCb
<u>Proximate, as received</u>		
Moisture	2.5	1.5
Ash	7.5	16.4
Volatile matter	9.2	9.7
Fixed carbon (by difference)	<u>80.8</u>	<u>72.4</u>
TOTAL	100.0	100.0
<u>Ultimate, dry</u>		
Carbon	84.4	75.8
Hydrogen	2.4	2.1
Nitrogen	1.5	1.3
Sulfur	1.0	1.3
Ash	7.7	16.6
Oxygen (by difference)	<u>3.0</u>	<u>2.9</u>
TOTAL	100.0	100.0
<u>Particle Size Distribution, (a)</u>		
<u>U.S. series mesh size</u>		
+10	70.7	2.9
-10+12	7.0	2.3
-12+16	8.7	9.0
-16+30	9.0	33.0
-30+50	3.2	31.9
-50	<u>1.4</u>	<u>20.9</u>
	100.0	100.0

(a) The chemical analyses above correspond to the +50 mesh fraction.

was -50+100 mesh (U.S. sieve series) but the char particle size was much larger, as shown in Table 1, due to swelling during hydrogasification. The average carbon conversion during dilute phase hydrogasification was 26 percent and the resulting chars had an average volatile matter content of about 10 percent. The variation in proximate and ultimate analyses of various chars was small. However, the mean particle diameter of the chars from Pittsburgh No. 8 coal was about three times (about 1800  $\mu\text{m}$ ) that of chars from Illinois No. 6 coal due to the higher FSI of Pittsburgh No. 8 seam coals.

Each of the eight char samples were hydrogasified at a fixed total pressure of 1000 psig (69 atm) at several different temperatures ranging from 700 C to 1000 C and employing three feed gas compositions: (a) 100 percent hydrogen, (b) 74 percent  $\text{H}_2$ -26 percent  $\text{CH}_4$ , and (c) 48 percent  $\text{H}_2$ -52 percent  $\text{CH}_4$ . To contain the samples in the 100 mesh screen basket, only the +50 mesh fraction, which nearly represented the bulk of the samples, was used. These experiments were preceded by studies on the effect of char particle size and gas velocity, employing chars produced at 800 C, to determine the influence of mass transfer on rate of hydrogasification.

In some experiments some carbon was deposited on the sample basket due to cracking of methane present in the feed gas. A correction was made for this deposition on the basket so as to obtain true char hydrogasification rate data.

## RESULTS AND DISCUSSION

### General Observations and Definitions

It is well recognized that bituminous coals exhibit an initial, transient period of extremely high hydrogasification reactivity followed by a rather slow rate of hydrogasification regime. The initial, high-reactivity period, which is generally over in a few seconds at temperatures above 850 C, consists of gasification of the volatile matter as well as some fixed carbon, the amount of which depends on the partial pressure of hydrogen (2). In the thermobalance, this regime lasts longer because of limitations on rate of heating of coal.

The rate of hydrogasification in the first kinetic regime is so much higher than the rate for the second regime that a "knee" is apparent in the curves showing fractional conversion, X, versus time as shown in Figure 3. The definition of X is

$$X = \frac{-\Delta W}{W_0} \quad 1)$$

where  $-\Delta W$  is the weight loss of as-received char due to gasification and  $W_0$  is the initial weight. Because of the heat up effects during the first minute the thermobalance is not suitable for determining the rate of hydrogasification in the rapid-hydrogasification kinetic regime. However, it is quite suitable for determining the onset of the slow-hydrogasification kinetic regime which is made possible by noting the "knee" in the X versus time curves. This boundary or "cut-off point" between the two regimes, designated as  $X_{cp}$ , was determined for each hydrogasification run. The cut-off reaction time was found to be as much as about 2.5 minutes at 700 C and as short as about 0.5 minutes at 1000 C. Johnson (11) used 2 minutes as the cut-off time for hydrogasification runs at temperatures of 850 C or higher.

The thermobalance data were correlated in terms of the conversion of base carbon which is that portion of the total carbon in char which is not associated with the ASTM volatile matter (10,11). The fractional conversion of base carbon is defined as

$$X_{BC} = \frac{X-V}{1-A-V} \quad 2)$$

where V is the ASTM volatile matter (including moisture) and A is the ash content of char, each expressed as weight fraction of as-received char. As mentioned above, a portion of the base carbon is hydrogasified in the rapid-hydrogasification regime. The total amount of this "rapid base carbon" is represented as  $X_{BC}^R$ . The remaining base carbon can be termed "slow base carbon". Now another fractional conversion term can be defined based on the slow base carbon content of char:

$$X_{SC} \equiv \frac{X_{BC} - X_{BC}^R}{1 - X_{BC}^R} = \frac{X - X_{CP}}{1 - X_{CP} - A} \quad 3)$$

It was assumed in writing Equations 2 and 3 that all volatile matter, including moisture, is hydrogasified during the rapid-hydrogasification regime and that the rate of carbon conversion relative to the rate of ash-free char conversion is constant after devolatilization. Both of the assumptions were found to be quite reasonable as determined by ultimate and proximate analyses data for chars hydrogasified to various levels of conversion.

#### Rapid Hydrogasification Regime

The effects of gas-film and pore diffusion on the yield of rapid base carbon conversion,  $X_{BC}^R$ , were investigated by varying the gas velocity and particle size, respectively. All experiments were performed at 1000 C temperature using a feed gas containing only  $H_2$ . Increasing the superficial gas velocity from 0.04 to 0.23 ft/sec resulted in only a slight increase in  $X_{BC}^R$  as shown in Figure 4. And increasing the mean particle diameter from 450 to 2100  $\mu m$  did not affect  $X_{BC}^R$  as shown in Figure 5. Anthony, et al, on the other hand, reported a significant increase in the yield of rapid base carbon with decreasing particle diameter. One explanation for this difference may be that Anthony, et al, worked with rather dense particles compared to the char particles used in this study which had a popcorn-like consistency in which case the internal surfaces of particle may be equally accessible to  $H_2$  for particles of varying outer diameters.

The +50 mesh samples denoted by closed symbols in Figure 5 were employed for determining the dependence of  $X_{BC}^R$  as a function of temperature, pressure, and feed gas composition as well as the char preparation (dilute phase hydrogasification) temperature. The char preparation temperature did not appear to affect  $X_{BC}^R$  for either type of coal.

Since the variation among the individual values of  $X_{BC}^R$  was small enough, the average values of  $X_{BC}^R$  for the eight chars were used to determine the effect of temperature and partial pressure of  $H_2$  and  $CH_4$ . The average  $X_{BC}^R$  values were found to depend on temperature and  $P_{H_2}$  but not on  $P_{CH_4}$ . Furthermore, temperature seemed to affect  $X_{BC}^R$  only below 800 C. The data were correlated using the following equation which is similar to the one given by Johnson (11) for temperatures exceeding about 850 C:

$$-\ln(1 - X_{BC}^R) = k_1 P_{H_2} \quad 4)$$

where  $k_1$  is a function of temperature. Figure 6 shows the dependence of  $X_{BC}^R$  on  $P_{H_2}$  for temperatures ranging from 800 to 1000 C. The  $k_1$  values obtained at different temperatures are summarized below:

<u>Temperature, C</u>	<u><math>k_1</math>, atm<sup>-1</sup></u>
700	0.0016
750	0.0023
≥800	0.0030

It should be pointed out that Johnson did not apply Equation 4 for temperatures below about 850 C.

The effect of temperature was found to be qualitatively similar to that observed by others (2,10,14,15), i.e.,  $X_{BC}^R$  increases with temperature until about 850 C and then levels off. Actually, the relationship between  $X_{BC}^R$  and temperature may be quite complex as shown by Pyricloch, et al (10), and Anthony, et al (2). At temperatures exceeding 850 C, Johnson found the value of  $k_1$  to be 0.0092 for air pretreated Ireland mine coal char, containing 28.4 percent volatile matter, as opposed to 0.0030 for this study. The difference in these  $k_1$  values is because some rapid base carbon is hydrogasified during dilute phase hydrogasification in the Hydrane Process.

#### Slow Hydrogasification Regime

It is necessary that a significant portion of the base carbon be gasified in the slow hydrogasification regime if the following conditions are to be met for a process involving the direct hydrogasification of high-volatile bituminous coal together with steam-oxygen gasification of char: (a) process operates at a total pressure of 1000 psig or lower, (b) the heat content of gas after methanation of the CO produced in the direct hydrogasification stage is equal to or greater than 950 Btu/scf, (c) there is no excess char produced. Therefore, the thermobalance data were analyzed to determine the kinetic parameters for the slow hydrogasification regime.

#### Rate Expression

The slow hydrogasification reaction has been studied by a number of researchers (10-12,15-19) and a number of rate expressions have been employed for the same. Most of these rate expressions can be written in the following generalized form:

$$-\frac{dX_{SC}}{dt} = k_2'(1-X_{SC})^{n_1} \exp(n_2 X_{SC})^{n_3} \quad (5)$$

where  $X_{SC}$  is the fraction of the base carbon that remains in the char after the rapid hydrogasification stage is complete, and  $k_2'$ ,  $n_1$ ,  $n_2$ , and  $n_3$  are parameters that depend on reaction conditions. Following are some specific forms of Equation 5 that appear in literature:

$$-\frac{dX_{SC}}{dt} = k_2''(1-X_{SC}) \quad (6a)$$

$$-\frac{dX_{SC}}{dt} = k_2'''(1-X_{SC})^{2/3} \exp(-\alpha X_{SC}^2) \quad (6b)$$

$$-\frac{dX_{SC}}{dt} = k_2(1-X_{SC}) \exp(-bX_{SC}) \quad (6c)$$

The first of these is the simplest, but not generally found to be applicable to hydrogasification (11,12). The second equation was used by Johnson who found the value of  $\alpha$  to be 0.97. At this value of  $\alpha$ , however, Equation 6b can be approximated by Equation 6a since the value of  $(1-X_{SC})^{1/3}$  is within 3 percent of the value of  $\exp(-0.97 X_{SC}^2)$  for  $X_{SC}$  values up to 0.6 which covers the range of interest. Equation 6c was developed by Gardner, et al, who assumed that  $bRT$  was independent of temperature (12), unlike the results of our study, discussed later.

Equation 6a, which is a good approximation for Equation 6b as discussed above, was found to be unsatisfactory for hydrogasification of Hydrane char, particularly at temperatures below 900 C. This is illustrated in Figure 7 which shows the plots of

$\ln(1-X_{SC})$  as a function of time, which are expected to be straight lines for Equation 6a to be valid. However, Equation 6c was found to be applicable at all conditions and was therefore used in this study. The basic hypothesis behind Equation 6c is that there is a continuous, exponential decay in the reactivity of the char as hydrogasification proceeds.

The determination of parameters  $k_2$  and  $b$  required rearranging Equation 6c and taking the integral of each side as follows:

$$\int_0^{X_{SC}} \frac{-\exp(bX_{SC})}{(1-X_{SC})} = k_2 t \quad 7)$$

where  $t$  is measured from the end of the rapid hydrogasification regime. The integral on the left hand side of Equation 7 was numerically evaluated for various values of  $b$  to give the best straight line when plotted against  $t$ . Samples of straight lines thus obtained are shown in Figure 8.

#### Effect of Gas-Film and Pore Diffusion

The effect of gas-film diffusion on the initial rate of hydrogasification,  $k_2$ , was found to be significant only below a gas velocity of about 0.15 ft/sec as shown in Figure 9. Wen, et al, similarly found that gas-film diffusion was not an important factor in their experiments with Hydrane char at 0.2 ft/sec (17). The gas velocities used for studying the effects of the variables discussed next were kept high enough so that gas-film diffusion was not a factor.

The effect of particle size on  $k_2$  for Hydrane char was found to be quite different from that found by others for preoxidized coal chars. Specifically, the value of  $k_2$  for Hydrane char was found to increase significantly with mean particle diameter as shown in Figure 10. But, Tomita, et al, found that changing the particle size range of low volatile coal char from -40+100 to -200+325 U.S. mesh resulted in a 1.6-fold increase in the hydrogasification rate at 400 psig and 980 C (19). Johnson, on the other hand, used a rate expression which assumed the rate to be independent of particle size (11). The reason for the peculiar behavior of the Hydrane char is yet unknown. It is suspected that the variation in internal surface properties with particle size will explain this peculiar behavior. Variation in the ash content was not found to be large enough to explain it.

#### Effect of Char Preparation Conditions and Coal Type

The char preparation temperature was not found to affect the initial rate of hydrogasification,  $k_2$ . However, the Pittsburgh No. 8 seam chars were found to be more reactive than Illinois No. 6 seam chars as shown in Figure 10. The difference in the reactivities of the +50 mesh fractions, which nearly represented the entire char sample as shown in Table 1, was even more pronounced due to the difference in the mean particle diameter. On the average, the +50 mesh Pittsburgh No. 8 chars were about 25 percent more reactive than the +50 mesh Illinois No. 6 chars. Johnson, on the other hand, using preoxidized chars found the Pittsburgh No. 8 chars to be about 10 percent less reactive than Illinois No. 6 chars (20). Again this difference is unexplained but is suspected to be due to variation in surface properties. For one thing, the bulk density of Pittsburgh No. 8 chars was found to be considerably lower than that of Illinois No. 6 chars.

In order to determine the effect of preoxidation on reactivity, the  $k_2$  values for Hydrane char from our study were compared with those reported in literature for other chars. The comparison, which was complicated due to variation in coal sources

and kinetic expressions used to determine rate constants, did not conclusively show that Hydrane char is more reactive than chars produced by preoxidation. For example, the  $k_2$  value for Pittsburgh No. 8 Hydrane char at 900 C using  $H_2$  only was found to be  $0.074 \text{ hr}^{-1} \text{ atm}^{-1}$ . On the other hand, Johnson (11) and Gardner, et al (12) reported  $0.021$  and  $0.117 \text{ hr}^{-1} \text{ atm}^{-1}$ , respectively, for preoxidized chars from similar coals. Also, we found that the  $k_2$  value for preoxidized Synthane char was  $0.037 \text{ hr}^{-1} \text{ atm}^{-1}$  for the same coal (13).

#### Effect of Pressure and Temperature

Since the char preparation temperature did not significantly affect the  $k_2$  values, these were averaged over the four types of chars for each coal source. Thus, for each set of temperature and pressure, two  $k_2$  values, one for each coal source, were obtained.

The back reaction of methane to form carbon on char was found to make a very significant contribution at higher temperatures and methane partial pressures. In fact, the value of  $k_2$  was found to be nearly zero at about 850 C when the partial pressures of  $H_2$  and  $CH_4$  were 33.1 and 35.9 atm, respectively. A simplified form of the following correlation, developed by Johnson, was used:

$$k_2 = \frac{k_3 P_{H_2}^2 \left[ 1 - \frac{P_{CH_4}}{P_{H_2} K^E} \right]}{1 + k_4 P_{H_2}} \quad (8)$$

where  $k_3$  and  $k_4$  are constants that depend on temperature only and  $K^E$  is the equilibrium constant for the formation of  $CH_4$  by reaction of  $H_2$  with  $\beta$ -graphite. However, at the conditions used in this study,  $k_4 P_{H_2}$  is expected to be large compared to one (11). Thus, Equation 8 can be simplified as follows:

$$k_2 = k_5 \left[ P_{H_2} - \frac{P_{CH_4}}{K^E} \right] \quad (9)$$

But,  $k_5$  is expected to show an Arrhenius type dependence on temperature. Thus,

$$k_2 = k_o \exp(-E_o/RT) \left[ P_{H_2} - \frac{P_{CH_4}}{K^E} \right] \quad (10)$$

Figure 11 shows that Equation 10 is applicable for Illinois No. 6 chars only above about 850 C. Below 850 C,  $k_2$  does not appear to be too sensitive to temperature. Similar results were found for Pittsburgh No. 8 chars. For this range of applicability the following values of  $k_o$  and  $E_o$  were determined for the two coal sources:

Coal Source	$k_o, \text{ min}^{-1} \text{ atm}^{-1}$	$E_o, \text{ kcal/mole}$
Pittsburgh No. 8 seam	106.2	26.5
Illinois No. 6 seam	1067.1	32.5

In Figure 11, the data points for higher  $CH_4$  partial pressures appear to fall somewhat below those at lower  $CH_4$  pressures. This suggests that the value of  $K^E$  for Hydrane char is somewhat higher than the value for  $\beta$ -graphite. This is also supported by the fact that the value of  $k_2$  for Hydrane char at 850 C,  $P_{H_2}$  and  $P_{CH_4}$  values of 33.1 and 35.9 atm, respectively, was positive, though nearly zero, while it is expected to be negative for  $\beta$ -graphite at temperatures above 840 C for the same partial pressures of  $H_2$  and  $CH_4$ .

It is easy to see from Equation 6c and 10 that  $E_0$  corresponds to the activation energy for hydrogasification at  $X_{SC}$  equal to zero. As  $X_{SC}$  increases, the effective activation energy,  $E_1$ , increases since bRT is positive and Equations 6c and 10 can be combined as follows:

$$\frac{dX_{SC}}{dt} = k_0(1-X_{SC}) \exp(-E_1/RT) \left[ \frac{P_{H_2}}{P_{H_2}} - \frac{P_{CH_4}}{E^K} \right] \quad (11)$$

where 
$$E_1 = E_0 + (bRT)X_{SC} \quad (12)$$

Equation 12 shows that the char becomes less reactive as  $X_{SC}$  increases. Gardner, et al, assumed but did not show that bRT is independent of temperature and pressure. However, bRT for Hydrane char was found to depend both on temperatures and partial pressure of  $H_2$  and  $CH_4$  as shown in Figure 12. The bRT values plotted in Figure 12 are average values based on eight chars since the coal source and char preparation temperature did not significantly affect bRT. Three things are to be noted in Figure 12. First, bRT decreases with temperature, i.e., higher temperatures help maintain the reactivity. Second, the bRT is more or less independent of temperature above 850 C which is the regime that Gardner, et al, operated in. And third, bRT decreases with increasing  $P_{H_2}$ . In other words, higher  $P_{H_2}$ , just as higher temperature, impedes decay of reactivity with increasing  $X_{SC}$ .

The value of bRT at 850 C or higher for 100 percent  $H_2$  case was found to be 3.6 kcal/mole. For these conditions one can write the apparent activation energy as a function of  $X_{SC}$  for Pittsburgh No. 8 chars as

$$E_1(\text{kcal/mole}) = 26.5 + 3.6 X_{SC} \quad (13)$$

Gardner, et al, on the other hand, found the following relationship for preoxidized Pittsburgh No. 8 char

$$E_1 = 29.3 + 2.43 X_{MAF} \quad (14)$$

where  $X_{MAF}$  can be approximated by  $X_{SC}$ . Thus, the initial activation energy,  $E_0$ , and rate of deactivation are not affected much on preoxidation of coal. This suggests that the kinetic data for the slow hydrogasification regime reported in this paper are generally applicable to direct hydrogasification processes whether they employ pre-oxidation or not.

Although the results on bRT are preliminary and somewhat sketchy, they provide important insight into the factors responsible for deactivation of chars during hydrogasification.

#### Conditions for Achieving Required Carbon Conversion

As mentioned earlier, about 50 percent of the carbon present in raw coal needs to be hydrogasified in the dilute phase and fluid bed stages for balanced operation. The conditions required to achieve this level of carbon conversion were therefore determined by combining the dilute phase and thermobalance data. Figure 13 shows the total carbon conversion, including 26 percent for dilute phase hydrogasification, as a function of time, temperature, and gas composition for Pittsburgh No. 8 char. The curves in Figure 13 are applicable when the second-stage hydrogasification takes place in a fluid bed reactor with perfect backmixing of gas. Under such conditions the product gas composition for the second-stage reaction is to be used to determine the appropriate curve in Figure 13. Note that the data for 100 percent  $H_2$  case are not plotted since the  $CH_4$  concentration in the gas from the fluid bed stage will be between

25 and 50 percent, probably greater than 40 percent.

#### CONCLUSIONS

Kinetic data were obtained on a thermobalance (TGA) for hydrogasification of chars produced in a dilute phase hydrogasifier, for designing a scaled-up, direct, fluid-bed hydrogasification reactor for the Hydrane process. Two distinct kinetic regimes were observed at any set of conditions. The first regime corresponded to rapid hydrogasification of volatile matter as well as some base carbon and was over in less than 2.5 minutes in the TGA. For this regime the yield of base carbon conversion,  $X_{BC}^R$ , was found to be practically independent of gas velocity, particle size, and char type. The yield of  $X_{BC}^R$  increased continuously with  $p_{H_2}$  which was the most important variable. The yield of  $X_{BC}^R$  was found to be independent of  $p_{CH_4}$ . Apparently the rate of the forward reaction between coal carbon and  $H_2$  was much higher than the rate of cracking of  $CH_4$  at all conditions. Increasing the temperatures resulted in an increase in  $X_{BC}^R$  until about 800 C, after which it did not change.

The second kinetic regime corresponded to the slow hydrogasification of base carbon. A kinetic model was employed that properly accounted for the fact that there was continuous deactivation of char with increasing fractional conversion. The rate of deactivation was found to be lower at higher temperatures and  $p_{H_2}$ . Again, the char preparation temperature did not affect the reactivity. But, there were two unexpected results. First, the initial rate of hydrogasification,  $k_i$ , increased with particle size. And second, the Pittsburgh No. 8 chars were found to be more reactive than Illinois No. 6 chars rather than the opposite. It is possible that these two unexpected results can be explained on the basis of differences in surface properties such as surface area, average pore size, etc. Although the surface properties of Hydrane char may be different from those of preoxidized chars, the initial activation energy and rate of deactivation with level of conversion are not. Also, it cannot be conclusively shown that initial rate of gasification of Hydrane chars is higher than that of pre-oxidized coal chars.

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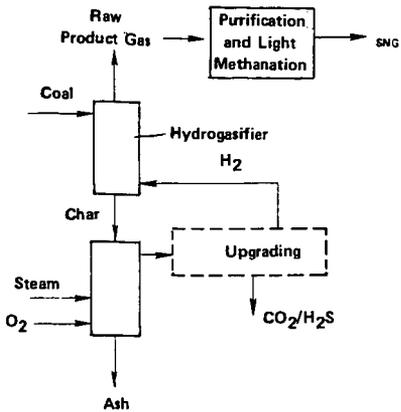


FIGURE 1. SCHEMATIC FLOWSHEET FOR DIRECT HYDROGASIFICATION OF COAL

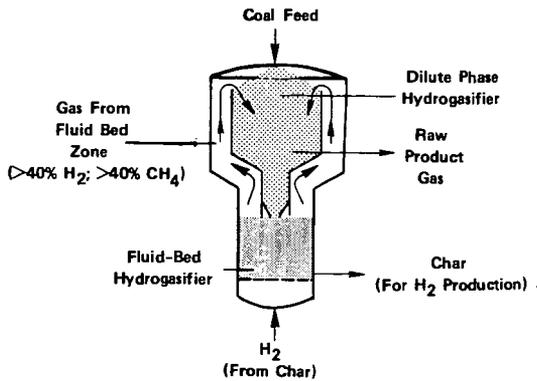


FIGURE 2. SCHEMATIC OF TWO-STAGE HYDROGASIFIER FOR THE HYDRANE PROCESS (Ref. 17)

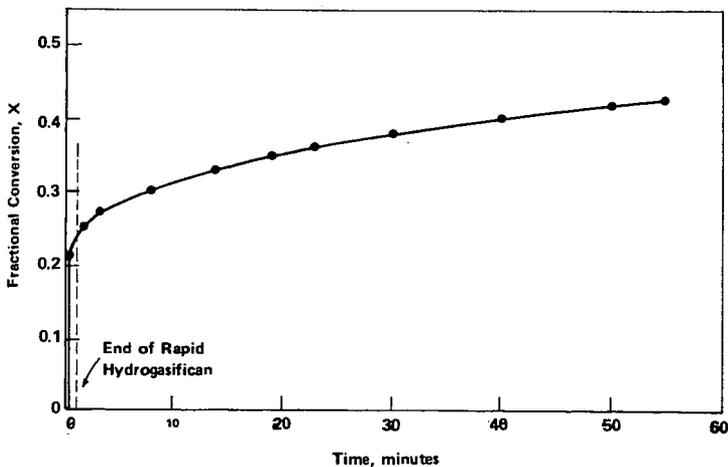


FIGURE 3. TYPICAL THERMOBALANCE DATA FOR HYDROGASIFICATION OF CHAR

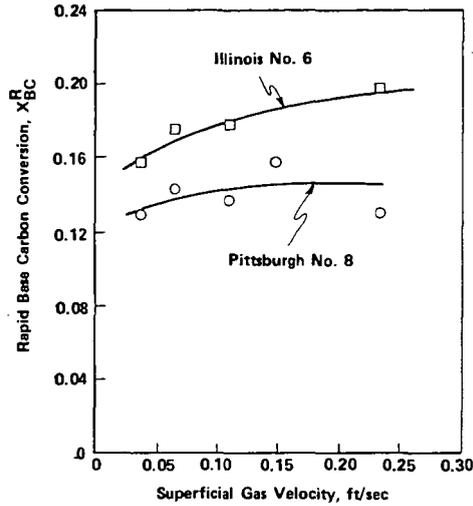


FIGURE 4. DEPENDENCE OF  $X_{BC}^R$  ON GAS VELOCITY FOR HYDROGASIFICATION OF -18+35 MESH CHAR AT 1000 C, 69 ATM, 100%  $H_2$

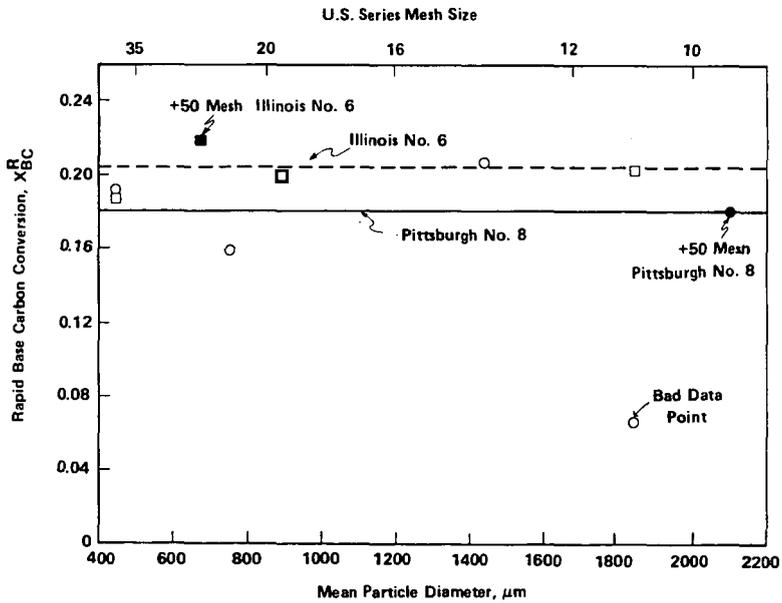


FIGURE 5. DEPENDENCE OF  $X_{BC}^R$  ON CHAR PARTICLE SIZE FOR HYDROGASIFICATION AT 1000 C, 69 ATM, 100%  $H_2$

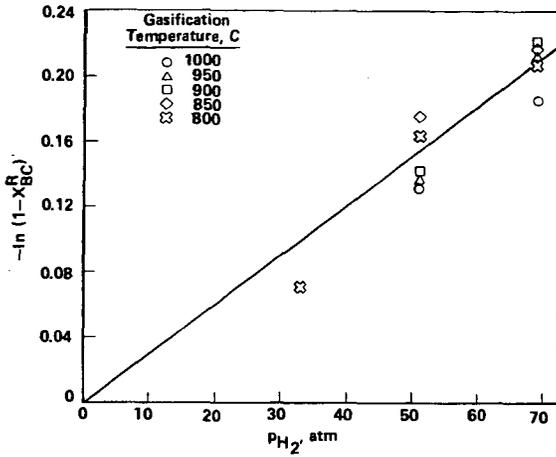


FIGURE 6. CORRELATION OF  $X_{BC}^R$  WITH HYDROGEN PARTIAL PRESSURE

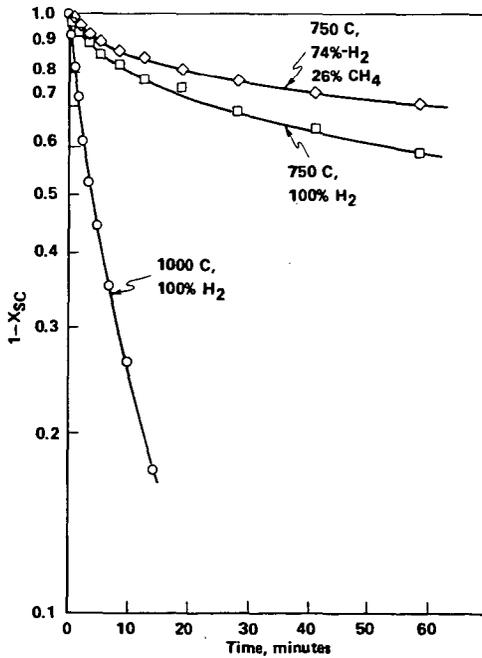


FIGURE 7.  $(1-X_{SC})$ , PLOTTED ON A LOGARITHMIC SCALE, VERSUS TIME FOR HYDRO-GASIFICATION OF PITTSBURGH NO. 8 CHAR AT 69 ATM TOTAL PRESSURE

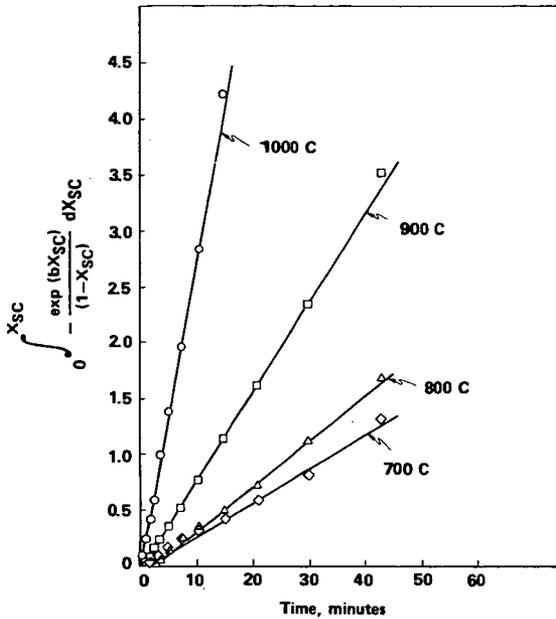


FIGURE 8.  $X_{SC} = \frac{-\exp(bX_{SC})}{(1-X_{SC})} dX_{SC}$  VERSUS TIME FOR HYDROGASIFICATION OF PITTSBURGH NO. 8 CHAR AT 69 ATM, 100% H<sub>2</sub>

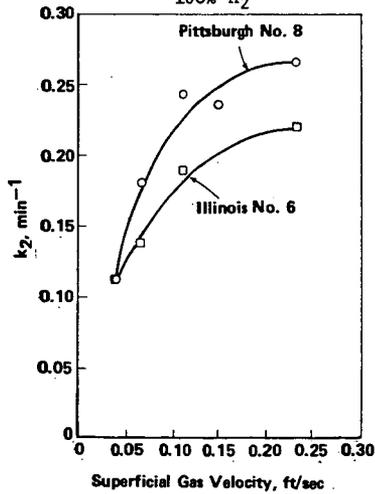


FIGURE 9. DEPENDENCE OF  $k_2$  ON GAS VELOCITY FOR HYDROGASIFICATION OF -18+35 MESH CHAR AT 1000 C, 69 ATM, 100% H<sub>2</sub>

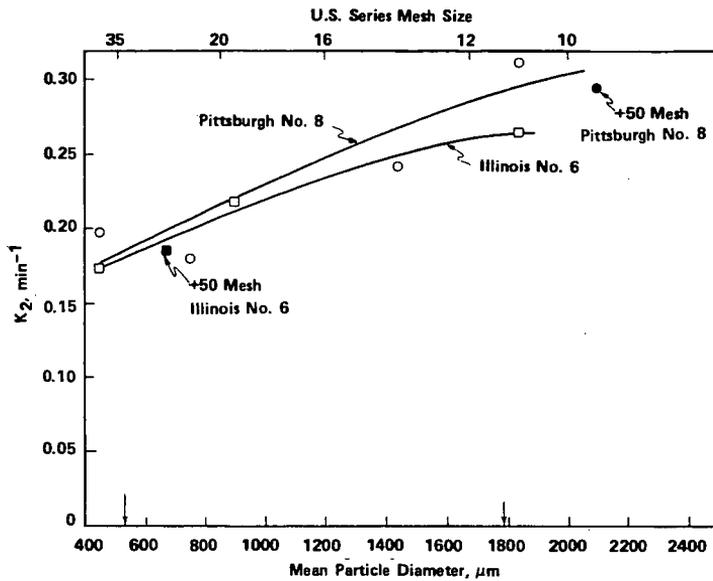


FIGURE 10. DEPENDENCE OF  $k_2$  ON CHAR PARTICLE SIZE FOR HYDROGASIFICATION AT 1000 C, 69 ATM, 100%  $\text{H}_2$

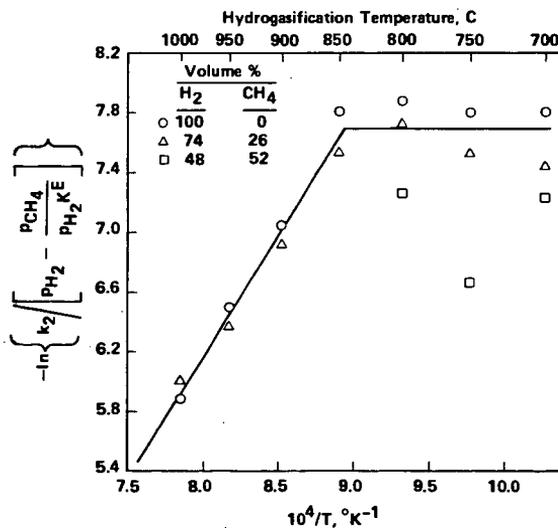


FIGURE 11. CORRELATION OF  $k_2$  WITH HYDROGASIFICATION CONDITIONS FOR CHARS DERIVED FROM ILLINOIS NO. 6 COAL. TOTAL PRESSURE = 69 ATM

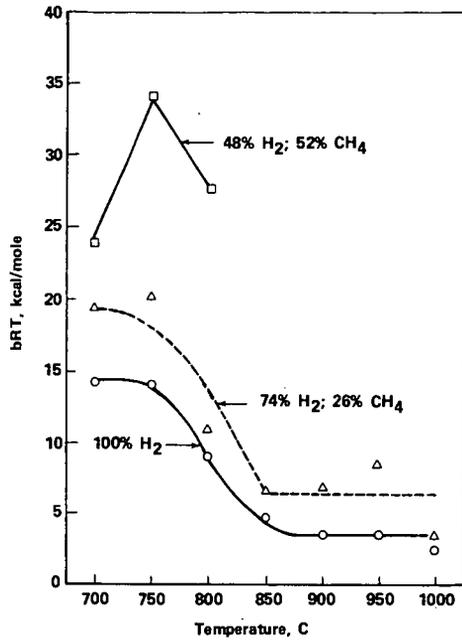


FIGURE 12. DEPENDENCE OF  $hRT$  ON REACTION CONDITIONS. TOTAL PRESSURE = 69 ATM

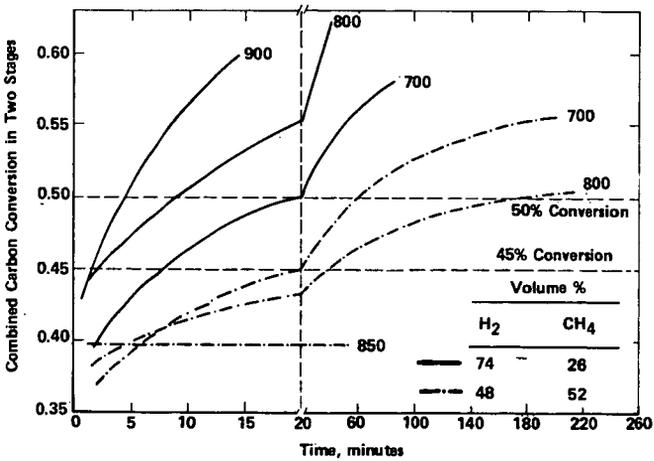


FIGURE 13. COMBINED CARBON CONVERSION IN FIRST STAGE (DILUTE PHASE) AND SECOND STAGE AS A FUNCTION OF TIME AT 69 ATM TOTAL PRESSURE FOR CHARs DERIVED FROM PITTSBURGH NO. 8 COAL