**Studies on Coal Devolatilization and
Char Reactivity Under PFBC Conditions**

Final Report

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ABSTRACT

Pressure affects many aspects of coal combustion: particularly, the kinetics of coal devolatilization and char oxidation. A fundamental combustion study was performed at Babcock and Wilcox's Alliance Research Center to characterize the combustion properties of Pittsburgh No. 8 and Texas lignite coals under conditions simulating pressurized fluidized-bed combustion (PFBC) using a bench-scale reactor.

Over 400 combustion tests were performed at temperatures ranging from 1425° to 1725°F, a maximum pressure of 280 psig, maximum superficial gas velocities of approximately 5 ft/sec to 20 ft/sec, and several oxygen concentrations using six coal particle sizes.

A database of combustion profiles at PFBC conditions was obtained. A fundamental model of the chemical kinetics of the coal combustion at elevated pressures was developed based on this database. The kinetic models were used to derive the rate constants and activation energies of coal combustion for the two coals.

For coal devolatilization, the effects of each test variable on the rate of reaction, the volatile yield, and the reaction order were evaluated. The apparent orders of coal devolatilization for Pittsburgh No. 8 and Texas lignite coals were determined to be less than one and vary with coal properties and test conditions.

For char oxidation, the rates were reported as apparent kinetic rates and were derived based on the information which was obtained at the early stage of char oxidation. The kinetic rate constant of Pittsburgh No. 8 coal was found to be insensitive to the tested particle sizes. Increasing temperature, pressure, and superficial gas velocity increased the kinetic rate constant. The kinetic rate constant of Texas lignite coal was found to be approximately 2.5 times that of Pittsburgh No. 8 coal. The kinetic data obtained from this study in the low-temperature range was comparable to those reported by others in the literature.

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SUMMARY

Pressure affects many operating parameters in pressurized fluidized-bed combustion (PFBC) units, such as concentration of oxygen in fluidizing air, gas diffusion coefficients, and cross-flow from rising bubbles in the bed. Pressure also affects the composition of the coal devolatilization products and the elutriation of particles from the bed. Most significantly, pressure changes the kinetics of coal devolatilization and char oxidation.

The objectives of this study were to characterize combustion properties of two coals under conditions simulating PFBC units using a bench-scale facility and to develop a kinetic model for the fuels.

In the course of this study, a 2-inch diameter bench-scale pressurized fluidized-bed (PFB) reactor was designed, fabricated, and installed at the Babcock & Wilcox (B&W) Alliance Research Center (ARC). The reactor was then modified to use a 1-inch diameter insert to accommodate higher gas velocities. The reactor was designed to be operated at a maximum temperature of 1800°F, a maximum pressure of 300 psig, and a maximum superficial gas velocity of about 5 ft/sec (for the 2-inch diameter reactor) and 20 ft/sec (for the 1-inch diameter reactor). Comprehensive shakedown testing of the PFB reactor on two coals was performed to determine the operational limits of the reactor.

Pittsburgh No. 8 and Texas lignite coals were selected for the combustion tests. The combustion tests were performed under different temperatures, pressures, oxygen concentrations, and coal sizes. In addition, over 40 tests of Pittsburgh No. 8 coal were performed specifically at higher superficial gas velocities of 4 ft/sec to 20 ft/sec. A database of PFBC profiles was obtained. These profiles indicated influences of each variable on coal combustion.

Based on the bench-scale PFBC results, information in the literature, reactor configuration, tests conditions, and kinetic information for coal combustion performed under atmospheric fluidized-bed combustion (AFBC) conditions, a fundamental model of the chemical kinetics of coal combustion at elevated pressures was developed. The kinetic models were used to derive the rate constants and activation energies of coal combustion.

For coal devolatilization, the results show that devolatilization consists of two stages. The early stage is more likely to involve release of aliphatic compounds. The later stage involves secondary reactions, such as converting tars to light hydrocarbons.

The rate of devolatilization increases for test conditions with high oxygen concentration, high superficial gas velocity, and smaller particle size. The rate of devolatilization and the volatile yield are affected by temperature and pressure. However, the rate of devolatilization did not have a linear relationship with temperature and pressure. The volatile yield for Texas lignite coal is greater than that for Pittsburgh No. 8 coal tested under similar conditions.

The volatile yields of the two coals obtained under the test conditions in this project are slightly less than the volatile matter determined from the ASTM coal analysis. This is because the temperature and the time of most tests performed in the project were less than the temperature and time used in ASTM coal analysis.

Accurate determination of the order of reaction of coal devolatilization is difficult, particularly during the early stage of coal devolatilization when the particle temperature is increasing during the heat-up period. An assumption of constant temperature for the later stage of coal devolatilization was used to determine the apparent order of coal devolatilization. The apparent orders of coal devolatilization for Pittsburgh No. 8 and Texas lignite coals are less than one and vary with coal properties and test conditions.

For char oxidation, the kinetic rate constant of Pittsburgh No. 8 coal is insensitive to particle size. This indicates that the coal was combusted in a temperature regime where both kinetics and diffusion play important roles in combustion. In other words, the density and the diameter of coal particle decrease as combustion proceeds.

Increasing temperature, pressure, and superficial gas velocity increases the kinetic rate constant. This is mainly attributed to either higher surface temperature or greater oxygen concentration and faster rate of mass transfer of oxygen to the coal surface or both. Comparing the combustion of the two coals, Texas lignite coal has a kinetic rate constant approximately 2.5 times that of Pittsburgh No. 8 coal.

The rates and rate constants are reported as apparent kinetic rates and rate constants, because the diffusion of oxygen into pores has not been separated from the intrinsic kinetic data. Also, all of the kinetic data is derived based on the information which is obtained at the early stage of char oxidation.

The char burning rates of Pittsburgh No. 8 coal at the low-temperature end of the fluidized-bed combustion regime obtained from this project are comparable to those obtained on various fuels under AFBC conditions by Combustion Engineering, Sandia National Laboratory, Field, et al., and Babcock & Wilcox.

The apparent activation energy for char oxidation of Pittsburgh No. 8 coal at 206 psig, 3% O₂, and 4 ft/sec is approximately 11.2 kcal/g-mole (or 4.69×10^7 joule/kg-mole). The frequency factor is approximately 0.043 gm of carbon/cm²-sec-(atm)^{0.2} (or 0.68 kg of carbon/m²-sec [MPa]^{0.2}). This apparent activation energy is less than most of the published true activation energies at pressures near one atmosphere. This difference may be attributed to the combustion nature of less porous char which is assumed to be formed in the temperature regime and higher pressures of this study. Apparent activation energy is independent of particle size in this regime.

The apparent order of char oxidation for Pittsburgh No. 8 coal was found to vary with the coal properties and test conditions. Also, for the same coal and test conditions, the order of reaction changes during the course of char oxidation. The apparent order of char oxidation for Pittsburgh No. 8 coal under the conditions tested in this project ranged from 0 to 0.35. This is less than the values most commonly used in the literature. However, the sensitivity of the order of reaction to the kinetic rate was evaluated and found to be small. A variation of 0.1 in the order of reaction showed only a 5% change in the value of kinetic rate constant. Therefore, an average order of reaction of 0.2 was used to simplify the calculations of the rate constants for various test conditions for Pittsburgh No. 8 and Texas lignite coals.

1.0 INTRODUCTION

Fluidized-bed combustion (FBC) is an attractive clean coal technology. It has the advantages of fuel flexibility and environmental control. Fuels with a wide range of fuel properties can be burned efficiently without slagging/fouling problems. Because combustion is performed at lower temperature in FBC units than in pulverized coal (PC) units, lower NO_x and SO_x emissions are produced in FBC units.

In pressurized fluidized-bed combustion (PFBC), the combustion process takes place at pressures in the range of 10 to 16 atmospheres. Pressure affects many operating parameters in a PFBC unit, such as the concentration of oxygen in the fluidizing air, gas phase diffusion coefficients, cross-flow from rising bubbles in the bed, and the elutriation of particles from the bed. Most significantly, pressure changes the kinetics of coal devolatilization and subsequently char oxidation.

PFBC has all the features of atmospheric fluidized-bed combustion (AFBC) plus some additional benefits. In PFBC units, due to high air pressure and mass flow, a deeper bed can be used and higher cycle efficiency is achieved. This increases the gas residence time for combustion and, hence, higher thermal efficiency is achieved. Because of increased mass flow of combustion gas, the PFBC units require smaller bed areas and volumes. This reduces the size of the combustion units.

Several versions of PFBC technology have been proposed for utility, cogeneration, and industrial applications. Babcock & Wilcox (B&W) and ASEA of Sweden have formed a joint venture company named ASEA-Babcock (AB) to supply supercharged PFBC units to the North American market. Design and performance information for these units have been provided by a 15-MWe PFBC pilot plant built at Malmö, Sweden, by ASEA PFBC and ASEA ATOM.^[1] Currently, startup of a commercial-scale (~70 MWe) combined-cycle (steam cycle and gas cycle) PFBC unit at the American Electric Power (AEP) Tidd Power Plant site at Brilliant, Ohio, is in progress. This unit will burn over 120,000 tons of Ohio coal per year. Demonstration is planned to run for at least two years.^[2] In addition, an AEP clean coal project for repowering of Units 3 and 4 of the 330-MWe Philip Sporn Plant with PFBC units in New Haven, West Virginia, was awarded for funding by DOE in the second round of clean coal technology development.

Although the PFBC technology has been developed to near-commercial scale, fundamental combustion information under PFBC conditions is still limited. Most fundamental work on coal combustion (coal devolatilization and char oxidation) has been performed under pulverized coal (PC) and AFBC conditions. Compared to these combustion technologies, many technical issues related to PFBC, such as fundamental information on coal combustion kinetics, heat transfer, ash handling, control of PFBC boiler system, and hot gas clean-up under pressure are not fully understood. Fundamental information on PFBC technology, in general, and combustion kinetics, in particular, are important to the design of the commercial PFBC units.

2.0 OBJECTIVES

The main objective of this study was to obtain fundamental combustion data on coal devolatilization and char oxidation on coals tested under conditions simulating PFBC units using a bench-scale PFB reactor. The more specific objectives of this study were to:

- Determine the effect of pressure, temperature, coal particle size, gas velocity, and oxygen concentration on coal devolatilization and char oxidation of a bituminous and a lignite coal.
- Develop kinetic expressions for PFBC using bench-scale test data as inputs.
- Fit test data to the model and derive rate constants and activation energies for coal combustion.

The information obtained in this study will be of use to those developing comprehensive PFBC performance models and advancing second-generation PFBC unit designs.

3.0 BACKGROUND

3.1 APPLICATION OF AFBC FUEL CHARACTERIZATION EXPERIENCE TO PFBC

Babcock & Wilcox (B&W) has conducted considerable research at the pilot-scale level using the 1-foot x 1-foot (1 x 1) (0.1 MWe) and the 6-foot x 6-foot (6 x 6) (2 MWe) AFBC facilities at B&W's Alliance Research Center (ARC). B&W built an 18-foot x 12-foot (20 MWe) demonstration AFBC facility at Paducah, Kentucky, for the Tennessee Valley Authority (TVA) under a program funded by the Electric Power Research Institute (EPRI). Although a considerable performance database for AFBC at the large-scale is available, there is still a lack of fundamental understanding regarding coal combustion under typical AFBC conditions. This has prevented the development of analytical methods to predict the performance of AFBC units.

Performing large-scale tests to obtain combustion and related information to guarantee the performance of FBC units is expensive and time-consuming. Using bench-scale facilities to obtain similar test information with relatively small fuel samples is more advantageous and effective. Over the past few years, EPRI has funded B&W to develop such a "Fuel Characterization" approach for AFBC. This approach consists of a performance code that utilizes results from inexpensive bench-scale tests to predict the combustion performance of large-scale AFBC units from a variety of coals. [3, 4, 5]

Determination of fuel flexibility under PFBC conditions is very important to the design and guarantees for PFBC units. Fundamental coal combustion information obtained under AFBC cannot be used to accurately predict coal combustion behavior in PFBC units. Pressure has a significant effect on volatile yield, the rates of coal devolatilization, and char oxidation. To optimize the design of first-generation and advanced PFBC combined cycle combustors to cleanly burn coals, it is necessary to thoroughly understand their combustion behavior at high pressure.

Laboratory and pilot data for PFBC is limited. Using bench-scale testing for fuel characterization and model development for PFBC has the advantages of using small quantities of fuels (grams) and well controlled conditions, as well as being cost- and time-effective. Therefore, in this project the bench-scale test data measured in a pressurized reactor were used to develop kinetic information. The kinetic information can be used as inputs to PFBC performance models for predicting the performance and reducing the risks in design of PFBC units. The general approach is described below.

3.2 PFBC FUEL CHARACTERIZATION

A major task of this project was to design, fabricate, and install a computer-controlled, high-pressure and high-temperature bench-scale facility. The reactor was designed to operate in a fixed bed mode. Temperature, pressure, particle size, and gas velocity closely simulated PFBC units. The inlet reaction gas stream was preheated by an electric furnace. The gas flow rate was controlled by the downstream back pressure regulators and was measured using mass flow controllers and rotameters. This facility was utilized to gather time-resolved data on coal devolatilization and char reactivity during heterogeneous combustion.

Two coals, Pittsburgh No. 8 and Texas lignite, with a wide range of properties were selected for testing. Before testing the coals, the flow in the reactor system was characterized by performing preliminary tests from which the operational limits of the bench-scale reactor were determined. Dispersion and time delay of the gases in the reactor system were determined using tracers.

A test matrix was then developed prior to formal testing to specify the appropriate testing ranges for each fuel. During the bench-scale combustion tests, evolved gases were analyzed on-line using CO, CO₂, O₂, and hydrocarbon analyzers. These test data were used to derive the combustion profiles in which carbon evolved was plotted against reaction time. The combustion profiles were corrected for dispersion and time delay before further kinetic information was derived.

Kinetic models were developed for tests performed at elevated pressures. The model development was based upon the bench-scale combustion test data, information in the literature, and an existing kinetic model for coal combustion under AFBC conditions. The reaction kinetics, and the heat and mass transfer processes occurring during coal combustion, were considered in developing the models. The test data were fitted to the models, and coal devolatilization rate constants, and char oxidation rate constants and activation energies were derived. The kinetic information obtained in this project was then compared to fundamental combustion information reported by others in the literature.

3.3 KINETIC THEORIES

In FBC, combustion of coal is characterized in two stages: devolatilization (or pyrolysis) and char oxidation. Upon heating, coal decomposes to yield a hydrogen-rich gas, called volatile matter, and a carbon-rich residue, called char. The relative yield of volatile matter and char depends on fuel properties and combustion conditions.

Figure 1 shows a typical combustion profile of Pittsburgh No. 8 coal obtained in a bench-scale PFB reactor. The combustion profile is a plot of the carbon content in the flue gas as a function of time of reaction. The first portion of the curve is coal devolatilization. The second portion is char oxidation.

Combustion of volatile matter is very rapid. Volatile matter liberated from inside the coal particles is very reactive and can undergo further cracking and/or polymerization. Early combustion models generally ignored volatiles and dealt with char combustion. However, the contribution of the volatiles to total energy released was later recognized and incorporated into models. In addition, volatile release influences the combustion split between in-bed and freeboard. [3,4]

Char oxidation depends on temperature and the amount of oxygen available to char particles. Generally, char burns at a much slower rate than volatile matter. Char oxidation is a highly exothermic process and, therefore, the temperature of char particles is normally higher than the surrounding gas temperature.

Figure 1. Typical Combustion Profile of Pittsburgh No. 8 Coal in a Bench-Scale PFB Reactor

In the B&W AFBC Fuel Characterization Program, rate expressions for coal devolatilization and char oxidation were developed. For simplicity in modeling, the devolatilization of coal was treated as a single overall and irreversible reaction. An Arrhenius-type rate expression was used for char oxidation. The models were incorporated in a performance code to predict the performance of AFBC units.

Most of the available data on char oxidation is decoupled from volatiles evolution. In this program, coal devolatilization and char oxidation were studied under the conditions similar to actual combustion conditions, i.e., the coal devolatilizes under oxidizing conditions, and devolatilization and char oxidation occur concurrently in the transition region. The detailed kinetics of coal devolatilization and char oxidation are discussed below.

3.3.1 Coal Devolatilization

Coal devolatilization can be described in a simplified scheme as shown in Figure 2. [6,7]

In Stage I, the parent "polymer" coal decomposes into smaller molecular units termed metaplast, i.e., metastable plastic intermediate. In this stage, breaking of weaker bonds, such as ether and aliphatic hydrocarbon linkages, between the polymer units occurs. During Stage II, three possibilities may occur to metaplast. It may evaporate to form tar products, it may lose

hydrocarbon gases by cracking of small aliphatic or olefinic side chains from the aromatic rings, or it may repolymerize to form char. During Stage III, the products can continue to react. The char can evolve secondary gas while undergoing ring condensation. The condensation process affects the reactivity of char toward combustion. The tars can crack to form soot, coke, and gases. The gases can crack to form lighter gases and soot. The yield and the compositions of the products vary widely with coal rank and with process variables, such as temperature, residence time, etc. The reactivity and usefulness of char depend on the reaction temperature. [8]

Figure 2. Coal Devolatilization Stages

During coal devolatilization, pyrolytic reactions in the presence of other substances, such as oxygen, can occur. [8] The cracking reactions involve dealkylation, dehydroxylation, and aromatization. [9]

Coal is extremely complex and can undergo a complex variety of reactions under different conditions. In addition, oxidation of volatile components is rapid compared to char oxidation. Detailed mechanisms for the overall devolatilization process are difficult to obtain. However, the evolution rate of the major volatile components is still important for combustion split in FBC units.

Modeling of kinetics of coal devolatilization is often based on the amount of gaseous products evolved. The evolution of volatiles can be modeled in a number of ways. The methods of modeling include single overall, two-competing, and multiple-parallel reactions. [10] Although the multiple-parallel reaction model appears to provide a more accurate result, it is very difficult and tedious to accurately obtain the rate constant for each major component. The volatile matter released from the inside of coal particles can further undergo secondary reactions. Modeling secondary reactions is complex and difficult to perform. In this study, coal devolatilization occurred under oxidizing conditions. The released volatiles were primarily combusted to CO, CO₂, and H₂O. The type and concentration of individual organic species were not measured. Therefore, the devolatilization reactions were treated as an overall reaction. No secondary reactions or parallel reactions were considered in the model.

Many investigators have simplified the overall process as a first-order decomposition occurring uniformly throughout the particle. This is inadequate. One attempt to improve the single first-order modeling was to describe devolatilization as a series of several first-order processes

occurring in different time intervals.[9] Another approach was to use nth order expressions.[9][11]

The most serious shortcoming of modeling the coal devolatilization using first or nth order kinetics is the failure to account for the change of temperature of the coal particle during devolatilization. In addition, the activation energy and pre-exponential factor in the Arrhenius rate equation are not constants during the course of devolatilization. This is more obvious for large coal particles than small particles. The change of temperature is actually a result of particle heat-up and changes in reaction at different temperature intervals.

In this study of fundamental PFB combustion, volatiles evolved from coal were treated as a lump sum, and the devolatilization of coal was modeled as nth order reaction. No secondary reactions were considered in the model. For simplicity, devolatilization was considered as an isothermal process at the later stage of devolatilization where the coal particle has been heated to near the gas temperature.

The expression for devolatilization can be described as:

$$-\frac{d(V_{\infty} - V)}{dt} = k_v (V_{\infty} - V)^n \quad (1)$$

where:

V_{∞} is the maximum amount of volatile released from the coal at test conditions

V is the amount of released volatile

k_v is the rate constant

n is the order of reaction

$$\text{Let } X \text{ (the fraction of released volatile)} = \frac{V}{V_{\infty}}, \quad (2)$$

then Eq. 1 becomes:

$$\frac{dX}{dt} = k_v V_{\infty}^{n-1} (1-X)^n \quad (3)$$

Taking the logarithm on both sides of Eq. 3, the equation becomes:

$$\ln \left(\frac{dX}{dt} \right) = \ln (k_v V_{\infty}^{n-1}) + n \ln (1-X) \quad (4)$$

Plotting $\ln \left(\frac{dX}{dt} \right)$ versus $\ln (1-X)$, n , and k_v can be determined from the slope and the intercept of the line.

The rate constant k_v is temperature dependent and can be expressed as an Arrhenius-type equation:

$$k_v = k_o e^{-Ea/RTp} \quad (5)$$

where:

k_o is a frequency factor

Ea is the apparent activation energy for devolatilization

R is gas constant

Tp is the absolute surface temperature of coal particle

Taking the logarithm on both sides of Eq. 5, then:

$$\ln k_v = \ln k_o - \frac{Ea}{RTp} \quad (6)$$

Plotting $\ln k_v$ versus $\frac{1}{Tp}$, Ea and k_o can be determined from the slope and intercept of the line.

In homogeneous reactions, the activation energy is independent of the extent of reaction. However, in devolatilization of coal, it is reasonable to assume that the apparent activation energy is dependent on the extent of reaction, because devolatilization occurs through many steps where molecules released by the coal change physically and chemically. In addition, devolatilization processes consist of many concurrent and consecutive reactions. Therefore, it is not possible to single out an activation energy of devolatilization. The apparent activation energy could change as the conversion continues. The change of the reactivity of coal during devolatilization was attributed to a decrease in the concentration of active sites, diffusion limitations, and the presence of inorganic impurities which act as catalysts. [12]

Calculation of Surface Temperature of Coal Particles (Tp)

Increase of surface temperature of coal particles during devolatilization is caused by gas-coal particle convection, wall-coal particle radiation, bed material-coal particle radiation, heat of combustion of volatiles, and heat of devolatilization. [13][14] This can be expressed as:

$$\begin{aligned} \frac{\pi d^3}{6} \rho C_p \frac{dT_p}{dt} = & \pi d^2 h_g (T_b - T_p) + \pi d^2 \sigma \epsilon [F_{12}(T_b^4 - T_p^4) + F_{13}(T_s^4 - T_p^4)] \\ & + f \left(\frac{dW}{dt} \right) (-\Delta H_r) - \left(\frac{dW}{dt} \right) (\Delta H_{dv}) \end{aligned} \quad (7)$$

where:

- T_p is coal surface temperature of coal particle
- $\frac{dT_p}{dt}$ is rate of increase of coal particle temperature
- d is diameter of coal (NOTE: Swelling factor should be considered)
- ρ is density of coal
- C_p is specific heat of coal
- h_g is heat transfer coefficient for gas-coal particles
- T_b is temperature of bed material
- T_s is temperature of surface of reactor
- σ is Stefan-Boltzmann constant ($= 5.6699 \times 10^{-12}$ Watt/cm² °K⁴)
- ϵ is emissivity of real body
- $\left(\frac{dW}{dt}\right)$ is rate of volatile generated from coal
- ΔH_r is heat of combustion of volatiles
- ΔH_{dv} is heat of devolatilization
- F_{12} is a fraction of coal particle's surface exposed to bed material (view factor)
- F_{13} is a fraction of coal particle's surface exposed to surface of reactor (view factor)
- f is the fraction of the energy acquired by coal particle

An emissivity of 0.85 was selected for coal. This number was selected by considering the mineral matter existing in coal and the emissivity decreasing with increasing temperature. Using emissivity of 0.85 instead of 1 has little influence on determining the particle temperature.

For a reactor with dimension of $\bar{D}$ (diameter) x H (height), the view factors for coal particles are:

$$F_{12} = \frac{\frac{\pi \bar{D}^2}{2}}{\left(\frac{\pi \bar{D}^2}{2} + \pi \bar{D} H\right)}, \text{ and } F_{13} = 1 - F_{12} \quad (8)$$

For this study, $\frac{dT_p}{dt}$, ΔH_r , and ΔH_{dv} are not known. Therefore, the coal particle temperature during devolatilization was not calculated. Calculation of coal particle temperature for char oxidation will be discussed later.

3.3.2 Char Oxidation

General Aspects

For heterogeneous reactions between char and oxygen, the observed rate of reaction is determined partly by its true chemical kinetics at the surface (exterior and interior) and partly by the rate of transfer of oxygen to that surface through diffusion. The heterogeneous reactions of char and oxygen can be described schematically in Figure 3. The major steps of the reactions are:

1. Mass transfer of oxygen across a relatively stagnant gas film between the exterior surface of the char and the main gas stream,
2. Mass transfer of oxygen from the exterior surface of char to an active site beneath the exterior surface of char,
3. Chemisorption of oxygen on the active site,
4. Rearrangement of chemisorbed species on the active site to desorbable products,
5. Desorption of products from active site,
6. Mass transfer of products from the interior of the char to the exterior surface of char,
7. Mass transfer of products from the exterior surface of char through the stagnant film of gas to the bulk gas.

Figure 3. Schematic Diagram of Major Steps Involved in Char Oxidation

The thickness of the stagnant layer is affected by the gas velocity and the particle size. If the mass transfer rates (Steps 1, 2, 6, and 7) are slow and the kinetic rates (Steps 3, 4, and 5) are fast, the reactions are diffusion controlled. If the reverse is true, the reactions are kinetically

controlled. For small coal particles, diffusion of oxygen is rapid and char oxidation is more likely to be kinetically controlled. For large coal particles, diffusion of oxygen in char is slow and char oxidation is more likely to be diffusion controlled.

The information on pore diffusion of oxygen and of gas products, mainly CO and CO₂, is difficult to determine. Many investigators have lumped Steps 2 to 6 as an apparent kinetic reaction. Information for Step 1 can be determined from the relationship of mass transfer with the gas flow dynamics. The rate of Step 7 is generally assumed to be fast in comparison with the rates of Steps 1 to 6.

Modelers have commonly dealt with the diffusion and the kinetic steps by using a pseudo-steady-state approach. In this approach, the rates of each step are set equal. Employing the pseudo-steady-state approach for modeling of coal combustion can have three typical cases depending on the magnitudes of the diffusion and the kinetic rates. These three typical cases are briefly described below. These three cases can be described through the effect of temperature on rate of char oxidation.

Temperature Regimes for Char Oxidation

Variation of reaction rate of char oxidation with temperature can be divided into three temperature regimes. These regimes are shown in the upper portion of Figure 4. [15] The marked effect of temperature on reaction rate is shown in the lower portion of Figure 4. The three regimes are not sharply delineated, but are separated by transitional regions.

In the low temperature regime (Regime I), the rate of gas diffusion is much faster than the kinetic rate. The concentration of oxygen in the interior of char is about the same as in the bulk gas. Eta (η), the ratio of the experimental reaction rate to the reaction rate which would be found if the oxygen concentration throughout the interior of char is equal to the oxygen concentration in the bulk gas, is near 1. In this temperature regime, combustion of the char proceeds at a constant particle size with decreasing density. [16][17] The reaction rate varies with particle size and shows true order of reaction and true activation energy. [15][18][18]

In the intermediate temperature regime (Regime II), the overall reaction is controlled by both diffusion and kinetics. The oxygen concentration profile varies depending on the magnitude of the rate of diffusion and the kinetics. The oxygen concentration goes to zero at a certain depth in the char. The ratio eta (η) is between zero and 1. As combustion proceeds, the char density and diameter decrease. The rate of reaction is independent of particle size and shows an apparent order n . The apparent order of reaction of n and the true order of reaction of m have the following relationship: [16]

$$n = (m + 1)/2 \quad (9)$$

For a special case where the oxygen concentration in the center of the char particle is zero, if the true order of reaction is one, the apparent order of reaction is also one. The apparent activation energy is about half of the true activation energy.

Figure 4. Oxygen Concentration Profile and Reaction Rate of Three Temperature Regimes of Porous Char

In the high temperature regime (Regime III), the kinetic rate increases to such an extent that it is not a controlling factor, but the diffusion rate is. The oxygen concentration at the exterior surface of char is near zero. η is near zero. The diameter of char decreases as combustion proceeds; however, the density of char remains constant. The apparent activation energy is much smaller than the actual activation energy.

The three temperature regimes for coal combustion can also be interpreted as three size regimes. For small particle size, diffusion of oxygen is fast and the reaction is more likely to be kinetically controlled. Therefore, combustion of small coal particles is more likely to be in temperature Regime I. For medium coal sizes, both diffusion and kinetic rates are important.

Combustion of medium size coal is more likely to be in temperature Regime II. For large coal particles, diffusion of oxygen is slow and the kinetic rate is relatively large. The combustion is more likely to be diffusion controlled, which is the characteristics of temperature Regime III.

Rate Expressions for Char Oxidation

As it is generally known, modeling char reactivity is complicated because not all chars show the same dependence on oxygen concentration. The order of reaction can change from char to char. The kinetics of char oxidation are described in detail below.

From a mass-balance point of view, the observed rate of char oxidation at a pseudo-steady-state equals the rate of oxygen diffused to the outer coal surface, which subsequently equals the kinetic rate of char carbon combustion at the outer coal surface. This can be expressed as:

$$r_{\text{obs}} = h_m ([C_{O_2}]_b - [C_{O_2}]_s) = k_c [C_{O_2}]_s^n \quad (10)$$

where:

r_{obs} is the observed rate for char combustion based on external char surface

h_m is the mass transfer coefficient of oxygen based on external char surface

$[O_2]_b$ is the oxygen concentration in bulk gas

$[O_2]_s$ is the oxygen concentration at the outer char surface

k_c is the kinetic rate constant based on external surface of char

n is an apparent order of reaction

Also, the observed rate of char oxidation equals the reaction occurring within the char and the reaction occurring on the exposed external surface of the char. This can be described by Eq. 11. [15]

$$r_{\text{obs}} = \eta \frac{A_{\text{sp}}}{A_s} k_i [C_{O_2}]_s^m + k_i [C_{O_2}]_s^m = (\eta \frac{A_{\text{sp}}}{A_s} + 1) k_i [C_{O_2}]_s^m \quad (11)$$

where:

η is the ratio of experimental (or actual) reaction rate to the attainable reaction rate if no pore-diffusion resistance existed

A_{sp} is the interior pore area of char

A_s is the external surface of char

k_i is the intrinsic rate constant per unit of total surface area

m is the true order of reaction

The intrinsic rate constant, k_i , is difficult to accurately determine because m and A_{sp} for oxygen are difficult to determine.

In general, the first term of Eq. 11 is greater than the second term, except at high rate of reaction and zero penetration of oxygen in the char.

$[C_{O_2}]_s$ is generally unknown and can be eliminated by manipulating Eq. 10. From Eq. 10:

$$[C_{O_2}]_s = [C_{O_2}]_b - \frac{r_{obs}}{h_m} \quad (12)$$

$$\text{Let } r_{mt} = h_m [C_{O_2}]_b \quad (13)$$

where r_{mt} is the maximum possible mass transfer rate based on outer char surface.

By substituting Eq. 13 into Eq. 12, Eq. 12 can be rewritten as:

$$[C_{O_2}]_s = [C_{O_2}]_b \left(1 - \frac{r_{obs}}{r_{mt}}\right) \quad (14)$$

Substituting $[C_{O_2}]_s$ from Eq. 14 into Eq. 10, Eq. 10 becomes:

$$r_{obs} = k_c [C_{O_2}]_b^n \left(1 - \frac{r_{obs}}{r_{mt}}\right)^n \quad (15)$$

$$\text{Let } r_c = k_c [C_{O_2}]_b^n = k_c' [P_{O_2}]_b^n \quad (16)$$

where r_c is the apparent kinetic rate based on the bulk oxygen concentration and k_c' is the rate constant based on external surface of char, while oxygen concentration is expressed in a pressure unit.

Then Eq. 16 simplifies as:

$$r_{obs} = r_c \left(1 - \frac{r_{obs}}{r_{mt}}\right)^n \quad (17)$$

This equation holds at any time during char oxidation.

Comparing Eq. 15 to Eq. 11, the r_c is not intrinsic kinetic rate. The r_c includes the pore diffusion and the chemical reaction, which is based on the oxygen concentration in the bulk gas, not on the oxygen concentration at the coal surface.

For a special case where $n = 1$, Eq. 17 simplifies as:

$$r_{\text{obs}} = r_c \left(1 - \frac{r_{\text{obs}}}{r_{\text{mt}}}\right) \quad \text{or} \quad \frac{1}{r_{\text{obs}}} = \frac{1}{r_{\text{mt}}} + \frac{1}{r_c} \quad (18)$$

Eq. 18 indicates that the resistance of observed char oxidation is the summation of the resistance of mass transfer and the apparent kinetics reaction.

Essenhight [19] has included the resistance of desorption of the product gas from char in his rate expression for char oxidation.

$$\frac{1}{r_{\text{obs}}} = \frac{1}{r_d} + \frac{1}{r_{\text{mt}}} + \frac{1}{r_c} \quad (19)$$

where r_d is the rate of desorption of product gas from char surface.

In actuality, the resistance of diffusion of the gas products, CO and CO₂, from the interior of the pore to the bulk should be included in the overall resistance of coal combustion. However, the resistance of diffusion of gas products is generally small and is neglected.

Determination of Observed Rate of Char Oxidation (r_{obs})

Char oxidation can be expressed as:

The rate equation for observed rate of char oxidation can be expressed as: [5]

$$r_{\text{obs}} = - \frac{d [\text{C}_{\text{char}}]}{dt} = k [\text{C}_{\text{char}}]^q [\text{C}_{\text{O}_2}]^n_b \quad (20)$$

where r_{obs} is the observed rate for char oxidation and k is the rate constant.

Let $q = 1$ and the fraction of char conversion is X , then:

$$X = \frac{[\text{C}_{\text{char}}]_0 - [\text{C}_{\text{char}}]}{[\text{C}_{\text{char}}]_0} \quad (21)$$

where $[\text{C}_{\text{char}}]_0$ is the initial char concentration.

By substituting Eq. 21 into Eq. 20, Eq. 20 becomes:

$$\frac{dX}{dt} = k (1-X) [\text{C}_{\text{O}_2}]^n_b \quad (22)$$

or

$$\frac{dX}{dt} = k' (1-X) [\text{P}_{\text{O}_2}]^n_b \quad (23)$$

where $[P_{O_2}]_b$ is the partial pressure of O_2 in bulk gas and k' is rate constant when the oxygen concentration is expressed in a pressure unit.

Characteristic Time of Char Combustion (t_c)

By rearranging and integration of Eq. 23 from $t=0$ to a characteristic time t_c where the conversion of char, X , is $(1 - \frac{1}{e})$ or 0.632, then Eq. 23 becomes:

$$\int_0^{X_c} \frac{dX}{1-X} = k' [P_{O_2}]_b^n \int_0^{t_c} dt \quad (24)$$

or

$$-\ln (1-X_c) = k' [P_{O_2}]_b^n t_c \quad (25)$$

By substituting $X_c = 1 - \frac{1}{e}$ in Eq. 25, the equation becomes:

$$1 = k' [P_{O_2}]_b^n t_c \quad \text{or} \quad t_c = \frac{1}{k' [P_{O_2}]_b^n} \quad \text{or} \quad k' = \frac{1}{t_c [P_{O_2}]_b^n} \quad (26)$$

By substituting k' from Eq. 26 into Eq. 23, Eq. 23 can be written as:

$$\frac{dX}{dt} = \frac{1-X}{t_c} \quad (27)$$

Eq. 27 holds for any time during the char oxidation. For $t = 0$, $X = 0$; then Eq. 27 becomes:

$$\left(\frac{dX}{dt} \right)_{X=0} = \frac{1}{t_c} \quad \text{or} \quad \frac{d(1-X)}{dt} = - \frac{1}{t_c} \quad (28)$$

Therefore, the characteristic time for char combustion, t_c , can be determined by plotting the char remaining, $1-X$, versus the char reaction time. The value of t_c can be determined by one of two methods:

Method 1: t_c is the time at which the fraction of char remaining, $1-X$, is equal to 0.368.

Method 2: Based on Eq. 28, t_c equals the reciprocal of the negative of the slope of the line tangential to the curve of $1-X$ versus t at $t=0$.

If the char reaction follows Eq. 20, the value of t_c determined by Methods 1 and 2 should be agreeable.

Multiplication of both sides of Eq. 28 by $[C_{\text{char}}]_0$ and substitution of Eq. 20 into Eq. 28, then Eq. 28 becomes:

$$[C_{\text{char}}]_0 \left. \frac{dx}{dt} \right|_{x=0} = - \left. \frac{d[C_{\text{char}}]}{dt} \right|_{t=0} = (r'_{\text{obs}})_{x=0} = \frac{[C_{\text{char}}]_0}{t_c} \quad (29)$$

or

$$\frac{(r'_{\text{obs}})_{x=0}}{[C_{\text{char}}]_0} = \frac{1}{t_c} \quad (30)$$

where $(r'_{\text{obs}})_{x=0}$ is the initial observed rate of char oxidation.

Specific External Surface Area of Char

The specific external surface area of char particles, A_s , can be expressed as follows assuming that the chars are spherical:

$$A_s = \frac{6}{\rho_{\text{char}} \cdot d} \quad (31)$$

where ρ_{char} is the char density and d is the diameter of the char.

An approximation of ρ_{char} can be determined from coal density, swelling factor (for swelling coals), and the fixed carbon of the coal. This can be expressed as:

$$\rho_{\text{char}} = \frac{\rho_{\text{coal}}}{(\text{swelling})^3} \times \frac{\% \text{ fixed carbon in coal}}{100} \quad (32)$$

ρ_{char} for each test can be more accurately determined by:

$$\rho_{\text{char}} = \frac{\rho_{\text{coal}}}{(\text{swelling})^3} \times \frac{\% \text{ total carbon in coal}}{100} \times \% \text{ char in total carbon} \quad (33)$$

where the % char in total carbon is determined from the fraction carbon remaining curve which is derived from coal combustion profile.

After dividing Eq. 30 by the specific external surface area of char particle, A_s , the equation becomes:

$$\frac{(r'_{\text{obs}})_{x=0}}{[C_{\text{char}}]_0 A_s} = \frac{1}{t_c \cdot A_s} = (r_{\text{obs}})_{x=0} \quad (34)$$

$(r_{\text{obs}})_{x=0}$ is the initial observed rate of char combustion based on the external surface of char.

Determination of Mass Transfer Rate of Oxygen to Char Surface

The relationship between mass transfer and dynamics of gas flow for char combustion was determined by measuring the weight loss of naphthalene balls tested under simulated gas dynamics as for PFBC conditions.

The relationship of weight loss and mass transfer coefficient of naphthalene balls can be expressed as:

$$\frac{\Delta W}{\Delta t} = h_m A_p (C_s - C_b) \quad (35)$$

where:

$\frac{\Delta W}{\Delta t}$ is the weight loss of naphthalene balls in time Δt

h_m is the mass transfer coefficient

A_p is the outer surface area of naphthalene balls

C_s is the naphthalene vapor concentration at ball surface

C_b is the naphthalene vapor concentration at bulk of gas stream.

In general, the approximations of $C_b \approx 0$, $C_s = C^*$ are assumed.

where C^* is the saturated vapor concentration under test conditions.

Then, Eq. 35 can be expressed as:

$$\frac{\Delta W}{\Delta t} = h_m A_p C^* \quad \text{or} \quad h_m = \frac{\Delta W / \Delta t}{A_p C^*} \quad (36)$$

and the mass transfer coefficient h_m can be calculated from Eq. 36.

The relationship of mass transfer of a single sphere in a gas flow stream can be described by the following equation which was originally proposed by Frössling:

$$Sh = 2 + 0.6 Re^{0.5} Sc^{0.33} \quad (37)$$

where:

$$Sh \text{ (Sherwood number)} = \frac{h_m d}{D} \quad (38)$$

d is diameter of the particle

D is diffusivity of gas of interest under test conditions

$$Re \text{ (Reynolds number)} = \frac{\left(\frac{u}{\epsilon}\right) \rho d}{\mu} \quad (39)$$

u is superficial gas velocity

ρ is bulk gas density under test conditions

μ is bulk gas viscosity under test conditions

ϵ is void volume of fixed bed

$$Sc \text{ (Schmidt number)} = \frac{\mu}{D\rho} \quad (40)$$

The experimental Sherwood number (Sh) was determined from Eqs. 36 and 38. The predicted Sherwood number (Sh) was determined from Eq. 37. The experimental and the predicted Sh numbers of the naphthalene balls were plotted versus Reynolds number (Re) and compared as shown in Figure 5. Detailed information is described in Appendix A of the report. As it will be discussed later, the experimental Sh number is much greater than the predicted Sh number. This indicates that the experimental Sh number versus Re number did not quite follow Eq. 37. A better correlation between experimental Sh number and Re number was found to be:

$$Sh = 2 + a Re^{0.7} Sc^{0.33} \quad (41)$$

where a is a constant. Eq. 41 will be discussed later in Section 5.2.3, Mass Transfer Coefficient.

Figure 5. Relationships of Mass Transfer With Gas Flow Dynamics

Determination of Mass Transfer Coefficient (h_m) of Oxygen for Char Oxidation

For char combustion, the Re and Sc numbers were calculated from Eqs. 39 and 40, respectively; the Sh numbers were calculated from Eq. 41 from which the mass transfer coefficient of oxygen can be calculated.

Determination of Diffusion Rate of Oxygen (r_{mt}) in Char Oxidation

As shown in Eq. 13:

$$r_{mt} = h_m [C_{O_2}]_b, \quad r_{mt} \text{ is in weight loss of } O_2 \quad (42)$$

In general, for particle size greater than 1 mm in diameter, the CO will burn near the surface to produce CO_2 . For coal particles less than 50 microns in diameter, the CO burns far away in the bulk gas. For coal particles between 1 mm and 50 microns in diameter, both CO and CO_2 are produced. [17] In previous B&W AFBC Fuel Characterization Program, the predicted surface temperature of coal particles based on CO is the only gas product from char oxidation matched with the experimental surface temperature of coal particles determined using a two-color pyrometer. Therefore, the CO is also assumed to be the only gas product of char oxidation under high pressures for all the coal sizes tested in this project.

With the assumption that the char oxidation goes to CO, then for one mole of O_2 diffused to the char surface, two moles of carbon are consumed. Therefore, the diffusion of oxygen in char oxidation can be expressed in terms of carbon losses, e.g.:

$$r_{mt} = h_m [C_{O_2}]_b \times \frac{24 \text{ (weight of 2 moles of carbon)}}{32 \text{ (weight of 1 mole of oxygen)}} \quad (43)$$

where r_{mt} is in weight loss of carbon.

In the previous AFBC Fuel Characterization Program, a shield factor of 0.45 was used in the calculation of the mass transfer rate of oxygen. This factor was used to account for the external coal surface area blocked by other coal particles during combustion. In this project, the combustion tests were performed at higher pressures. The mass transfer of oxygen from the bulk gas to the coal surface under PFBC conditions is faster than under AFBC conditions. The blockage of the external surface of coal particles by other coal particles is reduced in PFBC. Therefore, a shield factor of 1 is used in the calculation of mass transfer rate.

Determination of Apparent Kinetic Rate of Char Oxidation (r_c)

Based on Eqs. 17, 34, and 43, the apparent kinetic rate at the early stage of char oxidation, i.e., $(r_c)_{x=0}$, can be calculated provided the order of reaction for oxygen concentration, n , is known.

Determination of Apparent Order of Reaction (n)

The $(r_c)_{x=0}$ values can be calculated by assuming the apparent order of reaction, n , equals one initially. As shown in Eq. 16, a new apparent order of reaction can be determined by plotting $(\ln r_c)_{x=0}$ versus $[P_{O_2}]$ for

combustion tests performed at different oxygen concentrations. Then, the $(r_c)_{x=0}$ is recalculated using Eq. 16. A new "n" is obtained by plotting $\ln (r_c)_{x=0}$ versus $[P_{O_2}]$ again. Repetitions may be required until n does not vary significantly.

Calculation of Kinetic Constant of Char Oxidation (k_c)

The rate constant of the apparent rate of char oxidation can be determined from Eq. 16 or:

$$(r_c)_{x=0} = (k'_c)_{x=0} [P_{C_2}]_b^n \quad (44)$$

where $(k'_c)_{x=0}$ is the kinetic rate constant at the early stage of char oxidation in units of gm of carbon/(cm²-sec-atmⁿ).

Determination of Apparent Activation Energy of Kinetic Reaction (E_a)

$(k'_c)_{x=0}$ is temperature dependent. In general, $(k'_c)_{x=0}$ can be represented by an Arrhenius-type expression, i.e.:

$$(k'_c)_{x=0} = A e^{-\frac{(E_a)_{x=0}}{RT_p}} \quad \text{or} \quad \ln (k'_c)_{x=0} = \ln A - \frac{(E_a)_{x=0}}{RT_p} \quad (45)$$

where:

A is a frequency factor

$(E_a)_{x=0}$ is activation energy at the beginning of char oxidation

R is gas constant

T_p is surface temperature of char particle

By plotting $\ln (k'_c)_{x=0}$ versus $\frac{1}{T_p}$, the slope is $-\frac{(E_a)_{x=0}}{R}$, from which the activation energy $(E_a)_{x=0}$ can be determined. The frequency factor A can be determined from the intercept.

Determination of Surface Temperature of Coal Particle (T_p)

In char oxidation, the particle temperature stays relatively constant.^[17] Therefore, it is reasonable to assume that the particle temperature is constant throughout the particle.

The particle temperature of char can be determined from the energy balance of char particles. An equation similar to Eq. 7 can be used. At a steady state, the heat generated from combustion of char particles equals the convective heat loss from the particles and the radiation loss of heat from the particles to the fixed bed material and the surface of reactor. This can be expressed as:

$$-\Delta H \frac{dM_c}{dt} = h \pi d^2 (T_p - T_b) + \pi d^2 \sigma \epsilon [F_{12}(T_p^4 - T_b^4) + F_{13}(T_p^4 - T_s^4)] \quad (46)$$

where:

ΔH is heat of reaction

For $C + 1/2 O_2 \rightarrow CO$, $\Delta H = -2340$ cal/gm of carbon;
For $C + O_2 \rightarrow CO_2$, $\Delta H = -7900$ cal/gm of carbon. [18]

$\frac{dM_c}{dt}$ is char burning rate

h is heat transfer coefficient

σ is Stefan-Boltzmann constant ($= 5.6699 \times 10^{-12}$ Watt/cm² °K⁴)

ϵ is emissivity of real body (≈ 0.85)

T_p, T_b, T_s are temperatures of coal surface, bed material, and reactor surface, respectively

F_{12} is a fraction of char particles exposed to the bed material (view factor)

F_{13} is a fraction of char particles exposed to the surface of the reactor (view factor)

Again, F_{12} and F_{13} can be expressed by Eq. 8.

Determination of Heat Transfer Coefficient (h)

Similar to the correlation of mass transfer to gas flow dynamics for a single sphere (Eq. 41), correlation of heat transfer to gas flow dynamics for a single sphere can be written as:

$$Nu = 2.0 + a Re^{0.7} Pr^{0.33} \quad (47)$$

where:

$$Nu \text{ (Nusselt number)} = \frac{hd}{kg} \quad (48)$$

h is gas heat transfer coefficient

kg is gas conductivity

$$Pr \text{ (Prandtl number)} = \frac{Cp\mu}{kg} \quad (49)$$

Cp is specific heat of gas

μ is gas viscosity

For char particles tested at a preset condition, the heat transfer coefficient can be determined from Eq. 47.

Determination of Heat of Reaction (ΔH) of Char Oxidation

The heat of reaction for the overall reaction can be determined from:

$$\Delta H_t = \Delta H_{CO_2} Q + \Delta H_{CO} (1-Q) \quad (50)$$

where:

ΔH_t is the overall heat of reaction

ΔH_{CO_2} is the heat of reaction for $C + O_2 \rightarrow CO_2$

ΔH_{CO} is the heat of reaction for $C + 1/2 O_2 \rightarrow CO$

$$Q \text{ (fraction of carbon combusted to produce } CO_2) = \frac{CO_2}{2CO + CO_2} \quad (51)$$

In the previous AFBC Fuel Characterization Program, the coal particle temperature was calculated using the heat of formation of CO as the heat of reaction for char oxidation, since the carbon was mainly converted to CO in char oxidation. [18][20] The calculated particle temperature was comparable to the measured temperature as determined using a fiber optic temperature probe. [22] Therefore, the assumption of all carbon in char being converted to CO was applied in coal particle temperature calculations for PFBC tests.

With the assumption of CO is the only product of coal combustion for all the coal sizes and test conditions used in this project, the ΔH_t is approximately equal to ΔH_{CO} .

Calculation of Surface Temperature of Coal Particles (T_p)

Substituting appropriate information in Eq. 46, the surface temperature of coal particles can be calculated.

The combustion test data was collected and combustion profiles were obtained. The rate constants and activation energies were derived from the combustion profiles and the rate expressions.

4.0 TECHNICAL APPROACH

4.1 EXPERIMENTAL

One of the major tasks of this project was to design and install a bench-scale pressurized fluidized-bed (PFB) reactor. The reactor design was such that it could operate effectively at high pressure and high temperature, as well as meet stringent ASME code requirements. The following describes in more detail the PFB reactor design.

4.1.1 The PFB Reactor

The PFB reactor was designed and constructed at Babcock & Wilcox's Alliance Research Center (ARC). Figure 6 is a schematic diagram of the bench-scale fixed-bed PFB facility. Figure 7 is a photograph of the facility. The operational specifications of this facility are shown in Table 1.

Figure 6. Schematic Diagram of the Bench-Scale PFB Facility

Figure 7. Photograph of the Bench-Scale PFB Facility

Table 1

OPERATIONAL SPECIFICATIONS OF THE BENCH-SCALE PFB FACILITY

Gas Temperature	1400° to 1800°F
Gas Pressure	0 to 300 psig
Maximum Gas Flow Rate	26 SCFM
Gas Superficial Velocity	
(2-inch Diameter Reactor)	2 to 5 ft/sec
(1-inch Diameter Reactor)	4 to 20 ft/sec
Material of Gas Preheating Coil, Reactor, and Post Combustor	Inconel 600
Furnace Rating	26 kW

The reactor system has five major components:

- 1) a gas supply and preheating system
- 2) a coal injection system and a reactor
- 3) gas cooling
- 4) gas analysis
- 5) a control and data acquisition system

The components of the facility which experience high temperature and high pressure were made with Inconel 600 to minimize possible oxidation. A pressure relief valve was installed to prevent overpressuring of the system. A brief description of each component is given below.

Gas Supply and Preheating System

Nitrogen and oxygen are the sources of the reaction gases used in the tests. A reaction gas, pure nitrogen or a mixture of nitrogen and oxygen, is premixed before it goes into the preheating system. The gas flow rates and the ratio of nitrogen to oxygen in the mixture are controlled by master flow controllers. The percentages of oxygen in the mixed gas are verified using an oxygen analyzer.

The reaction gas is heated in a coil which is surrounded by a radiant-type electric furnace. The furnace heats the reactor and the post combustor. The preheating coil, the furnace, the reactor, and the post combustor are all enclosed in a pressure vessel. The gas is heated to a preset temperature and is discharged into the open space in the furnace before it goes into the reactor and the post combustor. This equalizes the pressure inside and outside of the preheating coil, the reactor, the post combustor, and the bypass. The furnace is insulated such that the skin temperature of the pressure vessel does not exceed 650°F. A pressure relief valve is installed in the pressure vessel to prevent overpressuring. Several temperature indication switches are installed in different areas of the system to prevent overheating.

Coal Injection System and Reactor

Figure 8 is a detailed drawing of the fixed bed reactor. The 2-inch inside diameter (ID) bed reactor is 10 inches high and sits in the top center of the preheating coil. The reactor slides into a sleeve which is connected to the post combustor and bypass system (see Figure 9). This allows the reactor to be easily removed from the pressure vessel. Four openings at the top of the reactor allow the preheated gas to go into the reactor and flow downward. A diffuser was installed on the top portion of the reactor to distribute the incoming gas.

Figure 8. Schematic Diagram of Bench-Scale PFB Reactor and Pressure Vessel

Figure 9. Photograph of the 2-Inch Diameter Fixed Bed Reactor

There are three penetrations through the top flange of the reactor. One penetration is used for thermocouples. Five thermocouples are used to measure the temperature of the bed material, gas above the bed material, gas below the bed material, the reactor surface, and the preheating coil (see Figure 9).

The second penetration is used for coal injection. The third is used for injecting tracer gases.

The coal particles are injected into the fixed bed reactor using a lock hopper operated with computer-actuated solenoids. The coal particles are injected by pressurizing nitrogen which is about 20 psi higher than the pressure in the vessel. Vibrating of the coal injection tube is necessary to prevent any possible hang-up or plugging of the coal particles.

Gas Cooling

The gas from the reactor travels through a water jacket where the gas is cooled to approximately 1200°F. The gas then goes to a high efficiency heliflow water cooler where the gas is further cooled to about 80°F. Backpressure regulators and valves are used to depressurize the gas to slightly over one atmosphere. The soot in the gas stream is collected in a filter.

Gas Analysis

Rotameters are installed downstream to recheck the gas flow rate and to insure no gas leaks in the system. Slip streams of gases from the post combustor stream are taken for determinations of CO, CO₂, O₂, and total hydrocarbon concentrations. Both CO and CO₂ analyzers are Model 864 non-dispersive infrared analyzers from Beckman Industrial Corporation. The total hydrocarbon analyzer is Model 400A from Beckman Industrial Corporation. The oxygen analyzer is Model 326RA-2 from Baker Industrial Equipment, Inc. The data are used to determine the volatile yield, rate of devolatilization, and rate of char oxidation.

Control and Data Acquisition

A modified IBM personal computer is used to control the solenoid valves for coal injection and the time intervals for monitoring gas concentration. This computer is also used to store the data from the gas analyzers and the temperatures at different locations of the reactor system.

4.2 OPERATION OF BENCH-SCALE PFBC FACILITY

During operation, the reaction gases, either pure nitrogen or a mixture of nitrogen and oxygen, are filtered and premixed before entering the preheating coil. The gas is then preheated to the desired test temperature and discharged into the pressure vessel. The heated reactor gas then flows through the openings in the top of the reactor, then to the bed and the post combustor. With this design, the pressure inside and outside of the reactor and the post combustor is equalized.

After the reactor reaches the desired temperature, the reactor vessel is pressurized by raising the gas delivery pressure to the prescribed pressure. When the system reaches a steady state, the coal particles are injected into

the fixed-bed reactor by pressurizing the coal injection tube and then opening the computer-actuated solenoid valves.

Following coal devolatilization and char oxidation, the products of combustion exit with the exhaust gas. The gas then exits through the water jacket, the cooler, and the filter before it goes to the gas analysis system. Slip streams of the exit gas are taken on-line for determining CO, CO₂, O₂, and hydrocarbon concentrations.

The gas concentrations and temperature readings are recorded by the data acquisition system. The data is reduced and a combustion profile of carbon concentration in exit gas is plotted against the reaction time.

4.3 MODIFICATION OF BENCH-SCALE PFBC FACILITY FOR HIGH GAS VELOCITIES

Because the second generation PFBC units could be a circulating pressurized fluidized-bed combustion (CPFBC) unit and operated at high gas velocities, coal combustion under high pressures and high velocities is of interest. The bench-scale PFBC facility was therefore modified for high gas velocities (from 4 to 20 ft/sec) testing after completing combustion tests in the 2-inch diameter PFB reactor at lower velocities (2 and 4 ft/sec).

In order to minimize changes of the facility to accommodate higher gas velocities, a reactor with a 1-inch diameter was fabricated and inserted in the 2-inch diameter reactor. With this modification, the superficial gas velocities were increased to a maximum of approximately 20 ft/sec. The combustion tests under high gas velocities were performed on Pittsburgh No. 8 coal.

4.4 COAL SELECTION AND PREPARATION

4.4.1 Coal Selection

Based on previous B&W fuel characterization results for AFBC units, it has been shown that the combustion efficiency and sulfur capture can suffer if a high-grade fuel is fed over-bed and burned in a unit designed for a low-grade fuel.^[3] However, if the high-grade fuel is fed under-bed, greater recycle-to-coal feed ratio and greater limestone-to-coal feed ratio are required for high-grade fuel than for low-grade fuel in order to meet AFBC unit design guarantees.^[3] Therefore, fuel flexibility of a given design unit is very important to the performance of FBC units. Also, different degrees of combustion split between in-bed and freeboard for different fuels can affect the thermal efficiency of the units.

In order to develop a fuel characterization method suitable to predict the fuel flexibility of PFBC designs, the combustion behavior of coals with a broad range of properties must be studied. Therefore, coals with a variety of properties in regards to volatile, ash, sulfur, and Btu content were considered as candidates for testing in this project.

In addition, factors such as seam location and production, applicability to PFBC, existing fundamental and pilot-scale PFBC data, relevance to DOE PFBC programs, and the availability were also considered for the candidate coals. An attempt was also made to select at least one coal previously tested under

the B&W AFBC Fuel Characterization Program so that the data obtained for AFBC characterization could be compared to results for PFBC.

Four candidates were selected based on these considerations. These were Pittsburgh No. 8, Kentucky No. 9, Texas lignite, and Beulah lignite. Pittsburgh No. 8 coal and Texas lignite coals were selected for testing after consultation with DOE.

4.4.2 Preparation of Coal Size Fractions

Char oxidation can be diffusion or kinetic controlled depending on combustion conditions and fuel properties. For small coal particles, diffusion of oxygen is rapid and char oxidation is more likely to be kinetically controlled. For large coal particles, diffusion of oxygen in char is slow, and char oxidation is more likely to be diffusion controlled. Therefore, coals with different particle size fractions were tested.

Coals were dried and then ground to the proper size ranges. Six size (4x5, 6x7, 10x12, 28x32, 48x60, 115x150 mesh) fractions were prepared by dry sieving. The corresponding sieve size and the diameter of the particles are shown in Table 2.

Table 2

COAL SIZE FRACTIONS USED IN COMBUSTION TESTS

<u>Mesh</u>	<u>Sieve Size</u>	<u>Diameter</u>	
		<u>Inch</u>	<u>Micron</u>
4x5	4x5	0.187x0.157	4750x4000
6x7	6x7	0.132x0.111	3350x2800
10x12	12x14	0.0661x0.0555	1700x1400
28x32	30x35	0.0234x0.0197	600x500
48x60	50x60	0.0117x0.0098	300x250
115x150	120x140	0.0049x0.0041	125x106

4.5 SHUTDOWN OF THE PFBC FACILITY

4.5.1 Shakedown Tests

After installation and equipment debugging of the pressurized fluidized reactor, comprehensive shakedown testing on coal was performed. The objectives of the shakedown tests were to:

- Determine the carbon mass balance of the combustion system
- Determine the degree of backmixing of the gas in the reactor system
- Calculate coal particle temperature
- Determine test methods and operational limits of the reactor

The electric furnace was cured for two days following the instructions from the vendor. After curing, the furnace was calibrated for automatic temperature control. The temperature of the reactor can be increased from room temperature to the test temperature in 1-1/2 hours. The system reduced the gas temperature to about 80°F before entering the gas analyzers. Plugging of the coal injection tube often occurred when 115x150 mesh particles were injected into the reactor. An air vibrator was installed next to the coal injection tube to reduce the possibility of coal plugging. The gas flow controllers were modified and calibrated to obtain stable output signal readings. Leak tests were done to insure no leakage of gas from the reactor system. The amount of gas flowing into the reactor was calculated and matched with the amount of the gas flowing out of the reactor. The data acquisition software was upgraded to allow more flexibility for recording gas concentrations and temperature and to allow control of the solenoid valves for coal injection, gas sampling, and the sampling time during combustion testing.

The amount of coal for the combustion test was selected to assure detectable CO₂ and CO peaks were observed on the analyzers, and at the same time the oxygen concentration was not significantly changed during combustion. In general, a 0.1 to 0.25 gram sample size (depending on gas pressure) was adequate for the tests. The optimum coal injection time was determined to be about 10 seconds.

Approximately 100 shakedown tests were conducted. The test conditions covered a range of approximately 1400° to 1750°F at pressures of 18 to 280 psig. Five different particle sizes were tested.

4.5.2 Determination of Mass Transfer Coefficient

The mass transfer rate of oxygen under combustion test conditions is difficult to measure. Small spheres of naphthalene representing coal particles were used to determine the relationship of mass transfer to the gas dynamics under conditions simulating the PFB tests. Naphthalene spheres (approximately 1/4-inch diameter) were attached to a thin wire and inserted in the reactor. The reactor was maintained at room temperature. The pressure was raised to 206 psig (15 atm), a typical pressure for PFBC conditions, and 17.5 psig (2.2 atm). The gas flow was adjusted such that the Reynolds number of the gas was in the same range as the Reynolds number for PFBC tests. The naphthalene sphere was then exposed to the gas flow for an hour before the pressure of the reactor was released and the naphthalene sphere was retrieved from the reactor. The loss of the weight and the diameter of the naphthalene sphere were recorded. The weight loss of the naphthalene sphere during the period of pressurizing and depressurizing of the reactor was also measured. The net weight loss of the naphthalene sphere during the actual test was used to determine the relationship of mass transfer to the dynamics of gas flow.

4.6 TEST MATRIX

The results of the shakedown tests were used to fully characterize the operational limits of the reactor and establish a reasonable range of test conditions for detailed devolatilization and char oxidation testing. The final test matrix was developed taking into account full-scale PFBC conditions.

4.7 PRESSURIZED COMBUSTION TESTS

All the tests were performed in a fixed-bed mode. Technically, there are several advantages of using a fixed-bed reactor. These advantages include minimizing backmixing of flue gas, minimizing attrition and elutriation of coal particles, and better tracking of the particle temperature. In the previous B&W AFBC Fuel Characterization Program, the test data was collected in fixed-bed mode. A kinetic model was developed based on accurate temperature and gas concentration measurements. The kinetic model was successfully incorporated in a performance model to predict the performance of AFBC units.

There are, however, some drawbacks to fixed-bed tests, such as neglecting the effects of actual hydrodynamics of the bed and changes in the mass and heat transfer caused by fluidization. This drawback was minimized in development of the overall AFB performance code by inputting additional information obtained under fluidized bed conditions in three other modules of the performance model, i.e., hydrodynamics, solids distribution, and transport phenomena. A similar approach of characterizing PFBC performance using fixed bed reactor tests seems technically feasible.

During testing, temperature, pressure, particle size, and gas velocity were controlled to simulate PFBC unit conditions. The combustion tests were performed by varying one test variable and maintaining other test variables constant. All of the tests were done in duplicate.

Many investigators study the coal devolatilization and char oxidation in a decoupled manner. In their studies, the chars are prepared in a separate step under N_2 before char combustion took place. In real system, devolatilization seldom occurs in a 100% N_2 environment. In actual coal combustion under FBC conditions, devolatilization of coal usually takes place in a gas environment with about 3% to 20% of oxygen. For this study, combustion tests were performed at small oxygen concentrations ranging from 0.5% to 10% in order to have a better differentiation of coal devolatilization from char oxidation.

4.8 MODELING KINETICS UNDER PRESSURIZED CONDITIONS

In this study, the kinetic modeling of the volatiles under PFBC conditions followed a global approach in which all the volatiles are lumped together. This approach simplified the kinetic model and eliminated detailed analyses of the composition of the volatiles released during devolatilization. The global kinetic approach can be easily incorporated into future performance models which might be developed for PFBC units.

Based on the combustion profiles, fundamental kinetic information was derived. The kinetic information included:

- Volatile yield
- Kinetic rate expression for devolatilization
- Rate constants for devolatilization
- Kinetic rate expression for char oxidation
- Rate constants for char oxidation
- Activation energies for char oxidation

The steps involved in deriving the kinetic information from the raw test data are described below:

- Step 1 Plotting the raw data of CO, CO₂, and total hydrocarbon concentration (in ppm) versus the reaction time in the form of combustion profiles as shown in Figure 10. (**NOTE:** The reaction time in Figure 10 has been corrected for time delay.) The gas concentrations corrected for backmixing using a computer algorithm developed at ARC are also shown in Figure 10.
- Step 2 Converting the combustion profile corrected for backmixing of the gas flow in the reactor system into milligrams of carbon as shown in Figure 11.
- Step 3 Plotting "Fraction of Carbon Remaining" versus corrected reaction time from the combustion profiles which have been corrected for backmixing and delay (Figure 12).

Figure 10. Combustion Profiles of Pittsburgh No. 8 Coal With and Without Corrections for Backmixing

Figure 11. Combustion Profiles of Pittsburgh No. 8 Coal With Corrections for Backmixing

Figure 12. Fraction of Carbon Remaining for Pittsburgh No. 8 Coal

- Step 4 Identifying the break point of coal devolatilization and char oxidation and determining the volatile yield and the amount of char produced. The break point is located near the intercept of the line tangential to the curves for coal devolatilization and char oxidation.
- Step 5 Plotting "Fraction of Volatile Remaining" versus corrected reaction time for coal devolatilization as shown in Figure 13.
- Step 6 Determining the order of reaction for coal devolatilization by plotting $\ln (dX/dt)$ versus $\ln (1-X)$ and calculating the slope. [NOTE: Figure 14 is a plot of (dX/dt) versus t .]
- Step 7 Calculating the rate constant for coal devolatilization from Eq. 4.
- Step 8 Plotting "Fraction of Char Remaining" versus corrected reaction time for char combustion as shown in Figure 15.
- Step 9 Determining t_c (where % char remaining is 36.8%) and $(\frac{dX}{dt})_{X=0}$ from "Fraction of Char Remaining" curve. If t_c is equal to the reciprocal of $(\frac{dX}{dt})_{X=0}$, this means the char reaction follows Eq. 28. If t_c is not equal to the reciprocal of $(\frac{dX}{dt})_{X=0}$, the value of the reciprocal of $(\frac{dX}{dt})_{X=0}$ was used as the characteristic time of char combustion.
- Step 10 Determining $(r_{obs})_{X=0}$ and r_{int} from Eqs. 34 and 43, respectively.
- Step 11 Assuming the apparent order for the kinetic reaction is 1 and calculating $(r_c)_{X=0}$ from Eq. 17.
- Step 12 Plotting $\ln (r_c)_{X=0}$ versus oxygen partial pressure (or oxygen concentration) to determine the apparent order for kinetic reaction.
- Step 13 Recalculate $(r_c)_{X=0}$ from Eq. 17 with the reaction order determined in Step 12.
- Step 14 Repeating Steps 12 and 13 until the apparent order of reaction does not change significantly.
- Step 15 Calculating $(k_c')_{X=0}$ from Eq. 44.
- Step 16 Calculating the surface temperature of coal particles, T_p , using Eq. 46 and appropriate information.
- Step 17 Plotting $\ln (k_c')_{X=0}$ versus $1/T_p$ and calculating activation energy, $(E_a)_{X=0}$, and the frequency factor, A , from the slope and the intercept of the line, respectively (see Eq. 45).

Figure 13. Fraction of Volatile Release for Pittsburgh No. 8 Coal

Figure 14. Rate of Devolatilization for Pittsburgh No. 8 Coal

Figure 15. Fraction of Char Remaining in Combustion for Pittsburgh No. 8 Coal

5.0 RESULTS AND DISCUSSION

5.1 COAL SELECTION AND ANALYSIS

5.1.1 Coal Selection

Based on the previously mentioned considerations on coal selection, Pittsburgh No. 8 and Texas lignite coals were chosen for this study.

Pittsburgh No. 8 coal is a high ash, medium sulfur, low VM/FC, and swelling bituminous coal. Texas lignite is a high ash, low sulfur, low alkali, high moisture, high VM/FC, and non-swelling lignitic coal. Both coals were tested at bench-scale and pilot-scale in the previous AFBC Fuel Characterization Program. These coals and the analyses were readily available at B&W for PFBC tests. Extensive fundamental combustion data obtained under AFBC conditions, which can be used to compare the reactivity and kinetics obtained under PFBC conditions, existed for both coals. In addition, Pittsburgh No. 8 coal was tested in a 15-MW pilot PFBC unit by ASEA PFBC. This coal has also been studied extensively under other DOE FBC programs.

5.1.2 Laboratory Analysis

The selected coals were analyzed for proximate, ultimate, and heating value using standard ASTM methods. This information was used for calculation of mass and heat balance. Free swelling index, an indirect indication for coal swelling during combustion, was measured and provided an indication of the coals' swelling behavior during devolatilization. Hardgrove grindability index provided information on attrition of the coal. Elemental ash analysis and ash fusion temperature determination on samples before and after PFBC testing were useful in assessing ash deposition and disposal characteristics of the different coals. The analyses can also be used in the future as inputs to a performance code.

A complete coal and ash analyses for each coal is shown in Tables 3 and 4.

5.2 SHAKEDOWN RESULTS

In general, the results of the shakedown tests indicated that the reactor and the furnace performed very well. The test results are described in the following paragraphs.

5.2.1 Gas Delay and Backmixing

The long distance and tortuous path traveled by the gas in the reactor gas cooling and gas analysis system induced backmixing and delayed the detection of the gas constituents by the analyzers. Also, gas analyzers had some built-in response delay. Therefore, the combustion profile measured by the gas analyzers was delayed and smeared, and did not represent the actual real time combustion profile in the reactor. This had to be corrected mathematically before further combustion information was derived.

Table 3

COAL ANALYSIS
(As Received)

<u>Description</u>	<u>Pittsburgh</u> <u>No. 8</u>	<u>Texas</u> <u>Lignite</u>
<u>Proximate Analysis, % (by wt)</u>		
Moisture	5.20	24.27
Volatile Matter	38.10	34.89
Fixed Carbon	48.10	30.75
Ash	8.60	10.39
Gross Heating Value (Btu/lb)	12,541	8,055
<u>Ultimate Analysis, % (by wt)</u>		
Moisture	5.20	24.27
Carbon	70.20	47.00
Hydrogen	4.90	3.48
Nitrogen	1.55	0.99
Sulfur	2.16	0.79
Ash	8.60	10.39
Oxygen (difference)	7.39	13.08
Free Swelling Index	4	0
Equilibrium Moisture	5.26	25.06
Grindability (ASTM D-409)	52	42

Table 4

ASH ANALYSIS

<u>Description</u>	<u>Pittsburgh</u> <u>No. 8</u>	<u>Texas</u> <u>Lignite</u>
<u>Ash Analysis (I.C.P.), %</u>		
Silicon as SiO ₂	50.58	39.10
Aluminum as Al ₂ O ₃	24.62	14.65
Iron as Fe ₂ O ₃	17.16	8.35
Titanium as TiO ₂	1.10	1.30
Calcium as CaO	1.13	15.66
Magnesium as MgO	0.62	3.08
Sodium as Na ₂ O	0.39	0.44
Potassium as K ₂ O	1.99	0.72
Sulfur as SO ₃	1.11	5.86
Phosphorus as P ₂ O ₅	0.39	<0.09
<u>Ash Fusion Temperature, °F</u>		
<u>Atmosphere</u>	<u>Red.</u> <u>Oxid.</u>	<u>Red.</u> <u>Oxid.</u>
A (I.D.)	2220 2560	2160 2200
B (S.T., Sp)	2440 2640	2220 2240
C (S.T., Hsp)	2470 2650	2230 2280
D (F.T., 1/16")	2570 2670	2260 2330
E (F.T., Flat)	2750+ 2750+	2360 2450

The delay and the backmixing of the gas in the bench-scale PFBC facility was corrected by using a method developed by Dr. Stuart Daw at Oak Ridge National Laboratory (ORNL).^[21] The detailed information of the method is described in Appendix B of this report. In this approach, the gas exiting from the reactor is treated mathematically as flowing through a plug flow reactor and two first order continuous stirred tank reactors connected in series (see Figure 16). The plug flow reactor is used to characterize the delay of the gas. The continuous stirred tank reactors are used to characterize the degree of backmixing of the gas. The time constant for the plug flow and the continuous stirred tank reactor can be determined by performing tracer studies.

Figure 16. Delay and Backmixing of Flue Gas

A tracer with a fixed concentration of CO , CO_2 , and methane was injected into the reactor by opening the solenoid valve of an injection tube for 10- to 20-second intervals to allow a step change in carbon concentration. The concentration profiles for CO , CO_2 , and total hydrocarbon were measured. The time constant for the plug flow reactor was determined by measuring the time at which the carbon concentrations started to decrease. This is equivalent to the close of the solenoid valve. A computer algorithm to determine the time constant for the continuous stirred tank reactors was developed by best fitting the predicted concentration profile with the measured concentration profile. The two time constants derived from tracer studies were then used to back-calculate the coal combustion profile which would exist without gas delay and backmixing. Figure 10 shows an example of the combustion profile of Pittsburgh No. 8 coal before and after correcting for backmixing. Tracer tests were done at different temperatures, pressures, and gas velocities prior to coal combustion tests. All the test data were corrected for gas backmixing and delay before further kinetic information was derived.

5.2.2 Carbon Mass Balance

The carbon mass balance for the combustor was also calculated. Examples of carbon mass balance results of several tests and the associated test

conditions are shown in Table 5. For most of the combustion tests performed during the shakedown test, the carbon mass balance was between 90 and 110%.

Table 5

CARBON MASS BALANCE AND SHAKEDOWN TEST CONDITIONS FOR PITTSBURGH NO. 8 COAL

<u>Size</u> <u>(mesh)</u>	<u>Temp.</u> <u>(°F)</u>	<u>Pressure</u> <u>(psig)</u>	<u>O₂</u> <u>(%)</u>	<u>Coal</u> <u>Weight</u>	<u>Gas</u> <u>Velocity</u> <u>(ft/sec)</u>	<u>Carbon</u> <u>Balance</u> <u>(%)</u>
48x60	1399	55	2.5	0.25	4	105
10x12	1725	18	3.0	0.257	4.4	93
4x5	1550	206	3.0	0.251	5	106

5.2.3 Mass Transfer Coefficient

Based on the shakedown data, the Sherwood number (Sh), a dimensionless term of mass transfer, at pressures of 205 and 17.5 psig was determined. The experimental Sh number was determined using Eqs. 36 and 38, and the predicted Sh number was calculated using Eq. 37. Comparison of the results is shown in Figure 5. The experimental Sherwood number is higher than the predicted Sherwood number calculated based on Eq. 37. The difference is mainly attributed to smaller gas diffusion coefficient at high pressure. The experimental Sherwood number is better represented by the following equation:

$$Sh = 2 + 0.92 Re^{0.7} Sc^{0.33} \quad (52)$$

5.2.4 Calculating of Coal Particle Temperature

During char oxidation, the surface temperature of coal is generally higher than the bed temperature. The surface temperature of coal is the temperature at which the kinetic reactions occur.

The surface temperatures of the coal particles were calculated from Eq. 46, which was based on the energy balance of the particle in the reactor. The char combustion rate in Eq. 46 was obtained from the combustion profile. Also, the heat transfer coefficient in the equation was calculated using the following equation:

$$Nu = 2 + 0.92 Re^{0.7} Pr^{0.33} \quad (53)$$

5.3 TEST CONDITIONS

The final bench-scale test conditions were developed based upon commercial PFBC operating conditions and inputs from the DOE technical project officer. The detailed test conditions for Pittsburgh No. 8 and Texas lignite coals are shown in Tables 6, 7, and 8. The rationale for selecting the ranges of test variables are discussed in the following paragraphs.

Table 6

TEST CONDITIONS FOR STUDIES ON
COAL DEVOLATILIZATION AND CHAR REACTIVITY UNDER PFBC CONDITIONS
(For Pittsburgh No. 8 Coal in 2-Inch Diameter Reactor)

Temperature °F	Pressure psig (atm)	Oxygen Conc. %	Superficial Gas Velocity ft/sec	Coal Particle Size Mesh (Sieve No.)
1425	18 (2.2)	10	4	4x5 (4x5)
1550	132 (10.2)	3	2	6x7 (6x7)
1725	206 (15.0)			10x12 (12x14)
	280 (20.0)			48x60 (50x60)
				115x150 (120x140)

Table 7

TEST CONDITIONS FOR STUDIES ON
COAL DEVOLATILIZATION AND CHAR REACTIVITY UNDER PFBC CONDITIONS
(For Texas Lignite Coal in 2-Inch Diameter Reactor)

Temperature °F	Pressure psig (atm)	Oxygen Conc. %	Superficial Gas Velocity ft/sec	Coal Particle Size Mesh (Sieve No.)
1425	18 (2.2)	3	4	4x5 (4x5)
1550	132 (10.2)	0.5	2	6x7 (6x7)
1725	206 (15.0)			10x12 (12x14)
	280 (20.0)			48x60 (50x60)
				115x150 (120x140)

Table 8

TEST CONDITIONS FOR STUDIES ON
COAL DEVOLATILIZATION AND CHAR REACTIVITY UNDER PFBC CONDITIONS
(For Pittsburgh No. 8 Coal in 1-Inch Diameter Reactor)

Temperature °F	Pressure psig (atm)	Oxygen Conc. %	Superficial Gas Velocity ft/sec	Coal Particle Size Mesh (Sieve No.)
1425	206 (15.0)	10	4	28x32 (30x35)
1550	280 (20.0)	3	12	48x60 (50x60)
1725			20	115x150 (120x140)

Pressure

In general, combustion results from pilot PFBC units have been operated at about 10 to 16 atm. The American Electric Power (AEP) PFBC demonstration units at the Tidd Plant at Brilliant, Ohio, and the Philip Sporn Plant at New Haven, West Virginia, are designed to operate near 15 atm. Pressures of 206 psig (15 atm) and 132 psig (10 atm) are included in the test conditions, so that the bench-scale data obtained from this study can be compared with the existing pilot PFBC data and demonstration results as they become available.

The bench-scale PFC reactor was designed to operate up to 300 psig. Combustion information at pressures near 300 psig is very limited and is of interest. Therefore, a pressure of approximately 280 psig was included in the test conditions. The test facility can also be operated near atmospheric pressure. However, because of the long gas preheating coil and extended plumbing in the gas cooling system of the PFBC bench-scale facility, a minimum gas pressure of approximately 18 psig (2.2 atm) is required in order to maintain a superficial gas velocity of 4 ft/sec in the reactor. This pressure was included in the test matrix.

Temperature

A typical operating temperature range for commercial, pressurized, fluidized bed combustion is between 1400° and 1800°F. The design limit of the electric furnace of the bench-scale PFB reactor is 1800°F. In this study, coals were characterized at approximately 1425°, 1550°, and 1725°F.

Oxygen Concentration

In fluidized-bed combustion of coal, the oxygen concentration in the bed varies from approximately 20% at the bottom of the bed to approximately 3% in the flue gas. The average concentration of oxygen is approximately 10%. Pittsburgh No. 8 coal was tested under 3% and 10% oxygen. However, the Texas lignite burned faster than Pittsburgh No. 8 coal. In order to differentiate coal devolatilization and char oxidation of Texas lignite, lower oxygen concentrations were required to slow down the combustion process. For Texas lignite, the coal was combusted at 0.5% and 3% O₂.

Coal Particle Size

The typical coal feed size to AFBC and PFBC pilot facilities is 1/4" x 0. Coal feed size can be further reduced to finer size fractions during feeding and combustion. This results in finer particle size distribution. The smaller coal size (approximately 60 microns) is of interest for second-generation PFBC design.

In this program, six particle sizes were included in the test matrix as described earlier in Section 4.4. The size fractions were the same as used in the previous B&W AFBC Fuels Characterization Program. For tests performed at high gas velocities in the 1-inch diameter reactor, three smaller size fractions (28x32, 48x60, 115x150 mesh) were used.

Superficial Gas Velocity

The typical range for the superficial gas velocity of commercial PFB combustor is approximately 2 to 5 ft/sec. The 2-inch diameter reactor was capable of a maximum gas velocity of 5 ft/sec. In this program, detailed combustion studies were performed at a superficial gas velocity of 4 ft/sec. Selected combustion tests were also performed at superficial gas velocities of 2 and 5 ft/sec.

After the reactor system was modified to 1-inch diameter for high pressure and high gas velocity tests, the combustion tests were performed at superficial gas velocities of 4, 12, and 20 ft/sec.

5.4 TEST MATRIX

Over 400 bench-scale combustion tests were conducted. The test matrix for Pittsburgh No. 8 and Texas lignite coals are listed in Tables 9, 10, and 11.

The results of the combustion tests are discussed in the following paragraphs. All of the test conditions shown in the figures and tables are approximate conditions. The exact test conditions are shown in Appendix C. All of the raw and reduced test data are stored on PC discs. These data are available upon request.

Table 9

TEST CONDITIONS FOR PITTSBURGH NO. 8 COAL (in 2-inch Reactor)

<u>File Name</u>	<u>Temp. °F</u>	<u>Press. psig</u>	<u>O₂ Conc. %</u>	<u>Gas Superf. Vel. ft/sec</u>	<u>Coal Sizes</u>
PITS100-111	1550	206	3	4	6 sizes*
PITS112-126	1550	206	10	4	6 sizes
PITS127-141	1550	18	3	4	6 sizes
PITS142-154	1550	18	10	4	6 sizes
PITS155-166	1550	132	3	4	6 sizes
PITS167-178	1550	132	10	4	6 sizes
PITS179-191	1425	18	3	4	6 sizes
PITS192-213	1425	18	10	4	6 sizes
PITS204-215	1425	132	3	4	6 sizes
PITS216-227	1425	132	10	4	6 sizes
PITS228-240	1425	206	3	4	6 sizes
PITS241-252	1425	206	10	4	6 sizes
PITS253-264	1725	18	3	4	6 sizes
PITS265-276	1725	18	10	4	6 sizes
PITS277-288	1725	206	3	4	6 sizes

* 4x5, 6x7, 10x12, 28x32, 48x60, and 115x150 mesh.

Table 9 (Continued)

TEST CONDITIONS FOR PITTSBURGH NO. 8 COAL
(in 2-inch Reactor)

<u>File Name</u>	<u>Temp. °F</u>	<u>Press. psig</u>	<u>O₂ Conc. %</u>	<u>Gas Superf. Vel. ft/sec</u>	<u>Coal Sizes</u>
PITS289-300	1725	206	10	4	6 sizes
PITS301-312	1725	132	3	4	6 sizes
PITS313-324	1725	132	10	4	6 sizes
PITS325-336	1550	206	3	5	6 sizes
PITS337-348	1550	206	10	5	6 sizes
PITS349-360	1425	206	3	5	6 sizes
PITS361-372	1550	18	3	2	6 sizes
PITS373-384	1550	18	10	2	6 sizes
PITS384-395	1550	132	3	2	6 sizes
PITS396-407	1550	132	10	2	6 sizes
PITS408-419	1550	206	3	2	6 sizes
PITS420-431	1550	206	10	2	6 sizes
PITS432-443	1425	206	3	2	6 sizes
PITS444-455	1425	206	10	2	6 sizes
PITS456-467	1425	132	3	2	6 sizes
PITS468-479	1425	132	10	2	6 sizes
PITS480-491	1725	206	3	2	6 sizes
PITS492-503	1725	206	10	2	6 sizes
PITS504-515	1725	132	3	2	6 sizes
PITS516-527	1725	132	10	2	6 sizes
PITS528-539	1725	18	3	2	6 sizes
PITS540-551	1725	18	10	2	6 sizes
PITS552-563	1425	18	3	2	6 sizes
PITS564-575	1425	18	10	2	6 sizes
PITS500-511	1550	206	3	4	6 sizes
PITS513-524	1550	280	3	4	6 sizes
PITS525-536	1550	280	10	4	6 sizes
PITS530-541*	1425	280	3	4	6 sizes
PITS542-553	1425	280	10	4	6 sizes
PITS554-565	1725	279	3	2	6 sizes
PITS566-577	1425	280	3	2	6 sizes
PITS578-589	1550	280	3	2	6 sizes
PITS580-591*	1725	235	3	4	6 sizes
PITS592-603	1725	240	10	4	6 sizes
PITS604-609	1550	280	3	4	1 size**

* File number is not in order

** 275x325 mesh

Table 10

TEST CONDITIONS FOR PITTSBURGH NO. 8 COAL
(in 1-inch Reactor)

<u>File Name</u>	<u>Temp.</u> <u>°F</u>	<u>Press.</u> <u>psig</u>	<u>O₂ Conc.</u> <u>%</u>	<u>Gas Superf.</u> <u>Vel. ft/sec</u>	<u>Coal Sizes</u>
PITS700-705	1550	206	3	4	3 sizes*
PITS706-711	1550	206	10	4	3 sizes
PITS711-716	1550	206	3	12	3 sizes
PITS717-722	1550	206	10	12	3 sizes
PITS723-728	1550	206	3	20	3 sizes
PITS729-734	1550	206	10	20	3 sizes
PITS736-741	1725	206	3	4	3 sizes
PITS742-747	1725	206	3	12	3 sizes
PITS748-753	1725	206	3	20	3 sizes
PITS754-759	1425	206	3	20	3 sizes
PITS760-765	1425	206	3	12	3 sizes
PITS766-771	1425	206	3	4	3 sizes
PITS772-777	1550	280	3	4	3 sizes
PITS900-905	1725	280	3	12	3 sizes
PITS906-911	1550	280	3	12	3 sizes
PITS912-917	1425	280	3	12	3 sizes

* 28x32, 48x60, and 115x150 mesh.

Table 11

TEST CONDITIONS FOR TEXAS LIGNITE COAL
(in 2-inch Reactor)

<u>File Name</u>	<u>Temp.</u> <u>°F</u>	<u>Press.</u> <u>psig</u>	<u>O₂ Conc.</u> <u>%</u>	<u>Gas Superf.</u> <u>Vel. ft/sec</u>	<u>Coal Sizes</u>
TEXL100-111	1550	206	3	4	6 sizes*
TEXL112-115	1550	206	0.5	4	6 sizes
TEXL116-129	1550	18	3	4	6 sizes
TEXL130-141	1550	18	0.5	4	6 sizes
TEXL142-153	1550	132	3	4	6 sizes
TEXL154-166	1550	132	0.5	4	6 sizes
TEXL167-178	1550	206	3	4	6 sizes
TEXL179-190	1550	206	0.5	4	6 sizes
TEXL191-204	1550	18	3	4	6 sizes
TEXL205-216	1425	18	0.5	4	6 sizes
TEXL217-228	1425	132	3	4	6 sizes
TEXL229-240	1425	132	0.5	4	6 sizes
TEXL241-252	1425	206	3	4	6 sizes
TEXL253-258	1425	206	0.5	4	3 sizes
TEXL259-271	1725	18	3	4	6 sizes
TEXL272-283	1725	18	0.5	4	6 sizes
TEXL284-295	1725	206	3	4	6 sizes
TEXL296-307	1725	206	0.5	4	6 sizes
TEXL308-319	1725	132	3	4	6 sizes
TEXL320-331	1725	132	0.5	4	6 sizes
TEXL332-343	1550	206	3	2	6 sizes
TEXL344-355	1550	206	0.5	2	6 sizes

* 4x5, 6x7, 10x12, 28x32, 48x60, 115x150 mesh.

5.5 COMBUSTION TEST RESULTS

5.5.1 Coal Devolatilization

Effect of Temperature

In general, in this study more CO is released during devolatilization at lower temperature than at higher temperature. The transition from coal devolatilization to char oxidation is less distinct at lower temperature than at higher temperature. This trend was observed for both Pittsburgh No. 8 and Texas lignite coals.

Figure 17 shows the logarithm of the rate of devolatilization versus the logarithm of the fraction of volatiles remaining in the coal on 28x32 mesh Pittsburgh No. 8 coal at 1427°, 1550°, and 1729°F. The rate of devolatilization shows a sharp increase initially. This is attributed to particle heat-up.

Figure 17. Effect of Temperature on Devolatilization of Pittsburgh No. 8 Coal (in 2-Inch Reactor)

The initial devolatilization rate is also greater for higher temperature than for lower temperature. This is attributed to faster particle heat-up rate at higher temperature. In the later stage of devolatilization, the coal devolatilization rate is the highest at temperatures near 1427°F. Howard, et al., also found that the volatiles produced by coals exhibit a maximum at around 600° to 700°C, and further increase in temperature results in production of more solids material from secondary cracking than volatiles from additional devolatilization.^[9] Talwalker mentioned that both the primary and secondary devolatilization reactions increase with temperature; however, the net effect of temperature on devolatilization rate and volatile yield is not obvious.^[23] Saxena indicated that the holding time at the peak temperature during devolatilization is important. As the holding time increases, the effect of temperature on devolatilization becomes less apparent.^[24] The volatile yields at 1427°, 1550°, and 1729°F were approximately 37%, 38%, and 43%, respectively. The volatile yield reported in Figure 17 and following figures is based on the total carbon in the coal.

The data shown in Figure 17 appears to have a transition near 50% of devolatilization. This suggests that there could be two types of volatile matter released. At the early stage of devolatilization where the particle temperatures are low, lighter molecular weight volatile, such as aliphatic compounds, are more likely to be released. At the later stage of devolatilization where the particle temperature is higher, secondary reactions of converting tars to light hydrocarbons are likely to occur. A two-stage reaction during devolatilization of North Dakota and Montana lignite coals was also reported by Nsakala, et al.^[25]

As mentioned previously, the particle temperature increases during the course of devolatilization. It is difficult to determine the order of reaction when the particle temperature is not constant. However, it may be reasonable to assume that the coal particle temperature is nearly constant in the later stage of devolatilization. Based on this assumption, the order of reaction is determined to be 0.43, 0.47, and 0.47 at 1427°, 1550°, and 1729°F, respectively. The order of reaction is less than one and is affected by temperature. Rai and Tran assumed that the activation energy for coal devolatilization is not a constant, but increased with degree of devolatilization. They found the order of devolatilization for Hanna coal was 0.24.^[11] Again, the order of reaction was much less than one.

A similar plot for 28x32 mesh Texas lignite coal at 1424°, 1572°, and 1730°F is shown in Figure 18. The devolatilization rate at 1572°F is greater than that at 1424° and 1730°F. However, the volatile yield decreases with increasing the temperature. The volatile yield is approximately 57%, 51%, and 48% at 1424°, 1572°, and 1730°F, respectively. The order of reaction is 0.49, 0.38, and 0.40 for 1424°, 1572°, and 1730°F, respectively. Again, the order of reaction is less than one.

Comparing Figure 17 with Figure 18, the data shows that for Texas lignite the transition from the primary to the secondary devolatilization occurs at a later stage than for Pittsburgh No. 8 coal. This appears to indicate that Texas lignite has more aliphatic volatile matter than Pittsburgh No. 8 coal.

Figure 18. Effect of Temperature on Devolatilization of Texas Lignite Coal (in 2-Inch Reactor)

Effect of Pressure

Figure 19 shows the logarithm of the rate of devolatilization versus the logarithm of the fraction of volatile remaining in the coal for 28x32 mesh Pittsburgh No. 8 coal at 20, 130, 207, and 277 psig gas pressure. The rate of devolatilization increased with pressure and reached a maximum at 130 psig. Further increasing pressure results in decreasing the rate of devolatilization. As indicated in Figure 19, the percentage of volatile matter released from coal decreases with increases in pressure up to 130 psig. When the pressure is above 130 psig, the volatile yield increases with pressure. The reason for having a minimum volatile yield is not known. The order of reaction is approximately 0.59, 0.14, 0.21, and 0.38 for 20, 130, 207, and 277 psig, respectively.

Figure 19. Effect of Pressure on Devolatilization of Pittsburgh No. 8 Coal (in 2-Inch Reactor)

Figure 20 shows the log-log plot of rate of devolatilization versus fraction of volatile remaining in Texas lignite coal. The rate of devolatilization increases slightly with pressure. The order of reaction is 0.42, 0.42, and 0.31 at 17.5, 132, and 206 psig, respectively. The percentage of volatiles released from Texas lignite coal increased only slightly with increasing pressure.

Suuberg, et al., reported that volatile yield under helium was higher at 1 atm than at 69 atm for Pittsburgh No. 8 and Montana lignite.^[26] Solomon and Hamblen reported that high pressure inhibits tar yields by reducing the evaporation and diffusion of heavy molecules.^[27] It was also reported that increasing pressure enhances the secondary reactions, thereby increasing the yield of char and light hydrocarbons at the expense of tar.^[9] In this project, the devolatilization tests were performed under nitrogen containing a small amount of oxygen. Combustion of the volatiles during devolatilization

at high gas pressure can induce more driving force for devolatilization than at low pressure. This could be one of the reasons why more volatile matter is released from the coal at higher pressure than at low pressure.

Figure 20. Effect of Pressure on Devolatilization of Texas Lignite Coal (in 2-Inch Reactor)

Effect of Particle Size

For the larger coal particles, the transition from coal devolatilization to char oxidation is less distinct than for smaller particles. Figure 21 is a log-log plot of rate of devolatilization versus the fraction of volatile remaining in coal for three particle sizes of Pittsburgh No. 8 coal. The rate of devolatilization for 10x12 mesh particles is much slower than that for 28x32 and 48x60 mesh particles. The order of reaction is 0.51, 0.39, and 0.30 for 10x12, 28x32, and 48x60 mesh particles, respectively. The volatile yield is approximately the same for the three sizes.

Figure 21. Effect of Particle Size on Devolatilization of Pittsburgh No. 8 Coal (in 2-Inch Reactor)

The effect of particle size on devolatilization rate for Texas lignite is shown in Figure 22. As the coal size decreases, the rate of devolatilization increases. The order of reaction is 0.41, 0.39, and 0.05 for 10x12, 28x32, 48x60 mesh particles. Nsakala, et al., [25] reported that the rate of devolatilization of North Dakota lignite at the initial stage increases with decreasing coal size. However, at the later stage of devolatilization, they found that the rate is not affected by coal size up to the largest size they have examined (180 microns).

The volatile yield is 41%, 51%, and 52% for 10x12, 28x32, and 48x60 mesh particles, respectively. The volatile yield increases with decreasing particle size. This is consistent with the observations on devolatilization rate and volatile yield for North Dakota lignite. [25]

Figure 22. Effect of Particle Size on Devolatilization of Texas Lignite Coal (in 2-Inch Reactor)

Effect of Oxygen Concentration

In general, more volatile is released at higher oxygen concentration than at low oxygen concentration. Figure 23 shows the effect of oxygen concentration on the rate of devolatilization of Pittsburgh No. 8 coal. The devolatilization rate increases with oxygen concentration. The volatile yield is 41% and 53% for 3% and 10% O₂. The order of reaction is 0.55 and 0.59 for 3% and 10% oxygen, respectively.

Figure 24 shows the effect of oxygen concentration on devolatilization rate of Texas lignite. The rate of devolatilization increases with increasing oxygen concentration. The order of reaction is 0.51 and 0.49 for 0.5% and 3% oxygen. However, oxygen concentration seems to have very little effect on the volatile yield of Texas lignite coal when oxygen concentration is 3% or less.

Figure 23. Effect of Oxygen Concentration on Devolatilization of Pittsburgh No. 8 Coal (in 2-Inch Reactor)

Figure 24. Effect of Oxygen Concentration on Devolatilization of Texas Lignite Coal (in 2-Inch Reactor)

The greater devolatilization rate for higher oxygen concentration than for lower oxygen concentration is attributed to larger driving force for devolatilization for higher oxygen concentration environment, which is caused by more complete combustion of volatiles at the external coal surface under higher oxygen concentration conditions.

Effect of Superficial Gas Velocity

Figure 25 shows the effect of superficial gas velocity on coal devolatilization of Pittsburgh No. 8 coal. The data shown in this figure was obtained from the 1-inch diameter reactor. The rate of devolatilization increases with increasing superficial gas velocity. The increase in devolatilization rate for higher superficial gas is attributed to two factors. First, there is a greater driving force for volatile release under higher gas velocity. Based on fluid mechanics, the faster the gas flows around the particle surface, the lower the static pressure on the particle surface. Secondly, oxygen is transferred faster to the coal surface at higher superficial velocity.

The volatile yield is 32%, 40%, and 32% for superficial gas velocity of 20, 12, and 4 ft/sec, respectively. The order of reaction of volatile in coal devolatilization is 0.19, 0.23, and 0.25 for superficial gas velocity of 4, 12, and 20 ft/sec, respectively.

Figure 25. Effect of Superficial Gas Velocity on Devolatilization of Pittsburgh No. 8 Coal (in 1-Inch Reactor)

Effect of Coal Type

Investigators have difference opinions on effect of coal rank on devolatilization. Some investigators have noted the differences in devolatilization of bituminous and lignite coals. Other investigators have suggested that the volatile yields can be related to the functional group distributions in coals and that the kinetics of evolution of a particular species are insensitive to coal rank. [23]

Based on the observations of the tests performed in this project, the transition from coal devolatilization to char oxidation is less distinct for Texas lignite coal than for Pittsburgh No. 8 coal. Comparing Figure 17 to Figure 18, the devolatilization rate of Pittsburgh No. 8 and Texas lignite coal were similar. However, the volatile yield is higher for Texas lignite coal than for Pittsburgh No. 8 coal.

Based on the ASTM coal analysis shown in Table 3, the volatile matter on a moisture and ash free basis is calculated to be 44.2 and 52.94% for Pittsburgh No. 8 and Texas lignite coal, respectively. As shown in Figures 17 to 25, the volatile yield of the two coals varies and depends on the physical properties of the coals and the test conditions. For most of the cases, the volatile yield is less than the volatile matter determined using the ASTM method. In determination of the volatile matter of coal in ASTM proximate analysis, the coal was dried and ground to 60 mesh top size and devolatilized at a temperature of $1742^{\circ} \pm 36^{\circ}\text{F}$ for 7 minutes. The size used in ASTM analysis is smaller than the size used in this project, and the temperature is greater than most of the test temperatures. Based on the previous discussions on the effect of size and temperature on coal devolatilization, it is not surprising to see that, in general, the volatile yields obtained in this project are less than the volatile matter determined by ASTM coal analysis.

Heating Rate

The effect of heating rate was not studied in this project. Many previous studies by other investigators indicated that heating rate affects the time-temperature history of the coal particles; however, it does not affect the volatile yield significantly. [27][28] Heating rate could also affect the properties of char produced. The chars produced by rapid heating were reported to have larger pore volumes and surface areas. [29]

The orders of reaction reported here are the apparent orders of reaction. The orders of reaction are not constant and are less than one. Also, they vary with the coal properties and devolatilization conditions. The actual order of reaction can be derived if the particle temperature history during devolatilization is known.

5.5.2 Char Oxidation

Char oxidation is the reaction of char with the oxygen which diffuses from the bulk gas to the surface of the char. Therefore, the oxygen concentration in the bulk gas can affect the rate of char oxidation. The order of oxygen concentration in the rate expression has been studied extensively by various investigators and different values have been obtained. Most investigators used 1 or 0.5 as the order of reaction. The order of oxygen

concentration in the reaction not only affects the rate of char oxidation, but also indicates the temperature regimes in which the char is combusted. Therefore, it is very important to discuss the effect of oxygen concentration on char oxidation.

Effect of Oxygen Concentration

Figure 26 shows the logarithm of the kinetic rate versus the partial pressure of oxygen in the bulk gas for three sizes (10x12, 28x32, and 48x60 mesh) of Pittsburgh No. 8 coal. The combustion conditions consisted of pressures of approximately 280 and 206 psig, bed temperatures of 1550°F, and a superficial gas velocity of 4 ft/sec.

Figure 26. Effect of Oxygen Concentration on Kinetic Rate of Pittsburgh No. 8 Coal

The test data shown in Figure 26 was taken at approximately the same bed temperatures. The surface temperatures of coal particles, however, are different. In high oxygen concentration environments, the coal particle temperature is greater than for lower oxygen concentration environments because of the increased surface oxygen concentration and the higher reaction rate. The difference in coal particle temperature affects the order of reaction and should be corrected in order to obtain a more accurate apparent order of reaction.

For higher oxygen concentration environments, the filled and open symbols in Figure 26 represent the data with and without a surface temperature correction, respectively. The corrections have been made such that the filled symbols for the higher oxygen concentration have the same coal surface temperature as the open symbols for the lower oxygen concentration. The details of the coal surface temperature correction will be described later under the section which discusses the "Effect of Temperature and Particle Size."

Based on Eq. 45, the slope of the line represents the apparent order of reaction for char oxidation. The orders of reaction for different coal sizes tested at different pressures with and without corrections for coal surface temperature are shown in Table 12.

Table 12

ORDER OF REACTION OF CHAR OXIDATION FOR PITTSBURGH NO. 8 COAL AT 1550°F

<u>Coal Size</u> <u>mesh</u>	<u>Pressure</u> <u>psig</u>	<u>Apparent Order of Reaction</u>	
		<u>Uncorrected</u> <u>for Surface</u> <u>Temperature</u>	<u>Corrected</u> <u>for Surface</u> <u>Temperature</u>
10x12	280	0.8	0.1
28x32	280	0.3	0.2
28x32	206	-0.15	0
48x60	206	0.35	0.25

Table 12 shows the differences in the order of reaction with and without corrections for the surface temperature caused by the difference between the lower and higher oxygen concentration environments. The table indicates that the smaller the particle, the smaller the magnitude of the correction for the order of reaction. The negative slope for 28x32 mesh particle tested under 206 psig is due to the difference in bed temperature for the low and high oxygen concentration conditions (see Appendix C) and is not caused by increasing oxygen concentration. For the other test cases, the bed temperatures were about the same. A similar situation applies to the negative slopes to be shown in Tables 13 and 14.

Figure 27 is a similar plot for 28x32 mesh Pittsburgh No. 8 coal combusted at a pressure of approximately 206 psig, a superficial velocity of 4 ft/sec, and three bed temperatures of 1425°, 1550°, and 1725°F. The orders of reaction for different temperatures with and without coal particle surface temperature corrections are shown in Table 13.

Figure 27. Effect of Oxygen Concentration on Kinetic Rate of Pittsburgh No. 8 Coal (28x32 Mesh; 206 psig)

Table 13

ORDER OF REACTION OF CHAR OXIDATION FOR PITTSBURGH NO. 8 COAL (28x32 Mesh; 206 psig)

Temperature °F	Apparent Order of Reaction	
	Uncorrected for Surface Temperature	Corrected for Surface Temperature
1425	0.35	0.25
1550	-0.15	0.0
1725	0.0	0.0

The limited test data in Figure 27 seems to indicate that the order of char oxidation varies with temperature.

Figure 28 shows the relationship of oxygen concentration to the reaction rate of 28x32 mesh Pittsburgh No. 8 coal burned at approximately 206 psig, 1550°F, at two superficial gas velocities, 12 ft/sec (in 1-inch diameter reactor) and 4 ft/sec (in 2-inch diameter reactor). The order of char oxidation for 28x32 mesh Pittsburgh No. 8 coal at 206 psig and 1550°F with and without coal particle surface temperature correction is shown in Table 14.

Figure 28. Effect of Oxygen Concentration on Kinetic Rate of Pittsburgh No. 8 Coal (28x32 Mesh; 206 psig; 1550°F Bed Temperature)

Table 14

ORDER OF REACTION OF CHAR OXIDATION FOR PITTSBURGH NO. 8 COAL
(28x32 Mesh; 206 psig; 1550°F Bed Temperature)

Superficial Gas Velocity, ft/sec	Diameter of Reactor, in	Apparent Order of Reaction	
		Uncorrected for Surface Temperature	Corrected for Surface Temperature
4	2	-0.15	0.0
12	1	1.0	0.35

Table 14 shows that the order of reaction for char oxidation increases with increasing superficial velocity. The correction for the coal particle surface temperature is greater for the high gas velocity environment than for the low gas velocity environment.

A survey of the literature suggests that the true order of reaction for oxidation of char at temperatures below 1350°F is in the range of 0.2 to 1.0. [30] Daw reported an order of char oxidation of 0.6 for Kentucky No. 9 coal. [17] An order of char oxidation of 0.17 for Pittsburgh No. 8 coal was reported. [31] Smith reported that the apparent order of reaction for char oxidation is between 0.5 and 1 if the true order of reaction is between 0 and 1 (see Eq. 9). [16] However, the orders of reaction obtained from this project do not fit the relationship (Eq. 9) reported by Smith. As shown in Figures 26, 27, and 28, there is not a fixed number for the order of reaction which covers a broad range of test variables. The order of char oxidation varies with char properties and test conditions. The sensitivity of the order of reaction to the kinetic rate was evaluated and found to be small. A variation of 0.1 in the order of reaction showed only about a 5% change in the value of the kinetic rate constant. Therefore, an average order of reaction of 0.2 was used to simplify the calculations of the rate constants for various test conditions for Pittsburgh No. 8 and Texas lignite coals. This number is between the two extremes of the order of reaction, i.e., 0 and 0.35, which was found for most of the combustion tests performed in the 2-inch diameter reactor.

Effect of Temperature and Particle Size

The surface temperature of a char particle is different under PFBC conditions as compared to AFBC conditions. This relates to increases in heat and mass transfer at higher pressures. Based on the calculations of the surface temperature of coal particle previously described in Section 2, the calculated coal surface temperature for the larger 4x5 mesh particles is about 310° to 425°C higher than the bed temperature. For the smaller 48x60 mesh particles, the coal surface temperature is about 65° to 220°C higher than the bed temperature.

Figure 29 shows the logarithm of the kinetic rate constant versus the reciprocal of the coal surface temperature for five sizes (4x5, 6x7, 10x12, 28x32, and 48x60 mesh) of Pittsburgh No. 8 coal. The test conditions were 206 psig, 3% O₂, superficial gas velocity of 4 ft/sec, and three bed temperatures (1425°, 1550°, and 1725°F). The data shows that for the same coal size, the rate constant increases as the coal particle temperature increases.

The larger coal particles usually burn slower than the smaller coal particles. This is mainly attributed to greater resistance of oxygen diffusion to the surface of the coal in the case of the larger coal particles. However, when the kinetic rate constant is expressed based on the external surface area of char, it is greater for the larger coal particles than for the smaller coal particles. This is because the specific external coal surface area (cm²/gm of coal) is much smaller for the larger coal particles than for the smaller coal particles.

However, in Figure 29, a single line can be used to fit the data points with some scattering. Part of the scattering may be attributed to the simplified calculation using 0.2 as the order of reaction for oxygen concentration. Figure 29 indicates that for the coal sizes used in this

project, the effect of coal size on the rate constant is small. This is most likely due to a high oxygen concentration at the char surface under high pressures which results in high kinetic rate. As previously described in Section 2 -- Temperature Regimes for Char Oxidation, the combustion of the particles in this project takes place close to Regime II where both diffusion and kinetics affect combustion significantly, and the diameter of char and the char density decrease as combustion proceeds.

Figure 29. Effect of Particle Size on Kinetic Rate Constant of Pittsburgh No. 8 Coal

Figure 30 is a figure reported by Patel, et al., [32] as a comparison of the literature data of char reactivity of a high volatile bituminous coal with their test data on the same coal. The test data shown in Figure 29 for Pittsburgh No. 8 under PFBC conditions is calculated based on $P_{O_2} = 0.1$ atm and included in this plot for comparison. The char reactivity obtained from this project at the lower temperature range is consistent with the data reported at $P_{O_2} = 0.1$ atm by Combustion Engineering, [32] Sandia National Laboratory, [33] Field, et al., [34] and Babcock & Wilcox. [35] However, the activation energy (slope of reactivity versus reciprocal of particle temperature) for PFBC data as determined in this project is less than the activation energies of other published data.

Figure 30. Comparison of Char Reactivity Reported by Different Investigators (Pittsburgh No. 8 Coal)

Figure 31 shows the comparison of the char reactivity for Kentucky No. 9 reported by Sandia National Laboratory, [33] Field, et al., [34] and Oak Ridge National Laboratory. [17] The PFBC data for Pittsburgh No. 8 (Figure 29) obtained from this study is calculated based on $P_{O_2} = 1$ atm and included in the figure. Although the published data and PFBC data in Figure 31 are for different coals, the PFBC data seems to be able to bridge the gap of the published data for low-temperature coal combustion. Again, the activation energy for PFBC data as determined in this project is less than the activation energies of other published data.

Figure 31. Comparison of Char Reactivity Reported by Different Investigators (Kentucky No. 9 Coal)

Smith, et al., studied the char reactivity of three sizes (89, 49, and 22 microns) of Yallourn brown coal in an entrainment reactor.^[36] They found that when the surface temperature of coal particles is above 1475°F (800°C), the rate constants for the three sizes are close. The effect of coal size on rate constant as found in this project is consistent with that reported by Smith and co-workers.

Abd El-Samed, et al., studied the char reactivity of five coals with a wide range of properties.^[37] In their tests, the char activities were determined during simultaneous devolatilization and combustion of coals in a drop-tube furnace. They found that as the coal burns, a transition occurs from the chemical and diffusion control state at the early stage of combustion to a chemical control state at the later stage of combustion. Therefore, the coal combusted in temperature Regime II in the early stage of combustion may shift to temperature Regime I in the later stage of combustion.

Using the slope of this line ($-E_a/R$) (see Eq. 45), the activation energy for the Pittsburgh No. 8 coal was calculated to be about 11.2 kcal/g-mole (or 4.69×10^7 joule/kg-mole). The pre-exponential term, A, was calculated to be $0.043 \text{ gm of carbon/cm}^2\text{-sec-(atm)}^{0.2}$ (or $0.68 \text{ kg of carbon/m}^2\text{-sec-(MPa)}^{0.2}$). Smith calculated the intrinsic kinetic rate constant for a wide range of coal chars and carbons which included petroleum coke, graphite, lignite, and bituminous coal char. The chars were prepared in a separate step prior to char combustion. He found that an overall activation energy of 42.8 kcal/g-mole for a range of coals [38]. Abd El-Samed, et al., found a lower activation energy (32.3 kcal/g-mole) from their char reactivity study than what Smith has reported. [37] They attributed the higher activation energy in Smith's data to more fragmentation in the chars which were prepared separately prior to the char combustion. A char which is prepared in a separate devolatilization step prior to the char combustion is more porous than coal. Diffusion of oxygen to this type of char particle is faster than it is to coal particles. Thus, the reactivity is expected to be greater.

The activation energy determined in this project for Pittsburgh No. 8 coal (11.2 kcal/g-mole) is lower than other literature values. This is attributed to three factors. First, some of the reported values for activation energy for char oxidation are the actual activation energies obtained from intrinsic kinetic rate constants. The char oxidation performed in this project occurred near temperature Regime II where the apparent activation energy is less than the actual activation energy. Secondly, the char particles were combusted while coal devolatilization was in progress. As discussed earlier, the activation energy for this type of char is less than that of char prepared independently of the char combustion test. Finally, the combustion tests performed in this project were under high pressures. As it will be discussed later, the reaction rate constant increases as the pressure increases. Thus, the activation energy of the reaction is likely to decrease with increasing pressure.

As described earlier in the paragraph entitled "Effect of Oxygen Concentration," the differences in the surface temperature of coal particles must be corrected before an accurate order of reaction can be determined. This correction was done by using Figure 29. The corrections have been made based on the assumption that the slope of the rate constant versus the reciprocal of particle temperature plot is the same for high and low oxygen concentrations. The surface temperatures of the coal particles at 3% and 10% O_2 were calculated using Eq. 46. The rate constants at the two coal surface temperatures were determined from the line in the figure. The correction factors were calculated by dividing the rate constant at the surface temperature where the oxygen is 3% by the rate constant at the surface temperature where the oxygen is 10%. The corrected rate constant for the tests performed at 10% O_2 at the same particle temperature as at 3% O_2 was obtained by multiplying the actual rate constant obtained at 10% O_2 by the correction factor. The comparison of the uncorrected and corrected rate constants for the tests performed at 10% O_2 and the details of the calculations are shown in Table 15.

Figure 32 shows the effect of coal particle size on the ratio of observed rate to the mass transfer rate for different sizes of coal particles. As the particle size increases, the ratio of the observed rate to the mass transfer rate increases. This indicates that when the coal size increases, mass transfer rate decreases and the reaction tends to be more diffusion controlled.

Table 15

CORRECTION OF KINETIC RATE FOR THE DIFFERENCE IN SURFACE TEMPERATURES
OF COAL PARTICLES

File No.	Pressure psig	% O2	1/Tp ok-1 (3% O2)	kc* g/cm2-sec-(atm)^n (3% O2)	1/Tp ok-1 (10% O2)	kc* g/cm2-sec-(atm)^n (10% O2)	Cor. Fac.	kc** g C/cm2-s/(atm)^n (10% O2)	Corrected (p O2) kc*** atm (10% O2)	Average Reaction (P O2)^n Order n	Rc+ g C/cm2-sg C/cm2-s (10% O2) (10% O2)	Rc++ g C/cm2-sg C/cm2-s (10% O2) (10% O2)	Corrected Reaction Order n		
PITS108	206	3													
PITS121	207	10	0.000865	0.000325	0.000857	0.00034	0.955882	0.000297	0.000283	1.508163	0.2	1.085649	0.000308	0.000322	0.25
PITS234	207	3													
PITS247	206	10	0.000911	0.00025	0.000897	0.00027	0.925925	0.000299	0.000276	1.50136	0.2	1.084668	0.000300	0.000324	0.25
PITS519	275	3													
PITS531	276	10	0.000828	0.000398	0.00081	0.00044	0.904545	0.000699	0.000632	1.977551	0.2	1.146107	0.000724	0.000796	0.2
PITS712	206	3													
PITS718	207	10	0.00084	0.000375	0.000739	0.000655	0.572519	0.002205	0.001262	1.508163	0.2	1.085649	0.001370	0.002394	0.35
PITS518	276	3													
PITS530	279	10	0.000763	0.000575	0.00057	0.00172	0.334302	0.002245	0.000750	1.9979	0.2	1.148457	0.000861	0.002579	0.1
PITS283	206	3													
PITS295	206	10	0.000778	0.000525	0.000784	0.0005	1.05	0.000272	0.000285	1.50136	0.2	1.084668	0.000309	0.000296	0
PITS107	206	3													
PITS120	207	10	0.000838	0.00038	0.000855	0.000345	1.101449	0.00027	0.000297	1.50136	0.2	1.084668	0.000322	0.000293	0

* Obtained from Figure 29 based on the calculated Tp

** Derived from test data

*** The correction factor times the kc which is derived from the test data

* Reaction rate after correction for the difference in the surface temperature of coal particles

** Reaction rate derived from test data without correction for the difference in surface temperature of coal particles

Figure 32. Effect of Particle Size on the Ratio of Observed Rate to Mass Transfer Rate of Pittsburgh No. 8 Coal

Effect of Pressure

Figure 33 shows the logarithm of the rate constant versus the reciprocal of coal particle temperature for 28x32 mesh Pittsburgh No. 8 coal. Test conditions consisted of 1550°F bed temperature, 3% O₂, a 4 ft/sec superficial gas velocity, and three pressures (277, 206, and 132 psig). The rate constant increases with pressure.

Figure 34 is the same plot for a larger coal size (4x5) mesh combusted at approximately 1725°F, 3% O₂, a superficial gas velocity of approximate 4 ft/sec, and three pressures (208, 132, and 18 psig). Figure 35 is a plot for 48x60 mesh Texas lignite combusted at approximately 1425°F, 3% oxygen, a superficial gas velocity of approximately 4 ft/sec, and three pressures (277, 207, and 130 psig). Both figures (Figures 34 and 35) show that as the pressure increases, the kinetic rate constant increases.

The density of gas is proportional to the total gas pressure, P . The diffusion coefficient of gas is inversely proportional to P . Based on Eq. 41, the mass transfer coefficient, h_m , is proportional to $P^{-0.3}$. The mass transfer rate, which is the mass transfer coefficient times the oxygen concentration, is proportional to $P^{0.7}$. Therefore, the mass transfer rate of oxygen to the coal surface is greater at higher pressure than at low pressure, even though the diffusion coefficient of oxygen is lower at higher pressure than at low pressure.

Figure 33. Effect of Pressure on Kinetic Rate Constant of Pittsburgh No. 8 Coal (28x32 Mesh; 1550°F Bed Temperature)

Figure 34. Effect of Pressure on Kinetic Rate Constant of Pittsburgh No. 8 Coal (4x5 Mesh; 1725°F Bed Temperature)

Figure 35. Effect of Pressure on Kinetic Rate Constant of Texas Lignite Coal

The increase in kinetic rate under high pressure is related to the fact both the oxygen concentration at the coal surface and the oxygen transfer rate to the coal surface are higher at higher pressure. This results in greater kinetic rate and higher surface temperature of coal particle, which subsequently increases the kinetic rate.

Turnbull, et al., studied the effect of pressure on char burnout time of various sizes of chars and cokes. It was found that the burnout time for chars and cokes decreases with increasing pressure. [39]

Superficial Gas Velocity

Figure 36 shows the effect of the superficial gas velocity on the kinetic rate constant of 28x32 mesh Pittsburgh No. 8 coal when combusted at approximately 206 psig, 3% O₂, and two temperatures with three superficial gas velocities (4, 12, and 20 ft/sec) in the 1-inch diameter reactor. Although data is limited, this figure clearly shows that as the superficial gas velocity increases, the kinetic rate constant increases. The increase in kinetic rate constant at high gas velocity is probably due to faster transfer of oxygen to the coal surface, resulting in lower diffusion resistance and a higher kinetic rate.

Figure 36. Effect of Superficial Gas Velocity on Kinetic Rate Constant of Pittsburgh No. 8 Coal

A combustion test performed at a superficial gas velocity of approximately 4 ft/sec in the 2-inch diameter reactor is also included in this figure for comparison. The rate constant is greater for the 2-inch diameter reactor than the 1-inch diameter reactor for the same size coal tested under similar conditions. This occurs because the same amount of coal was used in the tests conducted in both the 2-inch and 1-inch diameter reactors and the coal particles were spread over a larger area; thus, the particles are heated more effectively in the 2-inch diameter reactor than in the 1-inch diameter reactor. In addition, larger gas flows occurred through the reaction zone and more oxygen was available for reaction in the 2-inch diameter reactor. All of these contributed to the increase in the reaction rate in the 2-inch diameter reactor.

This data indicates that the bench-scale reactor has some influences on fundamental combustion kinetics. However, based on B&W previous experience for predicting combustion performance on AFBC units using 2-inch diameter reactor data, small changes in kinetic rate constant had little impact on coal combustion efficiency using B&W's FBC performance code. [4]

Effect of Coal Type

Figure 37 shows the effect of coal type on the rate constant. The rate constant for Texas lignite shown in this figure is in the same order of magnitude as reported by Nsakala, et al., [40] for 200x400 mesh particle Texas lignite combusted in a drop-tube furnace. The rate constant for Texas lignite is approximately 2.5 times the kinetic rate constant for Pittsburgh No. 8 coal for comparable test conditions.

6.0 CONCLUSIONS

Over 400 hundred combustion tests were performed in a bench-scale PFB reactor system on Pittsburgh No. 8 and Texas lignite coals. The combustion tests were performed over the following ranges:

Temperature:	1425° to 1725°F
Pressure:	18 to 280 psig
Oxygen Concentration:	0.5% to 10%
Superficial Gas Velocity:	2 to 5 ft/sec
Coal Size:	6 sizes (4x5 to 115x150 mesh)

Later, the reactor was modified to accommodate higher gas velocities. Additional combustion tests were performed at higher gas velocities (4, 12, and 20 ft/sec) on Pittsburgh No. 8 coal.

Based on the bench-scale PFBC results, literature information, and B&W's previous AFBC kinetic model, a global model for coal combustion at elevated pressures was developed. The kinetic model was used to derive the rate constants and activation energies of coal combustion.

The major conclusions of this study of coal devolatilization and char oxidation under pressurized conditions are listed below:

- For coal devolatilization, the rate of devolatilization increases with increasing oxygen concentration, increasing gas velocity, and decreasing particle size. The rate of devolatilization and the volatile yield are affected by temperature and pressure. However, the influence of temperature and pressure on the rate of devolatilization and volatile yield is not always a linear relationship.
- The apparent order of coal devolatilization was determined based on an assumption of a constant temperature for the later stage of coal devolatilization. The apparent orders of coal devolatilization for Pittsburgh No. 8 and Texas lignite coals range from 0.2 to 0.6 and vary with coal properties and test conditions.
- The volatile yields of the two coals obtained under the test conditions in this project are slightly less than the volatile matter determined from the ASTM coal analysis.
- For char oxidation, the kinetic rate constant of Pittsburgh No. 8 coal is not affected by coal particle size. This indicates that the coal combustion occurs in a temperature region where both kinetics and diffusion play important roles in the combustion reaction.
- Increasing temperature, pressure, and superficial gas velocity tends to increase the kinetic rate constant of char oxidation for Pittsburgh No. 8 coal.

- For char oxidation, the Texas lignite coal has a kinetic rate constant approximately 2.5 times that of the Pittsburgh No. 8 coal.
- The apparent activation energy of char oxidation of the Pittsburgh No. 8 coal at 206 psig, 3% O₂, and 4 ft/sec is approximately 11.2 kcal/g-mole (or 4.69×10^7 joule/kg-mole). The frequency factor is approximately 0.043 gm of carbon/cm²-sec-(atm)^{0.2} [or 0.68 kg of carbon/m²-sec-(MPa)^{0.2}].
- The apparent order of char oxidation for Pittsburgh No. 8 coal varies with the coal properties and test conditions. The apparent order of char oxidation for Pittsburgh No. 8 coal under the test conditions in this project ranged from 0 to 0.35. An average apparent order of char oxidation of 0.2 was used for calculating the apparent activation energy and rate constant for Pittsburgh No. 8 and Texas lignite coals.
- The char reactivity for the Pittsburgh No. 8 coal obtained at the low-temperature range of this study is comparable with the published AFBC data determined by other investigators.

7.0 RECOMMENDATIONS

7.1 CURRENT STUDY ON PFBC

7.1.1 Modifications of Coal Injection System

The smallest coal size fraction tested in the existing bench-scale PFBC reactor was 115x150 mesh (125x106 microns). However, the mass balance for this size fraction was often poor. Improvement of the coal injection system for smaller coal particles is needed, since a coal particle size of about 60 microns is of interest in DOE's second-generation of PFBC programs.

7.1.2 Reducing Gas Delay and Back Mixing

A major source of error in the test data is the delay and back mixing of flue gases in the gas cooling system and the gas analyzers. Although a computer program was developed based on a simplified flow model and corrections were applied to the test data, it is very difficult to verify the corrections were made properly. A way to minimize this type of error is to shorten the gas traveling time in the gas cooling systems and the gas analyzers. Slip streams of flue gases can be taken from the main gas streams and cooled quickly before they are analyzed by the analyzers.

7.2 FURTHER STUDIES ON PFBC

Several technical issues related to PFBC fuels characterization are important to the design of PFBC units. The major issues which may require further investigation as an extension of this program at B&W are briefly described below.

7.2.1 Link Between Bench-Scale AFBC and Bench-Scale PFBC Testing

Approximately 20 fuels have been characterized in a bench-scale AFBC reactor under the B&W AFBC Fuel Characterization. A performance model for in-bed combustion has been developed and validated with pilot test data obtained from three pilot sizes. A freeboard combustion model is being developed.

The successful development of a performance model for AFBC has laid the groundwork for developing a performance model for PFBC. There is a gap of how to use PFBC bench-scale data and an existing performance model for AFBC to predict performance of large-scale PFBC units. B&W is negotiating a contract with the Ohio Coal Development Office (OCDO) to perform PFBC fuel characterization on four Ohio and two Illinois coals. This work will derive a coal database and the chemical kinetics for the tested coals. The test data will be used to determine how to modify the AFBC performance model such that it will be suitable for PFBC use.

7.2.2 Link Between Bench-Scale PFBC and Pilot-Scale PFBC Testing

Limited information on fuel combustion behavior under PFBC conditions is available. Some PFBC pilot tests have been performed. However, the combustion and operational data available is limited to a few coals. This limits the development of a quick and inexpensive method for predicting the performance of large-scale units.

A kinetic model was developed based on bench-scale testing data. The other three modules in the B&W AFBC performance model, e.g., hydrodynamics, solid distribution, and transport phenomena, can be modified for PFBC conditions based on literature information and test data available from B&W current AFBC and PFBC Fuels Characterization programs. The PFBC kinetic model can be incorporated with the other three modules modified for PFBC conditions to form a preliminary PFBC performance model. The preliminary PFBC performance model can be used to predict the performance of a PFBC pilot unit and evaluated against some of the actual PFBC pilot test data for similar coals.

Therefore, the B&W/OCDO project will not only broaden the database on fuel characterization of PFBC technology, but also provide test data to modify the existing AFBC performance model for use with PFBC technology.

7.2.3 Sulfur Capture in PFBC Testing

Sulfur release is a function of the conditions of the combustion process and the nature of the sulfur in coal. The sulfur-containing products are also affected by the combustion environment. An understanding of the kinetics of sulfur release and sulfur capture mechanisms under PFBC conditions is important when considering the performance characteristics of PFBC design. Little fundamental information is available on the behavior of sulfur during PFBC combustion. Sulfur capture and its mechanism in PFBC was conducted at B&W under a separate contract entitled "Dynamic Kinetics of Sulfur Release in the Combustion of Ohio Coals." This project was also supported by OCDO. The objective of this project was to determine the effect of the chemical nature of sulfur in coal on sulfur release rate.

The tests involved injection of a known weight of coal particles into the bed and monitoring the product gases, especially SO_2 . The dynamic kinetics of sulfur release in several coals over a wide range of combustion conditions were studied under both AFBC and PFBC conditions. Time-resolved gas samples were collected via gas sampling train and analyzed for SO_2 , H_2S , COS , etc. using a gas chromatograph. The sulfur release profile data were analyzed to determine the relevant dynamic parameters. Semi-empirical correlations for sulfur release parameters were derived as a function of test variables. This information can be used in the future in PFBC performance models to address sulfur capture efficiency of FBC units.

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Appendix A

DETERMINATION OF MASS TRANSFER COEFFICIENTS

MASS TRANSFER COEFFICIENT OF NAPHTHALENE BALLS

The mass transfer coefficient of naphthalene was determined by inserting naphthalene balls in the PFB reactor. The tests were performed at room temperature, and pressures of 17.5 and 206 psig. The velocity of gas was adjusted such that the Reynolds number of gas in these tests was in the same range as that for PFB coal combustion tests performed at high temperature and pressure. The weight loss of naphthalene balls in a period of testing time was measured. The rates of weight loss of naphthalene balls were determined and used to calculate the mass transfer coefficients of naphthalene.

As described in the main body of this report in Section 3.3.2 -- Char Oxidation -- under "Determination of Mass Transfer Rate of Oxygen to Char Surface", the relationship of weight loss and the mass transfer coefficient of naphthalene balls can be expressed as:

$$\Delta W/\Delta t = h_m A_p (C_s - C_b) = h_m A_p C^* \quad (A-1)$$

where:

$\Delta W/\Delta t$ is the weight loss of naphthalene balls in time t

h_m is the mass transfer coefficient

A_p is the outer surface area of naphthalene balls which is πd^2

d is the diameter of naphthalene ball

C_s is the naphthalene vapor concentration at the ball surface

C_b is the naphthalene vapor concentration at the bulk of gas stream

C^* is the saturated vapor concentration under test conditions

Eq. A-1 can be rearranged as:

$$h_m = (\Delta W/\Delta t) / (A_p C^*) \quad (A-2)$$

The naphthalene balls were assumed spherical. The diameters of the balls were reported as an average of three measurements.

The C^* for naphthalene can be calculated from the ideal gas law:

$$C^* = P^* M_w / R T \quad (A-3)$$

where P^* is the saturation vapor pressure of naphthalene at gas temperature T and M_w is the molecular weight of naphthalene (which is 128).

The saturation vapor pressure of naphthalene can be calculated from:

$$\log_{10} P \text{ (in mm Hg)} = -0.005223A/T + B \quad (A-4)$$

where A and B are constant. For naphthalene, A is 71,401 and B is 11.450 at temperatures between 0 to 80°C.*

As described in the main body of this report under Section 5.2.3 -- Mass Transfer Coefficient, the experimental Sherwood number can be determined as:

$$Sh = h_m d/D \quad (A-5)$$

The Sherwood number can also be predicted from:

$$Sh = 2 + 0.6 Re^{0.5} Sc^{0.33} \quad (A-6)$$

where:

$$Sh \text{ (Sherwood number)} = h_m d/D$$

D is the diffusivity of the gas of interest

$$Re \text{ (Reynolds number)} = (u/\epsilon) \rho d/\mu$$

u is the superficial gas velocity

ρ is the bulk gas density under test conditions

μ is the bulk gas viscosity under test conditions

ϵ is the void volume of the fixed bed

$$Sc \text{ (Schmidt number)} = \mu/D \rho$$

The diffusion coefficient of gas at high pressure can be described by:**

$$D = D_o (T/T_o)^m (P_o/P) \quad (A-7)$$

where:

T_o is 273°K

T is gas temperature of the test conditions

P_o is 1 atm

P is the pressure of the test conditions

D_o is the diffusion coefficient of gas at 273°K

m is a constant which is between 1.5 and 2.0

For naphthalene diffused in air, D_o is 0.0513 cm²/sec and m is 2.0.**

* International Critical Tables, Vol. 3, McGraw-Hill, New York, 1933, p. 108.

** International Critical Tables, Vol. 5, McGraw-Hill, New York, 1933, p. 62.

The density of gas is calculated assuming the gas follows the ideal gas law:

$$\rho = P M_w / R T \quad (A-8)$$

The viscosity of gas was obtained from the *Handbook of Chemistry and Physics*.*

Table A-1 shows derivation of the experimental Sh and calculation of the predicted Sh using Eq. A-6. Comparison of the experimental Sh with the predicted Sh is shown in Figure A-1. This figure shows that Eq. A-6 does not have a good fit for the experimental values. The experimental data can be better represented by the following equation:

$$Sh = 2 + 0.92 Re^{0.7} Sc^{0.33} \quad (A-9)$$

MASS TRANSFER COEFFICIENT OF OXYGEN IN COAL COMBUSTION

Diffusion of oxygen to char surface in char combustion can also be represented by Eq. A-9. Re and Sc can be calculated from the test conditions for coal combustion. The mass transfer coefficient of oxygen can be obtained by substituting the diffusivity of oxygen in Eq. A-9. The diffusivity of oxygen in air at 0°C is 0.178 cm²/sec and m (for pressure effect) is 1.5.**

* *Handbook of Chemistry and Physics*, 63rd edition, CRC Press, 1982, pp. F-11, F-12, and F-49.

** *International Critical Tables*, Vol. 3, McGraw-Hill, New York, 1933, p. 62.

Table A-1

DETERMINATION OF MASS TRANSFER COEFFICIENT OF NAPHTHALENE IN AIR UNDER GAS FLOW CONDITIONS
SIMULATING PFB UNITS AND COMPARISON OF EXPERIMENTAL AND PREDICTED SHERWOOD NUMBER

Temp. cf	Pressure psig	Gas Flow Rate, CFM	Superf. Gas Vel. ft/sec	Ave. Particle dia., inch	dM/dt lb/hr	P* mmHg	C* lb/cu ft	Exp. hm ft/sec	Gas Vis. u lb/ft-hr	Gas Den. (rho) lb/cu ft	Diffusi. D ft ² /hr	Exp. Sh	Sc	Re	Pred. Sh [Eq A-6]	Pred. Sh [Eq A-9]
72	17.5	1.55	0.535456	0.2744	0.000015	0.065754	0.000028	0.093922	0.0423	0.157943	0.106102	72.87010	2.524123	365.7459	17.57533	79.75172
81	17.5	2.7	0.948510	0.2659	0.000036	0.106733	0.000045	0.145263	0.0431	0.155316	0.109723	105.6083	2.529075	605.9111	22.06010	112.7774
75	17.5	3.8	1.320135	0.2794	0.000043	0.077416	0.000033	0.214546	0.0428	0.157058	0.107302	167.5940	2.539638	902.3402	26.51382	148.5958
75	17.5	5	1.737020	0.2758	0.000060	0.077416	0.000033	0.301400	0.0428	0.157058	0.107302	232.4059	2.539638	1171.991	29.93754	178.0393
73	18.5	6.5	2.181923	0.2785	0.000057	0.069446	0.000030	0.316483	0.0426	0.162543	0.103294	255.9890	2.537255	1545.727	34.07435	215.6098
73	21	7.2	2.247649	0.2758	0.000052	0.069446	0.000030	0.292644	0.0426	0.174783	0.096060	252.0632	2.537255	1695.591	35.59325	229.9045
73	26	9.1	2.491788	0.2892	0.000043	0.069446	0.000030	0.220579	0.0426	0.199262	0.084259	227.1246	2.537255	2247.160	40.67306	279.5696
74	31	10.3	2.516513	0.2903	0.000040	0.073330	0.000031	0.193970	0.0427	0.223322	0.075322	224.2738	2.538449	2547.184	43.18026	305.0663
73	37.5	12.2	2.604675	0.2863	0.000070	0.069446	0.000030	0.362716	0.0426	0.255565	0.065696	474.2053	2.537255	2982.467	46.55324	340.4005
80	205	2.3	0.118203	0.2778	0.000005	0.101221	0.000043	0.026092	0.0431	1.061682	0.016022	135.7201	2.533759	539.2459	20.93595	104.1600
83	205	4.5	0.232551	0.2647	0.000005	0.118605	0.000050	0.019470	0.0433	1.055816	0.016200	95.43828	2.531453	1000.651	27.78722	159.4337
81	205	10.7	0.550919	0.2623	0.000014	0.106733	0.000045	0.058540	0.0431	1.059719	0.016081	286.4522	2.529075	2368.693	41.66277	289.6878
70	206	6.8	0.341444	0.2929	0.000007	0.058911	0.000025	0.040506	0.0426	1.086637	0.015364	231.6655	2.551617	1700.680	35.70635	230.8089
81	206	2.1	0.107634	0.279	0.000008	0.106733	0.000045	0.029751	0.0431	1.064543	0.016008	155.5559	2.529075	494.4818	20.12190	98.08829

Figure A-1. Relationships of Mass Transfer With Gas Flow Dynamics

Appendix B

CORRECTIONS FOR GAS DELAY AND BACKMIXING

INTERIM REPORT TO TVA ON THE ANALYSIS OF THE EPRI AFBC FUELS CHARACTERIZATION DATA: CORRECTION OF THE FIXED-BED REACTOR RESULTS

C. S. Daw

Abstract

A limited set of gas-tracer results from the B&W 5.1-cm(2-inch)-diameter fixed-bed reactor were analyzed to develop procedures for correcting measurement bias in the EPRI AFBC fuels characterization data. Measured responses of the reactor-analyzer system to step reactor inputs were found to be describable as pure deadtimes in series with second-order lags. The time constants associated with these processes have been derived from the gas-tracer data and used to correct typical devolatilization and combustion profiles. General procedures are recommended for standardized correction of the fuels characterization data base.

1. INTRODUCTION

Under an interagency agreement between the Tennessee Valley Authority (TVA) and the Department of Energy (DOE NO. 0737-0737-A1), Oak Ridge National Laboratory (ORNL) is responsible for participating on the advisory committee for the Atmospheric Fluidized Bed Fuels Characterization Program sponsored by the Electric Power Research Institute (EPRI). In conjunction with this responsibility, ORNL is assisting with the technical evaluation of bench-scale characterization data being generated by the Babcock and Wilcox Company (B&W) at B&W's Alliance Research Center.

This report summarizes the results of ORNL's investigation into potential biasing of data from the B&W fixed-bed reactor, a key component of the bench-scale characterization

tests. Specifically, it has been conjectured by B&W and some members of the advisory committee that, in some cases, the inherent dispersion and time lags associated with the reactor flow and gas-analysis instrumentation are distorting the measured devolatilization and combustion profiles. Such distortion could result in misleading conclusions and inaccurate rate estimates from the data base.

Recently, B&W made quantitative experimental measurements of the profile distortion during gas-tracer tests with the fixed-bed reactor. A small representative subset of the gas-tracer results was transmitted to ORNL for further analysis. These results have been used to develop a general systematic procedure for regenerating undistorted profiles from as-measured devolatilization and combustion data.

2. EXPERIMENTAL METHODS AND DATA ANALYSIS

The 5.1-cm(2-inch)-diameter fixed-bed reactor is illustrated schematically in Fig. 1. Detailed descriptions appear in Chandran et al (1987) and Chandran et al (1988). Briefly, the reactor is a vertically-mounted quartz tube enclosed in an electrically-heated furnace. Preheated gas flows into the top of the reactor, down through a bed of solids (on which the fuel sample is supported), and exits through a post-combustion zone into a gas-analysis train. Fuel samples are injected onto the bed from above by means of an electrically actuated solenoid.

Figure 1. Schematic Diagram of the B&W Fixed-Bed Reactor

During typical fuel characterization tests, temperature, pressure, gas composition, and flow are established prior to the injection of the fuel sample. Carbon-loss profiles for each sample are determined by recording the concentrations of CO₂, CO, and hydrocarbons (measured as CH₄ equivalent) in the exhaust gas as functions of time. Distortion of the profiles is expected to occur primarily as a result of gas mixing/dispersion in the reactor and exhaust piping and because of response lags in the gas analyzers.

2.1 Tracer data evaluation

The gas-tracer tests conducted by B&W consisted of "step" changes were made in the composition of the fixed-bed inlet gas. The steps were made using the electrically activated sample injection valve (response time < 0.025 s) and pre-mixed tracer gases containing known concentrations of CO₂ and CO (hydrocarbon tracer was not tested). Key parameters for the limited subset of gas-tracer test data received from B&W are summarized in Table 1.

Table 1

SUMMARY OF THE GAS-TRACER TEST DATA

<u>Test ID</u>	<u>Bed Temp (K)</u>	<u>% O₂</u>	<u>Gas Vel (m/s)</u>	<u>Comments</u>
RTD21	1121	3	1.68	CO analyzer off scale
RTD25	1121	10	1.60	CO analyzer off scale
RTD27	1117	10	1.60	Both analyzers on scale
RTD30	1041	10	1.56	CO analyzer off scale

Each test run consisted of measuring the gas analyzer outputs as the valve was opened, held open for 20 s, and then closed. Fig. 2 illustrates a typical measured "on/off" profile for CO₂ (RTD21). Note that the actual valve opening corresponds with time 0 on the graph. The complete lack of any initial analyzer response reflects the system dead time. The "spike" occurring in the early portion of profile is believed to be caused by the pressure pulse from the opening valve. In order to avoid complications associated with this pulse, only the "off" portion of the profile was used to develop the system response function. Inspection of the fixed-bed characterization data also indicates that the pulse effect is relatively insignificant for devolatilization and combustion.

Fig. 3 is a close-up view of the "off" portion of a CO₂ profile and a similar profile for CO (RTD27). It is clear that, in addition to the pure lag mentioned earlier, the step inputs have been spread out in the measured response. The response was spread more than 1s for CO₂ and 2s for CO.

2.2 System response model

In accordance with conventional reactor transient analysis [Smith(1981), Levenspiel(1972), Tyner and May(1968)], it is expected that the behavior of the fixed-bed reactor and its associated gas-analysis system can be modeled as a pure dead time followed by either a distributed-lag process (similar

(X 1000)

Figure 2. Overall Measured CO₂ Response for an "On/Off" Step Tracer Test

(X 100)

Figure 3. Detailed View of Step Response Profiles ("Off" Portion) for CO₂ and CO Showing the Spreading Effect

to tubular flow with axial mixing) or a series of first-order lags(similar to stirred tanks in series). The latter case was selected in this study because of its more convenient form.

For each first-order lag component in measuring gas concentration, the inlet and measured outlet concentrations (C_{in} and C_m) at any time t are related by

$$(C_{in})_i = (C_m)_i + \tau_i (dC_m/dt)_i \quad (1)$$

where τ_i is the characteristic time constant and i refers to the i th component. It is found through sequential substitution that for a series of n such lags the overall relationship between the original inlet and final measured outlet concentrations is

$$C_{in} = C_m + \sum_{i=1}^n \tau_i (dC_m/dt) + \sum_{i=1}^n \sum_{\substack{j=1 \\ i \neq j}}^n \tau_i \tau_j (d^2 C_m/dt^2) \\ + \dots + \sum_{i=1}^n \sum_{\substack{j=1 \\ i \neq j}}^n \dots \sum_{p=1}^n \tau_i \tau_j \dots \tau_p (d^n C_m/dt^n) \quad (2)$$

In simple terms, Eq. (2) states that the original inlet concentration at any time can be determined by correcting the measured value with terms proportional to time derivatives of that value. This is a reasonable behavior, since it is expected that distortion will increase for more rapidly changing inlet profiles. The effects of dead time can be included in Eq.(2) by recognizing that C_{in} is determined for time $t - \tau_d$ when C_m is evaluated at t ; i.e.,

a current measured concentration is determined by a past inlet concentration. Thus Eq. (2) can be rewritten as

$$C_{in}|_{t-r_d} = [C_m + \text{correction terms}]|_t \quad (3)$$

Dead time simply shifts the time of each observation; it does not change the basic profile shape.

The key problem in correcting fixed-bed data is thus to determine the appropriate number and values of the τ_i . The τ_i were estimated in this study by comparing the measured response to the step tracer inputs with the step response function derived from Eqs. (2) and (3). For all τ_i unique, the response for an input step from a finite value to 0 is

$$C_m|_t = (C_m|_{r_d}) \sum_{i=1}^n A_i \exp(-(t-r_d)/\tau_i) \quad (4)$$

for $t \geq r_d$. The quantities $C_m|_{r_d}$ and $C_m|_t$ are, respectively, the measured concentration at the end of the dead time (i.e., the concentration before there has been any response to the valve closing) and the measured concentration at some time t beyond r_d . The coefficients A_i are functions of the τ_i and are constrained by the initial condition so that their sum is 1. For cases where q of the τ_i are identical and equal to τ_j , Eq. (4) becomes

$$\begin{aligned} C_m|_t = & (C_m|_{r_d}) \sum_{i=1}^{n-q} B_i \exp(-(t-r_d)/\tau_i) \\ & + (C_m|_{r_d}) \exp(-n(t-r_d)/\tau_j) \\ & \times \left[\left(\frac{1 - \sum_{i=1}^{n-q} B_i}{\sum_{i=1}^{q-1} \left(\frac{q(t-r_d)}{\tau_j} \right)^i / i!} \right) \right] \end{aligned} \quad (5)$$

In fitting the gas-tracer results, it became clear that only a limited number of constants are needed to describe the measured response profiles. Models with up to three constants were tested, and it was found that a second-order lag (i.e., two first-order lags in series with two identical time constants) consistently gave fits with $R^2 > 0.99$ (R^2 = coefficient of determination). For a single first-order lag, Eq. (4) reduces to

$$C_m|_t = C_m|_{\tau_d} \exp(-(t-\tau_d)/\tau_1) \quad (6)$$

For two first-order lags in series Eq. (5) reduces to

$$C_m|_t = C_m|_{\tau_d} \exp(-(t-\tau_d)/\tau_2) [1 + (t-\tau_d)/\tau_2] \quad (7)$$

where τ_2 is the same time constant for both lags.

Fig. 4 illustrates typical goodness of fit for Eqs. (6) and (7) when applied to the CO_2 step response. Higher order models could not produce fits with greater statistical significance. Fitting results and time constants for all of the tracer runs evaluated are summarized in Table 2.

Table 2

SUMMARY OF THE MODELING RESULTS FOR THE GAS-TRACER TEST DATA

Run ID	CO_2			CO		
	$\tau_d(\text{s})$	$\tau_2(\text{s})$	R^2	$\tau_d(\text{s})$	$\tau_2(\text{s})$	R^2
RTD21	1.2	0.201	0.994	---	---	---
RTD25	1.2	0.201	0.994	---	---	---
RTD27	1.2	0.238	0.993	1.3	0.662	0.999
RTD30	1.2	0.232	0.995	---	---	---

Figure 4. Comparison of a Typical Measured CO₂ Step Response With Fits of First- and Second-Order-Lag Models

Note that the CO_2 time constants vary relatively little over the range of operating conditions tested, but the second-order-lag constant differs considerably from that of CO. It is believed that this difference is primarily due to variations in responsiveness between the CO and CO_2 analyzers. This also implies that analyzer response is the most important component in profile distortion. No tracer test data were available for determining the hydrocarbon response constants.

2.3 General correction procedure

With the estimated dead time and second order time constants described in 2.2, CO and CO_2 profiles generated during fuels characterization can be corrected with the following simplified form of Eq. (3):

$$C_a|_{t-r_d} = [C_m + 2r_2(dc_m/dt) + (r_2)^2(d^2c_m/dt^2)]|_t \quad (8)$$

where $C_a|_{t-r_d}$ is the actual CO or CO_2 concentration in the reactor at time $t-r_d$ and all of the right-hand-side terms are measured at time t .

In the example profile corrections done for this study, the value of r_2 used for CO_2 was 0.218, the average of the CO_2 values listed in Table 2. The value of r_2 used for CO was 0.662, the result for the single tracer test in which the CO analyzer was not off-scale. The value of r_2 assumed for hydrocarbons was the same as that for CO_2 . This assumption is based on the manufacturers specifications for

the hydrocarbon analyzer which reportedly characterize it as having similar dynamics to the CO₂ analyzer [Perna(1988)]. When the reactor oxygen level is ≥ 3 volume %, hydrocarbon concentration is usually much lower than that of CO and CO₂, and the CH_x contribution to the corrected carbon-loss profile is relatively unimportant anyway.

Eq.(8) can also be integrated with respect to time to yield the cumulative amount of CO₂, CO, and CH_x produced up to a given time. The result is

$$M_{ak}|_{t-\tau_d} = M_{mk} + 2\tau_{2k}C_{mk} + (\tau_{2k})^2(dC_{mk}/dt) \quad (9)$$

where M_{ak} and M_{mk} are the time integrated values of the actual and measured concentrations of species k (CO, CO₂, or CH_x), respectively. Note that M_{ak} is proportional to the cumulative mass of carbon lost from the sample via species k. (It is assumed here that the measured concentrations have already been corrected for instrument background bias).

The total corrected carbon-loss profile can also be determined by adding the M_{ak} for each of the three components. This yields

$$M_{at}|_{t-\tau_d} = M_{mt} + 2 \sum_{k=1}^3 \tau_{2k}C_{mk} + \sum_{k=1}^3 (\tau_{2k})^2(dC_{mk}/dt) \quad (10)$$

where M_{at} and M_{mt} now represent the time integrals of the total carbon lost from the sample. Eq.(10) is a convenient form of the correction equation because M_{mt} is typically calculated and stored in the fixed-bed data acquisition

files. It is also possible to use M_{at} in reexpressing the carbon-loss profile as:

$$\theta_{at} = 1 - M_{at}/M_{af} \quad (11)$$

where θ_{at} is the corrected fraction of total carbon remaining (FCR) in the sample and M_{af} is the final value of the time integral of the total carbon concentration in the exit gas.

The principal difficulty in applying Eqs.(8-11) to the fuels characterization data is evaluating the derivatives of the measured concentration profiles. This is a problem because of the noise in the as-measured data. As illustrated in Fig. 5, direct numerical differentiation of the data magnifies the noise. In order for the noise not to dominate the profile corrections, it is necessary to estimate "smoothed" values for the first and second derivatives. Two smoothing methods were successfully tried: 1) curve fitting the original profiles, and 2) application of auto-regressive-moving-average (ARMA) methods.

For curve fitting, it was found that the general function $at^{c-1}/(1+bt^c)^2$ can be used to represent typical fixed-bed concentration profiles. The parameters a , b , and c must be determined by least-square fitting of the observed profiles with a nonlinear least-squares procedure such as that developed by Marquardt (1963). The principal advantage of this smoothing method is that the profile derivatives can be determined analytically from the fitted function.

Figure 5. Illustration of Data Noise on the Estimated Devolatilization/Combustion Profile Derivatives

Two disadvantages of curve fitting are: 1) the original profile may have to be fitted in sections (for example, the devolatilization zone may require one set of parameters and the char burning zone may require another), and 2) nonlinear least-squares fitting can be time consuming due to the typically large number of data points and the large number of iterations required.

The other smoothing method, ARMA, is a commonly used time-series-analysis technique that involves correcting each measurement based on previous and future values [Box and Jenkins(1976)]. The method applied in this study is based on one of the simplest ARMA techniques, a simple moving average. For the fixed-bed data, the first derivative was evaluated numerically and a smoothed derivative profile was calculated by averaging 3 to 11 points centered on each measured point. Points on the ends were determined by linear extrapolation. This process was repeated to obtain the second derivative. Advantages of this method are: 1) it can operate directly on the as-measured data without the need to identify different zones of behavior, and 2) it is much faster than nonlinear least-squares fitting. A disadvantage is that the number of points needed in the moving average is somewhat subjective and may require adjustment from one data set to another.

Fig. 6 illustrates typical results of smoothing the first and second derivatives in Fig. 5.

Figure 6. Illustration of "Smoothed" Profile Derivatives

3. EXAMPLE APPLICATIONS

In demonstrating the effects of the proposed correction procedure, it is expected that fixed-bed characterization tests with Texas lignite at high temperature (above 1200 K or 1700 °F) would provide some of the best examples. This is based on the reasoning that Texas lignite is the fastest burning fuel yet tested, and thus the distortion due to measurement lags should also be greatest for this fuel.

Figs. 7-11 illustrate the effects of correcting Texas lignite data for selected B&W runs between T40 through T49 using the procedures described above. Note that the Figs. 8-11 are arranged in sequence so that the sample particle size increases in later figures. It can be seen that, as expected, the distortions present in the original data become less important as particle size increases. For particles sized 44 to 53 microns and 105 to 125 microns (Figs. 7-9), the distortions in the original data are clearly evident over the entire profile. For 500-595 micron particles (Fig. 10), the char burnout portion of the profile needs no significant correction, but the devolatilization zone has been significantly stretched by the system lags. For the 6350 micron particles (Fig. 11), no significant profile distortion is evident.

(X 1000)

Figure 7. Comparison of the Measured and Corrected CO₂ Profiles for Test No. T49 (Texas Lignite; 3% O₂; 44 to 53 Microns; 1212°K)

Figure 8. Comparison of the Measured and Corrected Carbon-Loss Profiles for Test No. T49

Figure 9. Comparison of the Measured and Corrected Carbon-Loss Profiles for Test No. T48 (Texas Lignite; 3% O₂; 105 to 125 Microns; 1211°K)

Figure 10. Comparison of the Measured and Corrected Carbon-Loss Profiles for Test No. T42 (Texas Lignite; 3% O₂; 500 to 595 Microns; 1210°K)

Figure 11. Comparison of the Measured and Corrected Carbon-Loss Profiles for Test No. T40 (Texas Lignite; 3% O₂; 6350 Microns; 1210°K)

The trend of increasing profile distortion with decreasing particle size is certainly reasonable and expected. Any condition which produces rapid fluctuations in the concentration profiles, such as small particle size, high temperature, high fuel reactivity, or high oxygen concentration, would be expected to result in greater variation between the measured and actual behavior. In light of this, it may be useful to establish data correction standards based on the maximum rate of change occurring in the measured concentration profiles; that is, the maximum slope in each concentration profile could be tested to determine if correction is necessary. Those profiles (or portions of profiles) with maximum slopes less than some critical value could then be left unaltered.

4. CONCLUSIONS

The results of this study lead to the following conclusions:

- The as-measured fixed-bed reactor data are distorted to varying degrees by the inherent response characteristics of the reactor and gas-analysis system. In some cases, these distortions can lead to large errors in estimating devolatilization and combustion rates and in deriving fuel characterization parameters.
- The gas-tracer tests evaluated in this limited study indicate that the reactor-analyzer response can be modeled as a dead time followed by a second order lag process (2 first-order lags in series with a single common time constant). The second-order time constants are different for CO and CO₂.
- Using the estimated values for the response dead time and second-order lag constants, typical as-measured fixed-bed data can be corrected to give what appear to be better estimates of the devolatilization and combustion profiles. The corrected profiles appear to follow reasonable trends.

5. RECOMMENDATIONS

It is recommended that the following action items be considered by EPRI and B&W for implementation:

- The remaining CO and CO₂ tracer data should be analyzed in the manner described by this report in order to confirm or improve the system response model and the estimated values of the appropriate time constants.
- Hydrocarbon tracer tests should be conducted on the fixed-bed reactor to establish the correct time constant or constants needed for this gas component.
- A computerized standard data correction procedure should be implemented as part of the data base so that users have access not only to the as-measured fixed-bed results but also the best estimates of the corrected values.
- All reported characterization parameters should be based on corrected data.
- Periodic tracer testing should be established as part of the standard fixed-bed operating procedure so that variations in the system response characteristics can be detected and accounted for.

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Appendix C

TEST CONDITIONS, KINETIC RATE CONSTANT CALCULATIONS, AND PARTICLE TEMPERATURE CALCULATIONS OF BENCH-SCALE PFBC TESTS

TEST CONDITIONS

File No.	Date	Pressure psig	Bed Temp. of	Reactor Surf. T. of	% O ₂	O ₂ Conc. g O ₂ /cm ³	Particle Diameter Size, mesh	Superf. V. ft/sec	Coal Wt gm	Rect. ID inch
OXYGEN CONCENTRATION EFFECT										
PITS108	2-22-89	206	1547	1665	3	0.000157	48x60	0.0275	4	0.257
PITS121	3-2-89	207	1531	1644	10	0.000532	48x60	0.0275	3.7	0.255
PITS234	3-14-89	207	1427	1491	3	0.000168	28x32	0.0549	4.1	0.256
PITS247	3-15-89	206	1419	1491	10	0.000561	28x32	0.0549	4	0.256
PITS519	10-5-89	275	1541	1617	3	0.000207	28x32	0.0549	4	0.256
PITS531	10-5-89	276	1505	1577	10	0.000707	28x32	0.0549	4	0.248
PITS712	1-25-90	206	1528	1566	3	0.000159	28x32	0.0549	12	0.25
PITS718	1-25-90	207	1527	1549	10	0.000533	28x32	0.0549	12	0.254
PITS518	10-5-89	276	1540	1616	3	0.000208	10x12	0.155	4	0.102
PITS530	10-5-89	279	1502	1574	10	0.000715	10x12	0.155	4	0.109
PITS283	3-20-89	206	1729	1839	3	0.000144	28x32	0.0549	4	0.259
PITS295	3-21-89	206	1717	1808	10	0.000484	28x32	0.0549	4.2	0.261
PITS107	2-22-89	206	1555	1670	3	0.000157	28x32	0.0549	4	0.25
PITS120	3-2-89	207	1520	1635	10	0.000535	28x32	0.0549	3.7	0.254
SIZE AND TEMPERATURE EFFECT										
PITS228	3-14-89	207	1419	1476	3	0.000169	4x5	0.4375	4.04	0.265
PITS230	3-14-89	206	1424	1489	3	0.000167	6x7	0.3075	4.07	0.259
PITS232	3-14-89	207	1424	1491	3	0.000168	10x12	0.155	4.05	0.263
PITS233	3-14-89	206	1422	1491	3	0.000168	10x12	0.155	4.06	0.117
PITS234	3-14-89	207	1427	1491	3	0.000168	28x32	0.0549	4.06	0.256
PITS236	3-14-89	206	1425	1494	3	0.000167	48x60	0.0275	4.07	0.263
PITS277	3-20-89	208	1727	1822	3	0.000146	4x5	0.4375	3.91	0.25
PITS279	3-20-89	208	1728	1830	3	0.000145	6x7	0.3075	4	0.26
PITS282	3-20-89	207	1727	1835	3	0.000145	10x12	0.155	4	0.11
PITS283	3-20-89	206	1729	1839	3	0.000144	28x32	0.0549	4	0.259
PITS285	3-20-89	206	1725	1842	3	0.000144	48x60	0.0275	4	0.259
PITS500	10-4-89	208	1551	1628	3	0.000158	4x5	0.4375	4	0.258
PITS502	10-4-89	206	1550	1623	3	0.000157	6x7	0.3075	4.03	0.251
PITS503	10-4-89	207	1550	1626	3	0.000158	6x7	0.3075	4.01	0.105
PITS504	10-4-89	207	1547	1623	3	0.000158	10x12	0.155	4.01	0.268
PITS505	10-4-89	206	1550	1624	3	0.000157	10x12	0.155	4.03	0.102
PITS507	10-4-89	208	1550	1622	3	0.000158	28x32	0.0549	4	0.109
PITS510	10-4-89	208	1550	1623	3	0.000158	48x60	0.0275	4	0.117
PITS105	2-22-89	206	1550	1666	3	0.000157	10x12	0.155	4	0.252
PRESSURE EFFECT										
PITS519	10-5-89	275	1541	1617	3	0.000207	28x32	0.0549	4	0.256
PITS107	2-22-89	206	1555	1670	3	0.000157	28x32	0.0549	4	0.25
PITS161	3-7-89	132	1556	1629	3	0.000104	28x32	0.0549	4.1	0.253
TEXL175	3-8-89	208	1583	1643	3	0.000156	48x60	0.0275	4	0.252
TEXL150	3-7-89	132	1564	1616	3	0.000103	48x60	0.0275	4.1	0.248
TEXL124	3-3-89	17.5	1569	1620	3	0.000022	48x60	0.0275	4	0.255
PITS277	3-20-89	208	1727	1822	3	0.000146	4x5	0.4375	3.91	0.25
PITS301	3-22-89	132	1725	1871	3	0.000096	4x5	0.4375	3.94	0.243
PITS253	3-16-89	18	1721	1842	3	0.000021	4x5	0.4375	4.38	0.26
SUPERFICIAL GAS VELOCITY EFFECT										
PITS766	1-26-90	208	1413	1432	3	0.000170	28x32	0.0549	4.2	0.254
PITS736	1-26-90	207	1725	1753	3	0.000145	28x32	0.0549	4.2	0.254
PITS742	1-26-90	206	1743	1779	3	0.000143	28x32	0.0549	12.4	0.252
PITS760	1-26-90	208	1423	1437	3	0.000169	28x32	0.0549	12.25	0.253
PITS723	1-25-90	209	1561	1561	3	0.000158	28x32	0.0549	19.9	0.25
PITS755	1-26-90	206	1398	1399	3	0.000170	28x32	0.0549	19.6	0.253
PITS234	3-14-89	207	1427	1491	3	0.000168	28x32	0.0549	4.1	0.256
PITS283	3-20-89	206	1729	1839	3	0.000144	28x32	0.0549	4	0.259
COAL TYPE EFFECT										
TEXL247	3-15-89	208	1424	1479	3	0.000169	28x32	0.0549	4	0.25
TEXL173	3-8-89	206	1572	1640	3	0.000155	28x32	0.0549	4	0.254

KINETIC RATE CONSTANT CALCULATIONS

$\rho(\text{char}) = \rho(\text{coal}) * \text{fixed carbon}/100/(\text{swelling})^{**3}$ (note: $\rho(\text{coal}) = 1.328$)
char specific area = $\rho(\text{char}) * d(\text{diameter of particle})/6$
 $T_c = 1/(dX/dt)$ = Time for the char to reduce its content to 36.8%
 $(R_{ob})_i$ (Initial observed rate) = $(dX/dt)/\text{char specific area}$
 $Sh = hm * d/D$, $Sh = 2.0 + 0.92 * Re^{0.7} * Sc^{0.33}$, $Sc = \mu(\text{vis.})/D/\rho(\text{density}) = 2.79$
 Sh = Sherwood no., Sc = Schmidt no., hm = mass transfer coeff.
 R_{mt} (Mass trans. rate) (g of C/ex. SA of char) = $hm * C(O_2) * 24g \text{ of C}/32g \text{ of } O_2$
 $R(c)$ (kinetic rate) (g of C/ex. S.A. of Char) = $R_{ob}/(1 - R_{ob}/R_{hm})^{**n}$
 Re (Reynold's Number) was based on actual gas velocity (superf. vel/0.45)
Conc. of O_2 (g O_2/cm^3) = PM/RT ($P \text{ } O_2 = \text{atm}$; $M = 32$; $T = ^\circ K$, $R = 82$)

KINETIC RATE CONSTANT CALCULATIONS (Continued)

File No.	Fixed C	Swelling	rho(char)	Spec. SA	1/(db/dt)	(Rob)	Gas Density	Gas Viscosity	Re	sh	Dp(diffu. h)	Rmt	n
			g/cm3	cm2/g	sec	g C/cm2-s	g/cm3	g/cm-sec			cm2/sec	g C/cm2-sec	
OXYGEN CONCENTRATION EFFECT													
PITS108	0.481	1.13	0.442698	492.8454	9	0.000225	0.004618	0.000422	92.15153	32.61885	0.141388	148.4124	0.017552
PITS121	0.481	1.13	0.442698	492.8454	6.3	0.000322	0.004723	0.00042	87.58929	31.54968	0.138791	140.9120	0.056250
PITS234	0.481	1.13	0.442698	246.8715	17.7	0.000228	0.004935	0.000405	209.9281	56.48621	0.126350	115.0454	0.014537
PITS247	0.481	1.13	0.442698	246.8715	12.5	0.000324	0.004982	0.000405	206.7912	55.91501	0.125982	113.5504	0.047814
PITS519	0.481	1.13	0.442698	246.8715	7.8	0.000519	0.006081	0.00042	243.3616	62.42459	0.107149	107.8190	0.016788
PITS531	0.481	1.13	0.442698	246.8715	5.1	0.000794	0.006275	0.000415	254.1791	64.29241	0.103440	107.2014	0.056854
PITS712	0.481	1.13	0.442698	246.8715	5	0.000810	0.004663	0.000419	561.1696	110.4433	0.139053	247.5541	0.029557
PITS718	0.481	1.13	0.442698	246.8715	1.7	0.002382	0.004733	0.000419	569.6119	111.5828	0.138304	248.7608	0.099502
PITS518	0.481	1.13	0.442698	87.44031	14.2	0.000805	0.006105	0.00042	589.8033	127.2982	0.106687	77.54003	0.012121
PITS530	0.481	1.13	0.442698	87.44031	4.5	0.002541	0.006350	0.000515	585.1440	113.6660	0.102110	66.26617	0.035561
PITS283	0.481	1.13	0.442698	246.8715	13.4	0.000302	0.004234	0.000442	161.0360	47.25676	0.164590	125.3767	0.013594
PITS295	0.481	1.13	0.442698	246.8715	13.7	0.000295	0.004300	0.000442	171.7131	49.33688	0.163013	129.6420	0.047115
PITS107	0.481	1.13	0.442698	246.8715	12.3	0.000329	0.004600	0.000422	183.2373	51.53897	0.142376	118.2829	0.013933
PITS120	0.481	1.13	0.442698	246.8715	13.8	0.000293	0.004749	0.000418	176.6731	50.28992	0.137452	111.4250	0.044726
SIZE AND TEMPERATURE EFFECT													
PITS228	0.481	1.13	0.442698	30.97885	66	0.000489	0.004956	0.000405	1655.463	233.2495	0.125414	59.17144	0.007508
PITS230	0.481	1.13	0.442698	44.07560	54	0.000420	0.004920	0.000406	1160.942	182.3868	0.126570	66.43568	0.008370
PITS232	0.481	1.13	0.442698	87.44031	23.5	0.000486	0.004942	0.000406	584.9534	113.6405	0.125999	81.75071	0.010346
PITS233	0.481	1.13	0.442698	87.44031	26.5	0.000431	0.004925	0.000405	585.8162	113.7558	0.126335	82.05170	0.010348
PITS234	0.481	1.13	0.442698	246.8715	17.7	0.000228	0.004935	0.000405	207.8800	56.11356	0.126350	114.2864	0.014441
PITS236	0.481	1.13	0.442698	492.8454	9.6	0.000211	0.004917	0.000405	104.0292	35.32993	0.126687	144.0345	0.018137
PITS277	0.481	1.13	0.442698	30.97885	54	0.000597	0.004277	0.000442	1266.953	193.7651	0.162851	63.82784	0.006989
PITS279	0.481	1.13	0.442698	44.07560	45	0.000504	0.004275	0.000442	910.5679	154.1794	0.162981	72.31715	0.007916
PITS282	0.481	1.13	0.442698	87.44031	28.7	0.000398	0.004257	0.000442	457.1334	95.94362	0.163585	89.60897	0.009769
PITS283	0.481	1.13	0.442698	246.8715	13.4	0.000302	0.004234	0.000442	161.0360	47.25676	0.164590	125.3767	0.013594
PITS285	0.481	1.13	0.442698	492.8454	7.3	0.000277	0.004242	0.000442	80.81241	29.93006	0.164064	158.0191	0.017165
PITS500	0.481	1.13	0.442698	30.97885	74.2	0.000435	0.004651	0.000422	1476.389	215.4409	0.140607	61.27457	0.007297
PITS502	0.481	1.13	0.442698	44.07560	32	0.000709	0.004612	0.000422	1036.599	168.6345	0.141758	68.79727	0.008124
PITS503	0.481	1.13	0.442698	44.07560	50	0.000453	0.004632	0.000422	1036.129	168.5815	0.141118	68.46543	0.008121
PITS504	0.481	1.13	0.442698	87.44031	33.3	0.000343	0.004639	0.000421	524.2997	105.4053	0.140750	84.70359	0.010062
PITS505	0.481	1.13	0.442698	87.44031	39	0.000293	0.004612	0.000422	522.5137	105.1586	0.141758	85.11049	0.010050
PITS507	0.481	1.13	0.442698	246.8715	13.5	0.000300	0.004653	0.000422	185.3579	51.93960	0.140485	117.6191	0.014015
PITS510	0.481	1.13	0.442698	492.8454	7	0.000289	0.004653	0.000417	93.96107	33.03850	0.140485	149.3618	0.017797
PITS105	0.481	1.13	0.442698	87.44031	35	0.000326	0.004612	0.000422	518.6241	104.6204	0.141758	84.67493	0.009999
PRESSURE EFFECT													
PITS519	0.481	1.13	0.442698	246.8715	7.8	0.000519	0.006081	0.00042	243.3616	62.42459	0.107149	107.8190	0.016788
PITS107	0.481	1.13	0.442698	246.8715	12.3	0.000329	0.004600	0.000422	183.2373	51.53897	0.142376	118.2829	0.013933
PITS161	0.481	1.13	0.442698	246.8715	20.3	0.000199	0.003056	0.000423	124.4864	39.79399	0.214381	137.5159	0.010762
TEXL175	0.3075	1	0.40836	534.2879	2.2	0.000850	0.004578	0.000427	90.27796	32.18175	0.144547	149.6956	0.017549
TEXL150	0.3075	1	0.40836	534.2879	4	0.000467	0.003044	0.000425	61.81779	25.15350	0.215872	174.7369	0.013620
TEXL124	0.3075	1	0.40836	534.2879	5.2	0.000359	0.000666	0.000426	13.17415	9.845908	0.987750	312.9622	0.005341
PITS277	0.481	1.13	0.442698	30.97885	54	0.000597	0.004277	0.000442	1266.953	193.7651	0.162851	63.82784	0.006989
PITS301	0.481	1.13	0.442698	30.97885	78.1	0.000413	0.002820	0.000444	837.9667	145.5806	0.246822	72.68298	0.005248
PITS253	0.481	1.13	0.442698	30.97885	167	0.000193	0.000629	0.000442	208.9676	56.31159	1.103760	125.7234	0.002027
SUPERFICIAL GAS VELOCITY EFFECT													
PITS766	0.481	1.13	0.442698	246.8715	25.4	0.000159	0.004994	0.000404	218.1721	57.97534	0.124154	116.0257	0.014837
PITS736	0.481	1.13	0.442698	246.8715	16.8	0.000241	0.004261	0.000443	169.7809	48.96339	0.163323	128.9052	0.014066
PITS742	0.481	1.13	0.442698	246.8715	10.9	0.000371	0.004207	0.000445	492.6944	101.0014	0.166437	270.9737	0.029194
PITS760	0.481	1.13	0.442698	246.8715	15.3	0.000264	0.004967	0.000405	631.3922	119.7732	0.125317	241.9463	0.030775
PITS723	0.481	1.13	0.442698	246.8715	5.2	0.000778	0.004649	0.000425	914.7504	154.6683	0.141199	352.0339	0.041907
PITS755	0.481	1.13	0.442698	246.8715	6.3	0.000642	0.004989	0.000403	1019.665	166.7242	0.123528	331.9821	0.042411
PITS234	0.481	1.13	0.442698	246.8715	17.7	0.000228	0.004935	0.000405	209.9281	56.48621	0.126350	115.0454	0.014537
PITS283	0.481	1.13	0.442698	246.8715	13.4	0.000302	0.004234	0.000438	162.5067	47.54567	0.164590	126.1432	0.013677
COAL TYPE EFFECT													
TEXL247	0.3075	1	0.40836	267.6305	6.5	0.000574	0.004965	0.000405	206.0594	55.78138	0.125433	112.7852	0.014338
TEXL173	0.3075	1	0.40836	267.6305	5.7	0.000655	0.004562	0.000425	180.4213	51.00480	0.144485	118.7912	0.013876

KINETIC RATE CONSTANT CALCULATIONS (Continued)

File No.	(1-Rob/Rmt) ⁿ	Rc	P O2	(P O2) ⁿ	Kc
	Rob/Rmt	g C/cm2-s	atm		g C/cm2-s/(atm) ⁿ

OXYGEN CONCENTRATION EFFECT

PITS108	0.997417	0.012844	0.000226	0.450408	0.852552	0.000265
PITS121	0.998852	0.005725	0.000322	1.508163	1.085649	0.000297
PITS234	0.996831	0.015742	0.000229	0.452448	0.853323	0.000269
PITS247	0.998640	0.006777	0.000324	1.501360	1.084668	0.000299
PITS519	0.993735	0.030933	0.000522	0.591224	0.900223	0.000580
PITS531	0.997190	0.013969	0.000796	1.977551	1.146107	0.000694
PITS712	0.994457	0.027409	0.000814	0.450408	0.852552	0.000955
PITS718	0.995164	0.023946	0.002394	1.508163	1.085649	0.002205
PITS518	0.986343	0.066443	0.000816	0.593265	0.900844	0.000906
PITS530	0.985279	0.071445	0.002579	1.997959	1.148463	0.002245
PITS283	0.995512	0.022236	0.000303	0.450408	0.852552	0.000356
PITS295	0.998741	0.006275	0.000296	1.501360	1.084668	0.000272
PITS107	0.995227	0.023635	0.000330	0.450408	0.852552	0.000388
PITS120	0.998684	0.006562	0.000293	1.508163	1.085649	0.000270

SIZE AND TEMPERATURE EFFECT

PITS228	0.986619	0.065136	0.000495	0.452448	0.853323	0.000580
PITS230	0.989752	0.050196	0.000424	0.450408	0.852552	0.000497
PITS232	0.990410	0.047036	0.000491	0.452448	0.853323	0.000575
PITS233	0.991516	0.041702	0.000435	0.450408	0.852552	0.000510
PITS234	0.996810	0.015847	0.000229	0.452448	0.853323	0.000269
PITS236	0.997658	0.011653	0.000211	0.450408	0.852552	0.000248
PITS277	0.982279	0.085519	0.000608	0.454489	0.854092	0.000712
PITS279	0.986924	0.063691	0.000510	0.454489	0.854092	0.000598
PITS282	0.991705	0.040789	0.000401	0.452448	0.853323	0.000470
PITS283	0.995512	0.022236	0.000303	0.450408	0.852552	0.000356
PITS285	0.996740	0.016192	0.000278	0.450408	0.852552	0.000327
PITS500	0.987782	0.059612	0.000440	0.454489	0.854092	0.000515
PITS502	0.981902	0.087271	0.000722	0.450408	0.852552	0.000846
PITS503	0.988567	0.055871	0.000459	0.452448	0.853323	0.000537
PITS504	0.993079	0.034128	0.000345	0.452448	0.853323	0.000405
PITS505	0.994095	0.029176	0.000294	0.450408	0.852552	0.000345
PITS507	0.995681	0.021408	0.000301	0.454489	0.854092	0.000352
PITS510	0.996721	0.016286	0.000290	0.454489	0.854092	0.000340
PITS105	0.993377	0.032678	0.000328	0.450408	0.852552	0.000385

PRESSURE EFFECT

PITS519	0.993735	0.030933	0.000522	0.591224	0.900223	0.000580
PITS107	0.995227	0.023635	0.000330	0.450408	0.852552	0.000388
PITS161	0.996263	0.018541	0.000200	0.299387	0.785682	0.000254
TEXL175	0.990110	0.048477	0.000859	0.454489	0.854092	0.001006
TEXL150	0.993033	0.034352	0.000471	0.299387	0.785682	0.000599
TEXL124	0.986144	0.067383	0.000364	0.065714	0.580138	0.000629
PITS277	0.982279	0.085519	0.000608	0.454489	0.854092	0.000712
PITS301	0.983727	0.078755	0.000420	0.299387	0.785682	0.000534
PITS253	0.980158	0.095349	0.000197	0.066734	0.581929	0.000338

SUPERFICIAL GAS VELOCITY EFFECT

PITS766	0.997841	0.010748	0.000159	0.454489	0.854092	0.000187
PITS736	0.996548	0.017141	0.000241	0.452448	0.853323	0.000283
PITS742	0.997441	0.012729	0.000372	0.450408	0.852552	0.000437
PITS760	0.998273	0.008602	0.000265	0.454489	0.854092	0.000310
PITS723	0.996254	0.018588	0.000781	0.456530	0.854858	0.000914
PITS755	0.996949	0.015160	0.000644	0.450408	0.852552	0.000756
PITS234	0.996831	0.015742	0.000229	0.452448	0.853323	0.000269
PITS283	0.995540	0.022100	0.000303	0.450408	0.852552	0.000356

COAL TYPE EFFECT

TEXL247	0.991850	0.040091	0.000579	0.454489	0.854092	0.000678
TEXL173	0.990367	0.047241	0.000661	0.450408	0.852552	0.000776

PARTICLE TEMPERATURE CALCULATIONS

$-H_t \cdot DM/Dt = h \cdot (3.1416 \cdot \#P \cdot d^2) \cdot (T_p - T_b)$
 $+ \text{Sigma} \cdot \text{Em} \cdot (3.1416 \cdot \#P \cdot d^2) \cdot [F_{12}(T_p^4 - T_b^4) + F_{13}(T_p^4 - T_f^4)]$
 $H_t(\text{CO}) = -9795 \text{ joules/g C} \quad H_t(\text{CO}_2) = -33086 \text{ joules/g C}$
 $Q = [\text{CO}_2 / (2\text{CO} + \text{CO}_2)]$
 $H_t = -33086 \cdot Q - 9795 \cdot (1 - Q)$
 (Note: With the assumption of all carbon goes to CO, $H_t = -9795 \text{ joules/g C}$)
 $(DM/Dt)_i$ (initial char burn rate) = $(dx/dt) \cdot C\%(\text{coal carbon}) \cdot \text{wt}(\text{sample weight})$
 $\#P$ (no. of particle) = $(\text{wt}/1.328) / (4/3 \cdot 3.1416 \cdot d^3)$ (d in cm)
 h (heat transfer coeff.) = $\text{Nu} \cdot \text{kg/d}$, $\text{Nu} = 2.0 + 0.92 \cdot \text{Re}^{0.7} \cdot \text{Pr}^{0.33}$
 $\text{kg}(\text{gas cond.}) = k_o(T_m/T_o)^{0.82} \text{ kw/m oK}$, $k_o = 2.27 \cdot 10^{-5} \text{ kw/m oK}$
 $\text{Pr}(\text{Prandtl}) = \text{Cp} \cdot \mu(\text{gas viscosity})/\text{kg} = 1.03$

 $\text{Sigma} = 5.7 \cdot 10^{-11} \text{ kw/m}^2 \text{ oK}^4$
 $\text{Em}(\text{emissivity}) = 0.85$

 $F_{12} = (3.14 \cdot D^2/2) / (3.14 \cdot D^2/2 + 3.14 \cdot D \cdot H)$, $F_{13} = 1 - F_{12}$
 D = diameter of reactor, H = effective height of reactor
 For $D=2"$, $H=4"$: $F_{12}=0.2$, $F_{13}=0.8$
 For $D=1"$, $H=4"$: $F_{12}=0.111$, $F_{13}=0.889$

PARTICLE TEMPERATURE CALCULATIONS (Continued)

File No.	(DM/Dt) i g/sec	Mt Joule/g	Nu	kg kw/m	h kw/m2	DP	Ht*DM/Dt kw	h*Tot kw	SA kw/°K^4	SI*E*SA kw/°K^4	Constant kw	Tp	diff	1/Tp, oK	Tp-Tb oC
OXYGEN CONCENTRATION EFFECT															
PITS108	0.013735	9795	24.03818			0.2221505	0.134536	0	2.6E-14	0.182123	1621.01	-0.13649	0.000865		74.01
PITS121	0.019469	9795	23.26864	0.000071	6.048093	2204.217	0.190699	0.003167	2.5E-14	3.738464	1638.585	-0.00000	0.000857		107.585
PITS234	0.006956	9795	41.21692	0.000068	5.135372	278.1219	0.068142	0.001352	1.3E-14	1.502598	1515.88	-0.00000	0.000911		88.88
PITS247	0.009850	9795	40.80579	0.000068	5.066461	278.1219	0.096489	0.001334	1.3E-14	1.505945	1545.73	-0.00000	0.000897		126.73
PITS519	0.015786	9795	45.49112	0.000071	5.947291	278.1219	0.154630	0.001566	1.3E-14	1.917178	1712.85	-0.00000	0.000828		171.85
PITS531	0.023389	9795	46.83550	0.000070	6.032542	269.4306	0.229103	0.001539	1.2E-14	1.928387	1762.44	-0.00000	0.000810		257.44
PITS712	0.02405	9795	80.05307	0.000071	10.40994	271.6034	0.235569	0.002677	1.2E-14	3.211299	1682.89	-0.00000	0.000840		154.89
PITS713	0.071867	9795	80.87320	0.000071	10.51225	275.9491	0.703937	0.002746	1.3E-14	3.754666	1973.415	-0.00000	0.000739		446.415
PITS518	0.003455	9795	92.18447	0.000071	4.266904	4.923992	0.033842	0.000158	1.8E-15	0.213082	1899	-0.00000	0.000763		359
PITS530	0.011650	9795	82.37260	0.000070	3.753223	5.261913	0.114120	0.000149	1.9E-15	0.279596	2697.1	-0.00000	0.000570		1195.1
PITS283	0.009296	9795	34.57394	0.000077	4.865523	281.3811	0.091063	0.001296	1.3E-14	1.700222	1852.6	-0.00000	0.000778		123.6
PITS295	0.009163	9795	36.07113	0.000076	5.053383	283.5539	0.089757	0.001356	1.3E-14	1.764918	1836.37	-0.00000	0.000784		119.37
PITS107	0.009776	9795	37.65610	0.000072	4.951212	271.6034	0.095760	0.001273	1.3E-14	1.544194	1687.82	-0.00000	0.000838		132.82
PITS120	0.008853	9795	36.75709	0.000071	4.764039	275.9491	0.086716	0.001244	1.3E-14	1.477848	1643.48	-0.00000	0.000855		123.48
SIZE AND TEMPERATURE EFFECT															
PITS228	0.001931	9795	168.4438	0.000068	2.624414	0.568884	0.018916	0.000089	1.7E-15	0.114769	1764.2	-0.00000	0.000809		345.2
PITS230	0.002307	9795	131.8349	0.000068	2.928784	1.601314	0.022597	0.000139	2.3E-15	0.171453	1694.7	-0.00000	0.000835		270.7
PITS232	0.005383	9795	82.35428	0.000068	3.629500	12.69617	0.052727	0.000347	4.6E-15	0.422887	1681.05	-0.00000	0.000840		257.05
PITS233	0.002123	9795	82.43723	0.000068	3.630072	5.648108	0.020801	0.000154	2.1E-15	0.185320	1650.7	-0.00000	0.000853		228.7
PITS234	0.006956	9795	40.94870	0.000068	5.101954	278.1219	0.068142	0.001343	1.3E-14	1.493375	1516.44	-0.00000	0.000911		89.44
PITS236	0.013177	9795	25.98950	0.000068	6.458866	2273.369	0.129072	0.003408	2.6E-14	3.816499	1491.2	-0.00000	0.000922		66.2
PITS277	0.002226	9795	140.0246	0.000077	2.470891	0.536683	0.021812	0.000079	1.6E-15	0.122578	2151.3	-0.00000	0.000689		424.3
PITS279	0.002779	9795	111.5324	0.000077	2.801213	1.607497	0.027221	0.000133	2.3E-15	0.195626	2054.5	-0.00000	0.000716		326.5
PITS282	0.001843	9795	69.61673	0.000077	3.467442	5.310187	0.018057	0.000138	1.9E-15	0.191811	1944.8	-0.00000	0.000748		217.8
PITS283	0.009296	9795	34.57394	0.000077	4.865523	281.3811	0.091063	0.001296	1.3E-14	1.700222	1852.6	-0.00000	0.000778		123.6
PITS285	0.017065	9795	22.10290	0.000077	6.200376	2238.793	0.167157	0.003297	2.6E-14	4.235713	1816.455	-0.00000	0.000790		91.455
PITS500	0.001672	9795	155.6259	0.000072	2.563567	0.553857	0.016381	0.000085	1.6E-15	0.114577	1862	-0.00000	0.000775		311
PITS502	0.003772	9795	121.9366	0.000072	2.856621	1.551853	0.036955	0.000131	2.2E-15	0.187856	2001.6	-0.00000	0.000731		451.6
PITS503	0.001010	9795	121.8985	0.000072	2.855727	0.649181	0.009893	0.000055	9.3E-16	0.073008	1844.6	-0.00000	0.000781		294.6
PITS504	0.003871	9795	76.42689	0.000071	3.547691	12.93754	0.037917	0.000346	4.7E-15	0.432309	1732.75	-0.00000	0.000821		185.75
PITS505	0.001258	9795	76.24933	0.000072	3.543788	4.923992	0.012322	0.000131	1.8E-15	0.162492	1709.5	-0.00000	0.000829		159.5
PITS507	0.003383	9795	37.94446	0.000072	4.978970	118.4191	0.038040	0.000558	5.4E-15	0.670731	1668.9	-0.00000	0.000845		118.9
PITS510	0.008039	9795	24.34023	0.000072	6.376105	1011.346	0.078747	0.001532	1.2E-14	1.809320	1641	-0.00000	0.000856		91
PITS105	0.003463	9795	75.86198	0.000072	3.525786	12.16515	0.033922	0.000323	4.4E-15	0.403616	1730.52	-0.00000	0.000821		180.52
PRESSURE EFFECT															
PITS519	0.015786	9795	45.49112	0.000071	5.947291	278.1219	0.154630	0.001566	1.3E-14	1.917178	1712.85	-0.00000	0.000828		171.85
PITS107	0.009776	9795	37.65610	0.000072	4.951212	271.6034	0.095760	0.001273	1.2E-14	1.544194	1687.82	-0.00000	0.000838		132.82
PITS161	0.005994	9795	29.20255	0.000072	3.841260	274.8626	0.058718	0.000999	1.3E-14	1.200331	1658.26	-0.00000	0.000849		102.26
TEXL175	0.035222	9795	23.72357	0.000073	6.298135	2178.285	0.345006	0.003259	2.5E-14	4.089029	1766.36	-0.00000	0.000808		183.36
TEXL150	0.019065	9795	18.66493	0.000072	4.917335	2143.709	0.186741	0.002504	2.5E-14	3.044788	1692.71	-0.00000	0.000836		128.71
TEXL124	0.015079	9795	7.647160	0.000072	2.018749	2204.217	0.147702	0.001057	2.5E-14	1.383371	1790.5	-0.00000	0.000800		221.5
PITS277	0.002226	9795	140.0246	0.000077	2.470891	0.536683	0.021812	0.000079	1.6E-15	0.122578	2151.3	-0.00000	0.000689		424.3
PITS301	0.001496	9795	105.3434	0.000077	1.857508	0.521656	0.014659	0.000058	1.5E-15	0.089444	2109	-0.00000	0.000700		384
PITS253	0.000748	9795	41.09123	0.000077	0.723468	0.558150	0.007335	0.000024	1.6E-15	0.040924	2089.5	-0.00000	0.000706		368.5
SUPERFICIAL GAS VELOCITY EFFECT															
PITS766	0.00481	9795	42.28873	0.000067	5.236827	275.9491	0.047113	0.001368	1.3E-14	1.485853	1473.06	-0.00000	0.000931		60.06
PITS736	0.007272	9795	35.80231	0.000077	5.030835	275.9491	0.071231	0.001314	1.3E-14	1.695198	1817.49	-0.00000	0.000790		92.49
PITS742	0.011120	9795	73.25715	0.000077	10.36338	273.7762	0.108923	0.002686	1.3E-14	3.425879	1814.53	-0.00000	0.000791		71.53
PITS760	0.007953	9795	86.76832	0.000068	10.79199	274.8626	0.077907	0.002808	1.3E-14	3.030720	1472.133	-0.00000	0.000931		49.133
PITS723	0.023125	9795	111.8843	0.000072	14.74703	271.6034	0.226509	0.003792	1.2E-14	4.503256	1666.385	-0.00000	0.000846		105.385
PITS755	0.019316	9795	120.5617	0.000067	14.83162	274.8626	0.189203	0.003860	1.3E-14	4.186735	1484.9	-0.00000	0.000925		86.9
PITS234	0.006956	9795	41.21692	0.000068	5.135372	278.1219	0.068142	0.001352	1.3E-14	1.502598	1515.88	-0.00000	0.000911		88.88
PITS283	0.009296	9795	34.78189	0.000077	4.894787	281.3811	0.091063	0.001304	1.3E-14	1.709702	1851.92	-0.00000	0.000778		122.92
COAL TYPE EFFECT															
TEXL247	0.011826	9795	40.70961	0.000068	5.065549	271.6034	0.115844	0.001302	1.2E-14	1.495337	1578.42	-0.00000	0.000883		154.42
TEXL173	0.013702	9795	37.27163	0.000072	4.934548	275.9491	0.134217	0.001289	1.3E-14	1.612172	1751.07	-0.00000	0.000814		179.07

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