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**INFLUENCE OF CHANGING PARTICLE STRUCTURE ON
THE RATE OF GAS-SOLID GASIFICATION REACTIONS**

Final Report for the Period July 1981—March 1984

April 4, 1984
Date Submitted

Work Performed Under Contract No. AC21-81MC16053

Vanderbilt University
Nashville, Tennessee

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Department of Chemical Engineering
Vanderbilt University
Nashville, TN 37235

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PREPARED FOR THE
UNITED STATES DEPARTMENT OF ENERGY
FOSSIL ENERGY PROGRAM

Under Contract No. DE-AC21-81MC16053

ABSTRACT

The objective of this work is to determine the changes in the particle structure of coal as it undergoes the carbon/carbon dioxide reaction, $(C + CO_2 \rightarrow 2CO)$.

Char was produced by heating the coal at a rate of $25^\circ\text{C}/\text{min}$ to the reaction temperatures of 800°C , 900°C , 1000°C and 1100°C . The changes in surface area and effective diffusivity as a result of devolatilization were determined. Changes in effective diffusivity and surface area as a function of conversion have been measured for reactions conducted at 800°C , 900°C , 1000°C and 1100°C for Wyodak coal char. The surface areas exhibit a maximum as a function of conversion in all cases. For the reaction at 1000°C the maximum in surface area is greater than the maxima determined at all other reaction temperatures.

Thermogravimetric rate data were obtained for five coal chars; Wyodak, Wilcox, Cimarron, Illinois #6 and Pittsburgh #6 over the temperature range 800 – 1100°C . All coal chars exhibit a maximum in reaction rate. Five different models for gas-solid reactions were evaluated. The Bhatia/Perlmutter model seems to best represent the data.

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LIST OF NOMENCLATURE

A	parameter in the Kasaoka equation
A'	adsorption potential (KJ/mol), or A constant (dimensionless)
A ₀	adsorption potential of reference (KJ/mol)
B	parameter in the Kasaoka equation
B ₀ , B ₁	moments of probability density ($\lambda(R_0)$), equations 23 and 24
C	concentration - moles/volume
$\bar{c}(z, s)$	Laplace Transform of $c(z, t)$
C _a	concentration of adsorbed gas (mol/cm ²)
C _{CO₂}	CO ₂ concentration in bulk gas (mol/cm ³)
C ₀	initial solid concentration (mol/cm ³)
C _S	concentration of adsorbed gas at saturation (mol/cm ²)
C _x (x,t)	sorbate concentration in microparticle (mol/cm ³)
C _y (y,t)	sorbate concentration in macroparticle (mol/cm ³)
C _z (z,t)	sorbate concentration in bulk gas (mol/cm ³)
d	exponent in the Chornet equation
D _{AB}	molecular binary diffusivity (cm ² /s)
D _e	effective diffusivity (cm ² /s)
D _e /r _c ²	diffusion parameter (s ⁻¹)
(D _e /r _c ²) ₀	diffusion frequency factor (cm ² /s)
D _x	microparticle diffusivity (cm ² /s)
D _y	macroparticle diffusivity (cm ² /s)
D _z	axial dispersion coefficient (cm ² /s)
e	exponent in the Chornet equation
E	characteristic energy (KJ/mol)

LIST OF NOMENCLATURE (continued)

E_0	activation energy in the Arrhenius equation
F	fraction of carbon in coal char
ΔH_0	enthalpy of adsorption (KJ/mol)
k	chemical rate constant (gm-cm/mol-s)
k_c	adsorption potential constant
k_f	mass transfer coefficient (cm/s)
k_1	chemical rate constant (s^{-1})
k_1'	chemical rate constant (mol/s-cm ³)
k_2	chemical rate constant (cm ³ /mol-s)
k_3	chemical rate constant (mol/s-cm ³)
k_3'	chemical rate constant (s^{-1})
K'	Arrhenius constant
K_a	dimensionless adsorption constant, defined in equation 21
K_c	constant of proportionality in Simons-Chornet model
K_d	rate constant in Dutta and Wen model
K_k	constant of proportionality in Kasaoka model
K_0	equilibrium constant pre-exponential
K_p	equilibrium constant, defined in equation 34
K_s	rate constant in Bhatia and Perlmutter model
L	packed bed length (cm)
L'	total length of overlapped capillary system
L_e	total length of non-overlapped capillary system
m	a constant (dimensionless)
M	atomic weight (g/mol)

LIST OF NOMENCLATURE (continued)

M_B	molecular weight of species "B"
N_{CO_2}	moles of CO_2 passed through char bed during reaction
N_{Ry}	sorbate flux at surface of macroparticle
Nu_{AR}	Nusselt mass transfer number
p	perimeter of pore cross section
P	ambient pressure (KPa)
P_a	atmospheric pressure (mm Hg)
P_o	pressure at saturation (KPa)
q	area of pore cross section
q'	increase in pore radius due to reaction Gavalas model
Q^i	mole ratio, CO/CO_2 , in product gas
r	pore radius (nm)
$\bar{r}$	mean pore radius (nm)
r_c	diffusion path length (cm)
r_t	reaction rate
R	ideal gas constant
Re	Reynold's number
R_o	initial capillary radius in Gavalas model
R_{po}	initial particle radius in Gavalas model
R_x	microparticle radius (cm)
R_y	macroparticle radius (cm)
S	specific area (m^2/g)
S'	specific surface area cm^2/cm^3
Sc	Schmidt number
S_e	total capillary surface

LIST OF NOMENCLATURE
(continued)

S_0	specific area at zero conversion (m^2/g)
S_x	specific area in microparticle (m^2/g)
t	time (s)
T	absolute temperature
$\underline{v}$	superficial velocity (cm/s)
v_s	pore surface velocity function (cm^2/s)
V	volume enclosed by reaction surface, per unit volume of space
$\bar{V}$	interstitial velocity (cm/s)
$\dot{V}$	volumetric flow rate (cm^3)
V_e	total capillary volume
W	volume of sorbat at equilibrium (cm^3)
W_i	weight of char after i th reaction
W_0	initial weight of char ₃ (g), or volume of sorbat at saturation per mass of carbon (cm^3/g)
x	microparticle radial coordinate (cm)
X	conversion
x_g^i	i th conversion based on gas analysis
x_w^i	i th conversion based on weight loss
x_i	i th unfiltered observation
y	macroparticle radial coordinate (cm)
y_{CO_2}	mole fraction of CO_2 in gas analysis
y_i	i th filtered observation
z	axial position in packed bed (cm)
$\bar{z}$	ratio of molal volume of product to reactant
α	lumped rate constant
β	lumped rateconstant, parameted in the Dutta and Wen model
γ	parameter in the Dutta and Wen model

LIST OF NOMENCLATURE (continued)

Γ	gamma function
$\delta(t)$	Gaussian function of time
Δ	sum of mass transfer resistances (s)
$\Delta H^\ddagger$	diffusion activation energy (KJ/mol)
ΔN_C^i	moles of carbon consumed in ith reaction
ΔP	pressure drop across char bed (inches of Meriam Red Oil 827)
ϵ	bed void fraction
ϵ_0	particle porosity
η	effectiveness factor
$\lambda(R_0)$	probability density function describing the porous medium
ϕ	a Thiele modulus defined: $1/3(K_d SC_{CO_2}(1-x)/D_e/r^{-2})^{1/2}$
θ	porosity Simons-Chornet model
θ_x	microparticle void fraction
θ_y	macroparticle void fraction
θ_z	bed void fraction
μ	viscosity of helium gas (cp)
μ_n	nth central moment (s^n)
μ_n'	nth absolute moment (s^n)
ρ	particle density (g/cm^3)
τ	dimensionless time in Simon-Chornet model
τ'	constant of proportionality in Bhatia and Perlmutter model
σ	size parameter in Bhatia and Perlmutter model
ψ	parameter in the Bhatia and Perlmutter model
<u>Subscript</u>	
o	time $t = 0$

CHAPTER I

SUMMARY

The reaction of carbon dioxide with Wyodak coal char to form carbon monoxide at 1073, 1173, 1273, and 1373°K was studied to determine the kinetic and mass transfer effects on the rate. Global reaction rates, specific areas, and diffusion parameters were determined at various conversions for each reaction temperature to apply experimental data to the rate model proposed by Bhatia and Perlmutter (7):

$$\frac{dx}{dt} = \frac{C_{CO_2} S_0 (1-x) \sqrt{1-\psi \ln(1-x)}}{1-\epsilon_0}$$

The specific area was related to conversion by a model proposed by Bhatia and Perlmutter (7):

$$S = S_0 (1-x) [1-\psi \ln(1-x)]^{1/2}$$

For each reaction temperature, carbon dioxide adsorption isotherms were obtained at 273°K for various conversion of coal char. The specific areas, average pore radii, and pore volume distributions were calculated by applying the Dubinin-Polanyi theory (44) and the method of Medek (81). Specific areas ranged from 180 to 650 m²/g and displayed a maximum around a char conversion of 0.35. The specific areas for each reaction temperature were correlated up to conversions of 0.5, 0.7, 0.6, and 0.4 by the following equations, respectively:

$$1073^{\circ}\text{K} \quad S = 225(1-X)[1-6.99 \text{ LN } (1-X)]^{1/2} \quad (\text{m}^2/\text{g})$$

$$1173^{\circ}\text{K} \quad S = 300(1-X)[1-8.67 \text{ LN } (1-X)]^{1/2} \quad (\text{m}^2/\text{g})$$

$$1273^{\circ}\text{K} \quad S = 301(1-X)[1-23.6 \text{ LN } (1-X)]^{1/2} \quad (\text{m}^2/\text{g})$$

$$1373^{\circ}\text{K} \quad S = 246(1-X)[1-11.2 \text{ LN } (1-X)]^{1/2} \quad (\text{m}^2/\text{g})$$

The range of conversion over which Bhatia's model applies is dependent on the sorbate-adsorbent pair. Average pore radii ranged from 0.688 to 0.74 nm which are close in value to those reported by other investigators (6.16).

Diffusion parameters D_e/r_c^2 were computed from a pulse chromatograph technique and the model of Haynes and Sarma (49) for CO_2/He , CO/He , N_2/He , CH_4/He at temperatures ranging from 323 to 523°K. An Arrhenius-type temperature dependency was assumed:

$$D_e/r_c^2 = (D_e/r_c^2)_0 \exp(-\Delta H_0^\ddagger/RT)$$

The above equation was used to determine the pre-exponential factor $(D_e/r_c^2)_0$ and the activation energy $\Delta H_0^\ddagger$ respectively. The parameters were used to estimate diffusion parameters at the reaction temperatures.

All of the carbon dioxide char reactions displayed a maximum in the rate at intermediate conversions. The rate model of Bhatia and Perlmutter, and values of ψ , determined from surface area measurements, were used to fit the reaction rate data and calculate reaction rate constants. The rate constants were fitted to the Arrhenius relation:

$$k = 86.2 \exp(-1.78 \times 10^4/T)$$

with an activation energy of 150 KJ/mole.

A Weisz-Prater analysis using measured global reaction rates and values of diffusion parameters extrapolated from calculated values of diffusion activated energies, $\Delta H_o^\ddagger$, and pre-exponential factors $(D_e/r_c^2)_o$, results in values of Thiele modulus of $< 10^{-2}$ indicating no intraparticle influence of diffusion on the global reaction rate. From the results of this work the carbon dioxide-Wyodak coal char reaction between the temperatures of 1073-1373°K was found to be chemical rate controlled.

Three bituminous coals, Illinois No. 6, Pittsburgh Bituminous, and Cimmeron Coal, as well as one lignite, Wilcox Lignite, were devolatilized in a helium atmosphere. The resulting coal chars were subsequently gasified in an atmosphere of pure carbon dioxide at atmospheric pressure. The rate of this C/CO₂ reaction was measured over a temperature range of 1073-1373°K.

Rate constant-temperature data from the coal chars were plotted on a logarithmic rate vs. reciprocal temperature scale according to the Arrhenius relationship. Deviation of data from a straight line on such a plot often suggests that mass transfer phenomena is affecting the global rate measurements. With these data no such deviation was found. Apparent activation energies ranged from 119-172 KJ/mole.

Several recent kinetic models for the coal char-carbon dioxide gasification reaction were discussed. The rate data obtained at 1073°K were fit to five of these models. These five models include three empirical equations, proposed by Dutta and Wen (25), Simons (98), and Kasoaka (60) in addition to two theoretical models proposed by Bhatia and Perlmutter (7) and Gavalas (38). The latter two models are shown to be equivalent. By the criteria of sum of the

squared errors the Kasaoka model (60) produced the best fits for all coals tested. The Dutta and Wen model (25) was consistently the least satisfactory model. The Wilcox Lignite data could not be interpreted very well by any of the models. The data from this coal and the Cimmeron coal could be interpreted by the theoretically derived models but resulted in model parameters which were physically inconsistent. Some speculations as to why these data might yield such model parameters are discussed.

CHAPTER II

INTRODUCTION

The formation of carbon monoxide by reaction of coal char with carbon dioxide has received considerable attention and is the subject of several reviews (27,54,118,126). The most significant feature of this gasification reaction is the microporous structure and, consequently, large specific surface area provided by the carbonaceous substrate. The observed, or global, gasification rate depends on the relative magnitudes of the various resistances in the overall reaction:

- (a) external diffusion of the reactant carbon dioxide and product carbon monoxide between the gas phase and the coal char's surface;
- (b) migration, either by gas phase or surface diffusion, of the reactant and product through pores, internal diffusion;
- (c) adsorption and desorption of the reactant and product at reactive sites on pore walls;
- (d) chemical reaction between the adsorbed reactant and solid substrate.

Since the pore structure is continuously changing during reaction, these resistances are functions of time, or equivalently, of conversion.

Various global rate models, which take into account conversion-dependent

effective diffusivity and specific area, have been proposed (1,25,62,67) (71,96,126) but, due to lack of experimental data, have not been extensively tested.

The global rate models are useful only if the specific area and the effective diffusivity can be related to conversion. In the case of specific area, correlation has been achieved either empirically (8, 48, 71) or with the aid of theoretical models (78,38,62). Specific areas were computed from carbon dioxide isotherms according to the adsorption theories of Langmuir (44) or Brunauer, Emmett and Teller (11). However, because of the very small mean pore radii encountered in coal char, the applicability of these adsorption theories is questionable. Thus far, a theoretical model relating effective diffusivity to conversion has not been developed. Very few attempts have been made to correlate diffusivity with conversion (19,22). Prior to this study, the influence of elevated reaction temperatures (800-1100°C) upon diffusion parameters obtained at ambient temperatures had been neglected.

This study is concerned with the kinetics and mass transfer of the reactions, at 800-1100°C of carbon dioxide with a packed bed of coal char particles. Particular attention is placed upon the determination of specific areas, pore radii and pore volume distributions, upon the estimation of reaction-temperature diffusion parameters and upon the correlation of specific areas and diffusion parameters with conversion. Though pore radii, pore volume distributions and diffusion parameters for CO, N₂ and CH₄ are not part of the rate model, these data were gathered to thoroughly characterize changes in the physical properties of the char during reaction.

The global rate model of Bhatia and Perlmutter (7) which includes the effects of variable specific area and variable diffusion, is tested.

The Dubinin-Polanyi theory (44) and the method of Medek (81) are used to calculate specific areas, mean pore radii and pore volume distributions from carbon dioxide isotherms obtained at 0°C and at different conversions. The specific areas are correlated with conversion by the theoretical model of Bhatia and Perlmutter (7). The diffusion parameters of carbon dioxide, carbon monoxide, nitrogen and methane are determined at various conversions and at different temperatures by the application of a pulsed chromatographic technique and a model developed by Haynes and Sarma (49). Arrhenius parameters at each conversion are calculated and are used to estimate the carbon dioxide diffusion parameters at reaction temperature.

Besides the Bhatia and Perlmutter rate model, there are many other rate equations for the coal char-carbon dioxide reaction available (1, 7, 8, 17, 25, 37, 38, 40, 41, 54, 60, 62, 69, 87, 90, 98). The most convenient of these equations express a relationship between reaction rate and the fraction of coal char gasified. Some rate models are empirical (1, 17, 25, 60, 62, 69, 98) and some are based on non-catalytic gas-solid reaction theory (6, 7, 37, 38, 129). A characteristic of most coal gasification reactions, regardless of the reactant gas, is a highly variable rate throughout the reaction (25, 54, 60, 118). If the rate is plotted as a function of conversion, or equivalently time, a maximum in reaction rate occurs. Any useful coal gasification model must predict this maximum.

Coal gasification rate models depend on either empirically determined parameters with no physical significance or theoretically derived parameters which describe the physical characteristics of the coal char. These parameters are difficult to measure and generally not available, but rate expressions containing them can be fit to rate-conversion data obtained experimentally. Parameters obtained in this way yield analytical rate expressions useful for accurate prediction of the coal char-carbon dioxide gasification trajectory. In addition those parameters which represent physical quantities may be evaluated experimentally. Examples of such quantities include surface area, porosity, effective diffusivity, etc. If the parameter magnitudes represent physically believable values, then the theoretical model from which they were derived gains credibility.

Five of these models, including the three semi-empirical models of Dutta and Wen (25), Simons (98), and Kasaoka (60), and the theoretical models of Bhatia and Perlmutter (7) and Gavalas (39) are examined for their ability to interpret global rate data for the coal Char-carbon dioxide reaction from several types of coal.

CHAPTER III

THEORY

Empirical Models

Most kinetic models are based upon the conversion of carbon in the coal char. Many workers simplify coal gasification by considering a process of two steps, pyrolysis and coal char-gas reaction. Coal is a complex hydrocarbon similar to the polymeric ring structure shown in Figure 1 (41). During the first phase of coal gasification this polymeric hydrocarbon structure disintegrates, and the volatiles escape. Only molecular carbon is assumed to remain. The kinetics of this process have been studied by many investigators. The next gasification phase is the reaction of the coal char with the reactant gas. Gases usually considered are oxygen, carbon dioxide, hydrogen, and steam. In this work only the carbon dioxide reaction is considered. It proceeds according to the following equation:

The coal char-carbon dioxide reaction is relatively slow even at temperatures as high as 1373 K. It is presumably a noncatalytic gas-solid reaction. The coal char is porous and the reactive surface area is not limited to the outer surface of the particle (7,29,90). For this reason the physical structure of the coal char as well as intra-particle transport phenomena must be carefully considered when proposing

Figure 1. The molecular structure of coal suggested by Given (1).

a kinetic model for the reaction. The reaction may proceed only when the reactant gas is adsorbed on the coal surface. Von Fredersdorf (110) has proposed the following mechanism for the coal char reaction.

The parenthesis indicate the sorbed species. Assuming Langmuir-Hinshelwood kinetics, the rate expression is

$$\text{rate} = \frac{k C_{\text{CO}_2}}{1 + \alpha C_{\text{CO}} + \beta C_{\text{CO}_2}} \quad (5)$$

where

$$K = k_1 k_2 / k_1'$$

$$\alpha = k_3' / k_3$$

$$\beta = k_1 / k_1'$$

As the rate expression predicts, the reaction is zero order with respect to the carbon dioxide concentration at high carbon dioxide partial pressures (1.5 MPa) and first order (25) with respect to carbon

dioxide at partial pressure of the gas below 100 KPa. In addition the reaction is inhibited by carbon monoxide (1). Experimentally the production of carbon monoxide or the disappearance of carbon dioxide is difficult to follow. Continuous monitoring of gas chromatographic data is possible (52), but the observation of weight change of the carbon char is more conveniently and directly measured.

Several coal char gasification models (7,25,38) include a carbon dioxide concentration term, but it is normally held constant throughout the reaction. By observing the coal char weight change in a continuous stream of gas the reaction rate can be determined. This procedure was the basis for the empirical model proposed by Dutta and Wen in 1977 (25).

$$dx/dt = \eta S_d K_d C_{CO_2} (1-x) \quad (6)$$

where

x = coal char conversion

t = time

η = a effectiveness factor (dimensionless)

S_d = relative surface area (dimensionless)

C = concentration of carbon dioxide.

This equation assumes an isothermal system and a gas flow rate high enough so that external mass transfer effects are negligible.

The term, η , the effectiveness factor, is the classical way of describing intrusion of mass transfer effects into the pure chemical rate. Based on the Thiele modulus, ϕ , η is for a first order reaction in a spherical particle (25):

$$\eta = 1/\phi (1/\tanh 3\phi - 1/3\phi) \quad (7)$$

where:

$$\phi = 1/3(K_d S_d C_{CO_2} (1-x)/D_e/r_c^2)^{1/2} \quad (8)$$

where D_e = the effective diffusivity, (m^2/s).

r_c = the radius of the particle (m).

At temperatures below 1273 K the effectiveness factor for many coal char reactions is approximately equal to one (25).

The " S_d " term in the Dutta and Wen (25) model is the ratio of surface at the beginning of the reaction to the surface area at any time during the reaction. It is a function of coal char conversion and is given as:

$$S_d = 1 \pm x^{\gamma\beta} e^{\beta(1-x)} \quad (9)$$

This function is an empirical relationship and has no theoretical basis. The parameter β has no physical significance. The parameter γ defines the fractional conversion of the coal char at which surface area is a maximum. This function for surface area is an important feature of the Dutta and Wen model because it allows their model to fit their rate versus conversion data. Previous gas-solid reaction models were based upon a constantly decreasing surface area of the reacting particle (106). For example, the shrinking core model assumed that, as the mass of the particle was reacted, less surface area was available for the reaction of the sorbed gas and the solid.

Earlier workers had suggested an increasing surface area of the

carbon particles as they reacted with carbon dioxide and other gases (45,87,89,117). Based on experimental evidence, it was reported that micropores existed in the carbon which were not available during the first part of the reaction. As the reaction proceeded, the micropores opened and the active surface area increased. The idea of a maximum surface area during the course of the reaction subsequently has been the basis for the modelling of many non-catalytic gas-solid reactions (7,37,38,40, 47,68,98,129).

The rate constant, " K_d ", of the Dutta and Wen model is a pseudo-first order rate constant for the intrinsic chemical reaction occurring on the changing surface of the coal char particle. The global reaction kinetics of the coal char gasification are not pseudo-first order. A reaction model in which a pseudo-first order reaction with respect to the carbon is combined with a relationship which describes the surface area as a function of conversion is proposed.

Other empirical models for coal char gasification have been proposed. Mahajan (69) fit coal char gasification data to a cubic polynomial. Other early attempts to model the reaction were power law forms (36,54). Later the general mathematical form of most models became the product of two functions of conversion (25,59,98). The authors of most of these heuristic attempts to mathematically describe coal gasification kinetics ascribe little or no physical significance to the form of the equations or to the adjustable parameters contained in these equations. In general these models are simple and predict reaction kinetics in which the reaction rate increases to a maximum. After this maximum rate, these models further predict a decreasing rate.

Empirically fitting data to polynomials or other similar expressions yields several models with two or three parameters. Mahajan (69) proposed that coal char gasification reactions could be normalized if the rate were expressed in dimensionless time. He proposed

$$\tau = \frac{t}{t_{x=0.5}} \quad (10)$$

where τ is dimensionless time, and t is real time. If x is conversion then in nested polynomial form:

$$dx/d\tau = ((x+a)x + b)x + c \quad (11)$$

Chornet (17) proposed a more compact model with variable exponents

$$dx/d\tau = K_c x^e (1 - x)^d \quad (12)$$

where $K_c = 1.763$, $e = 0.5$, and $d = 1.0$. This model is based on the idea of a reaction in which active sites increased during the first half of the reaction. Then as the coal char decomposed, the active sites collapsed and the rate of reaction decreased. Chornet did not identify the physical nature of the active sites, but the values for e and d were obtained by the method of Gorbachev (42) for determining kinetic parameters in an autocatalytic reaction. Simons (98) later showed that the Chornet model could be modified on a semi-theoretical basis to account for the surface area changes during the reaction. He contends (98) that:

$$S_p \propto \theta^{\frac{1}{2}}(1-\theta) \quad (13)$$

where S_p is the internal surface area, and θ is the porosity of the char particle. Then he proposed that reaction rates were proportional to available surface area:

$$dx/d\tau \propto \theta^{\frac{1}{2}}(1-\theta) \quad (14)$$

Thus:

$$x = \frac{\theta - \theta_0}{1 - \theta_0} \quad (15)$$

where θ_0 is the initial porosity. Therefore:

$$dx/d\tau = K_c (x + \theta_0(1-x))^{\frac{1}{2}}(1-x) \quad (16)$$

As θ_0 approaches zero this model reduces to equation 12, the Chornet model.

Kasaoka and others (60) have proposed a similar model in which the simple first order rate expression:

$$dx/d\tau = K_k(1-x) \quad (17)$$

has been relaxed to allow K_k to be a function of time or conversion.

$K_k(\tau)$ is defined:

$$K_k(\tau) = A B \tau^{B-1} \quad (18)$$

and $K_k(x)$ is:

$$K_k(x) = A^{1/B} B(-\ln(1-x))^{(B-1)/B} \quad (19)$$

The entire model cast into a form similar to other empirical models is:

$$dx/d\tau = A^{1/B} B(-\ln(1-x))^{(B-1)/B} (1-x) \quad (20)$$

There is similarity among all these models. Their mathematical form makes them appear as power law or polynomial formulas. Recent variations to this form include adjustable exponents or the insertion of logarithmic functions into the expressions. The more complicated algebraic form of the later model allows rate data to be fit using two parameters rather than three parameters required by the Mahajan or Dutta and Wen models.

Theoretical Models

Equations similar to the empirical equations previously summarized can be derived from a theoretical basis. Chornet implied his equation modeled an autocatalytic reaction, and Simons later showed this same equation could be expanded to account for structural changes of the coal char particle. Yet a rigorous model from basic physical considerations has been developed only recently by several workers (7,37,38,40,89,129). These models have been reviewed by Ramachandran and Doraiswamy (90). These models are based on two views of the way coal char particle structure effects the rate of reaction. One approach is to consider the particle as a cluster of grains (37,40). The other geometric model considers the particle to be comprised of a group of cylindrical pores (7,38,129). These two models apply generally to non-catalytic gas-solid reactions, and they assume there is no mass transfer resistance external to the particle.

If the reactive surface of a solid porous particle consists of a cluster of grains, shrinking core analysis can be applied to the individual grains. Each grain will have its surrounding product layer with its resistance to diffusion of reactants and products. Early models based on this idea were developed with their resulting rate expressions (12, 105). Similar analysis provided for shapes other than spheres such as long cylinders and infinite slabs. These models did not account for the existence of rate maxima during the course of the reaction. More recently other workers have proposed variable size grain models (99) which do predict rate maxima with the proper parameter values. One such model of Garza-Garza and Dudukovic (37) defines a coupled set of non-linear partial differential equations to describe a gas-solid reaction. The model contains four parameters which account for product layer diffusion and reaction resistances (a Damkohler number and a Thiele modulus) as well as structural and porosity measurements. While the model is attractive because of its generality, it is not presently useful because of its complexity. However, at various values of the four parameters this approach to gas-solid reaction kinetics will predict most observable rate trajectories.

The random pore model yields simpler rate expressions. Two recent approaches to the random pore model give identical equations for rate conversion data (7,38). Although these two derivations use the same coal char geometry, their approach is dissimilar. The model by Gavalas (38) assumes no diffusional control of the reaction and no dependence of the intrinsic surface reaction rate on

conversion. In addition Gavalas (38) assumes the char is a porous structure of infinitely long cylindrical capillaries with completely random axes. The other model, proposed by Bhatia and Perlmutter (7), also assumes no diffusional control, but they postulate cylinders of random size and parallel orientation. From these two points of view the same final rate expression has been derived.

Gavalas (38) begins his derivation of the structural mechanism of the char reaction by defining a probability function, λ , which describes the density of intersecting cylinders of any surface in the porous pellet. This function can be used then to develop an expression for the surface evolution. According to Gavalas the total porosity, $\epsilon_T(q)$, is:

$$\epsilon_T(q) = 1 - \exp \left[-2\pi \int_{R_1}^{R_2} (R_0 + q)^2 \lambda_0(R_0) dR_0 \right] \quad (21)$$

Where R_0 is the initial radius of the capillaries and q is a function of time which describes the increase in capillary radius.

The preceding equation is also equivalent to pore volume:

$$\frac{1 - \epsilon_T(q)}{1 - \epsilon_{T_0}} = \exp [-2\pi (B_0 q^2 + 2B_1 q)] \quad (22)$$

if

$$B_0 = \int_{R_1}^{R_2} \lambda(R_0) dR_0 \quad (23)$$

and

$$B_1 = \int_{R_1}^{R_2} R_0 \lambda(R_0) dR_0 \quad (24)$$

The zeroth moment, B_0 , is the total number of capillary axes intersecting a unit surface area while the first moment B_1 is equal to the product of B_0 and the mean pore radius. In order to relate this porosity function to surface area Gavalas (38) noted that

$$S(q) = \frac{dc_T}{dq} = 4\pi [1 - \epsilon_T(q)] (B_0 q + B_1) \quad (25)$$

In addition, the definition of fractional conversion, is the amount of carbon reacted divided by the initial amount of carbon. In terms of this analysis:

$$X_c(q) = 1 - (1 - q/R_{p0})^3 \frac{1 - \epsilon_T(q)}{1 - \epsilon_0} \quad (26)$$

Gavalas showed that q/R_{p0} was typically on the order of 10^{-3} so using this fact and combining equations 22 and 26:

$$X_c(q) = 1 - \exp [-2\pi (B_0 q^2 + 2 B_1 q)] \quad (27)$$

Now, v_s is the velocity at which a pore surface element recedes due to reaction,

$$v_s(c, c_s T) = 1/\rho_s r_t(c, c_s T) = q/t \quad (28)$$

where

c = concentration of the reacting gas,

c_s = concentration of active solid reacting sites,

T = temperature,

r_t = surface reaction rate.

Since Gavalas assumed that surface reaction rate and the concentrations of reacting gases were constant, then v_s was constant and:

$$dx_c/dt = 4\pi(B_0 v_s^2 + B_1 v_s) \exp(-2\pi B_0 v_s^2 t^2 + 2B_1 v_s t) \quad (29)$$

or combining equations 27 and 29:

$$\frac{dx_c}{dt} = 4\pi(1-x_c) \left[(B_1 v_s)^2 + \frac{B_0 v_s^2}{2\pi} \ln\left(\frac{1}{1-x_c}\right) \right]^{\frac{1}{2}} \quad (30)$$

This equation is a two parameter expression for rate and conversion. It is identical to a model proposed by Bhatia and Perlmutter (7) from the following argument. Bhatia and Perlmutter assume that the char particle is a set of overlapping parallel cylinders with a size distribution $f(r)$. $f(r)dr$ is the total length of cylindrical surfaces per unit volume of space with radii between r and $r + dr$.

Thus the total length is given:

$$L_e = \int_0^{\infty} f(r) dr \quad (31)$$

The total surface is:

$$S_e = 2\pi \int_0^{\infty} r f(r) dr \quad (32)$$

The total volume is:

$$V_e = \pi \int_0^{\infty} r^2 f(r) dr \quad (33)$$

If no cylinders are created or destroyed, the growth of cylinders yields this balance:

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial r} \left[f \frac{dr}{dt} \right] = 0 \quad (34)$$

Bhatia and Perlmutter also state that the intrinsic chemical rate on the changing surface area is constant (or in effect rate is proportional to surface area); therefore:

$$\frac{dr}{dt} = K_s C^n \quad (35)$$

where C is the concentration of the gas.

Combining equations (34) and (35):

$$\frac{\partial f}{\partial t} = K_s C^n \frac{\partial f}{\partial r} \quad (36)$$

Integrating with respect to r and combine with equation (31), and:

$$\frac{d L_e}{dt} = 0 \quad (37)$$

Multiplying equation 31 by $2\pi r$ and integrating with respect to r ,
Then using the definitions of L_e and S_e :

$$\frac{d S_e}{dt} = 2\pi K_s C^n S_e \quad (38)$$

Similarly $d V_e/dt$ is obtained by multiplication of equation (31) by πr^2 and integration with respect to r .

$$d V_e/dt = K_s C^n S_e \quad (39)$$

Now by solving the above differential equations:

$$S_e = \sqrt{S_{e0}^2 + 4\pi L_{e0} (V_e - V_{e0})} \quad (40)$$

also

$$V_e = V_{e_0} + S_{e_0} (K_s C^n t) + L_{e_0} (K_s C^n t)^2 \quad (41)$$

Bhatia and Perlmuter (3) used a geometric relation relating V_e , the non-overlapped volume, to V the volume of the particle (7),

$$dV = (1-V) dV_e \quad (42)$$

Note that as V_e approaches zero, V approaches zero. Then integrate with this boundary condition,

$$V = 1 - \exp(-V_e) \quad (43)$$

Since the change in the mass of the solids is accompanied by a proportional change in the volume of the reacting solid, and since the rate is proportional to the surface area, the equations:

$$dV_e = S_e (K_s C^n) dt \quad (44)$$

and

$$dV = S (K_s C^n) dt \quad (45)$$

are true. Combining equations 42, 44, and 45:

$$S = S_e (1-V) \quad (46)$$

The change in the length of the overlapping system is related to the change in the volume by:

$$dL' = \frac{L'}{1-V} dV \quad (47)$$

and as V approaches zero, $L' = L_e$. So integration with this boundary condition yields:

$$L' = L_e(1-V) \quad (48)$$

Now combining equations 43, 46, and 48 with equations 40 and 41 gives:

$$\frac{S}{S_0} = \left(\frac{1-V}{1-V_0}\right) \sqrt{1 - \frac{4\pi L'_0(1-V_0)}{S_0^2} \ln \frac{1-V}{1-V_0}} \quad (49)$$

$$1 - V = (1-V_0) \exp\left[-\frac{K_s C^n t}{1-V_0} (S_0 + \pi L'_0 K_s C^n t)\right] \quad (50)$$

and by the definition of conversion:

$$1-x = \left(\frac{1-V}{1-V_0}\right) \left(1 - \frac{K_s C^n t}{R_0}\right)^3 \quad (51)$$

Thus

$$S/S_0 = \frac{1-x}{(1-\tau'/\sigma)^3} \sqrt{1 - \psi \ln \left[\frac{1-x}{(1-\tau'/\sigma)^3} \right]} \quad (52)$$

Where

$$\tau'/\sigma = K_s C^n t / R_0 \quad (53)$$

and

$$\psi = 4\pi L'_0(1-V_0)/S_0^2 \quad (54)$$

When the size parameter, σ , is large as it is in many porous gas solid reactions, then

$$1 - \tau'/\sigma \approx 1 \quad (55)$$

Therefore,

$$S/S_0 = (1-x) \sqrt{1 - \psi \ln(1-x)} \quad (56)$$

Since S/S_0 is proportional to the rate of reaction:

$$dx/dt = \tau' (S/S_0) \quad (57)$$

and

$$dx/dt = \tau'(1-x) \sqrt{1 - \psi \ln(1-x)} \quad (58)$$

Noting the equivalence of this model to the Gavalas model one may observe how the parameters of the two models relate to one another. Consider the form of the final equations of the two models. Compare equation 30 to equation 58. When equation 30 is cast into the form of equation 50 it is:

$$\frac{dx}{dt} = 4\pi B_1 v (1-x) \sqrt{1 - \frac{B_0 v^2}{2\pi B_1^2 v^2} \ln(1-x)} \quad (59)$$

Thus:

$$\psi = B_0 / 2\pi B_1^2$$

and

$$\tau' = 4\pi B_1 v \quad (61)$$

Furthermore:

$$B_1 = B_0 R \quad (62)$$

where R is defined as the mean pore radius. So:

$$\tau' = 4\pi B_0 R r_t / \rho \quad (63)$$

where r_t is an intrinsic reaction rate function. Bhatia and Perlmutter denoted this function by:

$$r_t = K_s C^n \quad (64)$$

Also according to Bhatia and Perlmutter:

$$\tau' = K_s C^n S_0 / (1 - \epsilon_0) \quad (65)$$

Combining Equations 63 and 65:

$$\frac{S_0}{1 - \epsilon_0} = \frac{4\pi B_0 R}{\rho} \quad (66)$$

Therefore, by equating the constants of proportionality between surface area evolution and reaction rate obtained from the two different models, another relation for the zeroth moment of probability density from the Gavalas model emerges.

$$B_0 = \frac{\rho S_0}{(1 - \epsilon_0) 4\pi R} \quad (67)$$

Also by equating the parameter inside the radicals of the two models:

$$\psi = \frac{1}{2\pi B_0 R^2}$$

Physically, B_0 is a description of the density of intersection of random capillaries within the coal particle. It can be related to the density of the coal char multiplied by its specific surface area and divided by its mean pore radius. Since the two model derivations begin with the different geometric assumptions and lead to equations of the same form adds credence to the models.

Another significant conclusion concerning the two models is that surface evolution is the rate controlling factor in the kinetically controlled reaction. As was noted both models took the actual rate of disappearance of carbon atoms from the reactive surface as a constant. The only contribution to the kinetics which the chemical reaction actually made was to modify the reactive surface.

Bhatia and Perlmutter (8) later modified their model described above to yield:

$$\frac{dx}{dt} = \frac{\tau'(1-x)\sqrt{1 - \psi \ln(1-x)}}{1 + \left[\frac{2K_s \rho_B (1-\epsilon_o)}{bM_B D_e S_o} \frac{\bar{Z}}{\psi} (\sqrt{1 - \psi \ln(1-x)} - 1) \right]} \quad (69)$$

where

$\bar{Z}$ = the ratio of volume of the product to the reactant,

b = the stoichiometric coefficient of the solid,

M = the molecular weight of the solid,

D_e = the effective diffusivity,

ρ_B = density of the solid.

This model accounts for diffusion controlled reactions. Attempts are being made in this laboratory to collect surface and diffusivity data for the carbon dioxide-coal char reaction which may be useful in evaluating the validity of this model.

That the observed rates are not simply proportional to available area, as would be expected if the reaction were chemical rate controlled, indicates significant mass transfer intrusion (87). The intraparticle (intrapore) diffusion contributes by far the greatest resistance to mass transport. The diffusion parameter, D_e/r_c^2 , shows an Arrhenius-type dependence on temperature, that is, diffusion through pores of molecular dimensions is activated, with the largest energy of activation associated with the smallest pores (124). As gasification proceeds, the average pore radius increases and activated diffusion gives way to Knudsen diffusion. However, since no theoretical model has thus far been suggested to correlate the diffusion parameter with conversion, an empirical relationship is needed in order to use the model described by equations 6, 7, and 8.

Effective Diffusivity

A number of theoretical and experimental techniques have been exploited in the determination of the diffusivity of gases through porous media. The measurement of steady-state diffusion across a pressure gradient (112) or across a concentration gradient (55) has given way to the study of dynamic diffusion processes. For example, the unsteady-state release of a gas by a porous substance following a sudden reduction in pressure (84,84), or the unsteady-state elution of a sorbate (31,43) have yielded many useful data. Gorring and DeRosset (43) briefly reviewed some of the classical methods.

More recently, chromatographic techniques, which are especially applicable to unsteady-state diffusion in packed beds, have become very popular. Mathematical models which take into account axial dispersion, diffusion from the bulk fluid to the adsorbent surface (external diffusion),

diffusion within the porous particle (internal diffusion) and unsteady-state adsorption have been derived. The correlation of a tracer distribution, exiting the packed bed, with the model has been performed in the time or Laplace domains (39,80,93,94,114,115,116) or by applying Fourier analysis (18,34,50,51,113), frequency response (23) or analysis of moments (15,46,49,63,95,97,104). The method of moments is attractive mainly because it avoids a numerical solution to the model and because the experimental data need not be transformed to another domain. While the analysis of moments is relatively easily performed it is also often the least accurate, as delineated by Radeke (88), Wakao, et al. (116) and Gangwal et al. (35). Thus, the most objectionable error arises from high order moments which grossly over-weight the scattered tail segment of the measured peak. However, this shortcoming is of small consequence provided that the mathematical model is a priori adequate, the measurements are routine and not designed to confirm or improve the model, only a small number of parameters is to be estimated so that only a few moments must be analysed, and the tail section in the experimental curve is measured accurately (88). In this study all of the above criteria were satisfied, and the effective diffusivities were computed according to the method of moments.

The model presented here was developed by Schneider and Smith (95) and Haynes and Sarma (49), and applies to porous, bidisperse adsorbents. Consider a cylindrical bed packed with coal char particles and having length L . Each char particle is assumed to be a sphere of radius R_y , which is small compared to the bed radius, and composed of uniformly distributed microparticles having an average radius R_x .

The concentration of a sorbate in the bulk gas phase is a function of time and axial position along the bed:

$$D_z \frac{\partial^2 C_z}{\partial z^2} - \underline{v} \frac{\partial C_z}{\partial z} - \theta_z \frac{\partial C_z}{\partial t} + \frac{3(1-\theta_z)}{R_y} N_{R_y} = 0 \quad (70)$$

where

$C_z(z,t)$ = sorbate concentration in the bulk gas phase,

z = axial coordinate of packed bed,

t = time,

D_z = axial dispersion coefficient,

$\underline{v}$ = superficial velocity,

θ_z = bed void fraction,

R_y = radius of macroparticle

N_{R_y} = sorbate flux at surface of macroparticle, defined later in equation 75.

The four terms in equation 70 represent bulk diffusion, bulk flow, accumulation in the bed void space and accumulation in the particle, respectively. Initially, the bed is free of adsorbate:

$$C_z(z,0) = 0 \quad (71)$$

and

$$C_z(\infty,t) = 0 \quad (72)$$

In this study an input pulse of duration τ and amplitude C_0 was injected at time, $t=0$. In mathematical notation:

$$C_0(0, 0 < t \leq \tau) = C_0 \delta(t) \quad (73)$$

$$C_z(0, t > \tau) = 0 \quad (74)$$

where

$\delta(t)$ = Gaussian function of time.

The flux at the macroparticle surface may be written in terms of the mass transfer coefficient.

$$-N_{R_y} = k_f [C_z(z, t) - C_y(R_y, t)] \quad (75)$$

where

N_{R_y} = sorbate flux at the macroparticle surface,

$C_y(y, t)$ = sorbate concentration in macroparticle,

y = macroparticle radial coordinate.

Since the great majority of surface area suitable for adsorption is found in the microparticles, adsorption in the macroparticle is neglected. Diffusion in the macroparticle is given by:

$$D_y \left(\frac{\partial^2 C_y}{\partial y^2} + \frac{2}{y} \frac{\partial C_y}{\partial y} \right) - \theta_y \frac{\partial C_y}{\partial t} - \frac{3(1-\theta_y)}{R_x} D_x \frac{\partial C_x}{\partial x} \bigg|_{R_x} = 0 \quad (76)$$

where

D_y = macroparticle diffusivity,

θ_y = macroparticle void fraction,

D_x = microparticle diffusivity,

$C_x(x, t)$ = sorbate concentration in microparticle,

x = microparticle radial coordinate,

R_x = microparticle radius.

The sorbate concentration gradient at the particle center must be identically zero:

$$\frac{\partial C_y(0,t)}{\partial y} = 0 \quad (77)$$

Also:

$$C_y(y,0) = 0 \quad (78)$$

A mass balance on the microparticles gives:

$$D_x \left(\frac{\partial^2 C_x}{\partial x^2} + \frac{2}{x} \frac{\partial C_x}{\partial x} \right) - \theta_x (1 + K_a) \frac{\partial C_x}{\partial t} = 0 \quad (79)$$

where

θ_x = microparticle void fraction,

K_a = adsorption constant, defined in equation 80.

It has been assumed that adsorption is instantaneous and reversible, and that the concentration, C_x , is sufficiently small to allow the application of Henry's law:

$$K_a = \frac{\rho S_x}{\theta_x (1 - \theta_y)} \frac{C_a}{C_x} \quad (80)$$

where

ρ = particle density,

S_x = specific area in microparticles,

C_a = specific concentration of adsorbed gas.

Also, diffusion of the adsorbed gas along the adsorption surface has

been neglected, that is, all diffusion is assumed to occur only in the gas phase. The initial and boundary conditions are given analogously to equations 77 and 78 :

$$\frac{\partial C_x(0,t)}{\partial x} = 0 \quad (81)$$

$$C_x(x,0) = 0 \quad (82)$$

Solution of the model is achieved by transformation from the time to the Laplace domain:

$$\bar{C}(z,s) = \int_0^{\infty} C(z,t) e^{-st} dt \quad (83)$$

The resulting analytical solution is necessarily complicated and inversion to the time domain is not feasible. However, it is possible to obtain directly from $\bar{C}(z,s)$ explicit expressions for the moments of $C(z,t)$.

The n th absolute moment is defined as:

$$\mu'_n = \frac{m_n}{m_0} \quad (84)$$

where

$$m_n = \int_0^{\infty} t^n C(L,t) dt \quad (85)$$

and $C_z(L,t)$ is the sorbate concentration in the gas exiting the bed.

The n th central moment is given by

$$\mu_n = \frac{1}{m_0} \int_0^{\infty} (t - \mu'_1)^n C_z(L,t) dt \quad (86)$$

The first absolute moment, which is just the mode of $C_z(L,t)$ is:

$$\mu_1' = \frac{\int_0^{\infty} t C_z(L,t) dt}{\int_0^{\infty} C_z(L,t) dt} \quad (87)$$

and the second central moment, which provides a measure of the deviation of $C_z(L,t)$ from the mode, is:

$$\mu_2 = \frac{\int_0^{\infty} (t - \mu_1')^2 C_z(L,t) dt}{\int_0^{\infty} C_z(L,t) dt} \quad (88)$$

Now, the moments are related to $\bar{C}_z(L,s)$ by the expression

$$m_n = (-1)^n \lim_{s \rightarrow \infty} \frac{d^n}{ds^n} \left(\frac{\bar{C}_z(L,s)}{s} \right) \quad (89)$$

Application of equations 87, 88 and 89 to the model, and assuming the contribution made by macroparticles toward the overall diffusion process to be small, yields:

$$\mu_1' = \frac{L}{v} [\theta_z + (1 - \theta_z) \theta_x (1 + K_a)] \quad (90)$$

and

$$\begin{aligned} \mu_2 = \frac{2LD_z}{v^3} [\theta_z + (1 - \theta_z) \theta_x (1 + K_a)]^2 &+ \frac{2LR_y}{3\sqrt{k_f}} (1 - \theta_z) \theta_x^2 (1 + K_a)^2 \\ &+ \frac{2LR_x^2}{15\sqrt{D_x}} (1 - \theta_z) \theta_x^2 (1 + K_a)^2 \end{aligned} \quad (91)$$

The three terms on the right-hand side of equation 91 represent axial dispersion, external mass transfer and micropore diffusion, respectively. Equations 90 and 91 may be written more conveniently by transforming the superficial velocity to an interstitial velocity:

$$\bar{V} = \frac{v}{\theta_z} \quad (92)$$

and by letting

$$K_p = \theta_x (1 + K_a) \quad (93)$$

Hence,

$$\mu_1' = \frac{L}{\bar{V}} \left[1 + \frac{1 - \theta_z}{\theta_z} K_p \right] \quad (94)$$

and

$$\Delta = \frac{\theta_z}{\bar{V}^2 \theta_z} + \frac{1}{3} \frac{\theta_z}{1 - \theta_z} \left[\frac{R_y^2}{k_f} + \frac{R_x^2}{5D_x} \right] \quad (95)$$

where

$$\Delta = \frac{\mu_1'^2}{\bar{V}^2} \frac{L}{\bar{V}} \quad (96)$$

In deriving equation 95 it was assumed that:

$$\frac{1 - \theta_z}{\theta_z} K_p \gg 1 \quad (97)$$

Using equation 94, K_p is calculated from experimentally determined μ_1' , L , $\bar{V}$ and θ_z . The utility of equation 95 becomes apparent if data are collected at various gas velocities. A plot of Δ against $1/\bar{V}^2$ produces a linear graph having a slope equal to the axial dispersion

coefficient, D_z/θ_z . The intercept at $1/\bar{V}^2 = 0$ gives the microparticle diffusion parameter, D_x/R_x^2 , if k_f is independently estimated. The mass transfer coefficient, k_f , may be obtained from a correlation given by Bird, Stewart and Lightfoot (9):

$$Nu_{AB} = 2.0 + 0.60 Re^{1/2} Sc^{1/3} \quad (98)$$

where

Nu_{AB} = Nusselt mass transfer number,

Re = Reynolds number,

Sc = Schmidt number,

and

$$Nu_{AB} = \frac{2R_y k_f}{D_{AB}} \quad (99)$$

In this study the Reynolds number is very small so that $Nu_{AB} \approx 2$ and $k_f = D_{AB}/R_y$. The molecular diffusivity, D_{AB} , is calculated from the Lennard-Jones parameters as prescribed by Bird, Stewart, and Lightfoot (9). The axial dispersion coefficient, D_z , may be estimated by $D_z = 0.7 D_{AB} + \bar{V}R_y$ (97). This simplification then allows the direct computation of the microparticle diffusion parameter from data obtained at a single velocity.

In reality, diffusion in the microparticle does not occur exclusively in the radial direction, and the actual diffusion path length, r_c , is different from the microparticle radius, R_x . Hence, the microparticle diffusion parameter, D_x/R_x^2 , is replaced by the effective diffusion parameter, D_e/r_c^2 , where D_e is the effective microparticle diffusivity.

Surface Area and Pore Volume Distribution

The physical adsorption of gases by microporous solids presents special problems not encountered with nonporous or macroporous materials. In particular, adsorption sites reside mainly on the walls of pores having radii several times the kinetic diameter the sorbate molecule. Clearly, the assumptions of a uniform adsorption potential distribution and of non-interacting neighboring adsorption sites, which are implicit in the Langmuir (44) and Brunauer, Emmett and Teller (BET) (11) models, are not applicable. Indeed, the overlap of potential fields within the micropore results in an increase in the attractive force exerted upon the sorbate molecule. Hence, even at low relative pressures the pores become filled with the sorbate to a density approaching that found in the sorbate liquid state.

Pores which are very small or which have small entrances give rise to the phenomenon of "activated adsorption." Thus, the passage of the sorbate molecule through the pore opening is hindered. An activation energy, which is a strong function of both the sorbate and adsorbent (3,65,121), is associated with the process, and the attainment of adsorption equilibrium is often dominated by unfavorable kinetics. Hence, in the case of coal and coal chars, low adsorption temperatures and non-polar sorbates require very long equilibrium times. For example, adsorption of argon was incomplete even after 1,500 hours (72) and one week was required for the complete adsorption of nitrogen at -195°C (77). Surface areas obtained from low temperature studies are usually much smaller than those estimated at higher temperatures probably because insufficient time was allowed for equilibrium (2,3,4,33,65,119). The

use of carbon dioxide as sorbate is recommended because equilibrium is rapidly reached and because the isotherm may be obtained at low pressures (21,77,91,107,119,122). An adsorption isotherm typical of microporous solids is shown in Figure 1.

The classical concept of the adsorption mono- and multilayer, upon which the Langmuir and BET theories rest, is best abandoned altogether when considering microporous solids. A more meaningful approach considers the uptake of sorbate in terms of volumetric filling of pores having some size and shape distribution (13). The Dubinin-Polanyi (DP) theory, and modifications thereof, which advance this view have been developed (24,44,81,92,103) and successfully applied toward the calculation of both surface area (10,21,77,78,81,103,107,122) and pore volume distribution (13,21,81,103). The DP theory (44) and the method of Medek (81), deemed the most suitable for the work presented herein, are outlined below.

The adsorption volume within a collection of pores is characterized by a series of equipotential surfaces, and the potential for filling an incremental volume between these surfaces is given by:

$$A' = RT \ln (P_0/P) \quad (100)$$

where

A' = adsorption potential,

R = gas content,

T = absolute temperature,

P_0 = pressure at saturation,

P = equilibrium sorbate pressure.

Figure 2. Type I Adsorption Isotherm.

The adsorption potential is thought to depend only on the degree of pore filling and on the sorbate and adsorbent. Hence, for any given solid the adsorption potential of a sorbate is proportional to the potential of some standard sorbate:

$$A' = \beta A'_0 \quad (101)$$

where

A' = adsorption potential,

A'_0 = adsorption potential of reference,

β = affinity coefficient.

The theory postulates that the adsorption volume is a Gaussian function of the adsorption potential:

$$W = W_0 \exp(-\alpha'^2 A'^2_0) \quad (102)$$

where

W = equilibrium volume of sorbate,

W_0 = volume of sorbate at saturation,

α' = constant characteristic of the pore size distribution.

Combining equations 101 and 102, and letting $\beta/\sqrt{\alpha'} = E$, the characteristic energy, gives:

$$W = W_0 \exp\left[-\left(\frac{A'}{E}\right)^2\right] \quad (103)$$

or

$$W = W_0 \exp\left[-\frac{(RT \ln P_0/P)^2}{E^2}\right] \quad (104)$$

which is the Dubinin equation. A plot of $\ln W$ against $(\ln P_0/P)^2$ produces the total pore volume, W_0 , and the characteristic energy, E . The Dubinin equation has been successfully applied with relative pressures ranging from 10^{-5} to 0.2.

The pore volume distribution may be computed with the aid of a functional relation between the adsorption potential and pore dimensions (81):

$$A' = k_c / r^3 \quad (105)$$

where

k_c = constant depending on the sorbate and adsorbent,

r = average distance of the sorbate molecule from the pore wall.

In the case of the carbon dioxide-coal system k_c takes the value of 3.145 kJ/nm^3 (81). The "radius", defined as:

$$r = 2q/p \quad (106)$$

where

q = area of pore cross section,

p = perimeter of pore cross section,

is independent of the pore geometry. A comparison of equations 100 and 105 shows that the effective radius can be calculated at each observable relative pressure. The combination of equations 103 and 105 yields the expression relating volume adsorbed to pore radius:

$$W = W_0 \exp\left[-\left(\frac{k_c}{E}\right)^2 r^{-6}\right] \quad (107)$$

The pore size distribution follows from the differentiation, with respect to r , of equation 107,

$$\frac{dW}{dr} = 6 W_0 \left(\frac{k_c}{E}\right)^2 r^{-7} \exp\left[-\left(\frac{k_c}{E}\right)^2 r^{-6}\right] \quad (108)$$

Finally, the micropore area, S , may be obtained with the aid of equation 106. If dl is a differential element of pore depth, then:

$$r = \frac{2qdl}{pd} = \frac{2dW}{dS} \quad (109)$$

Substitution for dW in equation 108 followed by integration gives the micropore area:

$$S = 2W_0 \left(\frac{E}{k_c}\right)^{1/3} \Gamma(7/6) \quad (110)$$

and the mean pore radius:

$$\bar{r} = \frac{(k_c/E)^{1/3}}{\Gamma(7/6)} \quad (111)$$

where

Γ = gamma function.

CHAPTER IV

EXPERIMENTAL

This work involved the preparation of the coal char and its subsequent stepwise conversion to carbon monoxide by reaction with carbon dioxide. At each conversion the effective diffusivity, the bed void fraction and the total surface area and pore volume distribution were determined. The rate of reaction of char with carbon dioxide as a function of conversion was also obtained.

Preparation of Char Sample

A bulk sample of subbituminous coal, designated Wyodak, was taken from the Roland-Smith seam strip mine at Gillette, Wyoming. The composition of the dry coal was determined at the Oak Ridge National Laboratory and given in Table 1. To minimize the effects of oxidation, the coal was transported submerged under water in a hermetically-sealed metal cannister. Subsequent size reduction and classification were performed on coal slurried in water. A bulk sample was comminuted in a Waring blender and the resulting particles were screened on U.S.A. Standard Testing Sieves. The portion collected between sieve #35 (0.500 mm opening) and sieve #60 (0.250 mm opening) was dried in vacuo at 50°C. Approximately 20g of the dried coal were loosely packed into a quartz tube (2 cm x 45 cm) equipped with gas inlet and outlet ports. The assembly was placed in a Lindberg Sola Basic tube furnace and a stream of helium having a volumetric flow rate of 20 cm³/min, measured at

TABLE 1

PRINCIPLE ANALYSES FOR WYOMING SUBBITUMINOUS COAL

Analysis	Weight %
Moisture	6.17 ± 0.59
Ash (mf) ¹	6.84 ± 0.15
Volatile matter (maf) ²	46.40 ± 0.46
Carbon (maf)	72.50 ± 0.48
Sulfur (maf)	0.53 ± 0.08
Hydrogen (maf)	5.45 ± 0.18
Nitrogen (maf)	1.01 ± 0.08
Oxygen (maf) ³	20.49 ± 0.59
Heating Value (KJ/Kg,maf)	29000 ± 130

1. mf = moisture free

2. maf = moisture and ash free

3. by difference

ambient temperature and pressure with a soap film flow meter, was passed through the coal bed. The tube was heated to a final reaction temperature at a heating rate of 25°C/min, controlled by a Fisher Linear Temperature Programmer Model 360 equipped with a platinum II thermocouple. The final temperature was maintained for approximately two hours following the disappearance of the last visible traces of the ensuing coal gases and liquids. The resulting coal char was allowed to cool to ambient temperature and was stored at 50°C in a nitrogen atmosphere.

A 1.5561 g sample of the 35/60 mesh char was loaded into a quartz tube (ID 4.75 mm, length 158 mm) equipped with 10/30 male joints on both ends. The char, held in place by small quartz wool plugs, was packed to a maximum bulk density, yielding a bed length of 7.2 cm.

The char sample was gasified by stepwise reaction with carbon dioxide at 800°C. At each conversion the effective diffusivity, void fraction, surface area and pore volume distribution were determined.

Determination of Effective Diffusivity

Diffusivity measurements were made on the apparatus schematized in Figure 3. The quartz sample tube, a Gow-Mac Instrument Co., Model 10-301 thermal conductivity cell, a Valco Instrument Co. 6-port switching valve equipped with a 1 cm³ gas sampling loop and associated tubing were enclosed in a Perkin Elmer 880 Gas Chromatograph thermostated oven. Copper tubing and Swagelok fittings were employed throughout. The sample tube was held in place by quartz adaptors which were interfaced with the copper tubing by means of Swagelok fittings equipped with Teflon ferrules. The oven temperature was measured with a copper-constantan thermocouple positioned immediately above the sample tube. Output from the

Figure 3. Apparatus for the Determination of Effective Diffusivity

thermocouple was measured using a Leeds and Northrup Co. millivolt potentiometer and an ice-water reference. Power was supplied to the thermal conductivity cell by the Hot Wire Control unit of a Perkin Elmer 811 Gas Chromatograph, and the detector output was fed to a Sargent Model SR6 chart recorder and to the analog-to-digital converter input of a Digital Corp. MINC-11 computer. The area, the first absolute moment and the second central moment of a tracer distribution at the output of the char bed were numerically evaluated with the aid of a computer program called MOMEN9.¹

All gases used in this study were of high purity (>99.9%). A helium carrier gas volumetric flow rate of 20 cm³/min, measured with a soap film flow meter at ambient temperature and pressure, was used for all determinations. The diffusivity of each of the test gases nitrogen, carbon monoxide, carbon dioxide and methane was calculated from data obtained at temperatures of 50, 100, 150, 200 and 250°C.

Following each partial conversion, the char sample tube was fixed in position, the carrier gas flow rate was adjusted and the oven was brought to the required temperature. The gas injection loop was slowly purged with the test gas. The detector output was directed to the chart recorder and a constant baseline was established. Following initialization of MOMEN9, the switching valve was rapidly rotated to the injection position. In this configuration the carrier gas flow was channeled through the gas injection loop thereby introducing a rectangular pulse of test gas into the char sample tube. The resulting detector signal

¹Available from the Department of Chemical Engineering, Vanderbilt University.

directed to the analog-to-digital converter of the computer and was sampled at a frequency of ten observations per second. In the cases of carbon dioxide at 50 and 100°C long retention times were encountered (20-30 min), and the sampling frequency was reduced to one observation per second. In all measurements data acquisition was terminated after the output signal, having a peak maximum greater than 100 millivolts, returned to within 2 millivolts of the baseline. Each determination was repeated at least four times. The first absolute moments and the second central moments thusly obtained were employed in the calculation of the adsorption constant and the diffusion parameter, according to the method described in Chapter III.

Determination of Bed Void Fraction

The char sample was mounted in the surface area apparatus, shown in Figure 4, and a manometer filled with Meriam 827 Red Oil manometer fluid (density 0.827 g/cm^3) was connected across the sample tube. The volumetric flow rate of a helium stream passing through the sample and the attendant pressure drop were recorded. The experiment was repeated with a different flow rate. The Ergun equation (9) was solved for the void fraction using the Newton-Raphson algorithm. The void fraction determined in the two runs agreed to within $\pm 1\%$.

Determination of Surface Area and Pore Volume Distribution

The total surface area and pore volume distribution were calculated from volumes of carbon dioxide adsorbed at 0°C. Figure 4 shows the apparatus employed. The char sample tube was fixed vertically to form

Figure 4. Apparatus for the Determination of Surface Area.

one arm of a U-tube arrangement around which could be easily placed a tall 1-liter dewar flask. Quartz adaptors of the type previously described were used to hold the sample tube in place. The direction of gas flow was as indicated in Figure 4, allowing the gas to cool before entering the char bed. The detector and associated equipment have already been described. Output from the detector was directed to the Digital Corp. MINC-11 computer. A 6-port Valco Instrument Co. switching valve was equipped with a 5 cm³ gas sample loop.

In the majority of experiments the desired partial pressures of carbon dioxide were obtained by mixing helium and carbon dioxide in a Matheson R700 gas proportioner. However, the low carbon dioxide concentrations required could not be accurately measured with the proportioner, and therefore, the gas composition was determined by gas chromatography. Analyses were performed on a Baseline Industries, Inc. 1030A gas chromatograph equipped with a 6'x1/8" SS Porapak QS 50/80 mesh column and a 6'x1/8" SS Molesieve 5A 40/60 mesh column. All functions of the chromatograph were controlled by a self-contained microprocessor which was interfaced with the MINC-11 computer. Late in this work premixed carbon dioxide-helium gases, having mole fractions of 0.00913, 0.0139, 0.0213, 0.0321, 0.0516, 0.0866 and 0.161, were purchased from Union Carbide Corp., Linde Division. The composition of each of the gas mixtures was determined chromatographically by standardization against pure carbon dioxide. The carbon dioxide partial pressure was calculated from the equation:

$$P/P_0 = Y_{CO_2} (P_a + 0.5\Delta P)/P_0 \quad (112)$$

where

P/P_0 = relative pressure,

P_0 = saturated CO_2 pressure at 0°C ,

Y_{CO_2} = mole fraction of CO_2 in the adsorption gas mixture,

P_a = barometric pressure,

ΔP = pressure drop across the char bed.

The adsorption of carbon dioxide onto the char was effected by immersing the sample tube in an ice-water bath. Examination of a typical isotherm indicated that equilibrium was attained within one hour. The ice-water bath was replaced by a glycerol bath, resistively heated to approximately 180°C , and the area of the desorption peak was obtained using MOMEN9. Calibration against 5.0 cm^3 of pure carbon dioxide yielded the quantity desorbed.

Reaction of Char

The char was allowed to react with carbon dioxide in the equipment indicated in Figure 5. The char sample tube was secured with quartz tubing in a Lindberg Sola Basic tube furnace. The furnace temperature was controlled with a Fisher Linear Temperature Programmer, Model 360. A platel II thermocouple was positioned adjacent to the exterior surface of the sample tube and its output was measured with a Dana Digital Voltmeter. A 3-way Whitey Switching valve was situated on the inlet side of the sample whereby either helium or carbon dioxide could be selected to pass through the char. The carbon dioxide and helium flow rates were controlled with a Nupro model 4 MG needle valve and a Matheson rotameter, respectively.

Figure 5. Apparatus for the Reaction of the Char Bed with Carbon Dioxide.

Prior to heating the char to reaction temperature, the needle valve controlling the carbon dioxide flow was adjusted to maintain a flowrate of 20 cm³/min. The switching valve was then positioned to admit helium, also at a 20 cm³/min flow rate. The furnace was heated to reaction temperature at a rate of 25C°/min and held one hour. At this temperature heat transfer to the char occurs mainly through radiation. The temperature inside the char was measured and found to agree with the temperature near the external surface of the tube. A Saron gas collection bag was affixed to the sample tube outlet and the carbon dioxide stream was placed back on line. The reaction was allowed to proceed for a specific length of time, usually 10-30 minutes, after which the switching valve was positioned again in favor of helium. The bag was disconnected and the oven and contents were allowed to cool to ambient temperature. The sample tube was weighed on a Mettler B5C 1000 balance to a precession of ±0.1 mg, the contents were gently tamped to the maximum bulk density and the new bed length was measured to the nearest millimeter. The total conversion based on weight loss was calculated according to:

$$X_w^i = \frac{W_0 - W_i}{FW_0} \quad (113)$$

where

X_w^i = ith conversion based on weight loss,

W_0 = initial weight of char,

W_i = weight of char after the ith incremental reaction,

F = fraction of carbon in char, $F = 0.856$.

The collected product gas was analyzed on the gas chromatograph as

previously described. Separation of components was readily achieved on the Porapak column. Only the product carbon monoxide and unreacted carbon dioxide were detected. The average of five analyses was used to calculate conversion, according to equations 114, 115 and 116. Equations 114 and 115, based on reaction stoichiometry, are developed in Appendix A.

$$X_g^i = \frac{-(\Delta N_C^i + \Delta N_C^{i-1})M}{FW_0} \quad (114)$$

$$\Delta N_C^i = \frac{-Q^i N_{CO_2}}{2 + Q^i} \quad (115)$$

$$N_{CO_2} = \frac{P\dot{V}t}{RT} \quad (116)$$

where

X_g^i = ith conversion based on gas analysis,

ΔN_C^i = moles of carbon consumed in ith incremental reaction,

M = atomic weight of carbon,

Q^i = mole ratio CO/CO₂ in product gas,

N_{CO_2} = moles of CO₂ passed through char bed during reaction,

P = ambient pressure,

T = ambient temperature,

$\dot{V}$ = volumetric flow rate measured at T,P

t = time,

R = gas constant.

Reaction Rate Determination

A schematic diagram of the apparatus used in the study of the carbon dioxide reaction kinetics is shown in Figure 6. Figure 7 gives the detailed view of the reactor. The reactor consisted of two concentric quartz tubes, O.D. 15 mm and 21 mm, around which was placed a Fisher Model 260F tube furnace. Within the innermost tube was suspended, by means of a long nichrome wire one end connected to a Cahn RG electrobalance, a micro platinum stirrup pan. A Welch Duo-Seal vacuum pump was used to evacuate the reactor and balance chamber. An inlet at the top of the reactor allowed the passage of gas downward through the inner tube and upward through the annular space. The gas was vented to the atmosphere at the top of the reactor. A Whitey 3-way valve allowed the selection of either a helium or carbon dioxide stream, and the flow was controlled by a Matheson rotameter. The furnace temperature was controlled by a Fisher Linear Temperature programmer, Model 360. A platinum II thermocouple was positioned inside the inner tube of the reactor, immediately adjacent to the platinum stirrup pan, and the thermocouple output was monitored on a Dana Digital Voltmeter. Output from the electrobalance was directed to either a Fisher Recordall Series 200P Chart recorder or to the amplifier input of the Digital Corp. MINC-11 digital computer. Data collection and reduction were performed with the aid of a computer program designated KINET2.²

The gravimetric method of measuring the rate of a gas-solid reaction simply entails the determination of the weight of the solid,

²Available from the Department of Chemical Engineering, Vanderbilt University.

Figure 6. Apparatus for the Determination of Reaction Rates.

Figure 7. Detail of the Reaction Used in the Determination of Reaction Rates.

exposed to the gaseous reactant under reacting conditions, as a function of time. The reaction was studied at temperatures of 800 to 1100°C in 50° increments.

Following calibration of the electrobalance, approximately 8-10 mg of char were loaded into the platinum stirrup. The reactor and balance chamber were evacuated to a pressure of about 100 Pa (1 mm Hg) and then were carefully filled with helium. A helium flow rate of 60 cm³/min was maintained while the char was heated to reaction temperature at a rate of 25°C/min. Following initialization of KINET2 and the recording of the initial char weight, carbon dioxide was introduced into the reactor, also at a 60 cm³/min flow rate. This flowrate was chosen to achieve the same gas velocity as was employed in the diffusivity measurements and in the conversion reactions. Data were collected with signal averaging and the char weight, conversion and rate were tabulated at regular time intervals, depending on the duration of the experiment.

CHAPTER V

RESULTS AND DISCUSSION

Gasification of coal takes place in two steps: (a) pyrolysis or devolatilization, to form a char composed mostly of carbon and ash (10), and (b) reaction of the char with gaseous reactants to form gaseous products and ash. Pyrolysis is accompanied by an increase in pore surface area and a decrease in radii of the pore size distribution. Table 2 shows the effects of pyrolysis on the specific areas and effective diffusion parameters for Wyodak coal heated in a helium atmosphere at a rate of 25°C/min to final temperatures of 1073, 1173, 1273, and 1373°K. Pyrolysis was accomplished by heating each sample of coal to its reaction temperature and holding it at that temperature for one hour after signs of off gases had ended. The second step of gasification along with the changes in surface area and effective diffusivity, and their influence upon the global reaction rate, is the topic presented in this work.

Four samples of coal char were obtained by heating raw coal (35/60 mesh) to each sample's reaction temperature of 1073°K, 1173°K, 1273°K, and 1373°K, respectively, at a rate of 25°C per minute under a stream of helium. The coals were held at their reaction temperature for one hour after signs of off gases had ended. Utilizing the chemical analysis of raw coal, given in Table 1, the amount of carbon in the char was estimated to be 85.6%. Incremental reaction with carbon dioxide pro-

TABLE 2

EFFECTS OF PYROLYSIS ON WYOMING SUBBITUMINOUS COAL

Pyrolysis Temperature (°K)	Weight Ratio (Char/Coal)	Ratio of Specific Area (Char/Coal)	Ratio of Bed Porosity (Char/Coal)	Ratio of N ₂ Diffusion Measured at 323°K (Char/Coal)
1073	.5605	1.46	-	0.27
1173	.5855	2.41	.937	0.45
1273	.5749	2.10	.904	0.56
1373	.5527	1.52	.896	0.81

duced continuous changes in the internal structure of the char and in the physical characteristics of the char bed, Tables 3-6. The initial char particle density of 2.08 g/cm^3 is consistent with previously reported values which fall in the range $1.9\text{-}2.1 \text{ g/cm}^3$ (70). Tables 3-6 demonstrate that the particle density, defined as the mass of the particle per volume of the particle, including pores and fissures, decreases with conversion.

The conversions listed in Tables 3-6 were calculated by methods based on weight loss (equation 113) and on analysis of the product gas mixture (equations 114-116). The disagreement between the two methods suggests further pyrolysis may have occurred during the time the char was heated to reaction temperature or during gasification. However, attempts to detect further pyrolysis or reaction products other than carbon monoxide failed. No plausible explanation for these inordinately low conversions, based on gas analysis, can be given. Henceforth, all conversions reported herein are based on weight loss.

Changes in pore structure incurred during gasification are summarized in Tables 7-10. The specific area, S , is defined as the total surface area per mass of carbon in the char, and E is the characteristic energy which increases with the fineness of pore structure. Graphs of the logarithmic form of equation 104, the Dubinin plot, were prepared for each conversion and examples are given in Figures 8-11. Best lines were obtained by the method of least-squares. The characteristic energy and the total pore volume, W_0 , were extracted from the slope and intercept,

TABLE 3

WYODAK COAL CHAR REACTED AT 1073°K PHYSICAL
CHARACTERISTICS OF THE CHAR BED AT VARIOUS CONVERSIONS

Conversion		Length (cm)	Bed Void Fraction	Bulk Density (g/cm ³)	Particle Density (g/cm ³)
Weight Loss	Gas Analysis				
0	-	7.20	0.414	1.22	2.08
0.0608	-	7.00	0.417	1.19	2.04
0.100	-	7.00	0.397	1.15	1.90
0.176	0.157	6.80	0.392	1.10	1.80
0.247	0.228	7.20	0.412	0.96	1.63
0.357	0.316	7.10	0.398	0.86	1.43
0.473	0.450	6.70	0.348	0.74	1.14
0.583	0.512	6.00	0.359	0.74	1.15
0.701	0.532	5.20	0.304	0.64	0.92
0.778	0.563	4.60	0.234	0.60	0.78
0.849	0.569	3.90	0.313	0.57	0.82
0.865	0.575	3.30	0.268	0.64	0.87
0.902	0.590	2.40	0.214	0.75	0.96
0.926	0.599	2.30	0.241	0.59	0.78

TABLE 4

WYODAK COAL CHAR REACTED AT 1173°K PHYSICAL
CHARACTERISTICS OF CHAR BED AT VARIOUS CONVERSIONS

Conversion		Length (cm)	Bed Void Fraction	Bulk Density (g/cm ³)	Particle Density (g/cm ³)
Weight Loss	Gas Analysis				
0.0	-	7.80	.375	1.25	2.02
0.0643	-	7.70	.350	1.21	1.86
0.130	-	7.70	.329	1.13	1.68
0.213	-	7.50	.316	1.07	1.56
0.314	.294	7.50	.350	0.96	1.48
0.448	-	6.40	.332	0.93	1.39
0.535	.540	6.10	.285	0.86	1.20
0.643	.627	5.80	.308	0.75	1.08
0.740	.745	5.60	.297	0.63	0.90
0.821	.854	4.75	.216	0.61	0.78
0.918	.922	3.40	.199	0.61	0.76

TABLE 5

WYODAK COAL CHAR REACTED AT 1273°K PHYSICAL
CHARACTERISTICS OF THE CHAR BED AT VARIOUS CONVERSIONS

Conversion		Length (cm)	Bed Void Fraction	Bulk Density (g/cm ³)	Particle Density (g/cm ³)
Weight Loss	Gas Analysis				
raw	coal	13.30	0.386	1.29	2.10
0	-	7.80	0.349	1.26	1.94
0.0530	0.0519	7.65	0.345	1.23	1.88
0.134	0.147	7.35	0.345	1.19	1.81
0.373	0.243	5.90	0.237	1.02	1.34
0.478	0.445	5.40	0.237	0.97	1.27
0.590	0.564	5.10	0.281	0.86	1.19
0.719	0.697	4.80	0.270	0.71	0.97
0.845	0.843	4.20	0.174	0.58	0.71
0.990	1.000	3.00	0.115	0.28	0.32

TABLE 6

WYODAK COAL CHAR REACTED AT 1373°K PHYSICAL
CHARACTERISTICS OF THE CHAR BED AT VARIOUS CONVERSIONS

Conversion		Length (cm)	Bed Void Fraction	Bulk Density (g/cm ³)	Particle Density (g/cm ³)
Weight Loss	Gas Analysis				
raw	coal	12.30	0.374	1.27	2.04
0.0	-	7.40	0.335	1.17	1.76
0.0539	-	7.40	0.310	1.12	1.62
0.125	-	7.20	0.299	1.08	1.53
0.255	0.233	5.50	0.293	1.10	1.55
0.388	0.380	5.00	0.297	1.03	1.47
0.530	0.521	4.45	0.282	0.95	1.32
0.733	-	4.00	0.233	0.72	0.94
0.960	0.861	2.50	0.276	0.32	0.44

TABLE 7

WYODAK COAL CHAR REACTED AT 1073°K SPECIFIC
AREAS AND PORE CHARACTERISTICS AT VARIOUS CONVERSIONS

Conversion	Specific Area (m ² /g)	Mean Radius (nm)	E(KJ/mole)	W _o (cm ³ /g)
0	242	0.710	11.0	0.111
0.0608	261	0.698	11.6	0.091
0.100	273	0.705	11.3	0.096
0.176	289	0.707	11.2	0.102
0.247	280	0.706	11.2	0.099
0.357	293	0.713	10.9	0.105
0.473	281	0.714	11.1	0.100
0.583	209	0.693	11.9	0.071
0.701	183	0.679	12.7	0.062
0.778	429	0.735	9.95	0.157
0.849	444	0.733	10.1	0.163
0.865	312	0.698	11.6	0.109
0.902	424	0.718	10.7	0.152
0.926	529	0.730	10.2	0.194

TABLE 8

WYODAK COAL CHAR REACTED AT 1173°K SPECIFIC AREAS
AND PORE CHARACTERISTICS AT VARIOUS CONVERSIONS

Conversion	Specific Area (m ² /g)	Mean Radius (nm)	E(KJ/mole)	W _o (cm ³ /g)
0	399	0.707	11.2	0.143
0.643	403	0.726	10.4	0.146
0.130	318	0.714	10.9	0.113
0.213	459	0.733	10.1	0.168
0.314	309	0.727	10.3	0.112
0.448	395	0.725	10.4	0.143
0.535	424	0.717	10.7	0.155
0.643	382	0.741	9.70	0.142
0.740	251	0.709	11.1	0.089
0.821	387	0.732	10.1	0.141
0.918	358	0.729	10.2	0.131

TABLE 9

WYODAK COAL CHAR REACTED AT 1273°K SPECIFIC AREAS
AND PORE CHARACTERISTICS AT VARIOUS CONVERSIONS

Conversion	Specific Area (m ² /g)	Mean Radius (nm)	E(KJ/mole)	W ₀ (cm ³ /g)
raw	150	0.703	11.4	0.055
0	349	0.718	10.7	0.125
0.0530	394	0.731	10.2	0.144
0.134	269	0.709	11.1	0.095
0.373	653	0.752	9.30	0.246
0.478	634	0.750	9.40	0.238
0.590	579	0.747	9.50	0.216
0.719	661	0.743	9.60	0.246
0.845	717	0.742	9.70	0.266
0.990	-	0.717	10.7	0.945

TABLE 10

WYODAK COAL CHAR REACTED AT 1373°K SPECIFIC AREAS
AND PORE CHARACTERISTICS AT VARIOUS CONVERSIONS

Conversion	Specific Area (m ² /g)	Mean Radius (nm)	E(KJ/mole)	W _o (cm ³ /g)
raw	181	0.719	10.6	0.068
0	252	0.719	10.7	0.091
0.0539	241	0.698	11.7	0.084
0.125	392	0.745	9.60	0.146
0.255	362	0.738	9.90	0.133
0.388	386	0.737	9.90	0.142
0.530	446	0.737	9.90	0.164
0.733	524	0.733	10.1	0.192
0.960	911	0.733	10.0	0.334

Figure 8. Dubinin Plot for the Adsorption of Carbon Dioxide on Wyodak Coal Char reacted at 1073°K.

Figure 9. Dubinin Plot for the Adsorption of Carbon Dioxide on Wyodak Coal Char Reacted at 1173°K.

Figure 10. Dubinin Plot for the Adsorption of Carbon Dioxide on Wyodak Coal Char Reacted at 1273°K.

Figure 11. Dubinin Plot for the Adsorption of Carbon Dioxide on Wyodak Coal Char reacted at 1373°K.

respectively. The specific surface area and the mean pore radius, $\bar{r}$, were then calculated using equations 110 and 111. Pore volume distribution curves were constructed using equation 108, and are shown in Figures 12-15.

The Dubinin plots occasionally reveal a slight downward curvature in the graphs at high relative pressures. The literature contains many examples where downward or upward curvature occurs, and in some cases two or more distinct linear regions are found (10,13,19,44,77,78,92). The deviation from linearity is not surprising considering the empirical nature of the Dubinin-Polanyi equation. However, even if nonlinearity is observed, the DP theory is still useful in the comparisons of micropore structures provided all measurements are taken under the same conditions (3). The nonlinearities in the Dubinin plots are small and were neglected.

As seen in Tables 7-10, the micropores in coal char are small indeed, their diameters being only several times larger than the kinetic diameter of the carbon dioxide molecule. In his study of various coals and coal chars Medek (81) found mean pore radii ranging from 0.74 to 0.78 nm and characteristic energies between 9.3 and 11.5 KJ/mole. Debelak and Schrodtt (21) utilized the methods of Medek and Cranston and Inkley (20) on Kentucky coal and obtained similar distributions, though the Cranston and Inkley treatment consistently produced pore radius distributions slightly broadened in favor of larger radii. While other works have also reported pore radius distributions (10,20,32,54,55,103) the work presented here attempts to correlate pore radius with conversion.

An increase in pore radius, accompanied by a decrease in

Figure 12. Pore Volume Distribution of Wyodak Coal Char Reacted at 1073°K.

Figure 13. Pore Volume Distribution of Wyodak Coal Char Reacted at 1173°K.

Figure 14. Pore Volume Distribution of Wyodak Coal Char Reacted at 1273°K.

Figure 15. Pore Volume Distribution of Wyodak Coal Char Reacted at 1373°K.

characteristic energy and an increase in particle void fraction, would be expected in a chemical rate controlled reaction where gasification of pore walls occurs uniformly throughout the particle. On the contrary, the relative constancy of the mean pore radius, characteristic energy and particle porosity indicates that reaction occurred mainly near the surface thereby leaving the reactive core relatively unchanged. Consistent with the above, the distributions in pore radius indicate only a general broadening and tailing toward larger radii. Thus, significant mass transfer intrusion may occur.

Specific areas obtained in this work are similar to those previously reported. However, due to diminishing sample size, desorption isotherms at high conversions were difficult to obtain and specific areas obtained at greater than 70% conversion are not reliable. Nevertheless, local maxima at conversions between 0.35 and 0.5 are indicated in Tables 7-10. Hashimoto, et al. (48) and Dutta, et al. (25) reported similar maxima during the gasification of various chars with carbon dioxide and steam. In both cases the area-conversion data were accompanied by corresponding maxima in the reaction rates. It is very likely that the rate maxima documented by various workers (1,14,71,117) are a direct consequence of maxima in surface area. Bhatia's model for surface area is conveniently applied by recasting equation 56 in the form:

$$\left(\frac{S}{1-X}\right)^2 = S_0^2 - \psi S_0^2 \ln(1-X) \quad (117)$$

Figures 16-19 show the specific area data for each sample of char plotted according to equation 117. Least-squares analysis yielded an initial specific area of $225 \text{ m}^2/\text{g}$ and a structural parameter of 6.99 for the sample reacted at 1073°K , an initial specific area of $300 \text{ m}^2/\text{g}$ and a

Figure 16. Plot of Bhatia's Model for Specific Areas for Wyodak Coal Char Reacted at 1073°K.

Figure 17. Plot of Bhatia's Model for Specific Area for Wyodak Coal Char Reacted at 1173°K.

Figure 18. Plot of Bhatia's Model for Specific Area for Wyodak Coal Char Reacted at 1273°K.

Figure 19. Plot of Bhatia's Model for Specific Area for Wyodak Coal Char Reacted at 1373°K.

structural parameter of 8.65 for the char sample reacted at 1173°K, an initial specific area of 301 m²/g and a structural parameter of 23.6 for the char sample reacted at 1273°K, and an initial specific area of 246 m²/g and a structural parameter of 11.2 for the char sample reacted at 1373°K. In comparison, the measured initial specific areas are 242 m²/g, 399 m²/g, 349 m²/g, and 252 m²/g for the char samples reacted at 1073, 1173, 1273, and 1373°K, respectively. When the structural parameter has a value greater than 2.0, there is a maximum in the area-conversion curve. Bhatia's model has not been widely tested, and the range of conversion over which it applies is dependent on the adsorbent. The data of Hashimoto et al. (48) were correlated to a conversion of 0.75 in one char and to a conversion of 0.3 in another char. The data, herein, are correlated by equation 59 up to a conversion of 0.5.

The diffusion parameters, D_e/r_c^2 , and the adsorption equilibrium constants, K_a , determined by Equation 84 and 95, respectively, for the diffusion of carbon dioxide, carbon monoxide, nitrogen, and methane in helium for each char sample are displayed in Tables 11-26. The diffusion parameter and the adsorption equilibrium constants were determined for each char sample at each conversion at temperatures of 323, 373, 423, 473, and 523 K. Examination of the data reveals an increase in the diffusion parameter with conversion and an inverse relationship between the adsorption constant and the diffusion parameter. A similar effect was observed for the room temperature diffusion of nitrogen through coal chars at various conversions (19,22). Intuitively, as the pore structure becomes more open, or as the reactive core decreases in diameter, the resistance to mass transfer decreases.

TABLE 11

WYODAK CCAL CHAR REACTED AT 1073°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS FOR
CARBON DIOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	244	36.7	17.3	11.8	9.79	1.21	5.16	8.36	11.1	12.8
0.061	190	-	19.5	13.1	10.1	1.65	-	5.53	7.79	10.1
0.100	102	-	34.5	11.7	9.74	2.44	-	4.37	7.82	8.57
0.176	94.1	29.3	16.7	10.7	9.11	2.30	5.05	6.02	9.57	10.3
0.247	71.8	23.7	14.4	9.87	8.82	2.73	6.83	6.51	10.6	9.51
0.357	56.7	20.5	11.9	8.88	7.99	3.48	6.08	11.8	13.0	12.4
0.473	41.9	17.8	11.4	8.08	7.36	4.12	6.55	8.53	14.9	15.1
0.583	31.4	15.2	11.0	8.95	7.77	7.64	11.3	12.6	17.3	21.4
0.701	26.1	13.6	-	8.50	-	9.01	13.7	-	21.5	-
0.778	24.1	12.8	8.22	8.71	7.94	11.5	32.0	55.9	48.4	48.1
0.849	34.4	24.3	19.9	11.5	10.4	13.9	54.7	56.5	71.2	64.3
0.865	27.2	25.7	16.2	12.5	11.2	20.4	79.4	74.2	70.3	78.2
0.902	30.3	31.4	17.9	16.0	14.8	25.3	103	80.6	79.0	99.3
0.926	46.9	27.6	19.2	17.1	15.2	52.6	99.3	92.4	105	129

TABLE 12

WYODAK COAL CHAR REACTED AT 1073°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS FOR
CARBON MONOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	24.8	9.89	7.47	6.08	5.53	9.93	40.0	65.9	93.7	109
0.061	21.9	8.87	7.85	6.59	7.84	15.5	58.8	71.5	89.8	65.4
0.100	14.5	9.30	7.13	6.16	5.66	26.4	52.4	78.6	97.3	76.0
0.176	13.4	8.92	7.10	6.17	5.87	31.9	55.8	81.3	100.0	66.2
0.247	11.2	8.62	6.99	6.19	-	38.5	57.2	79.0	88.5	-
0.357	11.2	8.29	6.93	6.10	5.87	40.2	63.3	80.3	93.2	77.4
0.473	9.95	7.95	6.98	7.08	5.76	46.4	65.0	78.8	93.2	67.1
0.583	11.1	8.79	8.12	7.31	6.64	52.8	74.3	83.6	93.2	86.7
0.701	11.2	9.66	8.27	7.43	7.05	57.9	72.7	87.0	101	94.7
0.778	11.9	10.6	9.43	8.85	7.55	57.5	70.6	81.5	87.5	91.6
0.849	19.6	14.3	12.0	11.2	9.93	79.9	86.3	93.4	103	123
0.865	23.8	16.3	13.9	12.4	11.2	108	85.8	91.7	105	119
0.902	29.7	20.6	17.9	16.1	14.9	112	89.0	102	115	130
0.926	25.1	21.5	19.2	17.4	15.9	130	92.1	107	126	149

TABLE 13

WYODAK COAL CHAR REACTED AT 1073°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR NITROGEN IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	17.6	9.02	7.10	5.97	5.47	13.3	46.9	74.0	96.7	114
0.061	16.4	8.42	7.42	6.53	7.47	20.1	63.5	76.1	91.7	81.4
0.100	11.8	8.53	6.96	5.99	5.39	35.2	61.7	83.0	101	116
0.176	11.0	8.19	6.90	6.11	5.55	40.6	67.2	86.5	103	118
0.247	9.84	8.06	6.88	6.88	-	46.1	65.1	81.7	85.1	-
0.357	9.73	7.89	6.81	6.09	5.52	49.5	68.1	83.4	97.1	108
0.473	9.23	7.75	6.89	6.07	5.47	52.4	69.6	81.1	93.9	106
0.583	10.8	8.56	8.05	7.24	6.50	56.8	76.6	83.7	95.3	107
0.701	11.0	9.62	8.24	7.44	6.90	62.1	75.0	88.9	101	111
0.778	13.4	10.9	9.46	8.69	7.71	68.6	73.9	83.1	89.4	101
0.849	16.3	14.4	12.3	11.2	10.3	67.1	88.1	89.7	104	121
0.865	21.8	16.4	13.8	12.4	11.3	93.0	91.1	89.7	106	118
0.902	27.4	20.3	17.8	16.2	14.9	107	89.3	102	115	134
0.926	24.4	21.4	19.2	17.4	15.8	58.6	91.7	109	126	149

TABLE 14

WYODAK COAL CHAR REACTED AT 1073°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR METHANE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2 (s^{-1})$				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	44.7	14.9	9.41	6.80	5.99	3.86	14.2	33.8	64.4	82.9
0.061	66.2	12.5	-	7.26	6.68	5.95	31.5	-	69.1	82.7
0.100	41.3	15.7	8.99	6.81	5.61	10.4	27.7	53.8	76.2	99.2
0.176	38.5	14.2	8.36	6.62	5.74	14.5	36.2	58.7	83.3	99.9
0.247	31.0	12.5	8.05	6.54	-	19.8	37.8	62.2	76.8	-
0.357	5.87	10.9	7.73	6.36	5.69	68.7	44.2	68.8	84.6	97.4
0.473	19.6	9.54	7.46	6.27	5.52	28.3	50.7	68.5	83.7	96.1
0.583	17.3	9.69	8.30	7.33	6.49	31.2	60.8	74.4	85.5	99.7
0.701	14.3	10.2	8.45	7.41	6.86	38.8	62.7	79.6	92.3	100
0.778	17.7	12.0	9.14	8.75	7.71	49.8	67.2	70.4	83.0	89.5
0.849	23.6	16.3	12.5	11.1	9.86	60.7	86.8	86.2	96.7	113
0.865	28.5	20.6	13.9	12.4	11.2	78.5	102	81.6	97.0	111
0.902	35.3	20.5	-	15.9	14.6	92.2	73.2	-	101	116
0.926	32.9	21.9	19.2	17.4	15.7	173	84.3	100	118	134

TABLE 15

WYODAK COAL CHAR REACTED AT 1173°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON DIOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^9 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	-	23.0	11.3	6.52	4.78	-	4.78	9.87	11.0	13.4
0.0643	60.7	18.0	8.00	4.96	4.29	2.04	6.40	14.0	22.8	15.7
0.130	52.1	14.9	7.06	4.44	3.90	2.63	8.48	16.9	19.2	29.6
0.213	41.0	23.9	11.2	6.47	4.91	3.01	15.5	23.3	60.1	48.4
0.314	43.6	13.2	7.95	4.62	3.63	3.09	9.33	27.7	26.2	32.9
0.448	35.5	16.9	10.0	5.16	3.96	4.59	14.6	54.9	44.3	38.2
0.535	24.2	16.2	9.23	4.49	3.81	6.79	39.2	57.5	45.5	43.6
0.643	35.3	15.8	9.07	7.08	5.69	17.6	67.4	173	272	367
0.740	25.5	12.2	8.35	6.46	5.69	34.4	123	230	291	331
0.821	22.2	11.9	8.51	6.83	5.15	41.0	131	194	269	265
0.918	20.1	12.6	10.4	8.74	8.13	69.1	153	193	295	454

TABLE 16

WYODAK COAL CHAR REACTED AT 1173°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON MONOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2 (s^{-1})$				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	9.86	5.42	3.93	3.28	2.79	14.9	39.0	68.8	95.1	120
0.0643	8.63	5.19	3.86	3.26	3.25	18.9	39.2	69.8	89.7	92.9
0.130	7.88	4.69	3.48	3.05	2.72	22.0	47.4	76.3	94.1	114
0.213	7.14	6.68	4.94	3.28	2.84	29.9	89.8	122	112	118
0.314	7.67	4.60	3.89	3.24	2.88	24.7	60.5	82.1	103	113
0.448	7.36	6.68	4.50	3.97	3.41	41.0	57.0	88.0	93.2	125
0.535	5.88	6.96	4.55	3.88	3.52	47.1	125	72.8	100	108
0.643	11.0	8.06	6.44	5.49	4.95	123	164	197	216	333
0.740	4.87	7.79	6.63	4.57	5.18	167	170	203	153	349
0.821	10.8	8.44	7.05	6.10	6.14	124	140	161	218	379
0.918	12.7	8.94	8.03	7.53	7.63	108	97.4	128	183	336

TABLE 17

WYODAK COAL CHAR REACTED AT 1173°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR NITROGEN IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	7.36	4.80	3.70	3.17	2.74	21.7	47.7	76.3	101	126
0.0643	6.74	4.61	3.67	3.17	2.87	24.0	49.2	75.8	95.7	113
0.130	6.08	4.25	3.31	2.98	2.71	31.0	55.8	83.1	99.2	119
0.213	5.53	5.91	4.45	3.22	2.77	39.5	84.3	114	113	119
0.314	6.00	4.50	3.79	3.24	2.89	40.4	67.1	86.5	97.4	124
0.448	5.98	6.12	4.43	3.88	3.40	48.8	66.9	90.3	109	130
0.535	9.72	6.29	4.39	3.88	3.41	110	122	88.4	100	119
0.643	9.94	7.84	6.23	5.43	4.78	127	158	182	202	299
0.740	9.58	7.40	6.28	4.09	4.87	137	159	185	124	330
0.821	10.1	8.11	6.82	5.17	3.89	120	133	151	154	125
0.918	12.0	8.59	7.86	7.60	7.37	95.5	90.9	123	186	279

TABLE 18

WYODAK COAL CHAR REACTED AT 1173°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR METHANE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
0	16.4	8.02	5.04	3.77	3.02	6.38	15.0	35.1	61.9	92.4
0.0643	17.0	7.81	4.82	3.63	3.53	8.20	19.6	41.5	67.0	77.4
0.130	18.7	7.20	4.42	3.37	2.83	10.6	22.2	47.6	70.2	97.2
0.213	16.9	6.88	6.26	4.14	2.96	12.9	34.3	92.1	111	102
0.314	19.3	7.09	4.57	3.51	2.99	14.2	37.3	59.8	86.3	106
0.448	17.5	10.2	5.48	4.13	3.52	22.3	32.5	81.0	90.5	114
0.535	19.2	9.84	4.73	3.99	3.47	34.2	97.5	77.1	88.0	105
0.643	16.5	10.0	7.31	6.09	5.18	62.6	139	193	215	254
0.740	14.1	9.16	7.11	3.97	3.61	81.8	158	187	101	107
0.821	7.80	5.72	4.38	4.21	3.86	41.3	63.3	82.7	86.8	95.1
0.918	14.7	8.40	7.15	6.31	5.66	102	74.6	86.4	99.4	104

TABLE 19

WYODAK COAL CHAR REACTED AT 1273°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON DIOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	30.4	8.41	2.54	1.68	1.25	2.36	11.8	42.0	88.9	139
0	-	19.3	9.54	9.78	7.22	-	5.44	7.81	19.2	33.9
0.053	-	15.6	12.4	7.57	5.91	-	8.78	31.5	56.2	105
0.134	46.0	23.4	11.3	7.47	5.83	2.97	15.5	38.7	92.7	157
0.373	37.1	12.0	10.5	7.06	5.57	4.47	14.8	58.3	116	177
0.478	36.1	19.3	11.1	7.61	6.04	5.21	33.3	72.9	129	202
0.590	58.9	18.3	10.7	7.78	6.32	3.39	36.9	125	222	309
0.719	31.9	16.0	10.4	7.95	6.57	7.09	43.9	168	207	269
0.845	27.6	13.4	9.81	8.38	7.00	18.3	75.1	145	188	256
0.990	7.28	7.87	6.22	5.71	5.41	56.7	121	153	258	409

TABLE 20

WYODAK COAL CHAR REACTED AT 1273°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON MONOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	2.81	2.04	1.49	1.21	1.04	27.8	59.0	108	143	177
0	8.92	8.28	6.05	4.78	4.06	18.5	63.1	118	190	229
0.053	14.1	8.19	5.96	4.72	4.24	28.4	72.4	135	193	278
0.134	13.2	7.91	6.52	5.58	4.16	33.3	92.3	152	222	301
0.373	12.5	8.07	6.16	5.13	4.62	52.0	108	145	165	189
0.478	13.3	8.47	6.77	5.64	5.00	57.1	124	167	186	228
0.590	14.4	9.05	7.44	6.03	5.42	24.8	147	188	244	320
0.719	9.36	6.83	6.12	5.17	5.58	66.9	79.6	107	117	239
0.845	10.8	7.12	6.10	7.33	6.80	91.8	73.3	93.7	152	200
0.990	7.17	5.79	5.32	5.04	4.93	82.7	90.1	112	175	268

TABLE 21

WYODAK COAL CHAR REACTED AT 1273°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR NITROGEN IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s^{-1})				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	2.40	1.87	1.43	1.18	1.05	41.6	72.4	105	148	171
0	6.51	7.17	5.39	4.54	4.03	27.4	77.0	134	188	256
0.053	11.1	7.18	5.53	4.45	4.01	39.7	89.6	139	210	312
0.134	10.7	7.20	5.70	4.82	4.12	47.4	102	173	236	328
0.373	10.6	7.34	5.81	4.93	4.49	64.6	114	140	181	187
0.478	11.1	7.93	6.37	5.53	4.75	83.3	91.1	141	183	226
0.590	11.6	8.29	7.12	6.15	5.10	53.4	153	178	244	291
0.719	7.72	6.47	5.44	5.09	4.55	59.9	88.0	96.6	117	143
0.845	10.3	6.85	6.01	7.20	6.17	74.8	72.8	92.6	150	217
0.990	7.06	5.64	5.34	5.30	4.96	80.9	98.2	113	196	284

TABLE 22

WYODAK COAL CHAR REACTED AT 1273°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR METHANE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s^{-1})				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	3.61	2.47	1.67	1.29	1.08	13.4	29.7	73.8	116	150
0	13.5	10.4	6.96	5.37	4.48	10.4	29.3	63.2	111	166
0.053	13.6	10.3	6.98	5.26	4.38	12.3	39.8	77.5	129	193
0.134	13.1	10.5	7.52	5.61	4.45	13.7	35.2	87.6	149	192
0.373	20.4	10.6	7.17	5.66	4.55	20.7	57.9	101	134	154
0.478	21.0	10.9	7.95	6.17	5.16	23.4	68.7	117	160	176
0.590	14.7	11.5	8.54	6.59	5.54	59.2	75.5	131	173	217
0.719	17.2	8.88	5.95	6.39	5.44	48.2	69.4	83.1	150	160
0.845	15.5	8.97	5.91	6.16	5.14	51.7	74.2	71.6	88.5	91.1
0.990	7.28	5.70	5.05	4.47	3.99	58.8	72.6	87.8	103	120

TABLE 23

WYODAK COAL CHAR REACTED AT 1373°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON DIOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	22.2	8.02	4.03	2.59	2.01	3.46	14.7	53.3	153	300
0	30.8	20.2	9.54	6.29	5.91	3.59	8.36	33.1	54.9	85.7
0.0539	37.8	20.5	10.1	6.53	5.05	2.87	12.3	34.8	83.5	146
0.125	51.5	21.7	10.7	6.81	5.26	3.31	10.5	27.9	63.5	124
0.255	53.7	21.8	11.8	8.21	6.32	5.22	21.2	58.8	130	234
0.388	56.3	22.4	11.8	8.47	6.69	5.70	14.8	58.6	131	202
0.530	52.5	16.2	10.1	8.86	7.03	4.38	30.7	85.9	124	278
0.733	42.5	16.9	10.6	8.94	7.26	5.89	30.0	82.0	149	206
0.960	21.0	11.5	9.05	8.26	7.32	58.4	632	-	-	-

TABLE 24

WYODAK COAL CHAR REACTED AT 1373°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR CARBON MONOXIDE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s^{-1})				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	3.39	2.88	2.07	2.13	1.05	45.0	66.8	134	258	202
0	9.92	7.07	5.46	4.64	4.78	28.4	64.4	107	188	530
0.0539	11.3	7.32	5.62	4.51	4.19	33.6	73.2	113	157	236
0.125	12.4	7.66	5.49	4.52	4.19	29.3	67.6	103	149	212
0.255	14.1	9.36	7.29	5.81	4.90	37.4	87.6	137	180	212
0.388	13.9	9.68	7.49	6.29	5.58	36.8	76.5	123	151	209
0.530	12.1	7.90	7.67	6.25	5.65	47.8	77.7	109	164	227
0.733	12.7	8.32	7.27	7.02	6.36	46.6	74.8	95.7	128	176
0.960	9.27	7.91	7.07	6.40	5.75	124	259	888	-	-

TABLE 25

WYODAK COAL CHAR REACTED AT 1373°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR NITROGEN IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e/r_c^2$ (s ⁻¹)				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	2.49	2.16	1.99	1.42	1.56	55.7	89.2	144	171	289
0	7.87	5.89	5.15	3.82	3.64	39.4	79.9	123	150	240
0.0539	9.25	6.45	5.17	4.31	3.91	42.4	88.9	124	160	225
0.125	9.68	6.70	5.43	4.30	4.09	43.2	80.3	113	145	201
0.255	11.7	8.34	6.04	4.90	4.19	55.2	97.4	108	135	158
0.388	12.1	8.81	6.32	5.79	5.03	41.3	80.2	87.7	140	175
0.530	10.7	7.47	7.01	5.62	5.07	50.6	78.8	98.4	152	172
0.733	11.2	7.87	7.16	6.55	5.84	49.3	75.9	94.2	112	145
0.960	9.24	7.89	7.07	6.44	5.81	122	258	876	-	-

TABLE 26

WYODAK COAL CHAR REACTED AT 1373°K DIFFUSION PARAMETERS
AND ADSORPTION EQUILIBRIUM CONSTANTS
FOR METHANE IN HELIUM

Conversion	Adsorption Constant, K_a					Diffusion Parameter, $10^3 D_e / r_c^2$ (s^{-1})				
	323°K	373°K	423°K	473°K	523°K	323°K	373°K	423°K	473°K	523°K
raw	4.12	3.07	2.48	1.70	0.96	20.7	53.3	98.6	160	152
0	11.5	7.37	5.67	4.54	4.52	22.0	60.5	92.9	128	220
0.0539	14.8	8.50	6.23	4.74	4.14	22.1	48.3	79.0	121	156
0.125	16.9	9.23	6.22	4.84	4.28	16.0	43.5	84.4	121	165
0.255	19.5	11.1	8.18	5.80	4.72	18.2	56.8	92.5	122	127
0.388	20.2	10.9	7.97	6.99	5.53	17.5	48.7	90.2	130	157
0.530	18.4	12.0	8.96	6.99	6.22	25.8	49.1	95.1	177	214
0.733	19.2	10.5	8.75	7.92	7.12	25.3	65.2	105	139	208
0.960	12.2	8.40	7.12	6.57	5.76	90.3	213	405	-	-

Walker, et al. studied the diffusion of methane in coals and determined that diffusion is activated (83,86,120,123). Two models were proposed to explain the influence of temperature. In the occluded gas model, the diffusion rate is proportional to the concentration gradient of the adsorbed gas. Diffusion occurs predominantly along the pore walls and is governed by Arrhenius-type expression:

$$\frac{D_e}{r_c^2} = \frac{D_e}{r_c^2} \exp(-\Delta H_o^\ddagger / RT) \quad (118)$$

where

D_e/r_c^2 = diffusivity of some temperature, T,

$(D_e/r_c^2)_o$ = frequency factor,

$\Delta H_o^\ddagger$ = diffusion activation enthalpy,

R = gas constant,

T = absolute temperature.

In the adsorption-free gas model diffusion occurs via "free" molecules in the gas phase concurrent with adsorption-desorption on the pore walls. The diffusion rate is proportional to the concentration gradients in the gas phase. Application of a Langmuir isotherm for the adsorbed gas gave the overall temperature dependence of equation 119:

$$\frac{D_e}{r_c^2} = \frac{(D_e/r_c^2)_o \exp(-\Delta H_o^\ddagger / RT)}{\epsilon + C_s K_o \exp(-\Delta H_o / RT)} \quad (119)$$

where

ϵ = particle porosity,

C_s = concentration of adsorbed gas at saturation,

K_o = equilibrium constant pre-exponential factor,

ΔH_o = enthalpy of adsorption.

Two important limiting cases occur. At low temperature and high pressure the amount of adsorbed gas is large, so ϵ is small compared to $C_s K_o \exp(-\Delta H_o/RT)$ and equation 119 simplifies to:

$$\frac{D_e}{r_c^2} = \frac{D_e/r_c^2)_o}{C_s K_o} \exp [-(\Delta H_o^\ddagger - \Delta H_o)/RT] \quad (120)$$

Conversely, at high temperature and low pressures the quantity of adsorbed gas is small and equation 119 reduces to:

$$\frac{D_e}{r_c^2} = \frac{D_e/r_c^2)_o}{\epsilon} \exp(-\Delta H_o^\ddagger/RT) \quad (121)$$

Hence, in the adsorption-free gas model, an Arrhenius-type plot of $\ln D_e$ against $1/T$ will not be linear over a large temperature range.

Arrhenius plots for carbon dioxide, carbon monoxide, nitrogen and methane diffusing through char at 0.13 conversion are given in Figures 20-23. Similar plots (not given) were constructed for the char at various partial conversions. To extrapolate the data to reaction temperatures (800-1100°C) the data obtained at 100°C or greater were correlated with the high temperature limit given by equation 121. The resulting Arrhenius parameters are listed in Tables 27-30. For all gases the activation energy generally decreases with conversion, for char reacted at 1073K and 1173K. For chars reacted at 1273K and 1373K, activation energies generally decrease for nitrogen, carbon monoxide, and methane. However, for carbon dioxide there is an increase in activation energy at low conversion followed by a decrease at higher conversions. Patel, et al. (86) observed a decrease in the diffusion of methane through various activated anthracite coal. For comparison, Nandi and Walker (83) obtained diffusion activation energies for diffusion

Figure 20. Arrhenius Plot for Nitrogen Diffusion Parameters at 0.13 Conversion for Wyodak Coal Char Reacted at 1173°K.

Figure 21. Arrhenius Plot for Methane Diffusion Parameters at 0.13 Conversion for Wyodak Coal Char Reacted at 1173°K.

Figure 22. Arrhenius Plot for Carbon Monoxide Diffusion Parameters at 0.13 Conversion for Wyodak Coal Char Reacted at 1173°K.

Figure 23. Arrhenius Plot for Carbon Dioxide Diffusion Parameters at 0.13 Conversion for Wyodak Coal Char Reacted at 1173°K.

TABLE 27

WYODAK COAL CHAR REACTED AT 1073°K ARRHENIUS PARAMETERS
FOR DIFFUSION OF CARBON DIOXIDE, CARBON
MONOXIDE, NITROGEN, AND METHANE

Conversion	CO ₂		CO		N ₂		CH ₄	
	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)
0.0	9.94	0.13	11.0	1.46	9.68	1.09	19.6	8.26
0.061	12.9	0.20	6.18	0.42	5.36	0.35	10.7	1.00
0.100	9.16	0.070	11.2	1.79	6.89	0.57	13.8	2.46
0.176	10.5	0.13	9.84	1.27	6.08	0.48	11.1	1.35
0.247	8.64	0.082	7.29	0.59	5.40	0.36	11.8	1.64
0.357	9.78	0.14	7.15	0.60	5.03	0.34	8.54	0.72
0.473	9.70	0.15	9.88	0.40	4.87	0.32	6.95	0.48
0.583	6.97	0.10	3.34	0.22	4.25	0.28	5.29	0.33
0.701	7.33	0.13	4.69	0.33	4.13	0.29	5.13	0.33
0.778	3.93	0.13	3.32	0.20	2.66	0.18	3.97	0.23
0.849	2.40	0.12	2.84	0.22	3.82	0.28	3.85	0.27
0.865	-	-	3.58	0.26	-	-	6.00	0.45
0.902	3.83	0.24	4.15	0.33	-	-	4.93	0.36
0.926	6.14	0.52	5.15	0.47	5.19	0.48	5.03	0.42

TABLE 28

WYODAK COAL CHAR REACTED AT 1173°K ARRHENIUS PARAMETERS
FOR DIFFUSION OF CARBON DIOXIDE, CARBON MONOXIDE,
NITROGEN, AND METHANE

Conversion	CO ₂		CO		N ₂		CH ₄	
	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)
0.0	10.7	0.171	14.6	3.89	12.3	2.30	19.2	7.84
0.643	20.6	4.61	11.7	1.64	10.9	1.52	16.5	3.97
0.13	16.5	1.44	11.5	1.78	9.41	1.10	15.9	3.95
0.213	14.5	1.65	9.11	1.22	7.54	0.793	15.7	5.40
0.314	16.6	1.67	10.5	1.47	7.48	0.693	14.1	3.00
0.448	16.2	2.63	7.72	0.719	6.92	0.635	12.2	2.05
0.535	12.2	1.12	6.03	0.436	5.36	0.401	7.92	0.672
0.643	18.3	27.2	6.27	1.23	5.35	0.887	9.52	2.52
0.740	10.7	4.18	5.17	1.01	6.05	1.19	9.56	3.04
0.821	8.17	1.91	7.12	1.51	2.24	0.277	5.81	0.388
0.918	12.5	7.48	12.87	5.56	7.60	1.30	3.74	0.250

TABLE 29

WYODAK COAL CHAR REACTED AT 1273°K ARRHENIUS PARAMETERS
FOR DIFFUSION OF CARBON DIOXIDE, CARBON
MONOXIDE, NITROGEN, AND METHANE

Conversion	CO ₂		CO		N ₂		CH ₄	
	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\ddagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)
raw	29.2	139	13.2	4.08	10.1	1.86	17.7	9.90
0.0	20.4	3.37	17.8	16.5	15.5	9.77	19.6	16.0
0.053	26.3	46.6	15.9	11.3	14.1	7.88	19.2	17.0
0.134	27.8	103	15.2	10.8	13.5	7.45	19.2	18.3
0.373	26.9	99.4	8.82	1.59	7.54	1.16	14.2	4.81
0.478	25.1	79.1	9.30	2.10	9.76	2.17	14.3	5.77
0.590	23.0	71.3	8.36	2.10	11.3	4.36	9.62	1.95
0.719	19.0	25.2	7.87	1.10	5.73	0.519	8.84	1.23
0.845	18.1	19.9	11.2	2.58	12.0	3.21	3.79	0.224
0.990	13.2	7.71	8.06	1.39	8.63	1.72	5.00	0.371

TABLE 30

WYODAK COAL CHAR REACTED AT 1373°K ARRHENIUS PARAMETERS
FOR DIFFUSION OF CARBON DIOXIDE, CARBON
MONOXIDE, NITROGEN, AND METHANE

Conversion	CO ₂		CO		N ₂		CH ₄	
	$\Delta H_o^\dagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\dagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\dagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)	$\Delta H_o^\dagger$ (KJ/mol)	$(D_e/r_c^2)_o$ (s ⁻¹)
raw	31.9	467	12.5	4.46	11.0	3.25	14.8	5.88
0.0	23.4	20.2	15.7	9.90	12.1	3.63	15.3	7.05
0.0539	27.8	92.9	13.3	4.86	11.2	2.94	13.8	3.91
0.125	25.5	41.4	13.6	4.85	10.4	2.16	16.4	7.87
0.255	26.8	117	12.2	3.91	6.99	0.807	13.8	3.83
0.388	26.4	94.2	11.9	3.32	9.73	1.16	15.6	6.59
0.530	22.7	47.1	10.8	2.56	8.79	1.32	15.6	8.20
0.733	21.0	28.9	8.98	1.31	7.24	0.745	14.3	5.66
0.960	-	-	27.3	8.02	14.7	3.56	17.1	3.96

of methane through various activated anthracite samples which ranged from 16 to 23 KJ/mole (3.8 to 5.5 Kcal/mol).

Since activated diffusion involves pores, or pore entrances, whose radii are comparable to the size of the diffusing molecule, the activation energy should be a function of the kinetic dimensions of the diffusing molecule. Assuming nitrogen and carbon dioxide molecules to be ellipsoid, Kihara (64) utilized the Lennard-Jones potential to obtain the following dimensions: for nitrogen, major axis, 0.46 nm, minor axis, 0.35 nm; for carbon dioxide, major axis, 0.58 nm, minor axis, 0.37 nm. Tables 27-30 indicate that the activation energies are indeed greater for carbon dioxide than for nitrogen. Curiously, Nandi and Walker (82) obtained opposite results.

The objective in calculating the carbon dioxide diffusion Arrhenius parameters was the estimation of diffusivities at reaction temperatures. These estimated values are shown in Table 31. It was assumed that the Arrhenius parameters were constant at the elevated temperatures. These estimated values of D_e/r_c^2 at reaction temperatures of 1073 and 1173 increase only gradually as conversion proceeds. The values of D_e/r_c^2 at 1173 are approximately an order of magnitude greater than those at 1073K. At temperatures of 1273K and 1373K the estimated diffusion parameters increase rapidly at low conversion, reach a maximum, and then decrease at higher conversions. At low conversions, these diffusion parameters at 1273 and 1373K are approximately 20 to 30 times those at 1173K. This increase in diffusion parameter at reaction temperatures of 1273K and 1373K would indicate a more open pore structure than the pore structure developed at the lower reaction temperature of 1073K and 1173K. A more open pore structure would tend to decrease any influence of pore diffusion on the overall observed global rate.

TABLE 31 CARBON DIOXIDE DIFFUSION PARAMETERS

1073K		1173K		1273K		1373K	
Conversion	D_e/r_c^2	Conversion	D_e/r_c^2	Conversion	D_e/r_c^2	Conversion	D_e/r_c^2
0.0	0.043	0.0	0.057	0.0	0.49	0.0	2.60
0.061	0.048	0.064	0.557	0.053	3.88	0.054	8.13
0.100	0.025	0.13	0.266	0.134	7.48	0.125	4.43
0.176	0.039	0.213	0.374	0.373	7.83	0.255	11.13
0.247	0.031	0.314	0.305	0.478	7.36	0.388	9.35
0.357	0.048	0.448	0.500	0.590	8.09	0.530	6.47
0.473	0.501	0.535	0.320	0.719	4.19	0.733	4.18
0.583	0.046	0.643	4.160	0.845	1.52		
0.701	0.062	0.74	1.401				
0.778	0.084	0.821	0.828				
0.849	0.090	0.918	2.08				
0.902	0.155						
0.926	0.260						

The conversions and the corresponding rates, dX/dt , as functions of time appear in Figures 24-30. In order to smooth the raw data a second order exponential filter, which was implemented by cascading two first order filters, was employed (128). The first order exponential filter is given by:

$$y_i = (1-\alpha)y_{i-1} + \alpha X_{i-1} \quad (122)$$

where

y_i = i th filtered observation,

y_{i-1} = i th filtered observation,

X_{i-1} = i th unfiltered observation.

α = filter constant.

Equation 64 states that the filtered observation is a weighted sum of the current observation and the previous filtered observation. The value of α ranges from 0 to 1. An α value of 0.6 was found to provide optimal smoothing without significant attenuation or loss of detail.

Rates as functions of conversion are plotted in figures 31 and 32. That all the curves pass through the origin is an artifact of the experimental procedure since the actual initial rates must be nonzero. Therefore, the rate data at conversions less than 0.1 are not reliable.

Combining the expression for specific area (equation 56) with the general rate equation (equation 58) yields:

$$\frac{(dX/dt)(1-\epsilon)}{\eta C_{CO_2} [1-\psi \ln(1-X)]^{1/2}} = k S_0 (1-X) \quad (123)$$

The structural parameter, ψ , was determined previously from surface area measurements. If the reactions are kinetically controlled, $\eta=1$, then a plot of the left-hand side of equation 123 against $(1-X)$ should be rectilinear. Plots were created for each reaction temperature and

Figure 24. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 800°C.

Figure 25. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 850°C.

Figure 26. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 900°C.

Figure 27. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 950°C.

Figure 28. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 1000°C.

Figure 29. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 1050°C.

Figure 30. Conversion and Rate as a Function of Time for Reaction of Coal Char with Carbon Dioxide at 1100°C.

Figure 31. Rate as a Function of Conversion for Reactions of Coal Char with Carbon Dioxide at (1) 800, (2) 850, (3) 900 and (4) 950°C.

Figure 32. Rate as a Function of Conversion for Reactions of Coal Char with Carbon Dioxide at (5) 1000, (6) 1050 and (7) 1100°C.

are presented in Figures 33-41. The assumption of kinetic controlled appears correct, since the plots are linear for all the reaction temperatures. The slope of the plots are the product of the rate constant, k , and the initial surface area, S_0 . Table 32 lists the slope, the initial surface area, and the rate constant for each reaction temperature.

Figure 42 shows a plot of the rate constant as a function of temperature according to equation 7. The best line was drawn through the data points by the method of least-squares. Solving for the slope and intercept produced the expression:

$$k = 86.2 \exp (-1.78 \times 10^4/T) \quad (124)$$

with an activation energy of 150 KJ/mole.

The Weisz-Prater criterion (30) for a first order reaction which indicates the influence of diffusion is given by

$$\frac{(dX/dt)_{\text{observed}}}{D_e/r_c^2} = \phi \quad (125)$$

The maximum dX/dt observed at each temperature and the estimated diffusion parameter, D_e/r_c^2 , at that conversion and temperature are used to estimate the influence of pore diffusion. These are given in Table 33. From this analysis it can be concluded that diffusion has no effect on the overall observed rate since $\phi < 10^{-2}$ and therefore $\eta \rightarrow 1$. This is also supported by the linearity of the Arrhenius plot reaction rate constants.

Figure 33. Reaction of Coal Char with Carbon Dioxide at 1073°K. Data fitted to Equation 64, $\eta = 1$.

Figure 34. Reaction of Coal Char with Carbon Dioxide at 1123°K. Data fitted to Equation 64, $\eta = 1$.

Figure 35. Reaction of Coal Char with Carbon Dioxide at 1173°K. Data fitted to Equation 64, $\eta = 1$.

Figure 36. Reaction of Coal Char with Carbon Dioxide at 1223°K. Data fitted to Equation 54, $\eta = 1$.

Figure 37. Reaction of Coal Char with Carbon Dioxide at 1223°K. Data fitted to Equation 64, $\eta = 1$.

Figure 38. Reaction of Coal Char with Carbon Dioxide at 1273°K. Data fitted to Equation 63, $\eta = 1$.

Figure 39. Reaction of Coal Char with Carbon Dioxide at 1323°K. Data fitted to Equation 64, $\eta = 1$.

Figure 40. Reaction of Coal Char with Carbon Dioxide at 1323°K. Data fitted to Equation 64, $\eta = 1$.

Figure 41. Reaction of Coal Char with Carbon Dioxide at 1373°K. Data fitted to Equation 64, $\eta = 1$.

TABLE 32

RATE CONSTANTS AT VARIOUS REACTION TEMPERATURES

T(K°)	Slope	Initial Surface Area m ² /g	Rate Constant g-cm/mol-s (10 ⁶)
1073	21.3	225	9.46
1123	30.6	225 ¹	13.6
1123	28.5	300 ²	9.51
1173	45.7	300	15.2
1223	106	300 ²	35.2
1223	68.3	301 ³	22.7
1273	141	301	46.9
1323	265	301 ³	88.3
1323	356	246 ⁴	145
1373	1227	246	499

¹Surface area data from Wyodak coal char reacted at 1073°K

²Surface area data from Wyodak coal char reacted at 1173°K

³Surface area data from Wyodak coal char reacted at 1273°K

⁴Surface area data from Wyodak coal char reacted at 1373°K

Figure 42. Arrhenius Plot for the Rates Constants.

TABLE 33 ESTIMATION OF THIELE MODULUS

Temp. ($^{\circ}\text{C}$)	$\left(\frac{dx}{dt}\right)_{\text{max}} (\text{s}^{-1})$	x	$D_e/r_c^2 (\text{s}^{-1})$	ϕ
800	3.8×10^{-4}	0.18	.039	9.7×10^{-3}
900	0.8×10^{-3}	0.31	.305	2.6×10^{-3}
1000	3.2×10^{-3}	0.40	7.8	4.1×10^{-4}
1100	1.8×10^{-2}	0.45	7.9	2.3×10^{-3}

MODEL EVALUATIONS

The Coal

Rates were determined on carbon dioxide gasification reactions using coal chars derived from four types of coal. The coals were Illinois No. 6 coal, Pittsburgh Bituminous coal, Cimmeron coal from Hopkins County, Kentucky, and Wilcox Lignite from Texas. The first three coals were high volatile bituminous samples. Cimmeron coal was singular in its tendency to sinter and cake. During devolatilization 35 x 60 mesh Cimmeron coal agglomerated into one lump of coal char. The other coals did not agglomerate. Other properties of the coals relevant to this study are listed in the proximate analysis in Table 34.

As Table 34 shows the devolatilization process is a significant part of the gasification process. Although much of the coal mass is volatile matter, no attempt will be made to present data from the inert pyrolysis phase of the gasification reaction. Others have presented such data (6). Pyrolysis is not one but many heterogeneous reactions. Each reaction is a different function of temperature; yet during the course of the pyrolysis reaction the temperature is constantly increasing. The result is data which is difficult to analyse.

The Rate-Temperature Data

Data collected in this study confirmed the observation of many previous workers (25,54,60,69) that the rate of coal gasification increases

TABLE 34

PROXIMATE ANALYSIS OF COALS
USED IN THIS WORK

Coal	Rank	% Volatiles	% Fixed Carbon	% Ash
Wilcox	Lignite	54.7	31.3	14.0
Cimarron	Bituminous	50.2	43.3	6.4
Illinois	Bituminous	38.8	48.9	5.8
Pittsburgh	Bituminous	37.5	56.7	5.8

to a maximum and then decreases. Calculated rate data were plotted as a function of conversion. These data are shown in Figures 43-50. For each coal there is a plot of the carbon dioxide-char reaction at higher (1223-1373K) and lower (1073-1223K) temperatures. Three or four rate-conversion curves on each plot indicate how reaction temperature effects the trajectory of the reaction. Each reaction curve has a rate conversion maximum. The conversion at which this maximum occurs is a function of the temperature of the reaction and the type of coal.

In general, the faster reacting coals, Cimmeron and Wilcox, have broader maximum peaks than the more slowly reacting coals, Illinois and Pittsburgh. The order of the reactivity of these coals is:

Wilcox > Cimmeron > Illinois > Pittsburgh

In the case of Wilcox coal some of the reactions show such broad peaks that the trajectories of these reactions appear almost flat. While this result is most probably not evidence of zero order global kinetics, it may suggest that there are mass transfer or catalytic effects in the reaction which result in rate curves which are dissimilar to rate curves obtained from other coals.

Arrhenius Plots

One convenient way to unify rate data obtained at multiple temperatures is to plot the logarithm of the rate against the reciprocal of the absolute temperature. Although the Arrhenius expression was developed to describe the relation of the rate constant to temperature, it may be used to analyse rate data in the same way.

Figure 43. The reaction rate of Illinois coal char as a function of conversion (x). 1-reaction at 1123K; 2-reaction at 1173K; 3-reaction at 1223K.

Figure 44. The reaction rate of Illinois coal char as a function of conversion (x). 1-reaction at 1273K; 2-reaction at 1323K; 3 reaction at 1373K.

Figure 45. The reaction rate of Pittsburgh coal char as a function of conversion (x). 1-reaction at 1073K; 2-reaction at 1123K; 3-reaction at 1173K; 4-reaction at 1223K.

Figure 46. The reaction rate of Pittsburgh coal char as a function of conversion (x). 1-reaction at 1273K; 2-reaction at 1323K; 3-reaction at 1373K.

Figure 47. The reaction rate of Cimmeron coal char as a function of conversion (x). 1-reaction at 1123K; 2-reaction at 1173K; 3-reaction at 1223K.

Figure 48. Reaction rate of Cimmeron coal char as a function of conversion (x).
1-reaction at 1123K; 2-reaction at 1173K; 3-reaction at 1223K.

Figure 49. Reaction rate of Wilcox coal char as a function of conversion (x).
 1-reaction at 1073K; 2-reaction at 1123K; 3 reaction at 1173K; 4-
 reaction at 1223K.

Figure 50. Reaction rate of Wilcox coal char as a function of conversion (x).
1-reaction at 1273K; 2-reaction at 1323K; 3-reaction at 1373K.

$$\text{rate} = k(T)F(x) \quad (126)$$

where T is temperature, k is a rate constant, and $F(x)$ is some function of conversion. For any kinetic model, the rate evaluated at some specified conversion is the same as the intrinsic rate constant multiplied by a constant. For example:

$$\text{rate} = k(T) F(0.5) \quad (127)$$

Rate evaluated at 0.5 conversion was chosen for this study. This conversion is usually close to the maximum rate. Also, as noted previously, 0.5 conversion is a point around which data of widely different coals can be normalized so that they all nearly fall along the same curve (17,60,69). When one plots rate vs. temperature in this manner there is an important assumption made. This assumption is that all the parameters in the global kinetic expression which are functions of temperature can be separated from all the functions of conversion in a linear way.

Often useful information about the effects of mass transfer on the global kinetic rate can be obtained from the Arrhenius plot. If observed data significantly deviate from a straight line, this deviation is a necessary but not sufficient condition to suggest an intrusion of mass transfer effects into the global rate (105). However, if the data are linear one may only conclude that the parameters (e.g. intrinsic rate constant, effective diffusivity) which effect the global rate observation vary logarithmically with reciprocal absolute temperature.

The above statement is true for the data collected from the four

coal chars used in this work. Figures 51-54 show Arrhenius type plots for each coal char reaction. Linear regression coefficients for the straight lines through these data range from 0.98 to 0.995 (shown in Table 35). From the slopes of these lines pseudo-activation energies were calculated. These values are shown in Table 35 for the individual coals. They range from 119-176 KJ/Mol. This span is well within the range of "activation energies" obtained by similar methods from other coals and carbon sources (25,61). However, 119 KJ/mol, the "activation energy" for the reaction using Wilcox coal char, is a low value. It is even lower than the value reported by Kasaoka (61) for a barium (a good catalyst) impregnated sample of coal char. Perhaps this low energy of activation reflects the presence of a catalyst in the coal char ash. Alternatively this low value could be an artifact of a diffusion controlled reaction. Effective diffusivity is a temperature parameter which has a slope of an Arrhenius plot that would correspond to an "energy of activation" of around 20 KJ/mol (25,73). Possibly the low energy of activation of Wilcox coal char samples reflects a mean of the combined energies of activation for the diffusivity of the coal char and the intrinsic rate constant of the gasification reaction.

If an Arrhenius type of analysis is appropriate for the coal char--carbon dioxide reaction, then a rate constant can be generated from the rate vs. temperature data. The well-known Arrhenius relationship in logarithmic form is:

$$\ln(K) = \ln K' - E_0/RT \quad (128)$$

if K is a rate constant, K' is an Arrhenius constant, E is an activation

TABLE 35

ARRHENIUS DATA

Coal	Activation Energy (KJ/M)	$K'(F(X))$	K'	K_A	K_d	Linear Regression Coefficient
Illinois	172	3261	1.06E8	9.30	27.0	0.985
Pittsburgh	164	244	6.62E6	3.17	7.7	0.985
Cimмерon	176	6304	1.36E6	0.61	1.6	0.980
Wilcox	119	244	6.36E6	63.00	190.0	0.995

Figure 51. Rate-Temperature Data - Illinois coal char.

Figure 52. Rate-Temperature Data - Pittsburgh coal char.

Figure 53. Rate-Temperature Data - Cimmeron coal char.

Figure 54 . Rate-Temperature Data - Wilcox coal char.

energy, and R is the gas constant. Then in terms of this data analysis:

$$\ln(\text{rate}) = \ln(K' f(x)) - E_0/RT \quad (129)$$

since:

$$r = k f(x \text{ evaluated at } 0.5).$$

Here the term, $\ln(K' f(x))$ is the y intercept of the extrapolated straight line through the Arrhenius plot of rate vs. temperature data. The value of $f(x)$ is dependent upon the particular rate model considered. Since the Dutta and Wen (25) model has an explicitly defined chemical rate constant (denoted K_d) as an adjustable parameter, $f(x)$ was extracted from this expression. Thus, using the Dutta and Wen equation:

$$f(x) = S_d K_d C^n \quad (130)$$

K' was calculated for each coal char as shown in Table 35 from the y intercepts of the Arrhenius plots. Using the observed "energies of activation" and the Arrhenius expression, a global rate constant was generated for each coal. These constants are called K_A and are shown in Table 35. For comparison, the K_d parameter of the Dutta and Wen model is listed for each coal in Table 35. This parameter is a chemical rate constant for a first order reaction. The two constants have the same relative values to each other and are in the same range although the K_A 's are roughly one half to one third of the quantities of the K_d parameters. Considering that the K_d values are not directly measured but are one of three adjustable parameters resulting from a non-linear least squares regression routine, the two calculated rate constants

agree well. In more rigorous calculations of the values for K_A , the $f(x)$ should have been evaluated at all temperatures for which rate data were available. In this work $f(x)$ was evaluated at 1273K. Thus $f(x)$ is by assumption not a function of temperature. A direct evaluation of the Dutta and Wen model at all available temperatures would confirm or deny this assumption.

Model Evaluations

An evaluation of five of the available models for coal gasification was performed using the rate-conversion data collected at 1273K from the four coals described above. The temperature of 1273K was chosen because the rate data at this temperature were smooth, and yet 1273K is a temperature at which some authors contend the reaction rate is kinetically controlled (25). Data were fit to the rate expressions given by various models using a nonlinear least squares regression subroutine supplied by IMSL (53). The quality of the fit of data to the four models can be seen in figures 55-66, and the sum of the squared errors for each model and each coal is shown in Table 36. Parameter values for each model are listed for each coal in Table 37.

The fact that the collected data closely match the trajectories predicted by the various models is not highly significant. Each model has at least two adjustable parameters, and with the proper constraints, the IMSL curve fitting routine will converge to fit all of these models. The models fit the data because a sophisticated algorithm adjusted the parameters of the models until the model calculated values were little different from the measured data values and not because of any validity

TABLE 36

INDICATION OF THE ABILITY OF DIFFERENT MODELS TO FIT RATE DATA

Model	Coal	Sum of the Squared Errors
Bhatia & Perlmutter (Gavalas)	Illinois	0.207×10^{-6}
	Pittsburgh	0.201×10^{-7}
	Cimмерon	0.133×10^{-7}
	Wilcox	0.337×10^{-5}
Kasaoka	Illinois	0.491×10^{-7}
	Pittsburgh	0.5737×10^{-8}
	Cimмерon	0.311×10^{-8}
	Wilcox	0.242×10^{-5}
Dutta and Wen	Illinois	0.199×10^{-6}
	Pittsburgh	0.689×10^{-7}
	Cimмерon	0.184×10^{-7}
	Wilcox	0.502×10^{-5}

TABLE 36.--(Continued)

Model	Coal	Sum of the Squared Errors
Simmons Chornet	Illinois	0.142×10^{-6}
	Pittsburgh	0.134×10^{-7}
	Cimmeron	0.534×10^{-8}
	Wilcox	0.695×10^{-5}

TABLE 37

PARAMETERS OF MODELS DETERMINED FROM NON-LINEAR CURVE FITTING

Model	Coal	Parameters		
Bhatia & Perlmutter	Illinois	ψ 9.1	τ' 2.837E-03	
	Pittsburgh	19.5	6.761E-05	
	Cimmon	14699	7.695E-05	
	Wilcox	30424.0	6.084E-06	
Gavalas		Constants of this model are entirely equivalent to ψ and τ' of the Bhatia and Perlmutter Model.		
Kasaoka et al.	Illinois	A 0.9758E-04	B 1.26	(1-B)/B 0.21
	Pittsburgh	0.1314E-04	1.34	0.25
	Cimmon	0.4425E-05	1.66	0.40
	Wilcox	0.3238E-05	2.27	0.56
Dutta et al.	Illinois	K_d 27.24	γ 0.479	β 4.5
	Pittsburgh	7.7	0.4523	4.3
	Cimmon	1.89	0.999	0.62
	Wilcox	190	0.999	2.8
Simons-Chornet	Illinois	K_c 0.1137E-02	θ_o 0.0282	
	Pittsburgh	0.4212E-03	0.0136	
	Cimmon	0.1246E-02	0.3204E-06	
	Wilcox	0.9170E-02	0.6990E-04

Figure 55. The solid line is the Dutta and Wen model. The verticle slashes are the data collected from Illinois coal at 1273K.

Figure 56. The solid line is the Dutta and Wen model. The vertical slashes are the data collected from Pittsburgh coal at 1273K.

Figure 57. The solid line is the Dutta and Wen model. The verticle slashes are the data collected from Cimmeron coal at 1273K.

Figure 58. The solid line is the Dutta and Wen model. The verticle slashes are the data from Wilcox coal at 1273K.

Figure 59. The solid line is the Bhatia and Perlmutter (Gavalas) model. The knotted line is the Kasaoka model. The vertical slashes are data from Illinois coal at 1273K.

Figure 60. The solid line is the Bhatia and Perlmutter (Gavalas) model. The knotted line is the Kasacka model. The verticle slashes are data from Pittsburgh coal at 1273K.

Figure 61. The solid line is the Bhatia and Perlmutter (Gavalas) model. The knotted line is the Kasaoka model. The vertical slashes are data from Cimmeron coal at 1273K.

Figure 62. The solid line is the Bhatia and Perlmutter (Gavalas) model. The knotted line is the Kasaoka model. The verticle slashes are data from Wilcox coal at 1273K.

Figure 63. The solid line is the Simons-Chornet model. The verticle slashes are data from Illinois coal at 1273K.

Figure 64. The solid line is the Simons-Chornet model. The verticle slashes are data from Pittsburgh coal at 1273K.

Figure 65. The solid line is the Simons-Chornet model. The verticle slashes are data from Cimmeron coal at 1273K.

Figure 66 The solid line is the Simons-Chornet model. The verticle slashes are data from Wilcox coal at 1273K.

of the model. A more valuable criteria for evaluation of a model might be to determine whether the parameters needed to fit the data are physically credible.

The Bhatia and Perlmutter (7) model contains two parameters, ψ and τ' , which have physical significance. In Table 37 the values given for ψ are quite reasonable for Illinois coal char and Pittsburgh coal char (7). The value of the parameter ψ obtained from Cimmeron and Wilcox coal chars are seemingly high compared to typical values given in Bhatia and Perlmutter (7). Physically such values mean that the initial surface area of the coal char pores is small relative to the length of the entire pore system. Alternatively, the inordinately high values of the structural parameter may be caused by the fact that the gasification reaction for these two is not in the region of kinetic control. The large values of this parameter may reflect mass transfer limitations in this model, or they may be caused by a catalytic phenomenon not accounted for by this structural model. This effect has been suggested by Chornet (17) and Kasaoka (60).

The parameter τ' in the Bhatia and Perlmutter (7) and Gavalas (38) model is a constant of proportionality between surface area and reaction rate. It is defined by Gavalas in equation 63, and by Bhatia and Perlmutter in equation 65. Typical values of the constants in equation 65 are (7,13).

$$C^n = 9.5 \times 10^{-6} \text{ (ideal gas)}$$

$$S'_0 = 2.5 - 5.5 \times 10^6 \text{ cm}^2/\text{cm}^3$$

$$\epsilon_0 = 0.1 - 0.25$$

Therefore an estimate of the intrinsic chemical rate constant can be obtained by:

$$K_s = \frac{(9.5 \times 10^{-6})(2.5 \times 10^3(\tau))}{(0.9)} \quad (131)$$

The parameter K_s is 9.3, 432, 343, and 4342 $\text{cm}^4/\text{mol sec}$ for Illinois, Pittsburgh, Cimmeron, and Wilcox coals respectively. These values do not correlate with rate constants determined by methods discussed earlier. Alternatively, surface areas might be calculated using the rate constants listed in Table 3, but values obtained in this way would predict initial surface areas ($10^7 - 10^{11} \text{ cm}^2/\text{cm}^3$) which are far beyond values measured more directly by the Brunauer Emmet and Teller (BET) method (11). In terms of the Gavalas interpretation of this model τ is given as by equation 63. Using typical values for R , r_t , and ρ :

$$\bar{r} = 0.7 \times 10^{-3} \text{ mm (29)}$$

$$r_t = 0.5 \text{ (eqn. 64, Table 4, ideal gas)} \text{ g}\cdot\text{mol}/\text{cm}\cdot\text{s}$$

$$\rho = 1.1 \text{ gm}/\text{cm}^3$$

β_0 values for intersection density per square millimeter are 700, 17, 19, and 2 for Illinois, Pittsburgh, Cimmeron and Wilcox coal chars respectively. Since the moment, β_0 , is not a normally measured physically quantity but rather a geometric concept of how pores intersect with each other, a rational evaluation of this parameter is difficult. The ultrastructure of coal has been studied by scanning electron microscopy (25), but the quantification of pore intersections has never been approached. There

might be the great variability among coal chars predicted by the Gavalas analysis.

The parameters A and B of the Kasaoka model have no physical significance. The model is similar to the Bhatia and Perlmutter-Gavalas model; therefore, the Kasaoka proportionality constant, A, is of similar magnitude to the Bhatia and Perlmutter-Gavalas constant of proportionality, τ' .

The Kasaoka model approaches the form of the Bhatia and Perlmutter-Gavalas model when the term $(1-B)/B$ is equal to 0.5. In Table 37 values are given for $(1-B)/B$. Wilcox coal char has a value of 0.56, so for this char the two models are almost the same.

One of the Dutta and Wen model parameters, K_d , has already been discussed in conjunction with the Arrhenius analysis. As noted there the constants determined by the non-linear least squares method have the same relative magnitudes as those constants regenerated from the Arrhenius equation. The two other parameters occur in an empirical expression describing surface area. β has no significance, but as stated earlier γ is the parameter that represents the conversion at which the surface is maximum. The values listed in Table 37 for this parameter are reasonable, and they are the maxima of surface area predicted by equations for surface area as a function conversion. In the case of Illinois and Pittsburgh coal chars maxima in surface area are at around one-half conversion, but Wilcox and Cimmeron chars show surface maxima at full conversion. This latter situation is physical nonsense. Surface area cannot be maximum when there is no mass left, but the possibility that sites on which reactants might sorb increase dramatically even at later conversions might be true. In the case of Cimmeron coal which is highly sintered

during devolatilization this possibility may reflect the physical situation. Direct BET measurements of surface areas have shown increases in specific surface area late in the gasification reaction (73) although the workers who reported these measurements were hesitant to claim a high degree of confidence in the increasing values.

In the Simons-Chornet model, K_c is a constant of proportionality with no physical significance. θ_0 is a parameter which represents initial porosity. If this claim is true, all of the coal chars shown in Table 37 have low initial porosities. Illinois and Pittsburgh coal chars have about one-seventh to one-third the initial porosity reported by other measurements (73). Wilcox and Cimmeron chars have vanishingly small initial porosities predicted by the Simons model. Due to the sintering of Cimmeron coal it might have such a small initial porosity.

Simons noted that when the parameter, θ_0 , approaches zero, the model is the same as Chornet's model (17). Chornet stated that when the product of the constant, K_c , multiplied by the time necessary to reach one-half conversion equals 1.73, then his model fit an autocatalytic mechanism (17,42). For Wilcox coal, the parameter multiplied by the time to reach one-half conversion is 1.63. This value is 2.03 for Cimmeron coal. Wilcox and Cimmeron coal by this criterion may show autocatalytic effects.

The Bhatia and Perlmutter model and the Dutta and Wen model contain expressions for the quotient of the surface area of the char at some point of conversion divided by the initial surface area of the char. Figure 67 shows this dimensionless surface area as a function of conversion for Illinois and Pittsburgh coal using the Dutta and Wen surface area function. Dutta and Wen show a similar plot for the two coal chars. The

shapes of their curves are identical to those shown in Figure 67, but the magnitudes of the surface areas in Figure 67 are about twice the values given by Dutta and Wen. This difference could be a result of the different ways in which the coal chars were prepared. In this study coal was devolatilized in an inert atmosphere. Dutta and Wen pyrolysed their coal in the presence of carbon dioxide.

There are two different usages of surface areas in these models. The Bhatia and Perlmutter expression for surface area is simply the rate expression. As noted earlier, the y axis values must be divided by the parameter τ' , in order to model the evolution of surface area. Dutta and Wen describe rate as the product of surface area and the term $(1-x)$ as well as a constant. In Figures 55,63, the Bhatia and Perlmutter concept seems to fit the rate data better than the Dutta and Wen approach. Both of these models are conforming to the measured raw data.

Figure 67. The knotted line is the Dutta and Wen equation for surface area for Pittsburgh coal. The solid line is the same equation for Illinois coal.

CHAPTER VI

CONCLUSIONS

This study is concerned with the influence of intraparticle surface area and diffusion upon the global rate in the reaction of carbon dioxide with coal char. Analysis of the data leads to the following conclusions:

- (a) The specific area, mean pore radius and pore volume distribution are readily estimated by application of the method of Medek to carbon dioxide adsorption isotherms obtained at 0°C. Since the same gas was used as sorbate and as reactant, the reaction surface area may be taken to be equivalent to the specific areas calculated from the adsorption data.
- (b) Specific areas range from 180 to 650 m²/g depending on conversion, with a maximum near a conversion of 0.35. The random pore model of Bhatia and Perlmutter is able to correlate the specific area/conversion data to a conversions ranging from 0.5 to 0.7.
- (c) The mean pore radii range from 0.68 to 0.74 nm and almost all the pore volume is contained within pores having radii less than 1.2 nm. Both the mean pore radius and pore volume distribution do not vary greatly with conversion, suggesting that reaction occurs primarily near pore entrances.

- d) The diffusion parameters, D_e/r_c^2 , are conveniently estimated using the model of Haynes and Sarma and the method of moments. The diffusion of carbon dioxide, carbon monoxide, nitrogen and methane through a bed of coal char particles is activated, and adsorption onto pore walls is an integral part of the diffusion process. Diffusivities lie in the region of $10^{-5} \text{ cm}^2/\text{s}$, approximately one order of magnitude less than the region for Knudsen diffusion. The diffusion rates are inversely proportional to the adsorption equilibrium constants, increase nonlinearly with conversion and follow the order, $\text{N}_2 > \text{CO} > \text{CH}_4 > \text{CO}_2$.
- e) The reaction of carbon dioxide with coal char at temperatures between 1073 to 1373°K is kinetic controlled. The rate is proportional to the specific surface areas. The rate constants vary from $9.46 \times 10^{-6} \text{ g-cm/mole-s}$ at 1073°K to $4.99 \times 10^{-4} \text{ g-cm/mol-s}$ at 1373°K. The Arrhenius activation energy is 150 KJ/mole.
- f) There are negligible deviations from straight lines for the plots of logarithm of the rate versus reciprocal temperature data. Intrinsic rate constants can be regenerated from rate versus temperature data if one assumes that the rate models are linear functions of temperature.

- g) The reactivity of the coal chars tested is:

Wilcox > Cimmeron > Illinois > Pittsburgh.

Pittsburgh and Illinois coal chars are around fifty times less reactive than the Wyodak (subbituminous) coal char reported previously (29) and the lignite, Wilcox coal char, studied in this work.

- h) All coal chars reacted show rate maxima between 0.25 and 0.6 conversion.

- i) All coal char gasification data fit the four models tested.

The Kasaoka model and the Bhatia and the Perlmutter-Gavalas rate equations give the best fit to all data. The Dutta and Wen rate model is the least satisfactory model for generally predicting coal char gasification trajectories. Although the Bhatia and Perlmutter-Gavalas equation is readily fit to coal char reaction data, the physical constants obtained from these models are credible only in the case of the chars of Illinois and Pittsburgh coals. Curve fits of data obtained from Wilcox and Cimmeron coals do not yield physically credible parameters.

The assumptions about the coal chars used in the Bhatia and Perlmutter model may not apply to the Cimmeron and Wilcox coal chars. One important assumption of the model development is that all the pores in the coal char are accessible to the reactant gases at the beginning of the reaction. This may be true in the case of Illinois and Pittsburgh coals, but it is possibly invalid for Cimmeron and Wilcox coal chars. One might suggest that the rate of chemical reaction in Wilcox coal char is so fast that

many smaller pores are initially "blocked" due to mass transfer resistances. In the case of Cimmeron coal sintering during devolatilization is so significant that the coal char may be a semi-plastic substance which is not highly porous. Another possible variation from the model assumptions for these two coals is the possible existence of an autocatalytic phenomenon. As was noted, Wilcox and Cimmeron coal char reactions fit a proposed mathematical description of an autocatalytic reaction (17, 42). In addition, Wilcox coal is a lignite. The lignite coals are known to contain relatively high concentrations of barium (61). Kasaoka et al. (61) showed that barium was a highly potent catalyst for the coal char gasification reaction. Further experiments using the TGA technique might be useful to confirm or deny these possibilities.

- j) Surface area equations of the Dutta and Wen model and the Bhatia and Perlmutter model give similar surface evolution curves in the case of Pittsburgh and Illinois coals but not in the case of Wilcox and Cimmeron coals. The Bhatia and Perlmutter treatment of surface evolution yields a better prediction of rate data.

The precise mechanism of the coal char gasification reaction is probably affected by both geometric and catalytic characteristics of the coal char and its ash. No model is completely satisfactory for elucidating mechanisms or for predicting physically believable parameters for all types of coal. All five models tested in this work do yield accurate predictions of rate data when the proper parameters are selected. If these parameters are not functions of

temperature, then these rate equations would be useful for prediction of reaction rate under reactor conditions or other more complicated reaction schemes. Analysis of the rate data at other temperatures would determine this.

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APPENDIX A

DERIVATION OF EQUATIONS 56 AND 57 FOR CONVERSION BASED ON GAS ANALYSIS

APPENDIX A

DERIVATION OF EQUATIONS 56 AND 57 FOR
CONVERSION BASED ON GAS ANALYSIS

The following derivation is based on the stoichiometry of the reaction:

$$\begin{aligned} \Delta N_C^i &= -1/2 \Delta N_{CO}^i \\ &= -1/2 (N_{CO_f}^i - N_{CO_o}^i) \\ &= -1/2 N_{CO_f}^i \end{aligned}$$

where

ΔN_C^i = change in the number of moles of carbon during ith reaction.

ΔN_{CO}^i = change in the number of moles of carbon monoxide during ith reaction.

$N_{CO_f}^i$ = moles of carbon monoxide present at end of ith reaction.

$N_{CO_o}^i$ = number of moles of carbon monoxide present at beginning of ith reaction, $N_{CO_o}^i$.

Let

$$Q^i = N_{CO_f}^i / N_{CO_{2f}}^i \quad (A3)$$

where

$N_{CO_{2f}}^i$ = moles of carbon dioxide present at end of ith reaction.

Therefore,

$$\Delta N_C^i = -1/2 Q^i N_{CO_2f}^i \quad (A4)$$

The number of moles of unreacted carbon dioxide is:

$$N_{CO_2f}^i = N_{CO_2}^0 + \Delta N_C^i \quad (A5)$$

where

$$N_{CO_2}^0 = \text{moles of carbon dioxide passed through the char bed.}$$

Combining equations A4 and A5, and solving for ΔN_C^i gives:

$$\Delta N_C^i = - \frac{Q^i N_{CO_2}^0}{2 + Q^i} \quad (56)$$

Now, the conversion following the i th reaction is:

$$\begin{aligned} X^i &= \frac{W_C^0 - W_C^i}{W_C^0} \\ &= \frac{N_C^0 - N_C^i}{F W_O / M} \end{aligned} \quad (A7)$$

where

X^i = conversion at i th reaction.

W_C^0 = weight of carbon in the unreacted char.

W_C^i = weight of carbon in the char following the i th reaction.

N_C^0 = moles of carbon in the unreacted char.

N_C^i = moles of carbon in the char following the i th reaction.

F = fraction of carbon in the unreacted char.

W_0 = initial weight of unreacted char.

M = atomic weight of carbon.

The moles of carbon remaining in the char after the i th reaction is:

$$\begin{aligned} N_C^i &= N_C^0 + \sum_{j=1}^i \Delta N_C^j \\ &= N_C^0 + \sum_{j=1}^{i-1} \Delta N_C^j + \Delta N_C^i \end{aligned} \quad (A8)$$

Combining equations A7 and A8 yields:

$$X^i = \frac{-(\Delta N_C^i + \sum_{j=1}^{i-1} \Delta N_C^j)}{F W_0 / M} \quad (A9)$$

Letting $\sum_{j=1}^{i-1} \Delta N_C^j = \Delta N_C^{i-1}$ gives:

$$X^i = - \frac{(\Delta N_C^i + \Delta N_C^{i-1}) M}{F W_0} \quad (55)$$

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