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
•	Generalized Fuels Model
I	Fixed-Bed Model

(•) 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. ELEVENTH QUARTER PROGRESS

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

Work continued on the coal viscosity (fluidity) model. During the past quarter, the effects of different maceral groups on viscosity were addressed. The sensitivity of the model to the activation energy for the temperature dependence of the viscosity was also investigated. We have also obtained additional fluidity data on coals in the Exxon sample bank which will be used to test the model.

In view of the importance of macromolecular network models to the accurate predictions of coal processing behavior, we have assessed the assumptions and limitations of the proposed models. A comparison was made of the FG-DVC model and two other network decomposition models, namely the DISARAY model of Niksa and Kerstein and the CPD model of Grant and coworkers, both of which employ percolation theory. We are considering using percolation theory instead of Monte Carlo methods as the basis of our network decomposition model in order to reduce the computation time for running the FG-DVC model.

An independent investigation was made of the rank dependence of the pyrolysis kinetics by doing experiments in a TG-FTIR reactor over a series of heating rates (3, 30, 50, 100°C/min) with three coals (Pocahontas, Pittsburgh, No. 8, and Zap lignite) from the Argonne set. A comparison was done of the rank dependence of the rate constants for bridge breaking, tar evolution and CH_4 evolution at 450°C, determined from analyzing the TG-FTIR data at several heating rates and from fitting the FG-DVC model to fluidity, weight loss and methane evolution data at a single heating rate (3°C/min). The results indicated that the rates for tar evolution or bridge breaking vary by about a factor of 10 if the Pocahontas coal is excluded, which is consistent with previous results for coals from the same range of ranks. This corresponds to a difference in T_{max} for tar evolution of - 40°C at a heating rate of 30°C/min. If the Pocahontas coal is included, the rank variation for the tar evolution/bridge breaking rate is about a factor of 50. This corresponds to a difference in T_{max} for tar evolution of ~ 65°C at a heating rate of 30°C/min. The rates for tar evolution are consistent with those obtained by Burnham and coworkers at LLNL.

Work also began on adding the polymethylene species to the FG-DVC model. These are long chain aliphatic species which are important components of the tar in low rank coals.

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

Work continued on the instrumentation and testing of the high-pressure, controlled-profile (HPCP) reactor, preparation and characterization of char, and kinetics of char oxidation at high pressure. The reactor was tested by producing char from Pittsburgh No. 8 bituminous coal. The feeder was modified to reduce feed rates and eliminate plugging with sticky coals. The char separation and collection system was tested and shown during coal devolatilization to remove essentially all of the particles from the outlet stream of the reactor. Chars from this coal were prepared in the hot-tube reactor at pressures ranging from 1-10 atm and 1275-1530 K. SEM's were taken of all the samples for comparison with previous samples from other coals, and for comparison with chars produced in the HPCP. TGA and oxidation tests in the HPCP were conducted with sieved samples of one of the atmospheric pressure chars to determine reactivity. Analysis of the results is in progress. A research team member attended the ACERC First Symposium on Advances in Coal Spectroscopy in Salt Lake City, Utah, June 1989.

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

Discussions continued with BYU on the modeling of the Transparent Wall Reactor (TWR) experiments with the Montana Rosebud Coal. This work is being reported under subtask 3.a.

Work was also done to modify the TWR experiment to do pyrolysis and combustion experiments with FT-IR measurements of particle temperatures. During the past quarter, a series of pyrolysis experiments was done with Zap lignite and Pittsburgh seam bituminous coal. 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 temperature-time history. The pyrolysis yields were then simulated with the FG-DVC model and the results were consistent with the kinetic rates measured previously at high heating rates at AFR and Sandia for experiments where particle temperature measurements were made.

Subtask 2.d. Ash Physics and Chemistry Submodel

Work continued on improving the collection of ash from the entrained flow reactor experiments with the eight Argonne coals. It appears that most of the problem for the Upper Freeport coal, where low collections were obtained, was due to particles and ash sticking in the collection probe. This appears to be solved by rinsing the probe with acetone.

SEM/X-ray analysis was done on the extracted material and compared to that collected in the cyclone. It was found that there was some differentiation. The former material was higher in iron and sulfur, lower in aluminum and silicon and about the same in alkali content.

Work on the effects of minerals on char reactivity continued. As discussed in the previous quarterly, a particular area of interest is the investigation of the effects of Na on the reactivity of demineralized Zap coal. It was observed that a loading of 0.5 wt.% Na significantly increased the reactivity of a char produced at 900°C in a TGA but that a loading of 2.0 wt.% Na significantly reduced the reactivity of a char produced under the same conditions. In both cases, a comparison is being made to char produced from the demineralized Zap coal. Surface area analyses were done of the chars during the past quarter. It appears that a significant reduction in the CO_2 surface area can explain the low reactivity of the 2.0 wt.% Na char. The reason for this has not yet been determined. SEM photographs do not reveal anything unusual about the char morphology.

Subtask 2.e. Large Particle Submodels

The main modeling activity during the past quarter was to develop a revised version of the FG-DVC model which does not have a lot of extraneous variables which have accumulated over many years of development. This new version will be used by BYU in the Fixed-Bed Reactor Model and will eventually replace the version which is now in the Entrained Bed Model (PCGC-2). During the past quarter, discussions were held with BYU to reach an agreement on the features of the new version of the model. These discussions were completed and work on the new version began late in the quarter.

Work continued on testing the AFR fixed-bed reactor system. Some preliminary coal pyrolysis experiments were done with Zap lignite coal. The system appears to function properly except for an air leak that needs to be fixed.

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

This subtask has not been initiated and no work was conducted during the past quarter.

Subtask 2.g. SO_x-NO_x Submodel Development

An experimental program (independently funded) is currently in progress to collect data for evaluating the thermal NO mechanism of the revised NO_x submodel. PCGC-2 simulations of the reactor system are also in progress. Thermal NO data have been obtained from Karlsruhe University in West Germany for a natural gas flame. These data, although somewhat limited, will provide an independent source of data to compare with model predictions. One simulation was completed to compare an alternative empirical NO_x mechanism with the original fuel NO mechanism of PCGC-2 and experimental data. Additional comparisons will be completed for gasification tests of low-rank coals.

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

Work continued on the integration and evaluation of the FG-DVC submodel in PCGC-2. The relative effects of variability in coal offgas and enthalpy are being evaluated to assess the need for multiple solids progress variables. A previous case was repeated with the FG-DVC submodel and solving the full energy equation. A converged solution was obtained. A discrepancy, noted between the residual char fraction predicted by the FG-DVC submodel and that calculated by PCGC-2, was largely resolved. Problems experienced with the FG-DVC submodel never being called for small particles were resolved by calling the submodel at every time step. A problem noted in the calculation of time-average properties with the full energy equation option has been partially resolved by evaluating fluid intermittency terms assuming thermal isolation. Work also continued on the simulation of the transparent-wall reactor for submodel evaluation, and parametric calculations were carried out for inlet turbulence intensity varying from 5 to 15 percent. The code calculations are sensitive to the assumed value of intensity. Work was also initiated on developing a graphical user interface for the code. The interface is based on the Sun windowing system, and will make it much easer to use and interact with the program, both for input and output, and also for running the program and monitoring its progress.

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

Work continued on reviewing numerical techniques used in comprehensive fixed-bed models, obtaining validation data from the literature, and coding the chemical submodels. Three equilibrium-based, moving-bed submodel component codes were written, debugged, and partially validated. The three codes are based on total equilibrium, 1-zone partial equilibrium, and 2-zone partial equilibrium. The partial equilibrium models use the functional group model (FG model) to predict ultimate volatiles composition (including tar) and either the 2-step model or FG model to predict ultimate volatiles yield. The equilibrium models predict reasonable effluent properties and will be used to provide an initial guess for the 1-D, moving-bed model. The development of the equilibrium-based, fixed-bed models has provided familiarity with the chemical submodels to be used in the 1-D, moving-bed model, and has also provided insight into the moving-bed coal gasification process.

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

No work was planned or conducted on this subtask during the past quarter.

<u>Subtask 4.b. Application of Fixed-Bed Code</u>

This subtask was initiated during the past quarter. Fixed-bed technology and data were reviewed, and fixed-bed gasifiers of potential interest for simulation were identified. Design and test data were obtained for these gasifiers. Particular attention was paid to mild gasification data reported at the recent METC Ninth Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting. Effluent data, as well as limited available profile data, will be used as a basis for model evaluation. In order to obtain all the data potentially available for testing and validation of the advanced fixed-bed code, a questionnaire was prepared. The appropriate scope and format of the fixed-bed test data were also defined. This questionnaire will be sent to a number of organizations and individuals.