

Reactor Performance During Rapid-Rate  
Hydrogasification of Subbituminous Coal

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INTRODUCTION

In rapid-rate coal hydroxyprolysis, pulverized coal particles are contacted with hot, high-pressure hydrogen for a short period of time. Typical conditions include temperatures of 1,000°F to 2,000°F, hydrogen partial pressures of 500 to 3,000 psi, and particle residence times of 0.05 to 5 seconds. Reaction products are primarily methane, with smaller amounts of ethane, benzene and its derivatives, light oils, and carbon-oxides. Agglomeration of caking coals is avoided by rapidly heating the coal particles at rates in excess of 50,000°F/sec to reaction temperature.

Rapid-rate coal hydroxyprolysis involves a number of complex chemical and transport phenomena which are not well understood. These phenomena include devolatilization of the solid coal, hydrogenation of reactive volatile matter, hydrogenation of char, diffusion of volatile matter from the coal particles, and intrusion of hydrogen to stabilize the reactive volatiles or react with the active char.<sup>1</sup> Excellent reviews of the subject have been presented by Anthony and Howard<sup>2</sup> and by Pyrcioch et al.<sup>3</sup>

For the past several years, a number of studies have been conducted on the rapid-rate hydroxyprolysis of various rank coals. These studies have included laboratory-scale experiments at CUNY;<sup>4</sup> bench-scale experiments at Pittsburgh Energy Research Center (PERC),<sup>5</sup> Cities Service,<sup>6</sup> and Brookhaven National Laboratory;<sup>7</sup> and small pilot-scale experiments at Rocketdyne.<sup>8</sup> Some of these studies have emphasized the production of both gas and liquid products (hydroxyprolysis or hydrogenation); others have emphasized the production of only gas (hydrogasification).

Bechtel Corporation has conducted a program for the DOE (Contract EF-77-A-01-2565) to investigate the operability potential and scaleup feasibility of the Cities Service, Rocketdyne, PERC, and Brookhaven coal hydrogasification processes, relating to DOE plans for a hydrogasification process development unit (PDU). As part of the program objective, Bechtel has (1) collected bituminous, subbituminous, and lignite coal hydrogasification data from Rocketdyne, Cities Service, PERC, and Brookhaven, (2) performed a reactor model study for each of the processes, and (3) developed a conceptual full-scale hydrogasification reactor design for converting subbituminous coal to SNG. As part of the reactor model study, semiempirical correlations for predicting overall carbon conversion and carbon conversion to gaseous products have been fitted to the data. Results of the Bechtel program will be presented in a future publication.<sup>9</sup>

This paper presents (1) results of the reactor model study for the hydrogasification of subbituminous coal in the Rocketdyne and Cities Service reactor systems and (2) the design basis for a full-scale subbituminous coal hydrogasifier.

ROCKETDYNE AND CITIES SERVICE SUBBITUMINOUS COAL DATA

Bechtel has collected data from 12 Rocketdyne and 42 Cities Service hydrogasification tests using Montana Rosebud subbituminous coal feed. The data have been entered into a computerized data base for ease of evaluation and tabulation. A computer listing of all of the data contained in the data base will be presented in a future publication.<sup>9</sup> The Rocketdyne and Cities Service test programs were sponsored by the DOE under Contract EX-77-C-01-2518.

The Rocketdyne tests were conducted in an entrained-downflow tubular reactor system designed to feed coal at up to 1/4-ton/hr with coal fluxes to 20,000 lb/hr/ft<sup>2</sup>. Coal particles and hot (1,500°F to 3,000°F) hydrogen gas are mixed inside a high-efficiency injector element, which produces coal heatup rates in excess of 200,000°F/sec. The hydrogen gas is heated first in a fired heat exchanger, then by partial combustion through oxygen addition in a preburner. A more detailed description of the reactor system has been given by Oberg, et al.<sup>8</sup>

The Rocketdyne tests were conducted at reactor outlet gas temperatures of 1,420°F to 1,900°F, particle (or gas)\* residence times of 530 to 1,730 milliseconds, reactor pressures of 1,000 to 1,500 psig, and hydrogen-to-coal ratios of 0.33 to 0.71 lb/lb. The mass median coal particle size was approximately 45 microns. Overall carbon conversion for the tests ranged from 28 to 47 percent; carbon selectivity to gas ranged from 50 to 100 percent; and carbon selectivity to methane ranged from 25 to 87 percent. The maximum carbon conversion of 47 percent, carbon selectivity to gas of 100 percent, and carbon selectivity to methane of 87 percent were obtained at a reactor temperature of 1,760°F, a particle residence time of 1,420 milliseconds, and a hydrogen partial pressure of 1,390 psig.

The Cities Service bench-scale system incorporates an entrained-downflow tubular reactor system that is designed to feed coal at up to 5 lb/hr with coal fluxes to 15,000 lb/hr/ft<sup>2</sup>. Preheated hydrogen and coal are mixed inside a high-velocity coaxial injector nozzle to produce coal heating rates in excess of 100,000°F/sec. The mixture then passes through the reactor tube, which is electrically heated through the walls to maintain adiabatic operation. An injected stream of cryogenically cooled hydrogen at the reactor outlet quenches the reaction. The tests employed a number of helical and vertical reactor tubes designed to accommodate the desired residence times and feed flow rates. A more detailed description of the reactor system has been given by Greene.<sup>6</sup>

The Cities Service subbituminous tests were conducted at reactor outlet gas temperatures of 1,500°F to 1,750°F, particle (or gas) residence times of 303 to 3,510 milliseconds, reactor pressures of 500 to 1,600 psig, and hydrogen-to-coal ratios of 0.74 to 1.4 lb/lb. The mass median coal particle size was approximately 45 microns. Overall carbon conversion ranged from 26 to 55 percent; carbon selectivity to gas ranged from 59 to 84 percent; and carbon selectivity to methane ranged from 18 to 59 percent. The maximum carbon conversion of 55 percent was obtained at a gas temperature of 1,610°F, a residence time of 3,160 milliseconds, and a pressure of 1,600 psig.

Greene<sup>10</sup> has presented a series of plots for the Cities Service subbituminous data. These plots revealed that at larger residence times carbon conversion increases with increasing pressure, and at smaller residence times carbon conversion decreases with increasing pressure. The plots also showed that temperature and pressure interacted in the same manner as residence time and pressure. Greene has postulated that this reversal effect of pressure with residence time suggests a two-step mechanism for carbon conversion: pyrolysis-controlled devolatilization at short residence time, and pressure-controlled hydrogenation of char at longer residence time.

#### PROPOSED REACTOR MODEL

Rapid hydrolysis of coal is an extremely complex process, which involves a number of reversible heterogeneous and homogeneous reactions.<sup>2,3</sup> Coal (or carbon) conversion kinetics during rapid devolatilization and subsequent hydrogenation are not well understood, and a majority of the models developed to correlate carbon conversion data have been more or less empirical. The principal correlative tool in most

\* For a majority of the Rocketdyne and Cities Service entrained-downflow reactor tests, particle and gas residence times are nearly identical.

studies has been a simple first-order kinetic model for the irreversible reaction  $C + 2H_2 \rightarrow CH_4$ . An integration of this simple model, assuming the Arrhenius form for the reaction rate constant, gives:

$$X = 1 - \exp \left[ -k_0 \exp(-E/RT) P_{H_2} t_R \right] \quad (1)$$

where,

X = weight fraction overall carbon conversion  
 $k_0$  = forward reaction rate frequency factor  
 E = activation energy  
 R = gas constant  
 T = reaction temperature  
 $P_{H_2}$  = hydrogen partial pressure  
 $t_R$  = particle (or gas) residence time

The above model, however, has not satisfactorily correlated data from different sources, where pressure, residence time, hydrogen-to-coal ratio, coal particle size, or coal type have differed markedly.<sup>2</sup>

Bechtel has proposed the following model for correlating overall carbon conversion to the operating variables:

$$X = X^* \left[ 1 - \exp(-\psi) \right] \quad (2)$$

with

$$\psi = \alpha_1 (t_R)^{\alpha_2} \exp(\alpha_3 P_{H_2}) \exp(\alpha_4 P_{H_2}/t_R) \exp(\alpha_5 P) \exp(\alpha_6 H/C) \exp(-\alpha_7/T_G) \exp(-\alpha_8 P_{H_2}/T_G) (X^*)^{\alpha_9} \quad (3)$$

where,

$X^*$  = weight fraction overall carbon conversion at equilibrium, i.e., at infinite residence time  
 $\psi$  = fitted function of independent (operating) variables  
 $\alpha_1, \alpha_2, \dots, \alpha_9$  = fitted coefficients  
 P = total pressure  
 H/C = hydrogen-to-coal ratio  
 $T_G$  = maximum reactor gas temperature

The coefficients,  $\alpha_1$  through  $\alpha_9$ , have been fitted to the data using a computerized multiple-regression statistical analysis. The interaction terms,  $P_{H_2}/t_R$  and  $P_{H_2}/T_G$ , have been included in the model to account for the reversal effect of pressure with residence time and temperature reported by Greene.<sup>10</sup> Mean coal particle diameter was not included in the model, since particle size was not varied during the testing.

The proposed model, which consists of an equilibrium component,  $X^*$ , and a kinetic component,  $[1 - \exp(-\psi)]$ , satisfies a number of boundary constraints. For example, as residence time or temperature approaches zero, conversion approaches zero, and as residence time approaches infinity, conversion approaches the equilibrium conversion limit,  $X^*$ .

The form of Equations 2 and 3 has been influenced by the similar form of an integrated, first-order kinetic model for the reversible homogeneous reaction  $A \rightleftharpoons B$ , where one mole of reactant produces one mole of product. The analytical expression for conversion of A to B for this reaction, assuming the Arrhenius form for the forward rate constant, is:

$$X_A = X_A^* \left\{ 1 - \exp \left[ -(k_0/X_A^*) \exp(-E/RT) t_R \right] \right\} \quad (4)$$

with

$$X_A^* = k_1 / (k_1 + k_2) = K / (1 + K) \quad (5)$$

where,

$X_A$  = weight fraction carbon conversion of species A  
 $X_A^*$  = weight fraction carbon conversion of species A at equilibrium  
 $k_1$  = forward reaction rate constant  
 $k_2$  = reverse reaction rate constant  
 $K$  = equilibrium constant

The proposed model has also been used to correlate the available data for carbon conversion to gas and methane, as follows:

$$X_G = X_G^* \left[ 1 - \exp(-\psi_G) \right] \quad (6)$$

$$X_M = X_M^* \left[ 1 - \exp(-\psi_M) \right] \quad (7)$$

where,

$X_G, X_M$  = weight fraction carbon conversion to gas and to methane, respectively  
 $X_G^*, X_M^*$  = weight fraction carbon conversion to gas and to methane at equilibrium, respectively  
 $\psi_G, \psi_M$  = fitted functions of independent variables (assumed to have same form as  $\psi$  in Equation 3).

#### PREDICTION OF EQUILIBRIUM CARBON CONVERSION

Owing to the complexity of coal hydrolysis, a thermodynamic equilibrium computer model, PEP<sup>11</sup> (Propellant Evaluation Program), has been used to predict the thermodynamic equilibria for the test data. PEP considers a reaction system of carbon ( $\beta$ -graphite), hydrogen, oxygen, and hydrocarbon gases within a temperature and pressure range normally encountered in coal hydrolysis.

At a given temperature, pressure, and relative weights of initial reactants, PEP predicts the concentration of species that appear in significant amounts at equilibrium. For the operating range used in the hydrogasification reactor systems, the results from PEP indicate that methane is the major hydrocarbon product present at equilibrium. Higher hydrocarbon products, such as ethane, ethylene, or benzene, are present only in trace amounts. PEP also predicts that significant quantities of CO and CO<sub>2</sub> can be present in the gas phase at equilibrium. Note that for these conditions the equilibrium overall carbon conversion,  $X^*$ , and the equilibrium conversion to gas,  $X_G^*$ , are equal.

In Figure 1, predicted equilibrium conversions for the subbituminous coal are shown as a function of reaction temperature and hydrogen-to-coal ratio, at a reactor pressure of 1,500 psig. As expected,  $X^*$  increases with decreasing temperature (the overall reaction is exothermic) and with increasing hydrogen-to-coal ratio. Since there are fewer product gas moles than reactant gas moles during hydrolysis,  $X^*$  (or  $X_G^*$ ) will increase with increasing pressure. Similarly, predicted values for equilibrium conversion to methane for the subbituminous coal are shown in Figure 2 as a function of temperature and hydrogen-to-coal ratio at 1,500 psig.

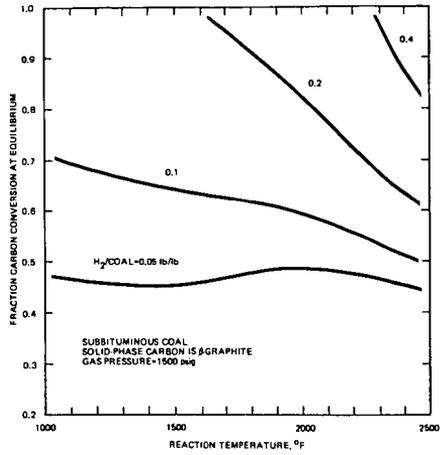


Figure 1. Predicted Fraction Carbon Conversion at Equilibrium for Subbituminous Coal

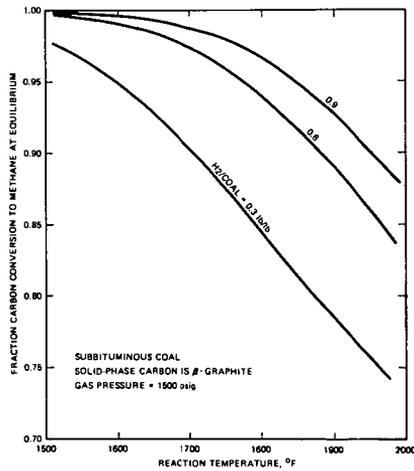


Figure 2. Predicted Fraction Carbon Conversion to Methane at Equilibrium for Subbituminous Coal

PEP predicts an equilibrium overall fraction carbon conversion and conversion to gas of unity for all of the Rocketdyne and Cities Service subbituminous tests; i.e., at infinite residence time, all of the carbon in the coal would be converted to methane and carbon-oxides. This is due primarily to the high levels of hydrogen-to-coal ratio, which varied from about 0.33 to 1.4 lb/lb (see Figure 1). PEP also predicts that the equilibrium fraction of carbon converted to methane is nearly unity for a majority of the Rocketdyne and Cities Service subbituminous tests (see Figure 2). For these conditions, Equations 2, 3, 6, and 7 simplify, with  $X^* = X_G^* = X_M^* = 1$ . The subbituminous data, therefore, were generated within a regime that is completely controlled by the kinetics of carbon conversion to products.

As mentioned previously, PEP assumes that the carbon present is  $\beta$ -graphite. Other studies<sup>12,13</sup> have indicated that the carbon present at equilibrium may be amorphous carbon, which has a higher reactivity than  $\beta$ -graphite. Therefore, the predictions of  $X^*$  and  $X_M^*$  shown in Figures 1 and 2 should be considered as approximate, and possibly on the low side.

#### FITTED CORRELATIONS

A statistical analysis of the fitted Rocketdyne and Cities Service subbituminous coal data showed that overall carbon conversion and carbon conversion to gas and methane were significant functions of gas temperature, particle (or gas) residence time, and hydrogen partial pressure. Carbon conversion was not significantly affected by reactor size or hydrogen-to-coal ratio within the region investigated.

As mentioned previously, the equilibrium computer model predicts that  $X^*$ ,  $X_G^*$ , and  $X_M^*$  have values of unity for all of the subbituminous tests. Therefore, the effect of equilibrium conversion on the kinetic components of Equation 2, 6, or 7 could not be obtained from the data; i.e., the value for the fitted coefficient  $\alpha_g$  in Equation 3 could not be determined. Similarly, it was not possible to verify the predicted effect (illustrated in Figures 1 and 2) of hydrogen-to-coal ratio on the equilibrium conversions. Additional data are required at reduced hydrogen-to-coal ratio (0.1 to 0.3 lb/lb) to determine these effects.

It was also not possible to determine separately the effects of both hydrogen partial pressure,  $P_{H_2}$ , and reactor pressure,  $P$ , on carbon conversion for the subbituminous tests. This is because  $P_{H_2}$  was nearly equal to  $P$  for a majority of the tests; i.e.,  $P_{H_2}$  and  $P$  are confounded. For convenience, the pressure variable is referred to as pressure or hydrogen partial pressure in this report. It should be noted that the separate effects of  $P_{H_2}$  and  $P$  could be determined by adding an inert gas (e.g., helium) and/or methane to the reactor recycle (feed) gas.

#### Overall Carbon Conversion

The correlation fitted to the Rocketdyne and Cities Service subbituminous coal carbon conversion data is:

$$X = 1 - \exp \left[ \frac{-2.53 \exp(-0.175 P_{H_2}/t_R) \exp(0.000393 P_{H_2})}{\exp(-3,820/T_G)} \right] \quad (8)$$

where  $P_{H_2}$  is in psig,  $t_R$  is in milliseconds, and  $T_G$  is in  $^{\circ}R$ .

As Equation 8 indicates,  $X$  increases with increasing coal particle residence time and gas temperature. At high particle residence times,  $X$  increases with increasing hydrogen partial pressure; at low particle residence times,  $X$  decreases with increasing hydrogen partial pressure. In addition, the effect of residence time on carbon conversion increases as pressure increases. The fact that overall carbon conversion

increases with residence time suggests that conversion of carbon to products occurs throughout the length of the reactor.

Equation 8 has a standard error of estimate of 3.3 percent in the predicted percent carbon conversion. The measured and predicted carbon conversions are shown in Figure 3. The statistics and Figure 3 indicate that within the experimental error, the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor achieve similar carbon conversions under comparable operating conditions.

As can be seen in Figure 3, the predictions of carbon conversion for the Rocketdyne reactor are, on the average, slightly higher than the measured values, whereas the predictions for the Cities Service reactor are, on the average, slightly lower than the measured values. With the data currently on hand, it is not possible to determine whether or not this discrepancy can be accounted for by (1) differences in the reactor sizes, (2) differences in the reactor operating conditions (e.g., the Rocketdyne feed gas contains water vapor), (3) differences in the accuracy of the values for maximum gas temperature, or (4) differences in the average levels of the hydrogen-to-coal ratio employed in the reactor systems.

In Figure 4, predicted overall carbon conversion from Equation 8 is plotted as a function of maximum gas temperature for selected levels of residence time and hydrogen partial pressure.

#### Carbon Conversion and Selectivity to Gas

The correlation fitted to the data for carbon conversion to gas is:

$$X_G = 1 - \exp \left[ -0.277 \exp(-0.178 P_{H_2}/t_R) \exp(0.00358 P_{H_2}) \exp(-6.57 P_{H_2}/T_G) \right] \quad (9)$$

where  $P_{H_2}$  is in psig,  $t_R$  is in milliseconds, and  $T_G$  is in  $^{\circ}R$ .

As can be seen from Equation 9,  $X_G$  increases with increasing residence time and gas temperature. At high residence time and/or at high temperature,  $X_G$  increases with increasing hydrogen partial pressure; at low residence time and/or at low temperature,  $X_G$  decreases with increasing hydrogen partial pressure. In addition, the effects of residence time and gas temperature on conversion increase as hydrogen partial pressure increases.

Equation 9 has a standard error of estimate of 3.0 percent in the predicted percent carbon conversion to gas. The measured and predicted conversions are shown in Figure 5. The statistics and Figure 5 indicate that the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor achieve similar carbon conversions to gaseous products under comparable operation conditions within the region investigated.

In Figure 6, predicted values for carbon selectivity to gas,  $\phi_G$ , obtained from Equations 8 and 9 (i.e.,  $\phi_G = X_G/X$ ) are shown as a function of gas temperature, for selected values of hydrogen partial pressure at a residence time of 1,000 milliseconds. Selectivity to gas is very insensitive to residence time for the subbituminous coal data. Note that a selectivity to gas of 100 percent is predicted at 1,900 $^{\circ}F$  and 1,500 psig.

#### Carbon Conversion and Selectivity to Methane

The correlation fitted to the data for carbon conversion to methane is:

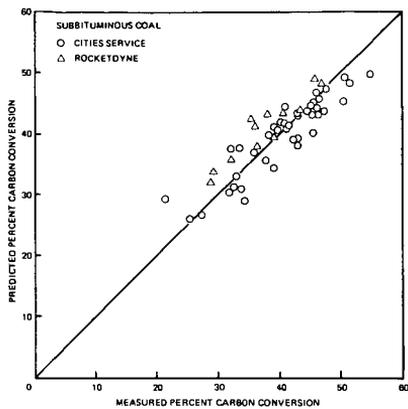


Figure 3. Comparison of Measured and Predicted Overall Carbon Conversion for Subbituminous Coal

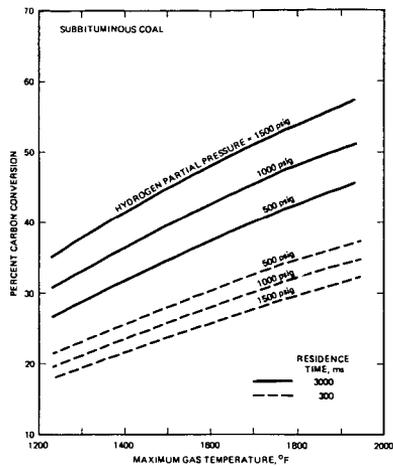


Figure 4. Predicted Overall Carbon Conversion for Subbituminous Coal

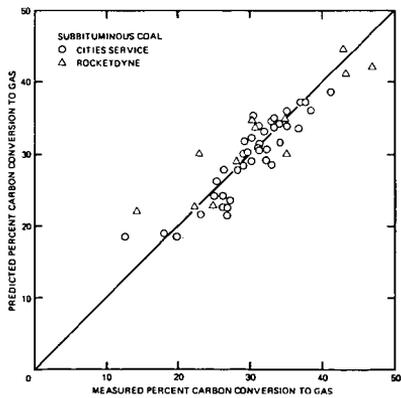


Figure 5. Comparison of Measured and Predicted Carbon Conversion to Gas for Subbituminous Coal

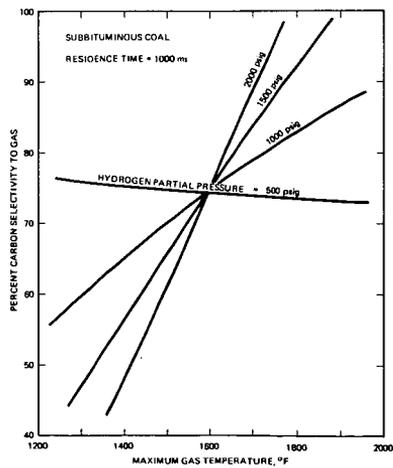


Figure 6. Predicted Carbon Selectivity to Gas for Subbituminous Coal

$$X_M = 1 - \exp \left[ -0.125 \exp(-0.286 P_{H_2}/t_R) \exp(0.00735 P_{H_2}) \exp(-13.9 P_{H_2}/T_G) \right] \quad (10)$$

where  $P_{H_2}$  is in psig,  $t_R$  is in milliseconds, and  $T_G$  is in  $^{\circ}R$ .

As can be seen from Equation 10,  $X_M$  increases with increasing particle residence time and reaction temperature. At high residence time and/or at high temperature,  $X_M$  increases with increasing hydrogen partial pressure; at low residence time and/or at low temperature,  $X_M$  decreases with increasing hydrogen partial pressure. In addition, the effects of residence time and gas temperature on conversion increase as hydrogen partial pressure increases.

Equation 10 has a standard error of estimate of 2.6 percent in the predicted percent conversion. The measured and predicted conversions are shown in Figure 7. The statistics and Figure 7 indicate that the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor achieve similar carbon conversions to methane under comparable operating conditions within the region investigated.

In Figure 8, predicted values for carbon selectivity to methane,  $\Phi_M$ , obtained from Equations 8 and 10 (i.e.,  $\Phi_M = X_M/X$ ) are shown as a function of gas temperature for different levels of residence time and hydrogen partial pressure. The fact that carbon selectivity to methane increases with increasing residence time suggests that the initial higher hydrocarbon products of devolatilization and, perhaps, products of direct char hydrogenation are cracked down to methane as gas residence time increases.

#### Comparison Between Predicted Values for Carbon Conversion and Carbon Selectivity to Products

In Figures 9 and 10, predicted carbon conversion to products and predicted carbon selectivity to products are shown, respectively, as functions of gas temperature for a particle residence time of 1,000 milliseconds, a hydrogen partial pressure of 1,500 psig, and a hydrogen-to-coal ratio of 0.7 lb/lb. It should be noted that above about 1,700 $^{\circ}F$ , the predicted value for  $X_M^*$  drops below unity at the selected operating variable levels (see Figure 2). Above 1,700 $^{\circ}F$ , therefore, the values for  $X_M$  shown in Figures 9 and 10 were obtained from Equation 7 using the calculated kinetic component from Equation 10 and the predicted equilibrium component from Figure 2.

#### DESIGN BASIS FOR CONCEPTUAL FULL-SCALE HYDROGASIFICATION REACTOR

This section presents the conceptual design basis for the hydrogasification stage of a proposed full-scale reactor facility for converting subbituminous coal to SNG. As currently envisioned, the reactor facility will consist of a hydrogasification stage to produce methane-rich product gas from the coal, and a hydrogen production stage to produce hydrogen-rich product gas from unreacted char and coal.

The conceptual full-scale hydrogasification stage will have a configuration similar to the Rocketdyne and Cities Service reactor assemblies, which incorporate entrained-flow tubular reactor chambers. The operating levels for temperature, pressure, and residence time have been based on predictions from the semiempirical correlations, which have been fitted to the Rocketdyne and Cities Service subbituminous coal data. The selected and calculated operating parameters are:

Overall carbon conversion	50 percent
Carbon selectivity to gas	100 percent
Reactor pressure	1,500 psig
Maximum reactor gas temperature	1,875 $^{\circ}F$
Particle (or gas) residence time	1,100 milliseconds
Carbon selectivity to methane	86 percent

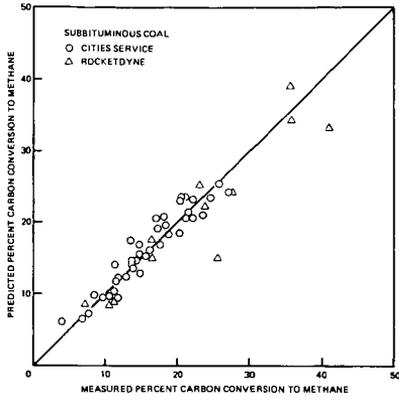


Figure 7. Comparison of Measured and Predicted Carbon Conversion to Methane for Subbituminous Coal

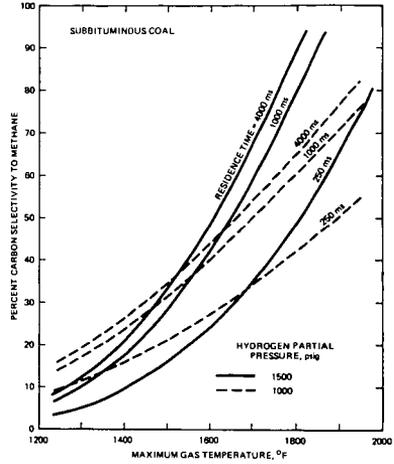


Figure 8. Predicted Carbon Selectivity to Methane for Subbituminous Coal

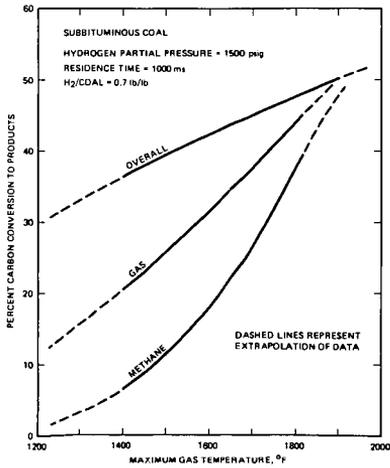


Figure 9. Predicted Carbon Conversion to Products for Subbituminous Coal

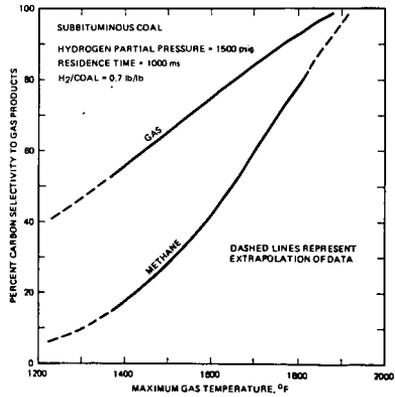


Figure 10. Predicted Carbon Selectivity to Gas Products for Subbituminous Coal

Greene<sup>14</sup> has shown that the cost of SNG produced from the reactor facility decreases as carbon conversion in the hydrogasification stage increases past the char balance point. (At the char balance point, the quantity of unreacted char from the hydrogasification stage is just sufficient to produce the required process hydrogen in the hydrogen production stages.) An overall carbon conversion of 50 percent was selected as the reactor design basis, since that value is close to the maximum conversion obtained to date in the Cities Service and Rocketdyne subbituminous coal testing, and is above the char balance point.

A carbon selectivity to gas of 100 percent was selected as the reactor design basis by the DOE. A reactor design pressure of 1,500 psig was chosen because at pressures less than 1,500 psig, the predicted maximum reaction temperature required for 100 percent carbon selectivity to gas is greater than 1,900°F (see Figure 6 and Equations 8 and 9). Temperatures greater than 1,900°F are considered excessive and are outside the range of the Cities Services and Rocketdyne subbituminous coal testing.

The selected hydrogen-to-coal ratio of 0.4 lb/lb is within the lower range investigated by Rocketdyne. A maximum gas temperature,  $T_G$ , of 1,875°F was calculated for the condition of 100 percent carbon selectivity to gas at a pressure of 1,500 psig. For the calculation, the predicted value for overall conversion (Equation 8) was equated to the predicted value for conversion to gas (Equation 9). Note that selectivity to gas is insensitive to residence time (see Figure 6).

A particle (or gas) residence time,  $t_R$ , of 1,100 milliseconds was computed, using Equation 8, for the condition of 50 percent overall carbon conversion, at a pressure of 1,500 psig and a temperature of 1,875°F.

The value of carbon selectivity to methane of 86 percent was obtained by dividing the predicted value for conversion to methane,  $X_M$ , by the predicted value for overall conversion,  $X$ , at a gas temperature of 1,875°F, a residence time of 1,100 milliseconds, and a pressure of 1,500 psig. The predicted value of  $X$  was obtained from Equation 8 and the predicted value of  $X_M$  from Equation 7. The kinetic component of Equation 7 was obtained from Equation 10 and the equilibrium component,  $X_M^*$ , is from Figure 2. It should be noted that for this relatively low hydrogen-to-coal ratio and relatively high temperature,  $X_M^*$  is approximately 0.86.

Bechtel has fitted carbon conversion to CO and CO<sub>2</sub> to the Rocketdyne and Cities Service data.<sup>9</sup> At the specified levels of the operating variables, the predicted values for carbon selectivity to CO and CO<sub>2</sub> were 13 and 0 percent, respectively.

#### CONCLUSIONS

The developed subbituminous coal correlations show that the Cities Service bench-scale reactor and the Rocketdyne 1/4-ton/hr reactor achieve similar values of overall carbon conversion and carbon selectivity to gaseous products under comparable operating conditions. Therefore, the results of testing at Rocketdyne and Cities Service should be scalable to a PDU or commercial-size reactor, within the region investigated.

The fitted correlations indicate that overall carbon conversion increases with increasing coal particle residence time and gas temperature. At high particle residence times, conversion increases with increasing hydrogen partial pressure; at low particle residence times, conversion decreases with increasing hydrogen partial pressure. This increase in overall carbon conversion with residence time suggests that conversion of carbon to products occurs throughout the length of the reactor. The reversal effects of pressure on carbon conversion suggests a two-step mechanism for hydrogasification: pyrolysis-controlled devolatilization at short residence time, and pressure-controlled hydrogenation of char at longer residence time.

The fitted correlations also indicate that carbon selectivity to methane increases with increasing temperature and particle residence time. The increase in selectivity to methane with increasing residence time suggests that the initial higher hydrocarbon products of devolatilization and, perhaps, the products of direct char hydrogenation are cracked down to methane as residence time increases.

The Rocketdyne and Cities Service subbituminous data were generated within a regime that is controlled by the kinetics of carbon conversion to products. This is due primarily to the relatively large hydrogen-to-coal ratios (0.3 to 1.4 lb/lb) used in the testing. For these hydrogen-to-coal ratios, the predicted carbon conversion at equilibrium is 100 percent for all tests; i.e., at infinite residence time, all of the carbon in the coal would be converted to methane and carbon-oxides.

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#### ACKNOWLEDGMENT

The work presented in this paper was sponsored by the DOE, Washington, D.C., under Contract No. EF-77-A-01-2565. The authors wish to express appreciation for technical support provided by L. Jablansky (DOE Technical Project Officer), M. I. Greene (Cities Service), J. A. Gray (PERC), and J. Friedman and L. P. Combs (Rocketdyne).