



MEASUREMENT AND MODELING OF ADVANCED COAL CONVERSION PROCESSES, VOLUME I, PART 1. FINAL REPORT, SEPTEMBER 1986--SEPTEMBER 1993

ADVANCED FUEL RESEARCH, INC. EAST HARTFORD, CT

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Final Report September 1986 - September 1993

Peter R. Solomon Michael A. Serio David G. Hamblen L. Douglas Smoot B. Scott Brewster Predrag T. Radulovic

September 1995

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For U.S. Department of Energy Office of Fossil Energy Morgantown Energy Technology Center Morgantown, West Virginia

By Advanced Fuel Research, Inc. East Hartford, Connecticut and Brigham Young University Provo, Utah



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By Advanced Fuel Research, Inc. 87 Church Street East Hartford, Connecticut 06108 and Brigham Young University Provo, Utah 84602

September 1995

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EXECUTIVE SUMMARY

The overall objective of this program was the development of a predictive capability for the design, scale up, simulation, control and feedstock evaluation in advanced coal conversion devices. This technology is important to reduce the technical and economic risks inherent in utilizing coal, a feedstock whose variable and often unexpected behavior presents a significant challenge. This program merged significant advances made at Advanced Fuel Research, Inc. (AFR) in measuring and quantitatively describing the mechanisms in coal conversion behavior, with technology developed at Brigham Young University (BYU) in comprehensive computer codes for mechanistic modeling of entrained-bed gasification. Additional capabilities in predicting pollutant formation were implemented and the technology was expanded to fixed-bed reactors.

The foundation to describe coal-specific conversion behavior was AFR's Functional Group (FG) and Devolatilization, Vaporization and Crosslinking (DVC) models, developed under previous and on-going METC sponsored programs. These models have demonstrated the capability to describe the time dependent evolution of individual gas species, and the amount and characteristics of tar and char. The combined FG-DVC model was integrated with BYU's comprehensive two-dimensional reactor model for combustion and gasification, PCGC-2, and a one-dimensional model for fixed-bed gasifiers, FBED-1. The program included: i) validation of the submodels by comparison with laboratory data obtained in this program, ii) extensive validation of the modified comprehensive codes by comparison of predicted results with data from bench-scale and process scale investigations of gasification, mild gasification and combustion of coal or coal-derived products, and iii) development of well documented user friendly software applicable to a "workstation" environment.

The progress during the program is summarized below.

For Subtask 2.a., the processes described were: 1) tar formation mechanisms and kinetics; 2) gas formation mechanisms and kinetics; 3) sulfur and nitrogen evolution mechanisms and kinetics; 4) coal and char fluidity (viscosity); 5) char swelling; 6) optical properties of coal and char; 7) the behavior of polymethylenes; 8) crosslinking; 9) char reactivity. These processes were embodied in the Functional Group - Depolymerization, Vaporization, Crosslinking (FG-DVC) model for coal conversion behavior. To provide the data for model development and for model parameters, several experimental methods were developed. These included: TG-FTIR (Thermogravimetric Analysis with analysis of evolved products by Fourier Transform Infrared spectroscopy) to determine coal composition, volatile evolutions, kinetics, and char reactivity and a transparent wall reactor (TWR) with in-situ FT-IR diagnostics to study rapid pyrolysis and combustion phenomenon. In addition, experiments were performed where coal was pyrolyzed in the inlet of a Field Ionization Mass Spectrometer (FIMS) apparatus.

The work has resulted in a successful method to characterize coal in the laboratory and predict its behavior over a wide variety of temperatures (100 to 1500°C), heating rates (10*/million years to 10^{5*}/sec), and pressures (vacuum to 10 atm). The work is described in a number of publications which were written as a result of this contract.

For Subtask 2.b., a high pressure facility (HPCP) was designed and constructed and char oxidation experiments were conducted at both atmospheric and elevated pressures. Approximately 100 oxidation experiments were performed with two sizes of Utah and Pitt. bituminous coal chars at 1, 5, 10, and 15 atm total pressure. Reactor temperatures were varied between 1000 and 1500 K and bulk gas compositions ranged from 5 to 21%, resulting in average particle temperatures ranged from 1400 to 2100 K with burnouts from 15 to 96%. Individual particle temperature, size and velocity were determined for approximately 75 particles at each test condition and overall reaction rates were independently determined from mass loss measurements.

The major findings of the study are as follows: 1) in spite of careful size classification and char preparation, the resulting particle population exhibited substantial variations in combustion behavior; 2) increasing total pressure in an environment of constant gas composition leads to modest increases in the

reaction rate and particle temperature; 3) significant kinetic control of the char oxidation process is exhibited at elevated pressures; 4) the global model kinetic parameters were found to be strongly dependent on the total pressure; 5) CO₂ formation must be accounted for at particle temperatures below about 1700 K; 6) independent particle temperature and mass loss measurements are both experimental necessities to fully describe combustion behavior.

For Subtask 2.c., studies of ignition, soot formation, and char burnout were performed in a Transparent Wall Reactor (TWR) which included in-situ FT-IR diagnostics. Experiments were done with several coal and char samples and the flame characteristics were compared to TGA measurements on the same samples. A comparison of the ignition of several samples suggested that the rate of ignition in the laminar flame correlated with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars was heterogeneous; ignition of the high rank coals was homogeneous; but low rank coals exhibited both homogenous and heterogeneous contributions to ignition. Soot formation in combustion correlated well with tar yields in pyrolysis, suggesting that tar is the chief precursor to soot.

For a Montana Rosebud flame, tomographic reconstruction techniques were applied to line-of-sight FT-IR Emission/Transmission (E/T) measurements to derive spectra that correspond to small volumes within a coal flame. From these spectra, spatially resolved point values for species temperatures and relative concentrations can be determined. The spectroscopic data are in good agreement with visual observations and thermocouple measurements. The data present a picture of the coal burning in a shrinking annulus which collapses to the center at the tip of the flame. It has been found that the preheated air velocity has a significant effect on the shape of the flame. Two cases were done for the Montana Rosebud coal (low velocity and high velocity) and a low velocity case for the Pittsburgh Seam coal was completed. The three flames showed both coal and flow dependent phenomena. Simulations of these results were done at BYU, as discussed under subtask 3.a. In addition, submodels for ignition, soot formation, and soot radiation were formulated.

For Subtask 2.d., work was performed in four areas: 1) laboratory studies of mineral-matter transformations; 2) laboratory studies of catalytic effects of minerals on char reactivity; 3) modeling of mineral effects on char reactivity; 4) literature review of mineral-matter transformations. The results for each of these areas are summarized below.

1) Argonne premium coal samples were characterized using a Scanning Electron Microscope (SEM) with dispersive energy x-ray analysis. In most cases, good agreement with elemental analysis data was obtained. Sampling of char/fly ash and subsequent TGA and SEM analyses were also performed. It was found that ash spheres present on the char surface were rich in Ca, moderately rich in Al and Si, and had varying amounts of Fe, K, and Mg. Many of the pure mineral particles were found to be of the same size as the starting coal particles.

2) The reactivity of chars prepared from raw and demineralized coals was measured. Above 10% oxygen, the mineral matter dominates the char reactivity through the catalytic effect of alkali metals, especially Ca.

3) The modeling of mineral effects on char reactivity was integrated into the overall char-reactivity model.

4) The relevant literature on mineral matter in coal as well as ash formation and deposition was reviewed. Emphasis was placed on research carried out at EERC, MIT and PSI. Several key areas have been identified and discussed. Application of advanced mineral-matter characterization techniques, such as CCSEM and chemical fractionation, is advocated. The review also includes modeling of ash formation and deposition.

For Subtask 2.e., a literature review of heat and mass transport effects in coal pyrolysis was completed. In addition, calculations were done to define regimes of internal and external heat and mass transport control for conditions of interest. This was done to define the boundary regions where such

considerations become important.

A single particle FG-DVC model was developed for use in the fixed bed reactor code. This version of the model is based on an ordinary differential equation (ODE) version of the 2- σ percolation FG-DVC model. The code was delivered to BYU for integration into the FBED-1 Model.

A model for the destruction of tar in fixed bed gasifiers was developed in order to account for the relatively low yield of tar from these systems. According to the predictions of the FBED-1 model, the tar evolution occurs in a relatively small region near the top of the reactor where the gas and particle temperatures are changing rapidly. While the coal particles are entering at room temperature, the exit gas temperature is close to 1000 K and is 1300 K in the region where tar evolves. Some experiments were done to assess the relative importance of tar gasification and tar cracking reactions. It was found that, while the thermal cracking effects were significant, the addition of CO_2 did not have much effect on the yield or composition of tar. Consequently, it was concluded that the tar destruction in the top part of a fixed-bed gasifier can probably be attributed primarily to thermal cracking rather than gasification reactions.

For Subtask 2.f., atmospheric char oxidation runs in platinum and porcelain crucibles were made. Char particles were prepared and oxidized from Utah bituminous, North Dakota lignite, Wyoming subbituminous, Illinois #6, Pittsburgh #8, and Colorado bituminous coals. In these tests, large particles (0.5-1 cm) were oxidized, one at a time, over 5-15 minutes for time periods up to two hours, in incremental steps. The cube root of particle mass declined linearly with time during the first 80-90% burnout. Ash layers formed and usually remained in place around the decreasing volume of carbon. Average mass reactivities increased with decreasing initial char particle mass. These observations are consistent with oxidation being controlled by diffusion of oxygen. However, some chemical kinetic control is indicated at lower temperatures.

The extension of the experimental char oxidation tests to include the variable of pressure was accomplished with the design and construction of a cantilever beam balance unit which was attached to the HPCP reactor of Subtask 2b. The mass loss of a reacting coal particle was followed continuously by the changing response of a force transducer connected to the reacting particles with a long-small-bore ceramic tube. Here also the cube root of particle mass declined linearly with time during the first 80-90% of char burnout. A significant influence of pressure was observed between one and five atmospheres but the burning characteristics at 5 and 7.5 atmospheres were about the same.

For Subtask 2.g., The fuel NO_x submodel in an existing 2-D comprehensive model for pulverized coal gasification and combustion (PCGC-2) was revised and extended to include thermal NO and to be applicable to fuel-rich systems. The effect of two different expressions for oxygen atom concentration was investigated. The fuel NO mechanism was revised to include parallel reaction paths through HCN or NH₃. An alternative global mechanism from the literature involving NH₃ was also investigated. The resulting model was evaluated by comparing model predictions with experimental data.

For Subtask 2.h., The cross-flow injection and mixing of sorbent were studied in a cold-flow facility, and the results were used to modify an existing entrained-flow gasifier for sorbent injection. Sulfurcapture studies were then carried out at pressure with limestone and four coals of varying sulfur content. Three methods were used to investigate the sorbent mixing in cold-flow. The results at relatively low jetto-free-stream momentum ratios showed that such flows are slower to mix with the free stream than flows with sufficient energy to impinge on the opposite wall. In such cases, increasing the number of cross-flow injectors was found to enhance the mixing. Sight windows were installed to permit optical access, and FT-IR temperature data were obtained with the assistance of AFR. There was no significant sulfur capture for three of the coals, and only a small effect with the highest-sulfur coal. The major cause of the low capture is believed to be the high temperature in the gasifier. For Subtask 3.a., a 2-D comprehensive model for pulverized coal gasification and combustion (87-PCGC-2) was extended to include the FG-DVC model as an option for predicting weight loss and volatiles enthalpy. Other improvements in the code include laminar flow effects, gas buoyancy, a user-friendly and reliable energy equation option, and a condensed-phase equilibrium algorithm. The improved model was extensively evaluated by comparing model predictions with experimental data from several reactors. A clear advantage of the FG-DVC submodel was shown to be coal generality. Needed model improvements were identified. User-friendly graphics options were developed for code input and output. A user's manual was prepared, documenting code theory and use. Under a closely related, but independent study, improvements were made to the radiation submodel and enthalpy balance closure was realized.

For Subtask 3.b., the principal objective was to develop, evaluate and apply an advanced, steady-state, one-dimensional model of countercurrent, fixed-bed coal combustion and gasification. Improvements included advanced treatment of devolatilization, separate gas and coal temperatures, axially variable solid and gas flow rates, variable bed void fraction, generalized treatment of gas phase chemistry, and SO_x/NO_x pollutants. The initial fixed-bed model, MBED-1, was evaluated through sensitivity analysis and comparisons to experimental data. The predicted temperature and pressure profiles were found to agree reasonably well with the measured values. In MBED-1, gas evolution rates are determined by the functional group (FG) submodel and the tar evolution rate is determined by the semi-empirical tar (SET) correlation. The MBED-1 results brought out the significant effect of tar yield on predictions and the need for a more rigorous devolatilization model.

The most important improvement in the final version of the fixed-bed model, FBED-1, is the inclusion of the advanced devolatilization submodel, FG-DVC. In this submodel, gas evolution rates are determined by the functional group (FG) submodel and the tar evolution rate by the depolymerization-vaporization-crosslinking (DVC) submodel. The final version of the fixed-bed code, FBED-1, provides also: improved predictions of product gas composition and temperature; improved prediction of tar production; modifications in the iteration scheme to satisfy the gas phase boundary conditions at the bottom of the gasifier; improved modularity, code structure, and use friendliness; and improved graphics output. The final fixed-bed model, FBED-1, was also evaluated through sensitivity analysis and comparisons to experimental data. The predicted effluent composition and temperature as well as the predicted temperature and pressure profiles were found to agree very well with the measured values.

For Subtask 3.c., the fuels feedstock submodel in PCGC-2 was generalized to feed particles in any inlet, and to feed sorbent particles as well as coal particles. The generalized feedstock submodel was tested with the sorbent reactions submodel developed under Subtask 2.g.

For Subtask 4.a., the applicability of 93-PCGC-2 to practical-scale processes of commercial interest was demonstrated by simulating two such reactors. One is the Coal Tech Corp. advanced, air-cooled cyclone combustor, and the other is the Solar Turbines, Inc. combustor. The latter simulation was performed under an independent study and is reported separately. The code was shown to be a useful tool for reactor design and simulation. A user's manual was prepared, the final code was installed at METC and a short course was given.

For Subtask 4.b., the fixed-bed coal combustion, gasification, and devolatilization codes, MBED-1 and FBED-1, developed in Subtask 3.b, were successfully demonstrated by simulating the four dry-ash, fixed-bed gasifiers of interest to METC: the high-pressure, oxygen-blown Lurgi gasifier, the medium-pressure, air-blown METC gasifier, the atmospheric-pressure, air-blown Wellman-Galusha gasifier, and the high-pressure, air-blow, PyGas[™] staged gasifier. The most comprehensive test data, including the temperature and the pressure profiles, were available for the atmospheric-pressure Wellman-Galusha gasifier. The Wellman-Galusha test data were used to validate the fixed-bed codes and the corresponding simulations were presented in Subtask 3.b. The simulations of the high-pressure Lurgi gasifier, the medium-pressure METC gasifier, and the high-pressure, air-blow, PyGas[™] staged gasifier, and spart of this subtask.

The user's manual was prepared for the FBED-1 code. The code was ported to a Silicon Graphics workstation and the sample case was successfully executed. The code, the user's manual, and the installation instructions were sent to METC. A short course on the use of the FBED-1 code was conducted at METC.

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SECTION I. INTRODUCTION

I.A. Program Background and Description

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During the past several years, significant advances have been made at Brigham Young University (BYU) in comprehensive two-dimensional computer codes for mechanistic modeling of entrained-bed gasification and pulverized coal combustion. During the same time period, significant advances have been made at Advanced Fuel Research, Inc. (AFR) in the mechanisms and kinetics of coal pyrolysis and secondary reactions of pyrolysis products. This program provided an opportunity to merge the technology developed by each organization in order to provide a detailed predictive capability for advanced coal characterization techniques in conjunction with comprehensive computer models to provide accurate process simulations.

The program streamlined submodels existing or under development for coal pyrolysis chemistry, volatile secondary reactions, tar formation, soot formation, char reactivity, and SO_x-NO_x pollutant formation. Submodels for coal viscosity, agglomeration, tar/char secondary reactions, sulfur capture, and ash physics and chemistry were developed or adapted. The submodels were first incorporated into the BYU entrained-bed gasification code and subsequently, into a fixed-bed gasification code, which was developed at BYU. These codes were validated by comparison with small scale laboratory and PDU-scale experiments. The validated codes can now be employed to simulate and to develop advanced coal conversion reactors of interest to METC.

I.B. Objectives

The objectives of this study were to establish the mechanisms and rates of basic steps in coal conversion processes, to integrate and incorporate this information into comprehensive computer models for coal conversion processes, to evaluate these models and to apply them to gasification, mild gasification and combustion in heat engines.

I.C. Approach

This program was a closely integrated, cooperative effort between AFR and BYU. The program consisted of four tasks: 1) Preparation of Research Plans, 2) Submodel Development and Evaluation, 3) Comprehensive Model Development and Evaluation, and 4) Applications and Implementation.

I.D. Critical Technical Issues

To achieve the goals of the program, the computer models must provide accurate and reliable descriptions of coal conversion processes. This required the reduction of very complicated and interrelated physical and chemical phenomena to mathematical descriptions and, subsequently, to operational computer codes. To accomplish this objective, a number of technical issues were addressed as noted below.

- Separation of Rates for Chemical Reaction, Heat Transfer, and Mass Transfer
- Particle Temperature Measurements Using FT-IR E/T Spectroscopy
- Functional Group Descriptions of Coal, Char and Tar
- Tar Formation Mechanisms
- Char Formation Mechanisms
- Viscosity/Swelling
- Intraparticle Transport
- Pyrolysis of Volatiles and Soot Formation
- Secondary Reaction of Tar
- Particle Ignition
- Char Reactivity
- Ash Chemistry and Physics

- Particle Optical Properties
- Coupling of Submodels with Comprehensive Codes
- Comprehensive Code Efficiency
- Turbulence
- SO_x and NO_x
- Generalized Fuels Models
- Fixed-Bed Model

These technical issues were addressed in three main tasks as described in Sections II-IV.

I.E. Summary

Subtask 2.a. Coal to Char Chemistry Submodel Development and Evaluation

The processes described in this work were: 1) tar formation mechanisms and kinetics; 2) gas formation mechanisms and kinetics; 3) sulfur and nitrogen evolution mechanisms and kinetics; 4) coal and char fluidity (viscosity); 5) char swelling; 6) optical properties of coal and char; 7) the behavior of polymethylenes; 8) crosslinking; 9) char reactivity. These processes were embodied in the Functional Group - Depolymerization, Vaporization, Crosslinking (FG-DVC) model for coal conversion behavior. To provide the data for model development and for model parameters, several experimental methods were developed. These included: TG-FTIR (Thermogravimetric Analysis with analysis of evolved products by Fourier Transform Infrared spectroscopy) to determine coal composition, volatile evolutions, kinetics, and char reactivity and a transparent wall reactor (TWR) with in-situ FT-IR diagnostics to study rapid pyrolysis and combustion phenomenon. In addition, experiments were performed where coal was pyrolyzed in the inlet of a Field Ionization Mass Spectrometer (FIMS) apparatus.

The work has resulted in a successful method to characterize coal in the laboratory and predict its behavior over a wide variety of temperatures (100 to 1500 °C), heating rates (10°/million years to 10⁵/sec), and pressures (vacuum to 10 atm). The work is described in a number of publications which were written as a result of this contract.

Subtask 2.b. Fundamental High-Pressure Reaction Rate Data

A high pressure facility was designed and constructed and char oxidation experiments were conducted at both atmospheric and elevated pressures. Approximately 100 oxidation experiments were performed with two sizes of Utah and Pitt. bituminous coal chars at 1, 5, 10, and 15 atm total pressure. Reactor temperatures were varied between 1000 and 1500 K and bulk gas compositions ranged from 5 to 21%, resulting in average particle temperatures ranged from 1400 to 2100 K with burnouts from 15 to 96%. Individual particle temperature, size and velocity were determined for approximately 75 particles at each test condition and overall reaction rates were independently determined from mass loss measurements. The results from the 1 atm Utah char oxidation results were shown to be consistent with results obtained by other researchers using the same coal. The chars were found to be burning mainly in a reducing density mode in a regime intermediate between the kinetic and pore diffusion zones, irrespective of total pressure. While the global model was used to correlate the results of the study, the extrapolation of the nth order rate equation to pressures higher than atmospheric was found to be invalid.

The effect of increasing total pressure on char oxidation at a constant gas composition can be summarized as follows. Raising total pressure also necessarily increases the bulk gas O_2 pressure, leading to an increase in the reaction rate. However, this increase is tempered by the decrease in oxygen diffusivity that also accompanies increases in pressure. The overall result is a slight increase in rate with increasing total pressure. Most of this change occurred by 10 atm and further increases in total pressure produce little effect on the rate.

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The major findings of the study are as follows:

- 1. In spite of careful size classification and char preparation, the resulting particle population exhibited substantial variations in combustion behavior.
- 2. Increasing total pressure in an environment of constant gas composition leads to modest increases in the reaction rate and particle temperature.
- 3. Significant kinetic control of the char oxidation process is exhibited at elevated pressures.
- 4. The global model kinetic parameters were found to be strongly dependent on the total pressure. This indicates that the empirical nth order equation is not completely valid over the range of pressures covered in the experiments.
- 5. CO₂ formation must be accounted for at particle temperatures below about 1700 K. This is true regardless of the pressure.
- Independent particle temperature and mass loss measurements are both experimental necessities to fully describe combustion behavior.

Subtask 2.c. Secondary Reaction of Pyrolysis Products and Char Burnout

Studies of ignition, soot formation and char burnout were performed in a Transparent Wall Reactor (TWR) which included in-situ FT-IR diagnostics. Experiments were done with several coal and char samples and the flame characteristics were compared to TGA measurements on the same samples. A comparison of the ignition of several samples suggested that the rate of ignition in the laminar flame correlated with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars was heterogeneous; ignition of the high rank coals was homogeneous; but low rank coals exhibited both homogenous and heterogeneous contributions to ignition. Soot formation in combustion correlated well with tar yields in pyrolysis, suggesting that tar is the chief precursor to soot.

A series of pyrolysis experiments was also done with Zap lignite and Pittsburgh seam bituminous coal in the TWR. These experiments included FT-IR gas and particle temperature measurements, thermocouple measurements of the gas temperature and collection of char samples with a probe at six different heights. The particle temperature measurements were used to reconstruct the particle time-temperature history. The pyrolysis yields were then simulated with the FG-DVC model and the results were consistent with kinetic rates measured previously at AFR and Sandia for experiments where particle temperature measurements were made.

For a Montana Rosebud flame, tomographic reconstruction techniques were applied to line-of-sight FT-IR Emission/Transmission (E/T) measurements to derive spectra that correspond to small volumes within a coal flame. From these spectra, spatially resolved point values for species temperatures and relative concentrations can be determined. The spectroscopic data are in good agreement with visual observations and thermocouple measurements. The data present a picture of the coal burning in a shrinking annulus which collapses to the center at the tip of the flame. It has been found that the preheated air velocity has a significant effect on the shape of the flame. Two cases were done for the Montana Rosebud coal (low velocity and high velocity) and a low velocity case for the Pittsburgh Seam coal was completed. The three flames showed both coal and flow dependent phenomena. Simulations of these results were done at BYU, as discussed under subtask 3.a.

In addition, submodels for ignition and soot formation were formulated. Work was also done on developing a radiative model for soot as part of the soot submodel. The inputs are the volume fraction of soot and the temperature. The output is the average soot emissivity. The main difficulty is to correct for the presence of CO_2 and H_2O . This work was done jointly with BYU since the radiation model is an

integral part of PCGC-2.

Subtask 2.d. Ash Physics and Chemistry Submodel

Under this subtask, work was performed in four areas:

- 1) laboratory studies of mineral-matter transformations
- 2) laboratory studies of catalytic effects of minerals on char reactivity
- 3) modeling of mineral effects on char reactivity
- 4) literature review of mineral-matter transformations

The results are summarized below.

1) Argonne premium coal samples were characterized using a Scanning Electron Microscope (SEM) with dispersive energy x-ray analysis. In most cases, good agreement with elemental analysis data was obtained. Sampling of char/fly ash and subsequent TGA and SEM analyses were also performed. It was found that ash spheres present on char surface were rich in Ca, moderately rich in Al and Si, and had varying amounts of Fe, K, and Mg. Many of the pure mineral particles were found to be of the same size as the starting coal particles. Small-particle shedding (< 10μ m was also observed. Sodium was nearly completely lost from the char, while magnesium was retained up to 30-50% burn-off. Sulfur was progressively lost as burn-off increased.

2) The reactivity of chars prepared from raw and demineralized coals was measured. For the rawcoal samples, an increase in reactivity with increasing coal-oxygen content was observed. Above 10% oxygen, the mineral matter dominates the char reactivity through the catalytic effect of alkali metals, especially Ca. This was confirmed by lower reactivities observed for demineralized samples. Loading demineralized samples with Ca and Mg ions restored the originally high reactivity.

3) The modeling of mineral effects on char reactivity was integrated into the overall char-reactivity model and is reported in section II.A.10

4) The relevant literature on mineral matter in coal as well as ash formation and deposition was reviewed. Emphasis was placed on research carried out at EERC, MIT and PSI. The following key areas have been identified and discussed: 1) the chemical and physical characterization of inorganic matter in coal; 2) the mechanisms of mineral-matter transformation into inorganic vapors, liquids and solids; 3) the physical properties of the intermediate ash species as a function of temperature, atmosphere, and residence time; 4) The mechanisms of ash transport to heat-transfer surfaces as a function of particle size and flow patterns in the combustor; 5) the heat-transfer characteristics coupled with the reactivity and melting behavior of the deposited ash material; 6) the characteristics of the liquid components in the deposit with respect to deposit growth and strength development; and 7) the physical characteristics of the deposit that influence its ability to be removed by conventional processes (e.g., by soot blowing). Application of advanced mineral-matter characterization techniques, such as CCSEM and chemical fractionation, is advocated. The review also includes modeling of ash formation and deposition.

Subtask 2.e. Large Particle/Thick Bed Submodels

A literature review of heat and mass transport effects in coal pyrolysis was completed. In addition, calculations were done to define regimes of internal and external heat and mass transport control for conditions of interest. This was done to define the boundary regions where such considerations become important.

A single particle FG-DVC model was developed for use in the fixed bed reactor code. This version of the model is based on an ordinary differential equation (ODE) version of the 2- σ percolation FG-DVC model. The code was delivered to BYU for integration into the FBED-1 Model.

Under this subtask, a model for the destruction of tar in fixed bed gasifiers was developed in order to account for the relatively low yield of tar from these systems. A compilation was made of literature data from laboratory reactors and full-scale moving bed gasifiers to help validate the model. The focus was on data for the Pittsburgh seam coal which shows the change in tar yield and/or composition with variations in heating rate, bed depth, flow rate, pressure, particle size, and reactor type.

According to the predictions of the FBED-1 model, the tar evolution occurs in a relatively small region near the top of the reactor where the gas and particle temperatures are changing rapidly. While the coal particles are entering at room temperature, the exit gas temperature is close to 1000 K and is 1300 K in the region where tar evolves. Consequently, the contribution of tar cracking and tar gasification (by CO₂) must also be accounted for and could be the dominant mode of tar loss under some conditions. Some experiments were done to assess the relative importance of tar gasification and tar cracking reactions. It was found that, while the thermal cracking effects were significant, the addition of CO₂ did not have much effect on the yield or composition of tar. Consequently, it was concluded that the tar destruction in the top part of a fixed-bed gasifier can probably be attributed primarily to thermal cracking rather than gasification reactions. A recommendation was made to assume that the rates of tar pyrolysis and gasification were the same as that for the coal and this feature was incorporated into the FBED-1 model.

Subtask 2.f. Large Char Particle Oxidation at High Pressure

<u>Atmospheric Char Oxidation in Simple Devices</u> - Atmospheric char oxidation runs in platinum and porcelain crucibles were made. Char particles were prepared and oxidized from Utah bituminous, North Dakota lignite, Wyoming subbituminous, Illinois #6, Pittsburgh #8, and Colorado bituminous coals.

Approximately 150 tests were made at atmospheric pressure in two different simple experimental devices using heat from Meker burners or a muffle furnace. In these tests, large particles (0.5-1 cm) were oxidized, one at a time, over 5-15 minutes for time periods up to two hours, in incremental steps. The cube root of particle mass declined linearly with time during the first 80-90% burnout. Ash layers formed and usually remained in place around the decreasing volume of carbon. Average mass reactivities increased with decreasing initial char particle mass. These observations are consistent with oxidation being controlled by diffusion of oxygen. However, some chemical kinetic control is indicated at lower temperatures.

Oxidation at Elevated Pressures in the HPCP Reactor - The extension of the experimental char oxidation tests to include the variable of pressure was accomplished with the design and construction of a cantilever beam balance unit which was attached to the HPCP reactor of Subtask 2b. The mass loss of a reacting coal particle was followed continuously by the changing response of a force transducer connected to the reacting particles with a long-small-bore ceramic tube. Here also the cube root of particle mass declined linearly with time during the first 80-90% of char burnout. A significant influence of pressure was observed between one and five atmospheres but the burning characteristics at 5 and 7.5 atmospheres were about the same.

Subtask 2.g. SO, - NO, Submodel Development

<u>NO, Submodel</u> - The fuel NO_x submodel in an existing 2-D comprehensive model for pulverized coal gasification and combustion (PCGC-2) was revised and extended to include thermal NO and to be applicable to fuel-rich systems. The effect of two different expressions for oxygen atom concentration was investigated. The fuel NO mechanism was revised to include parallel reaction paths through HCN or NH₃. An alternative global mechanism from the literature involving NH₃ was also investigated. The resulting model was evaluated by comparing model predictions with experimental data.

<u>SO_x/Sorbent Submodel</u> - An existing sulfation submodel was integrated into PCGC-2 and used to predict the reaction of injected sorbents with SO₂ and H₂S. The equilibrium approach for predicting sulfur species was evaluated. The use of the submodel was demonstrated by simulating a fuel-lean and a fuel-rich case. A sensitivity analysis of the sulfation submodel was performed.

Subtask 2.h. SO,/NO, Submodel Evaluation

The cross-flow injection and mixing of sorbent were studied in a cold-flow facility, and the results were used to modify an existing entrained-flow gasifier for sorbent injection. Sulfur-capture studies were used to investigate the sorbent mixing in cold-flow: 1) Smoke injection for visualization, 2) tracer gas injection and sampling, and 3) laser-Doppler anemometry (LDA). The results at relatively low jet-to-free-stream momentum ratios showed that such flows are slower to mix with the free stream than flows with sufficient energy to impinge on the opposite wall. In such cases, increasing the number of cross-flow injectors was found to enhance the mixing. Three injection ports were therefore used in the gasifier. Sight windows were installed to permit optical access, and FT-IR data were obtained with the assistance of AFR. There was no significant sulfur capture for three of the coals, and only a small effect with the highest-sulfur coal. The major cause of the low capture is believed to be the high temperature in the gasifier. Temperature determined by FT-IR ranged from approximately 1510 to 2480 K. Also, slag samples taken at various axial locations indicated that interactions between the slag, sulfur, and sorbent were occurring, probably reducing the amount of sorbent available for sulfur capture.

Subtask 3.a. Integration of Advanced Submodels into Entrained-Flow Code, with Evaluation and Documentation

A 2-D comprehensive model for pulverized coal gasification and combustion (87-PCGC-2) was extended to include the FG-DVC model as an option for predicting weight loss and volatiles enthalpy. Other improvements in the code include laminar flow effects, gas buoyancy, a user-friendly and reliable energy equation option, and a condensed-phase equilibrium algorithm. The improved model was extensively evaluated by comparing model predictions with experimental data from several reactors. A clear advantage of the FG-DVC submodel was shown to be coal generality. Needed model improvements were identified. User-friendly graphics options were developed for code input and output. A user's manual was prepared, documenting code theory and use. Under a closely related, but independent study, improvements were made to the radiation submodel and enthalpy balance closure was realized.

Subtask 3.b. Comprehensive Fixed-Bed Modeling Review, Development, Evaluation, and Implementation

The principal objective of this project was to develop, evaluate and apply an advanced, steadystate, one-dimensional model of countercurrent, fixed-bed coal combustion and gasification. Improvements included advanced treatment of devolatilization, separate gas and coal temperatures, axially variable solid and gas flow rates, variable bed void fraction, generalized treatment of gas phase chemistry, and SO_x/NO_x pollutants. The initial fixed-bed model, MBED-1, was evaluated through sensitivity analysis and comparisons to experimental data. The predicted temperature and pressure profiles were found to agree reasonably well with the measured values. In MBED-1, gas evolution rates are determined by the functional group (FG) submodel and the tar evolution rate is determined by the semi-empirical tar (SET) correlation. The MBED-1 results brought out the significant effect of tar yield on predictions and the need for a more rigorous devolatilization model.

The most important improvement in the final version of the fixed-bed model, FBED-1, is the inclusion of the advanced devolatilization submodel, FG-DVC. In this submodel, gas evolution rates are determined by the functional group (FG) submodel and the tar evolution rate by the depolymerization-vaporization-crosslinking (DVC) submodel. The final version of the fixed-bed code, FBED-1, provides also:

improved predictions of product gas composition and temperature; improved prediction of tar production; modifications in the iteration scheme to satisfy the gas phase boundary conditions at the bottom of the gasifier; improved modularity, code structure, and use friendliness; and improved graphics output. The final fixed-bed model, FBED-1, was also evaluated through sensitivity analysis and comparisons to experimental data. The predicted effluent composition and temperature as well as the predicted temperature and pressure profiles were found to agree very well with the measured values.

Subtask 3.c. Generalized Fuels Feedstock Submodel

The fuels feedstock submodel in PCGC-2 was generalized to feed particles in any inlet, and to feed sorbent particles as well as coal particles. The generalized feedstock submodel was tested with the sorbent reactions submodel developed under Subtask 2.g.

Subtask 4.a. Application of Generalized Pulverized Coal Comprehensive Code

The applicability of 93-PCGC-2 to practical-scale processes of commercial interest was demonstrated by simulating two such reactors. One is the Coal Tech Corp. advanced, air-cooled cyclone combustor, and the other is the Solar Turbines, Inc. combustor. The latter simulation was performed under an independent study and is reported separately. The code was shown to be a useful tool for reactor design and simulation. A user's manual was prepared, the final code was installed at METC and a short course was given on June 29-30, 1993.

Subtask 4.b. Application of Fixed-Bed Code

The fixed-bed coal combustion, gasification, and devolatilization codes, MBED-1 and FBED-1, developed in Subtask 3.b, were successfully demonstrated by simulating the four dry-ash, fixed-bed gasifiers of interest to METC: the high-pressure, oxygen-blown Lurgi gasifier, the medium-pressure, airblown METC gasifier, the atmospheric-pressure, airblown Wellman-Galusha gasifier, and the high-pressure, airblow, PyGas[™] staged gasifier. The most comprehensive test data, including the temperature and the pressure profiles, were available for the atmospheric-pressure Wellman-Galusha gasifier. The Wellman-Galusha test data were used to validate the fixed-bed codes and the corresponding simulations were presented in Subtask 3.b. The simulations of the high-pressure Lurgi gasifier, the medium-pressure METC gasifier, and the high-pressure, air-blow, PyGas[™] staged gasifier were presented as part of this subtask.

The user's manual was prepared for the FBED-1 code. The code was ported to a Silicon Graphics workstation and the sample case was successfully executed. The code, the user's manual, and the installation instructions were sent to METC. A short course on the use of the FBED-1 code was conducted at METC.

SECTION II. TASK 2. SUBMODEL DEVELOPMENT AND EVALUATION

Objectives

The objectives of this task were to develop or adapt advanced physics and chemistry submodels for the reactions of coal in an entrained-bed and a fixed-bed reactor and to validate the submodels by comparison with laboratory scale experiments.

Task Outline

The development of advanced submodels for the entrained-bed and fixed-bed reactor models was organized into the following categories: a) Coal Chemistry (including coal pyrolysis chemistry, char formation, particle mass transfer, particle thermal properties, and particle physical behavior); b) Char Reaction Chemistry at high pressure; c) Secondary Reactions of Pyrolysis Products (including gas-phase cracking, soot formation, ignition, and char burnout); d) Ash Physics and Chemistry (including mineral characterization, evolution of volatile, molten and dry particle components, and ash fusion behavior); e) Large Coal Particle Effects (including secondary reactions within the particle and in multiple particle layers; f) Large Char Particle Effects (including oxidation); g) SO_x-NO_x Submodel Development (including the evolution and oxidation of sulfur and nitrogen species); and h) SO_x and NO_x Model Evaluation.

II.A. SUBTASK 2.a. - COAL TO CHAR CHEMISTRY SUBMODEL DEVELOPMENT AND EVALUATION

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Objective

The objective of this subtask is to develop and evaluate, by comparison with laboratory experiments, an integrated and compatible submodel to describe the organic chemistry and physical changes occurring during the transformation from coal to char in coal conversion processes.

Accomplishments

The processes described in this work were:

- tar formation mechanisms and kinetics
- gas formation mechanisms and kinetics
- sulfur and nitrogen evolution mechanisms and kinetics
- coal and char fluidity (viscosity)
- char swelling
- optical properties of coal and char
- the behavior of polymethylene
- crosslinking
- char reactivity

These processes were embodied in the Functional Group - Depolymerization, Vaporization, Corselinking (FG-DVC) model for coal conversion behavior.

To provide the data for model development and for model parameters, several experimental methods were developed. These included:

- TG-FTIR (Thermogravimetric Analysis with analysis of evolved products by Fourier Transform Infrared spectroscopy) to determine coal composition, volatile evolutions, kinetics, and char reactivity.
- Transparent wall reactor (TWR) with in-situ FT-IR diagnostics to study rapid pyrolysis and combustion phenomenon.
- Pyrolysis of coal in a Field Ionization Mass Spectrometer (FIMS) apparatus.

The work has resulted in a successful method to characterize coal in the laboratory and predict is behavior over a wide variety of temperatures (100 to 1500°C), heating rates (10⁰/million years to 10⁵°/sec), and pressures (vacuum to 10 atm).

The work is described in a number of publications which were written for this contract.

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These topics are discussed in the sections that follow.

II.A.1. Coal Characterization

Characterization of the coal samples for this program was performed by quantitative FT-IR analysis, pyrolysis, and char reactivity. Analyses were run on ampoules of Argonne samples 1-7 and 9, listed in Tables II.A.1-1 and II.A.1-2. Also, six jars containing bulk samples of coal were received from the Argonne National Laboratory for coals 1, 2, and 4-7. Due to the broad particle distribution, each jar was well mixed and a small representative sample was removed, handground and sieved to obtain the 200 x 325 mesh fractions. Additional samples of these six coals were obtained from BYU after grinding. For Rosebud subbituminous coal, samples have been obtained from METC. Bulk samples of the Beulah lignite were obtained from UNDERC. Bulk samples of Illinois #6 have been ordered from the Illinois State Geological Survey. Measurements have been made on raw coals and coals demineralized in HCI and HF.

Quantitative FT-IR Analysis

The coal samples were subjected to FT-IR analysis using approximately 1 mg of dry ground sample in approximately 300 mg of alkali halide. To obtain optical properties for the coals, CsI pellets were prepared in addition to the KBr pellets. Figures II.A.1-1a and 1b to II.A.1-9a and 9b show the dry

Coal Name	Rank	Mine/Location	Source
1. Upper Freeport	Medium Volatile Bituminous	Pennsylvania	ANL
2. Wyodak	Subbituminous	Wyoming	ANL
3. Illinois #6	High Volatile Bituminous	Macoupin, Illinois	ANL
4. Pittsburgh #8	High Volatile Bituminous	Washington, Penn	ANL
5. Pocahontas #3	Low Volatile Bituminous	Virginia	ANL
6. Utah Blind Canyon	High Volatile Bituminous	Utah	ANL
7. Utah Blind Canyon	Medium Volatile Bituminous	Eastern, WV	ANL
8. Zap	Lignite	Mercer, N. Dakot	a UND
9. Rosebud	Subbituminous	Montana	METC

Table II.A.1-1. AFR/BYU Program Coal Samples.

Table II.A.1-2.

ELEMENTAL COMPOSITION (MAF)

•	<u>COAL</u>	NAME	С	н	0	S*	ASH*
	1.	Upper Freeport (UF)	87	5.5	4	2.8	13
	2.	Wyodak (WY)	74	5.1	19	0.5	8
	3.	Illinois #6 (Ill. #6)	77	5.7	10	5.4	16
	4.	Pittsburgh #8 (Pitt #8)	83	5.8	8	1.6	9
	5.	Pocahontas #3 (Poc #3)	91	4.7	3	0.9	5
	6.	Utah Blind Canyon (UT)	79	6.0	13	0.5	5
	7.	Upper Knawha (WV)	81	5.5	11	0.6	20
	9.	North Dakota (Zap)	73	5.3	21	0.8	6
	10.	Rosebud	72.1	4.7	20.3	1.2	10

.

* Dry Basis



Figure II.A.1-1. FT-IR Spectra of Bulk Upper Freeport Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-2. FT-IR Spectra of Bulk Wyodak Subbituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-3. FT-IR Spectra of Bulk Illinois #6 Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-4. FT-IR Spectra of Bulk Pittsburgh Seam Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-5. FT-IR Spectra of Bulk Pocahontas Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-6. FT-IR Spectra of Bulk Blind Canyon Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-7. FT-IR Spectra of Bulk Upper Knawha Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-8. FT-IR Spectra of Bulk North Dakota Zap Lignite. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.



Figure II.A.1-9. FT-IR Spectra of Bulk Montana Rosebud Subbituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

uncorrected KBr and CsI pellet spectra for the nine coals. Seven of the spectra are for bulk samples and two are for amouple samples. In general, the bulk and ampoule samples are quite similar as shown in Figs. II.A.1-10 to II.A.1-16. The exception is the Upper Knawha which was a much higher mineral concentration in the bulk sample.

To obtain quantitative functional group and mineral matter data, a spectral synthesis routine was applied to the dry mineral matter and baseline corrected spectra (see Figs. II.A.1-1c to II.A.1-9c). The organic functional group data are shown in Tables II.A.1-3 and II.A.1-4 for bulk and ampoule samples, respectively. Tables II.A.1-5 and II.A.1-6 list the mineral matter data for the bulk and ampoule samples, respectively. The two sets of samples are similar except for the Upper Freeport and Pittsburgh No. 8 where the bulk samples are poorer in hydrogen and the Upper Knawha in which the bulk sample has a higher clay and quartz content.

Pyrolysis in Thermogravimetric Analyzer (TGA)

Pyrolysis experiments on the ampoule and bulk samples were performed using the TGA. With a N_2 flow of 400 cc/min and a N_2 purge flow of 20 cc/min, the coal particle temperatures reached 900°C with heating rates of 30°C/min. Plots of the TGA pyrolysis runs are shown in Figs. II.A.1-17 to II.A.1-21. The bulk samples and ampoules are similar except for some differences in moisture and mineral content for Wyodak, Upper Knawha, and North Dakota (Zap) lignite.

Char Reactivity in TGA

The reactions in chars prepared from both raw and demineralized coals were measured. The chars were prepared by pyrolysis as described above. The char reactivity measurements were made by employing a non-isothermal technique using the TGA. With an air flow of 40 cc/min and a N_2 purge flow of 40 cc/min, the samples were heated at a rate of 30°C/min until 900°C was reached. The resulting critical temperatures (defined as the temperature at which the derivative of the weight loss reaches 0.11 weight fraction/min) are listed in Table II.A.1-7 and are also plotted in Fig. II.A.1-22 as functions of oxygen in the parent coal.

Figure II.A.1-22a compares the bulk and ampoule sample. There is a good agreement between the two and the trend is an increase in reactivity (decreasing T_{cr}) with increasing oxygen.

Figure II.A.1-22b compares the raw bulk samples with the demineralized samples. The reactivities show interesting trends. Above 15% O_2 , the ash content of the coal dominates the char reactivity, increasing the char's reactivity (lower T_{cr}) compared to the demineralized samples. The reason for this increase appears to be the catalytic activity of the organically bound alkali metals as will be discussed in Section II.D. Below 10% O_2 , the raw coals have a lower reactivity (higher T_{cr}) than the demineralized samples. The reason for this is not known and is being investigated.

Determination of Percent Ash

Ash percent values ascertained through three different analytical techniques are listed in Table II.A.1-8. The values are in good agreement for the Argonne ampoule samples. These samples (excluding Montana sample) which were from amber borosilicate glass ampoules flame sealed under nitrogen were subjected to x-ray analysis, TGA analysis and Argonne's proximate analysis. There is more scatter for the bulk samples and the Montana Rosebud subbituminous which were not as well homogenized as the Argonne ampoule samples. The ash in the bulk sample of the Upper Knawha coal is much higher than in the ampoules.

Pyrolysis in Entrained Flow Reactor (EFR)

The 200 x 325 mesh sieved fractions of 6 of the Argonne coals were pyrolyzed in the entrained flow reactor. The coals were vacuum dried at 105°C for 1 hour prior to the pyrolysis runs. The coal was

Table II.A.1-3.Data on Bulk Coals (weight Percent dmmf)*

	Hyd	rogen		<u>Aromatic Hydrogen</u>			<u>Carbon</u>	Carbonyl	Oxyge	n		
Sample	H _{al}	H _{oh}	H _{ar}	H _{total}	H _{ar} /H _{total}	1 Adj	2 Adj	3 or More	C _{al}	Units (Abs. x cm ⁻¹)	0 _{oh}	0 _{ether}
UF	2.84	0.14	1.59	4.57	0.35	0.50	0.59	0.50	18.93	1.69	2.23	1.11
WY	3.10	0.34	1.74	5.18	0.34	0.54	0.78	0.42	20.67	26.65	5.50	4.53
PITT#8	3.02	0.11	1.57	4.70	0.33	0.54	0.63	0.40	20.13	8.38	1.75	1.44
POC#3	1.96	0.13	2.19	4.28	0.51	0.68	0.75	0.76	13.06	1.09	2.06	0.40
UT	4.65	0.20	1.96	6.81	0.29	0.52	0.89	0.55	31.00	11.17	3.25	4.00
WV	3.77	0.19	1.59	5.55	0.29				25.13	7.35	3.09	2.48
ZAP	2.31	0.33	1.66	4.30	0.39	0.50	0.69	0.46	15.40	25.59	5.25	5.5
ROSEBUD	2.79	0.45	1.62	4.86	0.33	0.48	0.71	0.43	18.60	26.64	7.22	6.31
	122245212222222222222222	IFTERD TELEPENEERS (#11		0003552510341392511319788	#0417#92#31281342# 4# \$#141121212#340241		XIBAIT (1126210885)./1.9281)	TINGTISIYNYNANNAN CIG	COCICILIZEUREIXEXIEIRZARIERA	***************************************	1925558110151111111111111111	1621

* Except Carbonyl: Relative Peak Area

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Table II.A.1-4.

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Data on Ampoule Samples (weight Percent dmmf)*

		Hyd	rogen		Ar	omatic	Hydroge	<u>n</u>	Carbon	<u>Carbonvl</u>	Oxyg	en
Sample	H _{al}	H _{oh}	Har	H _{total}	H _{ar} /H _{total}	1 Adj	2 Adj	3 or More	C _{al}	Units (Abs. x cm ⁻¹)	0 _{oh}	0 _{ether}
UF	3.43	0.11	2.08	5.62	0.37	0.66	0.71	0.71	22.87	0.63	1.75	0.75
WY	3.03	0.33	1.73	5.09	0.34	0.52	0.78	0.43	20.20	23.86	5.25	5.0
ILL#6	3.41	0.23	2.07	5.71	0.36	0.69	0.78	0.60	22.73	4.48	3.75	2.25
PITT#8	3.60	0.16	2.07	5.83	0.36	0.67	0.80	0.60	24.00	0.86	2.5	1.88
POC#3	1.97	0.06	2.19	4.22	0.52	0.60	0.73	0.86	13.93	1,92	1.0	1.25
UT .	4.79	0.16	1.90	6.85	0.28	0.51	0.80	0.58	31.93	8.70	2.5	4.0
wv	3.48	0.23	2.12	5.83	0.36	0.67	0.67	0.79	23.20	3.59	3.75	1.75
ZAP	2.02	0.34	1.58	3.94	0.40	0.46	0.74	0.37	13.47	24.67	5.5	5.0

* Except Carbonyl: Relative Peak Area

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Table II.A.1-5. Data on Bulk Coals (dry weight percent)

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Sample	Mixed Clay	Quartz	Calcite	Kaolin	Total
UF	9.06	0.86	1.98	2.63	14.53
WY	3.52	1.34	0.59	2.00	7.45
PITT#8	5.65	0.64	1.49	2.90	10.68
POC#3	4.91	0.53	3.88	0.45	9.76
UT	3.31	0.48	2.23	0.24	6.26
WV	21.40	4.79	1.08	8.44	35.71
ZAP					
ROSEBUD	3.42	1.00	1.92	2.51	8.86

<u>Minerals</u>

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Table II.A.1-6.

Data on Ampoule Samples (dry weight percent)

<u>Minerals</u>

Sample	Mixed Clay	Quartz	Calcite	Kaolin	Total
UF	10.40	0.93	2.97	3.60	17.90
WY	2.57	0.76	1.04	2.11	6.48
ILL#6	8.50	2.26	3.98	2.29	17.02
PITT#8	7.74	1.00	2.01	2.72	13.47
POC#3	4.28	0	4.83	0.99	10.11
UT	2.90	0.12	2.40	0.17	5.59
wv	15.50	1.24	1.46	7.74	25.95
ZAP	2.36	· 0.73	1.38	0.71	5.18

Table II.A.1-7.

Data on Char Reactivity

	0°C N ₂ C	har							
Coal Name	Abbreviation	Rank	Wt. % Oxygen in Original Coal Sample by Difference (DMMF)	Am T _C	poules %Ash	Bulk Tcr	Sample %Ash	Demi Bulk T _C	neralized Sample %Ash
1. Upper Freeport	UF	Medium Volatile Bituminous	<u>4</u>	644	13.81	641	11.63	513	1.93
2. Wyodak	WY	Subbituminous	19	436	8.07	440	11.13	503	0.40
3. Illinois #6	ILL.	High Volatile Bituminous	10	519	15.02				
4. Pittsburgh #8	PITT	High Volatile Bituminous	8	586	9.61	600	9.01	542	1.44
5. Pocahontas #3	POC	Low Volatile Bituminous	3	697	5.10	611	4.83	564	
6. Utah Blind Canyo	on UT	High Volatile Bituminous	13	527	4.45	528	4.68	516	0.80
7. Upper Knawha	wv	Medium Volatile Bituminous	11	529	19.49	544	26.44	498	1.24
9 North Dakota	ZAP	Lignite	21	443	8.98	434	7.54	550	0.26
10. Rosebud	£44 X.£ 19123215211121414(0122101545555511111	Subbituminous	20			478	14.72	508	3.47

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*HF/HCL demineralized.

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Analysis Type	Upp Free	er eport	Wyódak	Illinois No.6	Pittsburgh No.8	Pocohontas No.3	Utah Blind Canyon	Upper Knawha	North Dakota Lignite	Montana Rosebud	
TGA Ampo	ule	13.81	8.07	15.02	9.61	5.00	4.45	19.49	8.98		
TGA Bulk		11.63	11.13		9.01	4.83	4.68	26.44	7.54	14.72	
X-Ray Ampoule		12.49	9.02	16.14	8.51	4.40	3.41	21.48	9.60	12.33	
Argonne Proximate (ampoule)	Ŧ <u>ş</u> ŧŧvezsikese;	13.16	8.95	17.76	9.44	4.90	4.68	19.81	6.53		

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Table II.A.1-8. Ash in Dry Weight Percent

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Figure II.A.1-10. Dry Uncorrected FT-IR Spectra of Upper Freeport Bituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-11. Dry Uncorrected FT-IR Spectra of Wyodak Subbituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-12. Dry Uncorrected FT-IR Spectra of Pittsburgh Seam #8 Bituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-13. Dry Uncorrected FT-IR Spectra of Pocahontas #3 Bituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-14. Dry Uncorrected FT-IR Spectra of Utah Blind Canyon Bituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-15. Dry Uncorrected FT-IR Spectra of Upper Knawha Bituminous Coal. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-16. Dry Uncorrected FT-IR Spectra of Beulah Zap Lignite. a) Bulk Sample and b) Ampoule Sample.



Figure II.A.1-17. Pyrolysis of a) Upper Freeport Bituminous Coal and b) Wyodak Subbituminous Coal in TGA at 30°C/min in N2. Solid, Dashed, and Dotted Lines Represent Bulk, Ampoule and Demineralized Samples, Respectively.



Figure II.A.1-18. Pyrolysis of a) Illinois #6 Bituminous Coal and b) Pittsburgh Seam Bituminous Coal in TGA at 30°C/min in N2. Solid, Dashed, and Dotted Lines Represent Bulk, Ampoule and Demineralized Samples, Respectively.



Figure II.A.1-19. Pyrolysis of a) Pocahontas #3 Bituminous Coal and b) Utah Blind Canyon Bituminous Coal in TGA at 30°C/min in N2. Solid, Dashed, and Dotted Lines Represent Bulk, Ampoule and Demineralized Samples, Respectively.



Figure II.A.1-20. Pyrolysis of a) Upper Knawha Bituminous Coal and b) Zap North Dakota Lignite in TGA at 30°C/min in N₂. Solid, Dashed, and Dotted Lines Represent Bulk, Ampoule and Demineralized Samples, Respectively.



Figure II.A.1-21. Pyrolysis of Upper Montana Rosebud Subbituminous Coal in TGA at 30°C/min in N2. Solid, Dashed, and Dotted Lines Represent Bulk, Ampoule and Demineralized Samples, Respectively.



Figure II.A.1-22. Variation of Reactivity with Coal Rank for Chars Prepared by Heating in Nitrogen at 30°C/min to 900°C.

fed at rates of 1½ to 2 g/min with a N₂ carrier. Particle residence time was approximately 0.66 seconds with the injector height position adjusted to 24" and the furnace operated at 1400°C. 1100°C, and 700°C. The gas analyses were performed using two analytical techniques: 1) FT-IR calibration program and 2) Gas Chromatograph.

The data are presented in Tables II.A.1-9 to II.A.1-11. The data are plotted for each coal as a function of temperature in Figs. II.A.1-23 to II.A.1-28. The yields show the expected dependence on temperature. These data, as well as data from the TG-FTIR will be modeled using the FG/DVC model during the next year.

II.A.2. FG-DVC Model

The FG-DVC model has been developed as a stand alone PC-based predictive model as well as a submodel for comprehensive combustion and gasification codes. FG-DVC is a general model for coal pyrolysis which predicts the coal's decomposition into tar, char, and gas, given the ambient pressure and the time-temperature history of an isothermal coal particle. The model predicts the amount, functional group composition, elemental composition, and molecular weight distribution of tar and char and the amount and composition of the gas.

The FG model considers certain functional groups in the coal which decompose to form the light gas species. At the same time, the DVC model describes the overall depolymerization of the macromolecular network which combines bridge breaking and crosslinking to produce fragments of the coal macromolecule. These fragments are then subjected to transport behavior, specifically the vaporization of the lightest fragments to form tar. The tar fragmentation process provides a second mechanism for the removal of functional groups from the coal. The model, whose parameters are determined in the laboratory at moderate temperatures and one atmosphere, can then be used to extrapolate away from the laboratory conditions to predict pyrolysis and combustion in high temperature reactions, or liquefaction at high pressure. Recently, we have explored extrapolation of the kinetics and reactions to low temperature geological transformations in coal beds.

The model for coal thermal decomposition has six basic concepts.

- Functional Groups (decompose to produce light gases)
- Macromolecular Network (decomposes to produce tar and metaplast)
- Network Coordination Number (possible number of attachments per cluster)
- Bridge Breaking (limited by hydrogen availability)
- Crosslinking (related to gas evolution)
- Mass Transport of Tar (evaporation of light network fragments into light gases)

The first concept is that light gases are formed by the decomposition of certain functional groups in the coal. For example, methyl groups can lead to the formation of methane, carboxyl groups can lead to the formation of CO_2 , etc. The second concept is that coal consists of a macromolecular network. This network is made up of fused aromatic ring clusters (which are described by their molecular weight) linked by bridges, some of which are relatively weak. There are some unattached parts of the network which can be extracted. Sometimes, there is also a second component of high polymethylene content. When heated, this network decomposes to produce smaller fragments. The lightest of the fragments evaporate to produce tar and the heavier fragments form the metaplast. These heavier molecules are the primary liquid fragments in liquefaction or the fragments that make coal fluid.

The third concept is that one of the most important properties of the network is its coordination number $(1 + \sigma)$. The coordination number describes the geometry of the network, and specifies how many possible attachments there are per aromatic ring cluster. For example, a linear polymer chain has a coordination number of 2, because each fused aromatic ring has two possible attachments to link it in the chain. On the other hand, a square "fish net" has a coordination number of 4, because there are four possible attachments at each ring cluster. The coordination number of weight

Table II.A.1-9.
Pyrolysis in the Entrained Flow Reactor in Nitrogen at 700°C, 24".
Values in Ash Free Weight Percent.

STITUT PERCENTER AND))))	·····	21	22	23	24
AFR/BYU Run #	19	Zv Unnor Knawha	Pittsburgh #8	Wyodak	Pocahontas #3	Utah Blind Canyon
Species	Upper Freeport				03453642425268688999984666655288489686688888888888	aceceraza 5566,000 de 2000 035206004 a 2000 2340 2662 a 2662 a 2662 a 2662 a 2662 a 2662
Char	64.88	66.95	57.49	59.56	80.64	54.8
Tar & Soot	22.07	17.22	30.5	13.09	10.29	25.8
Gas	5.85	6.95	7.44	13.46	3.83	13.62
H_O	6.68	3.62	5.96	2.27	2.71	.95
Missing	.53	5.27	-1.4	11.62	2.52	4.83
CH	.92	.678	1,1	.696	.784	1.25
CO	.122	.449	.506	2.44	.118	1.04
Ho	0	0	0	0	0	0
COn	.408	1.16	.331	4.82	.81	3.47
CoHo	.021	.002	.006	.007	1.4×10^{-4}	0.1
$C_{2}H_{4}$.372	.271	.433	.452	.095	.623
CoHo	.373	.169	.393	.198	.201	.66
$C_3 H_c$.305	,591	.589	.703	.106	.83
CcHG	.002	.609	.217	.406	.338	.24
CS	.145	.107	.108	.134	.074	.07
SO ₂	.024	0	.014	.01	0	.01
HCN*	.094	0	0	0	0	.12
Paraffins	1.93	2.17	2.46	1.73	1.09	3.54
Olefins	1.57	.744	1.32	1.77	,208	1.77

* HCN values not included in gas totals or missing totals.

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Table II.A.1-10. Pyrolysis in the Entrained Flow Reactor in Nitrogen at 1100°C, 24". Values in Ash Free Weight Percent.

AFR/BYU Run # Species	10 Upper Freeport	11 Wyodak	12 Upper Freeport	13 Upper Knawha	, 14 Utah Blind Canyon	15 Pittsburgh #8	16 Pocahontas #3
Char	52.50	43.16	52.14	56.52	40.94	47.91	73.50
Tar & Soot	21.65	7.71	16.59	14.35	13.40	21.84	11.69
Gas	25.99	40.14	24.94	21.49	39.28	28.62	14.17
H ₂ O	1.73	2.85	3.40	5.64	7.02	4.58	3.58
Missing	-1.88	6.14	2.93	2.60	64	-2.95	-2.94
CH ₄	4.37	1.86	4.01	3.80	5.34	5.55	3.23
CO	5.46	12.27	5.40 .	4.16	8.85	6.04	1.82
H_2	1.38	.99	1.22	.77	1.5	1.21	1.04
CO_2	1.91	9.29	2.02	1.02	6.07	1.62	1.03
C_2H_2	1,49	2.09	1.21	.73	2.01	1.06	1.23
$C_2 H_4^-$	1.95	2.27	1.76	1.84	2.84	2.29	.96
C_2H_6	.005	.006	.009	.15	.05	.08	.08
C ₃ H ₆	.15	.24	.15	.20	.24	.25	.06
C ₆ H ₆	3.32	5.26	3.45	3.23	3.97	3.98	2.08
CS_2	.18	.24	.25	.14	.164	.16	0.097
so_2	.03	.012	.029		.002	.018	
HCN*	2.16	1.49	1.93	1.36	2,98	2.07	.70
Paraffins	.56	.44	.59	.83	.55	.61	.33
Olefins	3.05	3.66	2.89	3.26	4.68	3.68	1.51

* HCN values not included in gas totals or missing totals.

Table II.A.1-11. Pyrolysis in the Entrained Flow Reactor in Nitrogen at 1400°C, 24". Values in Ash Free Weight Percent

	1		200623383998858589202038492020201955766559338328688 3		5	6	8	9
AFR/BYURUN#	Pocahontas #3	Pocahontas #3	Upper Knawha	Wyodak	Upper Freeport	Utah Blind	Wyodak	Pittsburgh #8
Species		Re-run of Run #1				Canyon	Re-run of Run #4	
Char	70.03	70.19	51,22	44.82	46.64	35.24	42.82	37.38
Tar & Soot	13.54	13.22	20.05	15.54	25,85	28.52	13.44	29.75
Gas	14.22	15.34	22.28	43.0	21.91	33.49	45.18	30.64
H ₂ O	.58	2,23	1.37	2.40	.64	.85	1.46	1.80
Missing	1.23	99	5.08	-3.36	4.94	1.90	-2.90	.43
CH ₄	.24	.19	.16	.16	.14	.28	.41	.19
CO	7.21	8.27	15.80	30.25	12.95	22.72	31.12	18.92
H_2	4.38	4.11	4.22	4.17	4.55	5.19	4.0	4.82
co_2	.49	.70	1.80	5.75	1.28	1.42	6.74	1,96
$\overline{\mathbf{C_2H_2}}$	1.83	1.87	.03	2.36	2.59	3.72	2.59	4.33
$C_2 H_4$.56	.04	.06	.04	.05	.12	.054	.10
$C_2 H_6$	1.73×10^{-5}	.02	4.86×10^{-6}	.01	.01	6.34×10^{-4}	.001	2.91×10^{-3}
C_3H_6	.03	.01	.02	.04	.03	.03	.01	-1.14×10^{-2}
C ₆ H ₆	.01	.01	.01	.01	.01	.01	.006	$1.25 \mathrm{x} 10^{-2}$
CS ₂	.08	.17	.17	.20	.26	.11	.183	.28
so_2	.00	.01	.01	.01	.01	.01	.009	$1.11 \ge 10^{-2}$
HCN *	2.22	2.20	3.96	3.30	4.36	5.65	3.56	5.54
Paraffins	0	.109	0	0	0	0	.06	.00
Olefins	0	0	0	· 0	0	.03	0	07
		₩₩₽₽₩₩₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽₽	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	222224996428 864 888648966688	98#661\$1#1#6#1¥¥##\$\$67#669#2#663#66#3#6####	***************************************	***************************************	8598888888881088138888810810888 8

* HCN values not included in gas totals or missing totals.

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Weight Percent Product

Fyfolysis Temperature (C)

Figure II.A.1-23. Pyrolysis Results for Upper Freeport Bituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.



Figure II.A.1-24. Pyrolysis Results for Wyodak Subbituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.



Figure II.A.1-25. Pyrolysis Results for Pittsburgh Seam Bituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.



Figure II.A.1-26. Pyrolysis Results for Pocahontas Bituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.



Figure II.A.1-27. Pyrolysis Results for Utah Blind Canyon Bituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.



Figure II.A.1-28. Pyrolysis Results for Upper Knawha Bituminous Coal, 200 x 325 Mesh, in the Entrained Flow Reactor at a Reaction Distance of 24". The Coal was Fed at Rates of 1-1/2 - 2 g/min with an N₂ Carrier. Particle Residence Time was Approximately 0.66 Seconds.