

MECHANISM OF SHORT RESIDENCE TIME HYDROLYSIS  
REACTION FOR MONTANA ROSEBUD SUBBITUMINOUS COAL

by

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A. Introduction

Research into short residence time hydrolysis of coal has been in progress at Cities Service Research and Development Company since 1974. More than 150 individual coal runs were performed in this time period using a bench-scale reactor recently described (1). Cost estimates for SWG and benzene production were also published (2)(3).

Some 50 runs were performed on Montana Rosebud Subbituminous coal at various reactor conditions. The results of these runs were reported elsewhere (1)(4)(5). In this report, a kinetic model originally proposed by Feldmann (6) is used to calculate reaction rate constants for carbon conversion for these 50 runs, at four distinct temperature zones. Also, the effect of reactor conditions are statistically correlated with gas and liquid hydrocarbons and the results of this analysis is reported.

B. Kinetics of Carbon Conversion

High heat up rates of finely divided coal particles and short residence time of less than 2 seconds at 500-1500°C under hydrogen atmosphere (7) were shown to promote carbon conversion into gas and liquids. Several reaction models were proposed to explain the kinetics of this phenomenon. Recently, Russel et al (8) illustrated that the role of mass transfer by bulk flow and diffusion including kinetics of devolatilization in single particles of coal can be explained by assuming a first order devolatilization reaction with instantaneous heatup to isothermal state and relatively long reaction time. Their model consists of three sets of reactions: primary devolatilization, secondary deposition and hydrogenation. This model was shown to fit data generated by Anthony and Howard (9) from hydrolysis of single discrete coal particles in a batch reactor.

For continuously operating reactors a simpler model has been used by several investigators including Wen, Feldmann, et al (6)(10). In this model the rate of gasification is proportional to the hydrogen partial pressure and to the rapid-rate carbon material remaining in the coal. For coal gasification into methane this simple model can be used by assigning the carbon in the coal into three categories (6). Type 1 carbon is a highly reactive specie which is almost instantaneously flashed off during the rapid heatup step. Type 2 is the solid carbon which readily hydrogasifies and type 3 is the low reactivity char carbon which will react upon long duration exposure (in order of minutes) to the hot hydrogen atmosphere. Type 1 and 2 carbon are classified "rapid rate carbon" and in this report are considered as a single specie.

For hydrogasification reaction the "rapid rate carbon" and hydrogen interaction follows the rate reaction (6):

$$\frac{dX}{dt} = k P_{H_2} (\alpha - X) \quad (1)$$

where X is the fractional carbon conversion,  $P_{H_2}$  the hydrogen partial pressure,  $\alpha$  the fraction of carbon available for reaction in the regime of consideration and k the reaction rate constant. Best fit for conversion data were found by Feldmann (6)(12) when  $\alpha = 1$ . Hence, at any given constant temperature:

$$\int_0^X \frac{dX}{1-X} = \int_0^t k P_{H_2} dt \quad (2)$$

$$\ln(1-X) = -k P_{H_2} t \quad (3)$$

where  $t$  is the coal/hydrogen contact time in the reactor. From equation 3, the reaction rate constant  $k$ , can be calculated.

### C. Particle Residence Time in the Reactors

The Cities Service R & D Co. short residence time bench-scale reactor system shown in Figure 1 was previously described (4). It can accept interchangeable reactors to investigate the effect of wide spans of residence time on the extent of carbon conversion into gas hydrocarbons and liquid hydrocarbon products. When short residence times are desired, straight vertical reactors of different diameters are fitted inside the electric furnace cavity. For longer residence times, helical reactors can be fitted.

The problem of estimating particle residence time in vertical entrained straight reactors can be solved by estimating the terminal velocity of a single char particle, and then correcting this value for entrained flow. This method was used by Gray et al (11) who used the equation:

$$U_T = \left[ \frac{3.1g (\rho_s - \rho_g) \bar{d}_p}{\rho_g} \right]^{1/2} \quad (4)$$

to estimate the terminal settling velocity (14). Correction factors which were applied following Wen and Huebler (10) increased the final particle velocity by a factor of about 3. For helical reactors, the problem of estimating particle residence time is further aggravated by the almost total lack of experimental or theoretical data. In our work, we met these shortcomings with glass cold-flow models of straight and helical reactors and measured average particle velocities in these models. The same flow regimes that were experienced in the bench-scale apparatus were used in the model studies. The average average particle velocities were found by feeding coal-char at controlled rate from feed hoppers located above the glass model. Coal char was used because in most of these tests particle residence time exceeded 0.5 seconds. Coal is converted into char-like material within 0.200 seconds at the temperature regimes of 825-1000°C.

Holdup of particles in the model, at constant flow conditions, was measured by simultaneously closing plug valves at the inlet and exit. The velocities were calculated from the weight of the solids trapped in the section and the feed rate to the model. This work was done by Ming-Tsai Shu and C. B. Weinberger of Drexel University (15).

With the glass model for the vertical straight reactor of length  $L$ , (4) we found that the average average particle velocity is very close to that of the superficial gas velocity. This greatly simplified the task of calculating particle residence times  $t$ :

$$t = L/\bar{V}_p(dp) \quad (5)$$

where  $\bar{V}_p(dp)$  is the average average particle velocity in m/sec. For helical reactors, at gas velocity in the excess of 6.3 m/sec. the following semi empirical equation was derived by Shu (15) to estimate the average average particle velocity:

$$\frac{\bar{v}_g - \bar{v}_p(dp)}{\bar{v}_g} = k_o \text{Re}^a R^b \left(\frac{D_H}{D_T}\right)^c \cdot \left(\frac{dp}{d\bar{p}}\right)^d \quad (6)$$

where for char of Montana Rosebud subbituminous coal:

$$\begin{aligned} k_o &= 0.323 \\ a &= 0.139 \\ b &= 0.185 \\ c &= -.102 \end{aligned}$$

When calculating the average average flow velocity of char:

$$dp/\bar{d}p = 1 \quad (7)$$

and  $t$ , residence time, is calculated from equation 5. A plot of the average variable size particle velocity for a constant gas velocity of 6.3 m/sec is shown in Figure 2. The plot indicates that selective classification occurs in the helical reactor. This was also observed visually. The large particles tend to settle at the glass model wall and because of wall friction move slower than the fine particles. Also, when the feeding rate of particles into the model is increased, the average average particle velocity in it decreases. This is because the particles are not uniformly dispersed and tend to concentrate at the outer periphery of the helix.

When the superficial gas velocity is below 6.3 m/sec, equation 6 becomes increasingly unreliable and velocity of the particles must be interpolated from specific flow measurements generated by Shu (15). However, even at somewhat lower velocity the equation may be used to predict average average particle residence times. For example, workers at the University of Utah (17) using iron filings as tracer in coal which was treated in a helical reactor in hydrogen at 122 atm. and 482°C reported residence time of 9 seconds. The reactor was a tube of 0.48 cm internal diameter, 14.5 meters long which was coiled into a 12.7 cm diameter helix. The gas velocity in their tests was only 5.6 m/sec. Yet even with this low velocity, equation 6 predicts residence time of 10 sec.

#### D. Hydrogasification Kinetics of Montana Rosebud Subbituminous Coal

Fifty subbituminous coal runs were performed (4) over a range of conditions summarized in Table 1. The data was further divided into four temperature ranges from 827°C to 1000°C. Plot of  $-\ln(1-x)$  versus  $P_{H_2} t$  in sec. atm is displayed in Figure 3. Table 2 summarizes the equations of each of the lines indicating the quality of fit of each as obtained by regression analysis.

A plot of  $\ln k$  vs.  $1/T$  on Figure 4 for Montana Rosebud Subbituminous coal is compared with results for Pittsburgh Seam bituminous coal (11). The Arrhenius activation energies for both coals are relatively high: about 15 kcal/mole for the Pittsburgh seam coal and 27 kcal/mole for Montana Rosebud Subbituminous coal. This indicates that both reactions are chemically controlled.

#### E. Statistical Correlation of Factors Affecting The Formation of Products

Statistical treatment of the data from the fifty runs is used to determine which of the reactor variables: temperature, pressure, vapor residence time, coal to hydrogen ratio, solids residence time or particle diameter are most likely to affect the degree of carbon conversion. The treatment can be extended to the effects of conditions on the yield of the various product

FIGURE 1

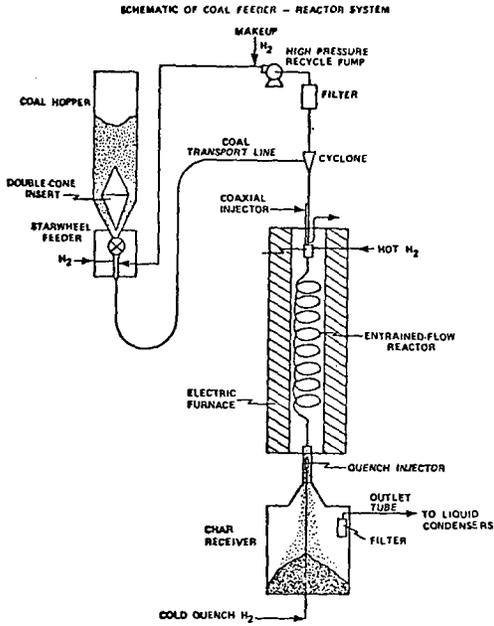


FIGURE 2

CHAR PARTICLES VELOCITY IN THE HELICAL REACTOR AS PREDICTED BY EQUATION

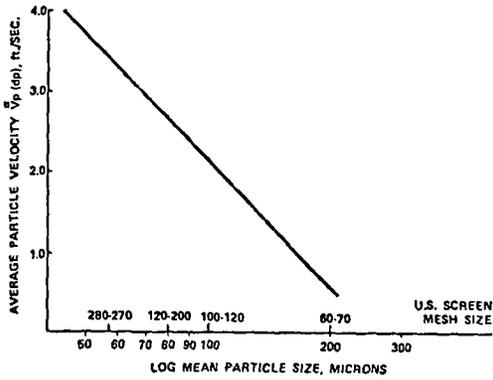


TABLE 1

RANGE OF OPERATING CONDITIONS FOR HYDROGASIFICATION  
OF MONTANA ROSEBUD SUBBITUMINOUS COAL

	<u>Range</u>
Temperature - °C	825-1000
Pressure - atmospheres	34-160
Particle Residence Time - sec.	0.4-14.0
Superficial Gas Residence Time - sec.	0.3-4.0
Superficial Gas Velocity m/sec.	5.0-8.0
Hydrogen to Coal Weight Ratio	0.7-1.2

TABLE 2

DATA SUMMARY FOR EACH TEMPERATURE RANGE

<u>Temperature</u> °C	<u>No. of</u> <u>Data</u> <u>Points</u>	<u>Equation of line of best fit</u>	<u>r</u>	<u><math>\frac{k}{\text{atm}^{-1} \text{hr}^{-1}}</math></u>	<u>Equation</u> <u>No.</u>
827 ± 10°	15	$\ln(1-x) = 1.483 \times 10^{-4} P_{\text{H}_2} t + .3974$	.861	.53	(8)
877 ± 10°	19	$\ln(1-x) = 2.36 \times 10^{-4} P_{\text{H}_2} t + .4036$	.915	.85	(9)
902 ± 10°	8	$\ln(1-x) = 4.108 \times 10^{-4} P_{\text{H}_2} t + .3668$	.892	1.48	(10)
927 ± 10°	8	$\ln(1-x) = 3.88 \times 10^{-4} P_{\text{H}_2} t + .3859$	.972	1.40	(11)

FIGURE 3

PLOT OF  $-\ln(1-X)$  vs.  $P_{H_2} t$  - The slope of each of the lines is the reaction rate constant for Montana Rosebud Subbituminous Coal at the designated temperature

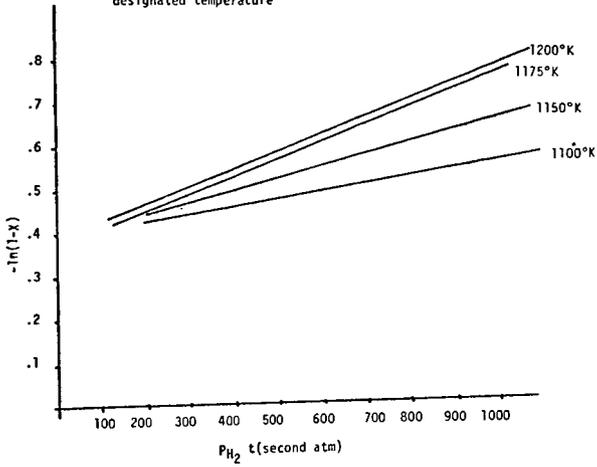
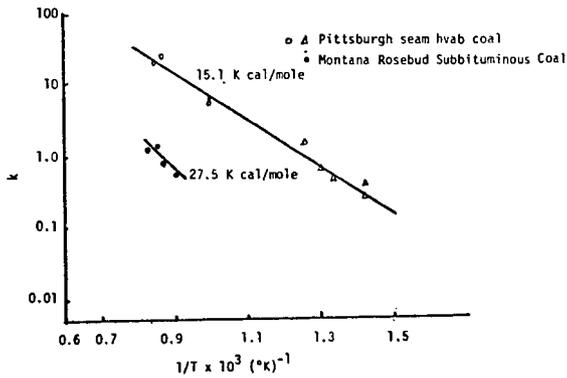


FIGURE 4

TEMPERATURE DEPENDENCE OF THE HYDROGASIFICATION REACTION RATE CONSTANTS FOR PITTSBURGH SEAM COAL (6) AND MONTANA ROSEBUD SUBBITUMINOUS COAL



fractions: gas, liquids, BTX and methane plus ethane. The computer program used for the analysis is available from IBM (16). It is capable of performing a stepwise linear regression followed by a polynomial fitting with orthogonal polynomials. With it, it is possible to analyze the effect of up to 40 variables. The results of the regression is expressed in a form of a linear equation:

$$y = b_0 + b_1x_1 + b_2x_2 + \dots b_nx_n \quad (12)$$

where  $x_1, x_2, \dots, x_n$  can be entered as independent transformation functions. The program selects the most effective functions to be fitted into the polynomial equation (12). In addition, it presents each dependent variable in order of importance and re-calculates the curve fitting correlation coefficient with each variable introduced. The forty functions shown in Table 3 were selected for each of the six independent variables:

T - temperature in degrees Kelvin  
 $P_{H_2}$  - hydrogen partial pressure - atmospheres  
 $t$  - residence time of solids in the reactor - gaseous  
 $X_g$  - gas residence time in the reactor - msec.  
 $X_{H/C}$  - hydrogen to coal ratio - gm/gm  
 $dp$  - mean particle size - microns

and regressed against each of the dependent variables:

$x$  - total fraction of carbon converted  
 $y_g$  - fraction of carbon converted to methane plus ethane  
 $y_e$  - fraction of carbon converted to liquid hydrocarbons  
 $y_b$  - fraction of carbon converted to BTX.

The following equations and correlation coefficients were obtained:

For total fraction of carbon converted:

$$X = \exp \left[ \frac{-3276}{T} + .1282 \ln t + 1.761 \right] \quad r = 0.91 \quad (13)$$

For fraction of the carbon conversion into methane plus ethane:

$$y_g = \exp \left[ \frac{-9428}{T} + .4457 \ln P_{H_2} + \ln t + 4.63 \right] \quad r = 0.93 \quad (14)$$

For fraction of the conversion into liquid hydrocarbons:

$$y_e = \exp \left[ 0.273 \ln P_{H_2} + 0.96 \ln t - 4.373 \right] \quad r = 0.67 \quad (15)$$

For fraction of carbon conversion to BTX:

$$y_b = \exp \left[ \frac{-6814}{T} + .265 \ln t + 2.899 \right] \quad r = 0.87 \quad (16)$$

These results indicate that within limits of experimental conditions, and for the transformation functions selected gas residence time, hydrogen-to-coal ratio and mean particle diameter have no apparent effect on the degree of carbon conversion into any of the four products  $x$ ,  $y_g$ ,  $y_e$ , and  $y_b$ . The two most important variables seem to be temperature and solids residence time followed by the effects of pressure. Future work with other transformation functions and better modelling may however show that gas residence time may have effect on  $y_e$ .

Figure 5 illustrates the effects of temperatures and solids residence times on the total fraction of carbon converted. As expected, the effects of solids residence time are marginal compared to that of temperature. For example, in order to achieve  $x = 0.3$ , solids residence time of 15 seconds is required at 827°C but only 0.5 seconds if the temperature were to increase by 150°C.

Figure 6 illustrates the effect of temperature and pressure on conversion of carbon to methane and ethane. At constant pressure, the conversion rises steeply with the temperature but the effects of solids residence time are somewhat less pronounced than in Figure 5. At 880°C,  $x = 0.3$  and only 60°C rise in temperature is required to drop the required solids residence time from 15 seconds to 0.5 seconds. The effect of pressure on conversion may even be smaller than that of solids residence time. When the pressure is reduced by about 34 atmospheres, the average reduction in conversion is less than 10% even at the high range of temperature. This is within the overall accuracy of gas analysis that can be claimed for this data.

Figure 7 illustrates the dependence of liquid yields on the partial pressure of hydrogen and on residence time. Because of poor correlation ( $X = .67$ ), which indicates scatter in data and poor modelling, it is hard to draw more definitive conclusions. But when viewed with Figure 6 which has steeper slopes of carbon conversion to gas, it seems that optimum yield of liquid may be obtained at moderate temperatures, say 900°C and at hydrogen partial pressures which are as high as practicable.

Figure 8 suggests that conversion of carbon to BTX depends on the fraction of liquid hydrocarbons cracked to methane and ethane. Given long solids residence time with increasing temperature, most of the carbon will eventually be converted to gas probably undergoing intermediate liquefaction. BTX could be a product of liquid hydrocarbons which crack to produce methane and ethane. This may explain the positive slope of the yield curves and the relatively large effect of solids residence time on conversion.

TABLE 3

TRANSFORMATION EQUATIONS FOR REGRESSION ANALYSIS

X(1) - Dependent Variable  
 X(2) - Temperature  
 X(3) - Total Reactor Pressure  
 X(4) - Hydrogen Partial Pressure  
 X(5) - Particle Residence Time  
 X(6) - Gas Residence Time  
 X(7) - Hydrogen/Coal Ratio  
 X(8) - Mean Coal Feed Particle Size

X(11) =  $\text{ALOG}(X(1))$   
~~X(12) =  $-1/X(2)$~~   
~~X(13) =  $\text{ALOG}(X(3))$~~   
~~X(14) =  $\text{ALOG}(X(4))$~~   
~~X(15) =  $\text{ALOG}(X(5))$~~   
~~X(16) =  $\text{ALOG}(X(6))$~~   
~~X(17) =  $\text{ALOG}(X(7))$~~   
~~X(18) =  $\text{ALOG}(X(8))$~~   
~~X(19) =  $X(2)/X(3)$~~   
~~X(20) =  $X(2)/X(4)$~~   
~~X(21) =  $X(2)/X(5)$~~   
~~X(22) =  $X(2)/X(6)$~~   
~~X(23) =  $X(2)/X(7)$~~   
~~X(24) =  $X(2)/X(8)$~~   
~~X(25) =  $X(3)/X(4)$~~   
~~X(26) =  $X(3)/X(5)$~~   
~~X(27) =  $X(3)/X(6)$~~   
~~X(28) =  $X(3)/X(7)$~~   
~~X(29) =  $X(3)/X(8)$~~   
~~X(30) =  $X(4)/X(5)$~~   
~~X(31) =  $X(4)/X(6)$~~   
~~X(32) =  $X(4)/X(7)$~~   
~~X(33) =  $X(4)/X(8)$~~   
~~X(34) =  $X(5)/X(6)$~~   
~~X(35) =  $X(5)/X(7)$~~   
~~X(36) =  $X(5)/X(8)$~~   
~~X(37) =  $X(6)/X(7)$~~   
~~X(38) =  $X(6)/X(8)$~~   
~~X(39) =  $X(7)/X(8)$~~   
~~X(40) =  $X(2) \times X(3)$~~   
~~X(41) =  $X(2) \times X(4)$~~   
~~X(42) =  $X(2) \times X(5)$~~   
~~X(43) =  $X(2) \times X(6)$~~   
~~X(44) =  $X(2) \times X(7)$~~   
~~X(45) =  $X(2) \times X(8)$~~   
~~X(46) =  $X(3) \times X(4)$~~   
~~X(47) =  $X(3) \times X(5)$~~   
~~X(48) =  $X(3) \times X(6)$~~   
~~X(49) =  $X(3) \times X(7)$~~   
~~X(50) =  $X(3) \times X(8)$~~   
~~X(51) =  $X(4) \times X(5)$~~   
~~X(52) =  $X(4) \times X(6)$~~   
~~X(53) =  $X(4) \times X(7)$~~   
~~X(54) =  $X(4) \times X(8)$~~   
~~X(55) =  $X(5) \times X(6)$~~   
~~X(56) =  $X(5) \times X(7)$~~   
~~X(57) =  $X(5) \times X(8)$~~   
~~X(58) =  $1/X(2)$~~   
~~X(59) =  $1/X(3)$~~   
~~X(60) =  $1/X(4)$~~

FIGURE 5

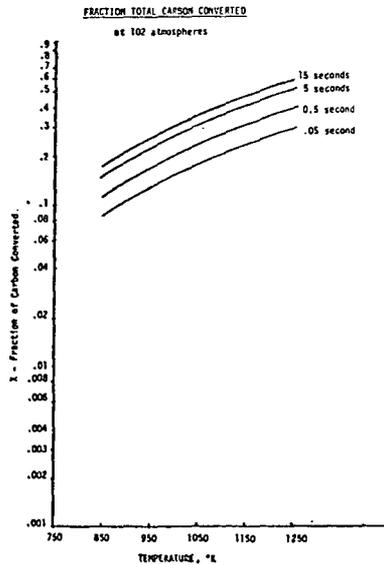


FIGURE 6

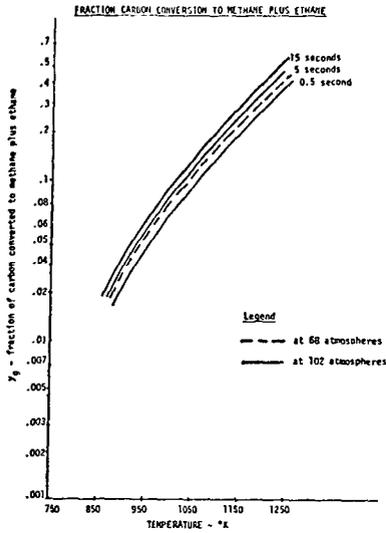


FIGURE 7

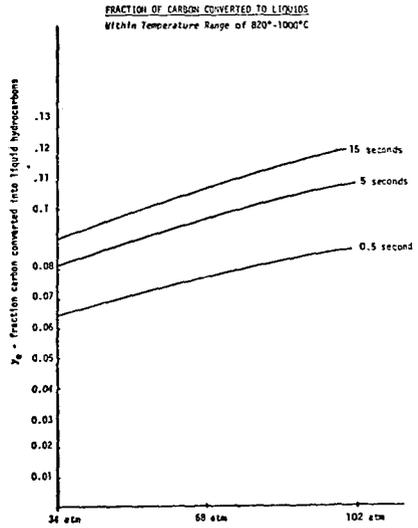
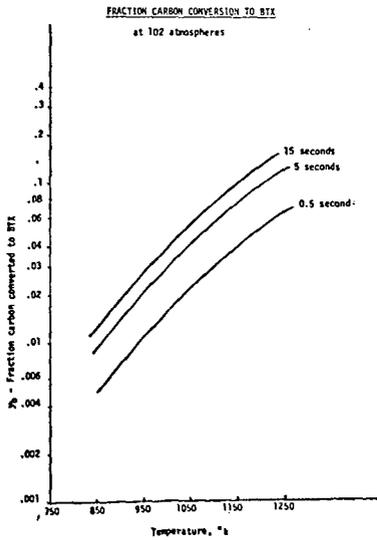


FIGURE 8



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### G. Nomenclature

- BTX - benzene, toluene and xylene
- $\bar{d}_p$  - average particle diameter -  $m^3$
- $D_H$  - helix diameter - microns
- $D_T$  - helix tube internal diameter - m
- $g$  - gravity constant -  $m/sec^2$
- $k$  - reaction rate constant -  $atm^{-1} hr^{-1}$
- $L$  - reactor length - m
- LHC - liquid hydrocarbons produced, including the BTX fraction as analyzed in the gas
- $P_{H_2}$  - partial pressure of hydrogen
- $r$  - correlation coefficient of regression of the line of best fit by the root mean square through the experimental data points
- $Re$  - Reynold's number
- $R$  - char to gas weight ratio
- $t$  - time - sec.
- $U_T$  - terminal settling velocity -  $m/sec.$
- $\bar{V}_g$  - average gas velocity -  $m/sec.$
- $\bar{V}_p(dp)$  - average average particle velocity -  $m/sec.$
- $X$  - fraction of carbon converted
- $X_g$  - gas residence time - msec.
- $X_{H/C}$  - hydrogen to coal ratio gm/gm
- $y_p$  - fraction carbon converted to methane plus ethane
- $y_e$  - fraction carbon converted to LHC
- $y_b$  - fraction carbon converted to BTX
- $\rho_s$  - particle density -  $kg/m^3$
- $\rho_g$  - gas density -  $kg/m^3$
- $\alpha$  - fraction of carbon available for reaction