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. THIRD YEAR PROGRESS

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

A significant amount of work was done in the area of tar transport during the past quarter. The current vapor pressure law does a good job of predicting the relative amounts of the oligomers in each size classification from FIMS pyrolysis experiments. However, it predicts a shift in the temperature range of the oligomers as the size range increases in the case of bituminous coal pyrolysis/FIMS, which is not observed in the actual data. We believe this results from restricted diffusion of the large oligomers as the coal begins to resolidify.

Work was resumed on the addition of polymethylenes to the FG-DVC model. Some predictions were made of the tar hydrogen composition for coals of different rank and compared to measurements made by Freihaut et al. (1988). Good agreement was obtained except for the two lowest rank coals (Zap lignite, Wyodak subbituminous), where the predicted hydrogen composition was too high.

Work also continued on the swelling model. Additional bubble types (sizes) were introduced into the model in order to improve the prediction of surface area. However, this did not lead to better predictions, so other modifications to the model will be tried.

Work continued on examining a percolation theory approach to doing the network decomposition calculations. A version of the model was developed which incorporates two different types of bonds, the so-called two-σ model. Three important new features in our two-σ percolation theory are: (i) tar vaporization, (ii) molecular weight distribution of monomers, and iii) an approximation which allows the removal of tar. These features are basically treated the same way as in the original DVC model. The Monte Carlo and two-σ predictions of the tar yield and of the coal fluidity data agree reasonably well with each other and with the data.

Work also continued on the rank dependence of the pyrolysis kinetic rates. So far, comparisons have been made with Pittsburgh Seam bituminous coal TG-FTIR data from experiments at four different heating rates. In this case, rank dependent kinetics have been determined which provide an excellent fit to the evolution profiles and yields for each heating rate.

A comparison was made of intrinsic reactivity measurements for Montana Rosebud coal determined from the non-isothermal test to the plot developed by Smith for a range of carbons over a wide range of temperatures. The agreement at low temperatures was within a factor of two when compared to the data of Smith (1982) for brown coal chars. When the results were extrapolated to high temperatures using E = 35 kcal/mole, again good agreement was obtained with Smith's data for coal chars (within a factor of two).

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

Work continued on developing the optical particle-imaging system for the HPCP reactor. A mass flow meter and flow controllers were installed in the inlet streams to enable more rapid testing. A new particle injection probe with smaller diameter and thicker insulation is being fabricated to reduce the thermal impact of the probe on the preheated inlet stream. A suction pyrometer for reactor centerline temperature characterization is also being fabricated. The facility was modified to enable insertion of the pyrometer from the bottom of the reactor. Work continued on the analytical procedure to measure titanium content for determining char burnout.

Under independent funding, work continued on the collection of tar/char/gas from devolatilization runs in the HPCP reactor. Four devolatilization runs were made with North Dakota lignite at atmospheric and elevated pressures. The collection system is being modified to improve the separation.

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

Work continued on doing coal flame experiments in the transparent wall reactor (TWR). An attempt was made to use the Pittsburgh Seam bituminous coal.

However, some problems were experienced in feeding the coal and with flame stability. Consequently, a switch was made back to Montana Rosebud subbituminous coal.

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. Values for particle temperature, relative particle density, relative soot concentration, the fraction of ignited particles, the relative radiance intensity, the relative CO_2 concentration and the CO_2 temperature have been obtained as functions of distance from the flame axis and height above the coal injector nozzle. Initial measurements (reported last quarter) were made at 6 cm and 12 cm above the coal injector nozzle, with the ignition point occurring at 10 cm. During this quarter, two more slices of data, at 16 cm and 20 cm above the nozzle were collected and tomographically reconstructed. An in-depth discussion of the four measurement positions can be found in Appendix A, which is a copy of our paper entitled "FT-IR Emission/ Transmission Tomography of a Coal Flame", which has been submitted to the 23rd Symposium (Int) on Combustion, France, (1990).

Subtask 2.d. Ash Physics and Chemistry Submodel

The work on the study of mineral transformations in the entrained flow reactor (EFR) was temporarily suspended due to manpower and funding constraints.

Temperature Programmed Desorption (TPD) experiments were done in air for chars produced from all of the Argonne coals. The CO_2 desorption and the O_2 adsorption show a consistent trend with the char reactivity as measured by the Critical Temperature (T_{cr}). The more reactive chars adsorb more O_2 and give off CO_2 earlier. These experiments will be repeated with chars produced from demineralized samples of these coals and experiments will also be done in CO_2.

Samples of char were collected from the Montana Rosebud coal flame experiments in order to do reactivity measurements. Since the samples at high levels of burnout had high ash contents, the non-isothermal reactivity measurement technique (which determines the "critical" temperature) had to be modified to account for this.

Subtask 2.e. Large Particle Submodels

The work on the AFR fixed-bed reactor (FBR) system was continued. Experiments were done at two bed depths and two flow rates with samples of Illinois No. 6, Pittsburgh No. 8, and Upper Freeport bituminous coals. Over the range of bed depths examined, there did not appear to be a large effect on tar yield and composition. We were restricted from using larger bed depths because problems with tar deposition in the gas cell. However, the ability to bypass some of the tar from the cell has recently been added which will allow larger samples to be used.

It was also found that the temperature of the maximum evolution rate of tar and CH_4 decreased with increasing bed depth. This was due to low levels of oxygen contamination. The contamination problems have recently been solved.

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

Work was initiated on this subtask. A literature search of large particle oxidation and high-pressure reactor systems was conducted. An experimental approach was selected which includes using reactor tubes containing fixed beds of large char particles inserted in the HPCP reactor from Subtask 2.b.

Subtask 2.g. SO_x-NO_x Submodel Development

Work continued on evaluating the thermal NO submodel using data from the BYU/ACERC laboratory-scale reactor. Problems with the high gas temperature previously predicted by PCGC-2 have been resolved, and thermal NO predictions have been compared with experimental data. The presence of prompt NO in gaseous hydrocarbon flames has made it difficult to evaluate the results. Relatively high levels of HCN and NH_3 have been measured in the near-burner region, which supports the formation of prompt NO on the fuel-lean side of the flame. The NO concentration is underpredicted by approximately 30 percent, but it is not certain that this disparity is a result of neglecting prompt NO. Expressions for estimating radical oxygen, for example, have been shown to be sensitive to temperature. Several coal gasification cases have been simulated, and the gas temperature and major species concentrations agree reasonably well with the experimental data. Evaluation of the combined fuel and thermal NO mechanism is ready to begin.

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

Several improvements in PCGC-2 were made during the last quarter. A major error was discovered and corrected in the radiation submodel. This correction apparently resolved the previously reported problem with unreasonably high temperature predictions in some cases. A new option was also added to the code for solving the radiation submodel for gaseous combustion (no particles). Other improvements were made in the full energy equation option, the SIMPLE-based numerical algorithm used for solving the fluid flowfield, and the tri-diagonal matrix solver used by SIMPLE. Converged solutions were then obtained for several cases being used in Subtask 2.g to evaluate the extended NO_x submodel, and for the gasification case chosen previously as a standard test case. Additional model validation data were also obtained from AFR, and work continued on modeling the TWR reactor facility. Development of a user-friendly, graphical interface on the Sun workstation was also continued.

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

Work continued during the last quarter on coding chemical and physical submodels and model validation. Improved temperature profiles and pressure profiles have been obtained from the one-dimensional, fixed-bed code. The fixed-bed model considers separate gas and solid temperatures, partial equilibrium in the gas phase, variable bed void fraction, coal drying, devolatilization based on chemical functional group composition, oxidation and gasification of residual char with an ash layer, and axially variable solid and gas flow rates. Predictions and comparisons to experimental data include effluent gas compositions and temperatures, temperature profiles, and axial pressure variation. Additional predictions with comparison to limited data include carbon conversion, variable particle size, and species concentration profiles. The relative importance of char oxidation resistances to bulk film diffusion, ash diffusion, and chemical reaction are identified. For the cases examined, chemical resistance dominates in the cool regions at the bottom and top of the reactor while ash diffusion resistance competes with chemical resistance throughout most of the reactor. The importance of adequate treatment of devolatilization, gas phase chemistry, and variable bed void fraction is identified.

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 from organizations and individuals involved in fixed-bed research. Eighteen sets of data have been obtained, but some of the most important ones have not been obtained yet. Requests for data were sent again to a number of individuals and organizations who had not responded to the first request. Work also continued on collecting fixed-bed experimental data from the open literature. Further testing and validating of the advanced fixed-bed code developed in Subtask 3.b was performed. The test case was the same as one used before - the test run of the Wellman-Galusha gasifier with Jetson high volatile B bituminous coal. Improved predictions of temperature and pressure profiles were obtained, but the need for further improvement of the advanced fixed-bed code is still evident.