SECTION I. INTRODUCTION

I.A. PROGRAM BACKGROUND AND DESCRIPTION

During the past 5 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. The proposed program presents a unique opportunity to merge the technology developed by each organization to provide detailed predictive capability for advanced coal conversion processes. This predictive capability will incorporate advanced coal characterization techniques in conjunction with comprehensive computer models to provide accurate process simulations.

The program will streamline 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 would be developed or adapted. The submodels would first be incorporated into the BYU entrained-bed gasification code and subsequently, into a fixed-bed gasification code (to be selected and adapted). These codes would be validated by comparison with small scale laboratory and PDU-scale experiments. The validated code could then be employed to simulate and to develop advanced coal conversion reactors of interest to METC.

I.B. OBJECTIVES

The objectives of this proposed study are 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 will be a closely integrated, cooperative effort between AFR and BYU. The program will consist 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 will require 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 must be addressed as noted below. The status of each of these tasks is also indicated.

A Separation of Rates for Chemical Reaction, Heat Transfer, and Mass Transfer
A Particle Temperature Measurements Using FT-IR E/T Spectroscopy
A Functional Group Description of Coal, Char, and Tar
A Tar Formation Mechanisms
I Char Formation Mechanisms
I Viscosity/Swelling
I Intraparticle Transport

I Pyrolysis of Volatiles and Soot Formation
I Secondary Reaction of Tar
I Particle Ignition
I Char Reactivity
I Ash Chemistry and Physics
A Particle Optical Properties
I Code Efficiency and Compatibility for Submodels
I Coupling of Submodels with Comprehensive Codes
I Comprehensive Code Efficiency
I Turbulence
I SO_x and NO_x
o Generalized Fuels Model
I Fixed-Bed Model

(o) to be addressed; (I) initiated; (A) almost completed.

These technical issues are addressed in the three Tasks as described in Section II-IV.

I.E. SECOND YEAR PROGRESS

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

Additional characterization of the coal samples for this program was performed by pyrolysis experiments in a TG-FTIR and in Field Ionization Mass Spectrometry (FIMS) apparatus. The FG-DVC model was used to predict baseline pyrolysis data for the eight Argonne coals from these two reactors as well as from an Entrained Flow Reactor (EFR). In general, the model did a good job in predicting the data for gas, tar and char yields and for the tar molecular weight distributions. Additional improvements were made in the FG-DVC model. In addition, work was done on comparing the FG-DVC model to the statistical model of Pugmire and Grant at the University of Utah which is based on percolation theory.

A review of internal pore transport models was prepared by Professor Eric Suuberg of Brown University. It was determined that differences in the pressure drops calculated by the Simons and Gavalas approaches to internal transport were primarily due to different assumptions regarding the pyrolysis rate. The geometry of the Simons approach makes it the easiest model to use in predicting swelling based on knowledge of the pressure inside pores and so it will be used in the future swelling model. In order to refine the combined kinetic/mass transport submodel used in the FG-DVC model, a search was made of literature pyrolysis data for the Pittsburgh Seam coal, starting with heated grid experiments. When a comparison was made of data produced by heating at 1000 K/s to various peak temperatures, it was found that the results of different investigators did not agree, even when obtained from the same laboratory. We begin an experimental and theoretical study into possible reasons for these variations, which we are doing in conjunction with Professor Eric Suuberg of Brown University.

To examine the effect of product evolution, char viscosity, and transport on the swelling of char, drop tube experiments have been done with a Pittsburgh coal at temperatures varying from 475-600°C in 25°C intervals. The chars collected from these experiments have been characterized for volatile content and reactivity in a TGA. Selected chars were potted and polished for analysis of their morphology by SEM.

Preliminary measurements were made of the spectral emissivity for coals of varying particle size and rank. The average emittance increased with increasing rank and particle size. The total extinction efficiency for scattering out of the aperture of our instrument needs to be measured before more accurate values of the spectral emissivity can be determined.

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

The design of the high-pressure, controlled-profile (HPCP) reactor was completed, and fabrication of major reactor components was also finished. The reactor test bay was modified for high pressure application and for use of the laser-based instrumentation. The reactor support and optical table have been fabricated prior to installing the particle sizing and temperature instrumentation. Assembly of the reactor facility is in progress, with initial char tests planned for next January.

Char preparation was continued with the objectives of understanding the experimental details associated with char preparation at elevated pressures as well as at atmospheric pressure and comparing the physical properties of chars prepared with different reactors in anticipation of the availability of the HPCP reactor. The rationale for the time and effort used for char preparation with a simple, hot-tube reactor has been outlined. Char samples prepared from a Utah bituminous coal at various residence times, temperatures, and pressures are compared by C and H analyses, SEM micrographs, and surface area measurements. One observation of a structural feature in this comparison is that the influence of pressure is to diminish the porosity of the char for a particular coal.

Five coals were selected for detailed char oxidation measurements in the HPCP reactor: 1) Utah bituminous, 2) North Dakota lignite, 3) Wyoming subbituminous, 4) Illinois #6 bituminous, and 5) Pittsburgh #8 bituminous. These coals were chosen because of their variation in properties, widespread use in research, and extensive commercial applications. All of the coals are included in the Argonne premium coal bank.

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

Studies of ignition and soot formation in flames were continued in the transparent wall reactor (TWR) in experiments which include in-situ FT-IR diagnostics. Attention is being focused on what controls ignition (heterogeneous or homogeneous oxidation) and soot formation. Seven additional samples were completed in addition to the four reported in the First Annual Report. Flame properties were compared with characteristics of the samples to determine the factors which control flame behavior. A comparison of the ignition of several samples suggests that the rate of ignition correlates with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars is heterogeneous; ignition of high rank coals is homogeneous; but low rank coals exhibit both homogeneous and heterogeneous contributions to ignition. Soot formation in combustion correlates well with tar yield in pyrolysis suggesting that tar is the chief precursor of soot.

In order to obtain in-situ data from an actual gasifier, an FT-IR spectrometer was temporarily installed at BYU on their high pressure gasifier.

Subtask 2.d. Ash Physics and Chemistry Submodel

During the second year, two sample collection probes were constructed that can be inserted into the transparent wall reactor (TWR) to allow for the collection of char with its transforming mineral matter from the flame at various stages of burnoff, and of fly ash from above the flame. Both probes result in no visual disruption of the stability, size or ignition delay time of the flames. Sample collections were performed using these probes from Zap lignite and Montana Rosebud coal flame experiments. SEM/dispersive x-ray analysis was performed on individual ash spheres that were recovered from the preseparator and the eight stages of the cascade impactor for an "in stack" ash collection from 200 x 325 mesh Zap lignite.

In order to further understand the role played by ion-exchanged cations on char reactivity, samples of demineralized Zap coal were subjected to ion-exchange experiments with Ca, Na, Mg, and K. The reactivity of the resultant chars was measured in air and CO_2.

Subtask 2.e. Large Particle Submodels

A literature review of models which account for heat and mass transport effects in coal pyrolysis was completed. A critical evaluation was made of two models from the literature that have been used to describe coupled reaction and transport in large particles. The formulation of our own single particle model was begun. Discussions were also held with BYU on the interface between the single particle model and the advanced fixed bed reactor model.

The design and construction of a small scale fixed-bed reactor was completed. This reactor will have on-line analysis of evolved volatile products and on-line measurement of char functional group composition and particle temperature.

Subtask 2.g. SO_x-NO_x Submodel Development

Incorporation of the Zeldovich thermal NO_x mechanism into the existing NO_x submodel has been completed. The revised NO_x submodel can now predict the joint contribution of fuel and thermal NO. Evaluation of this submodel is in progress. One case for coal gasification has been completed. The contribution of thermal NO improves the predicted formation of total NO. A gas-phase laboratory reactor was also simulated and thermal NO was shown to correctly predict the experimental data where the predicted temperature profile also matched the experimental data. The importance of including the reverse reaction rates of the Zeldovich mechanism was also determined from this case. Preliminary plans were made to measure additional data in a BYU-ACERC reactor to provide cases for a complete model evaluation.

A sorbent-particle reaction model is currently being incorporated in PCGC-2, under independent funding. Prediction of the gaseous sulfur species has also been studied and a reaction mechanism has been identified. To begin, predictions using an equilibrium approach will be evaluated. The data collected under subtask 2.h will be used in this effort.

Subtask 2.h. NO_x/SO_x Submodel Evaluation

Modifications were completed on the cold-flow facility designed to replicate the geometry of the entrained-flow gasifier, and mixing data were obtained for the crossflow injection of sorbent. Three testing techniques were used: 1) Smoke injection for flow visualization to obtain qualitative information of the trajectory and mixing patterns of the crossflow injectors, 2) trace gas injection and gas extraction at different locations in the flow chamber (analysis of the gas samples provided quantitative data on the mixing of the two streams), and 3) laser-Doppler anemometer (LDA) measurements to determine representative velocity and turbulence characteristics of the flows.

The cold-flow testing has been completed, and analysis of the data is nearly complete. Photographs of injected smoke illustrate the deflection of the jet plume as it was entrained in the free stream. The jets can be made to penetrate to any desired distance by adjusting the diameter of the jet and the momentum flux ratio. Contour maps of normalized tracer gas concentration were obtained to quantify the mixing patterns of the crossflow jets. The tracer gas tests conducted at relatively low jet-to-free-stream momentum ratios confirm the observation from the flow visualization studies that such flows are slower to mix with the free stream than flows with sufficient energy to impinge on an opposing jet or the opposite wall. In cases employing low momentum ratios, increasing the number of crossflow injectors was found to improve the mixing of the jet fluid with the free stream. Velocity profiles obtained with LDA along a horizontal plane at the main duct centerline and at the free stream inlet are typical of fully-developed flow.

Based on the results obtained in the cold-flow study, modifications to allow sorbent injection in the entrained-flow gasifier were completed, and testing was initiated. A new reactor section was constructed with three sorbent injection ports. Another reactor section was fitted with sight windows to permit optical access with FTIR. A pressurized, rotary-plate feeder was designed and built for the sorbent. A flash drum was also designed, built and integrated into the scrubber system to prevent gases entrained in the quench water from being carried down the sewer.

Tests were conducted with four coals of varying sulfur content: Utah bituminous (0.45% S), Illinois No. 6 bituminous (3.6% S), Pocahontas No. 3 bituminous (0.64% S), and Alberta subbituminous (0.07% S). Pulverized limestone (6 microns mass mean diameter) containing 93.3% calcium carbonate ($CaCO_3$) was used for the sorbent. FTIR data were obtained for the Utah and Alberta coals with the assistance of Robert Carangelo from AFR. The data are currently being analyzed.

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

Work continued on incorporating the FG-DVC devolatilization submodel being developed under Subtask 2.a and the SO_x-NO_x submodel being developed under Subtask 2.g into PCGC-2, implementing the advanced code on computers, and evaluating the comprehensive code. Modifications were made in PCGC-2 to test the Multiple Solids Progress Variables (MSPV) method with two solids progress variables independently tracking coal offgas, and converged solutions were obtained for a swirling combustion case and a non-swirling gasification case. The results clearly show the importance of accounting for variability in coal offgas composition, enthalpy, or both. The FG-DVC submodel was integrated into PCGC-2 assuming constant coal offgas composition and enthalpy, and work is continuing to investigate the effects of variability in the offgas. A laminar option in the code is being developed for submodel validation in the comprehensive code in the absence of turbulence effects. A method for evaluating the comprehensive code has been outlined.

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

A detailed review of existing fixed-bed coal gasification codes was accomplished previously and described in the First Annual Report. The proposed features of the advanced model were reviewed by external consultants and, based on their written comments, an extensive plan for developing the model was formulated. Evaluation of existing models continued during the second year. Predictions were compared with experimental values and a sensitivity analysis was performed. Preliminary reviews of flow, mass, and heat transfer processes in fixed beds as well as fixed-bed technology were completed. A comprehensive review of fixed-bed combustion and gasification was initiated. A simplified version of the advanced model, incorporating separate gas and solids temperatures but not the advanced coal chemistry and bed hydrodynamics submodels planned for the advanced model, was formulated and coded. This improved model is similar to the existing two-dimensional fixed-bed codes but extended to include separate gas and solid temperatures, accumulation of energy and mass in the gas phase, radial dispersion of mass in the gas phase, and motion of the solid phase. Based on this experience, development of the advanced fixed-bed model was also initiated. The key model assumptions were determined. The governing equations and the boundary conditions are being derived. The flow of solids, as a particularly critical issue in fixed-bed modeling, is being considered.

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

The FG-DVC model was successfully integrated with PCGC-2. This was described in the Fifth Quarterly Report under Subtask 4.a. and is summarized under Subtask 3.a. of this report.

Subtask 4.b. Application of Fixed-Bed Code

No work was scheduled.