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
A	Viscosity/Swelling
A	Intraparticle Transport
I	Pyrolysis of Volatiles and Soot Formation
I	Secondary Reaction of Tar
I	Particle Ignition
A	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 Sections II-IV.

I.E. FOURTEENTH QUARTER PROGRESS

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

Work continued on examining a percolation theory approach instead of Monte Carlo for doing the network decomposition calculations in order to increase computational speed. Using percolation theory, we can get comparable predictions of the tar and gas rates. For the same set of bridge breaking parameters, there are some slight differences in the shape of the tar peak and in the fluidity predictions. The fluidity predictions appear to be the most sensitive to the choice of percolation theory over the Monte Carlo approach, as the definition of the fluid fraction is model dependent.

Work also continued on the incorporation of rank dependent pyrolysis kinetic rates. We have completed a first round of fits to the TG-FTIR data obtained from all eight Argonne coals at four different heating rates and the fluidity data obtained for six of the coals at one heating rate. This procedure provides a set of rank dependent kinetic parameters for gas evolution (CH_4, CO_2) and the breaking of weak bridges (required for tar evolution). For the lower rank coals, we still need to get better resolution of the paraffin/olefin peak from the main tar peak in order to determine the rank dependent parameters. The next step is to try this set of kinetic parameters in the percolation theory version of the model in order to arrive at a consistent set and to complete the work on the other major gas species (CO, H_2O, H_2).

Work continued on the particle swelling model. Additional sets of equations were examined to describe the driving force for swelling and one was chosen which we feel is the most consistent with the physics. Work was also done to solve some numerical problems which make the predictions sensitive to the choice of the time step. It is planned to obtain additional swelling data, to find more relevant data on the gas diffusivity and to make some measurements of pore wall thickness.

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

During the last quarter, the suction pyrometer for reactor centerline temperature characterization was fabricated and temperature profiles for the HPCP facility were measured. Also, the smaller diameter injection probe was installed, and development of the optical particle imaging system was continued. Under independent funding, the char/tar/gas separation and collection system was modified to improve the separation and collection of tar, char and gas, and the quenching of secondary tar reactions.

Significant improvement was made in particle size classification and characterization by using aerodynamic and screen separation, along with an optical particle sizer. Devolatilization runs were made with North Dakota lignite, at atmospheric and elevated pressure, to continue evaluation of the effectiveness of reaction quenching and of the separation of the char and tar in the collection system during devolatilization runs. The detailed interpretation of these data is being made as part of a related, independent project. Carefully sized North Dakota lignite char particles (64-75 μm) were also oxidized under a variety of pressures and heating conditions. SEM and ash and titanium analyses were performed for comparison with previously oxidized samples.

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

Additional work was done on the coal flame experiments in the TWR using the FT-IR Emission/Transmission Tomography technique. It has been found that the preheated air velocity has a significant effect on the shape of the flame. At low velocities, the ignition point of the flame has a donut-shaped ring of ignition with a cooler center. At high velocities, there appears to be a solid ball of ignited particles. Two cases are being done for the Montana Rosebud coal (low velocity and high velocity) and a low velocity case for the Pittsburgh Seam coal is also being done. The three flames showed both coal and flow dependent phenomena. The slow flow cases showed reduced mixing (more soot and more variations in flame properties with radius) compared to the fast flow case. The Pittsburgh Seam coal showed higher soot, higher swelling, lower particle temperatures, lower char reactivity, and higher volatility compared to the Rosebud coal.

A paper based on this work was accepted for presentation at the 23rd International Symposium of the Combustion Institute.

Subtask 2.d. Ash Physics and Chemistry Submodel

Work began on characterizing the reactivity of chars collected from the coal flame experiments. These chars have been analyzed by the standard TG-FTIR analysis which directly provides information on the reactivity index ($T_{critical}$) and the active site concentration (based on the amount of oxygen chemisorbed). A correlation was found between these two measurements, which was expected since the theory on which $T_{critical}$ is based relates it to the inverse of the product of the active site concentration and the accessible surface area. In order to apply this technique on high ash chars from the coal flame, a method was developed to correct the $T_{critical}$ for the char ash content. This is described in Appendix A. Our next step is to do Temperature Programmed Desorption (TPD) measurements on these chars, which will provide additional information on the reactivity and the distribution of active sites.

Subtask 2.e. Large Particle Submodels

The experimental work on the AFR fixed-bed reactor (FBR) system continued with the Pittsburgh Seam bituminous and Zap lignite coals. For both coals, we have not observed a strong effect of bed depth on tar yield over the range of conditions studied. For the Pittsburgh coal, there was some effect on tar composition, with the deeper beds giving tars which were more aliphatic (less aromatic). A second series of pyrolysis experiments was done with the FBR using Pittsburgh Seam bituminous coal. The reactor was modified so that the coal could be held in two separate layers on top of each other with a gap in between. The lower bed is at - 150°C lower in temperature. The experiments were done at two different flow rates. The higher flow rate resulted in an increase in tar and a decrease in CH_4 and char yields in both the single and dual bed experiments.

Discussions were held with BYU about the single particle FG-DVC model. Work was completed on a percolation theory version which is based on a system of ordinary differential equations which describes the creation and loss of n-oligomers. This version will be the basis for the single particle FG-DVC model which will be input into the Advanced Fixed Bed Model being developed at BYU. Our current tests indicate that this version is somewhat slower than the original version. Work is currently being done to make it more efficient.

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

Design of a large-particle insert for the HPCP reactor was continued. Analytical procedures for monitoring the rates of large particle oxidation are being evaluated. Preliminary oxidation experiments were conducted with a set of large particles of Utah bituminous coal, and mass reactivities were determined.

Subtask 2.g. SO_x-NO_x Submodel Development

Thermal NO predictions were found to be sensitive to the method of estimating radical oxygen concentration, wall temperature, chemistry/turbulence interactions, swirl number, and overall equivalence ratio. A scheme was developed to allow the code to check the local equivalence ratio at each node in the computational domain and choose either of two expressions to estimate the radical oxygen concentration. Unfortunately, it was not possible to specify a single value of critical local equivalence ratio which is applicable to all cases and fuel types. Therefore, the recommended approach is to assume oxygen radicals to be in equilibrium with oxygen atoms, unless experimental data are available. In the latter case, it may be possible to determine a critical value of local equivalence ratio that can be used to select between the fuel-lean and fuel-rich expressions for determining local oxygen radical concentration. Thermal NO increased with increasing wall temperature due to a proportional increase in local gas flame temperature. The strong sensitivity of the model to wall temperature may lead to erroneous predictions and the inability to match trends when inadequate wall temperature data are available. As with fuel NO formation, predicted thermal NO was considerably higher when chemistry/turbulence interactions were taken into account. Predicted concentrations of sulfur species based on local instantaneous equilibrium in the gas phase were also obtained and compared with experimental data for gasification of North Dakota lignite and Utah bituminous coal.

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

Work was temporarily suspended on the integration of the FG-DVC submodel awaiting the development of a new submodel version by AFR. The new version will replace the time-consuming Monte Carlo approach with the faster two-sigma percolation theory, leading to increased efficiency and numerical stability in PCGC-2. Work continued on simulating the transparent wall reactor (TWR). The calculational grid was refined and gas buoyancy and laminarization effects were investigated. Both were found to be definitely important in the TWR. The ignition point is extremely sensitive to inlet coal stream diameter, with a diameter of 3 mm giving good agreement with measured burnout and visual observation of the flame. The observed convergence of the particle stream after ignition has not been predicted in the simulations, but may be due to the dampening effect of particles on gas turbulence. This effect is being investigated. Several minor improvements in the energy equation as well as additional insight into the energy equation coupling between the gas and solid phases led to the successful convergence of a high-pressure gasification case that is being considered for code validation. In addition, the robustness of the code for gaseous combustion simulations with radiation was improved. Work continued on the development of a graphical user interface (GUI) for PCGC-2 on the Sun workstation, and a window was added for specifying inlet stream composition and temperature. The thermodynamic input data file is now generated automatically by the GUI. Work was also initiated on applying two graphics programs developed under independent funding, a pre- and post-processor, to PCGC-2. These two programs assist with grid generation and analysis of code results.

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

Work continued on reviewing, coding, and validating the well-mixed, partial-equilibrium submodel used for estimating effluent composition and temperature for the 1-D fixed-bed code. Predictions were compared with measured effluent temperature and composition from fixed-bed reactors, and quantitative agreement was obtained for a wide range of coal types. The interface between the fixed-bed code and FG-DVC submodel was considered, and a plan was formulated for incorporating the percolation theory version of the DVC model while retaining the current implementation of the FG model. The algorithm for solving the DVC equations will be compatible with the LSODE solver currently used by the code. A freeboard submodel was added to the code to account for heat loss in the void space above the bed. A paper was submitted to Combustion Science and Technology.

Subtask 3.c. Generalized Fuels Feedstock Submodel

This subtask has not been initiated.

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

This subtask has not been initiated.

Subtask 4.b. Application of Fixed-Bed Code

Work continued on collecting fixed-bed design and test data, and on testing and validating the 1-D code. Twelve additional responses to the questionnaire were received, seven of which were positive, and seven additional data sets were obtained. However, some of the more important data sets are still unavailable.