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. This 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 will be developed or adapted. The submodels will 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 will 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 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 is a closely integrated, cooperative effort between AFR and BYU. The program consists 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$_x$

I Generalized Fuels Model

I Fixed-Bed Model

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

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

I.E. SEVENTEENTH QUARTER PROGRESS

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

During the past quarter, most of the effort was on using the set of rank dependent kinetic parameters obtained from low heating rate experiments to predict high heating rate data from pyrolysis experiments in our Transparent Wall Reactor (TWR) and Heated Tube Reactor (HTR). We also did simulations of high heating rate pyrolysis data from the literature such as the heated grid experiments of Gibbins, the wire grid experiments of Fong and coworkers of MIT, and the TWR experiments of Fletcher at Sandia.

Some problems were obtained in predicting the changes in the tar yield and tar molecular weight distributions with heating rate for low rank coals using the current version of the model. In addition, we could not predict the extractables yields for the high heating rate data of Fong and coworkers on the Pittsburgh Seam coal with the current kinetic parameters. It was decided to re-examine the assumptions on the model input parameters, such as 1) the bridge breaking rate, 2) the crosslinking efficiencies, 3) the tar vaporization law, and 4) the ΔP parameter. It was found that a modest change in the activation energy for the bridge breaking rate (from 25 to 27 kcal/mole) allowed for good predictions of the Fong data. Changes in the crosslinking efficiencies were thoroughly evaluated and found to be largely unnecessary. A decision was made to use 10^{14}sec^{-1} for the bridge breaking pre-exponential and values of the crosslinking efficiencies = 1.

The effects of the tar vaporization law and the ΔP parameter were found to be very important. The change in the original vaporization law from the expression proposed by Suuberg to a factor of 10 higher was found to be mainly responsible for the inability to predict the high heating rate Zap data. By changing to Suuberg X1, and allowing ΔP to be the sole adjustable parameter, the predictions are much better. A decision was initially made to use the law proposed by Fletcher, since it had been subjected to a rather thorough validation with model compounds. However, in the intermediate molecular weight range where the model is sensitive to the vaporization law, the two models are comparable. Therefore, either Fletcher or Suuberg X1 can be employed. The main unresolved question is the appropriate choice for ΔP and how this could be functionalized. It appears that the model predictions of the FIMS data are very sensitive to the choice of this parameter. At low heating rates, a choice of $\Delta P = 0$ gives the best prediction of the tar yield. A choice of $\Delta P = 0.2$ gives the best prediction of the tar MWD. Possible solutions would be to: 1) parameterize ΔP; 2) improve the description of the external transport of tar to resolve the problem of the higher molecular weight tars coming out earlier than expected.

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

During the last quarter, progress was made in increasing the signal-to-noise ratio of the optical particle imaging system so that small particles at low temperature can be measured. The modified reactor collection system was operated successfully under devolatilization conditions. The time required for size classification of pulverized coal was further reduced, the quality of the classification was improved, and sufficient quantities of narrow size ranges of three of the five test coals were produced for upcoming char preparation and oxidation tests. Under independent funding, coal devolatilization tests were successfully conducted using the modified reactor collection system. Computer software was written to support the data acquisition and heater control hardware that was previously interfaced to the reactor instrumentation and heaters, and was successfully used during the devolatilization tests.

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

Discussions were held with BYU on the future direction of the work on modeling the tomography data from the TWR coal flame experiments. Some discrepancies exist in the measured and predicted particle temperatures which could result from problems with the measurements and/or the model. A rate limiting step in comparing the model with the data is the generation of suitable plots. A new approach which involves output of the predictions of the model into a spreadsheet format was agreed upon.

Subtask 2.d. Ash Physics and Chemistry Submodel

No work scheduled during the past quarter.

Subtask 2.e. Large Particle Submodels

The work on the modified AFR fixed-bed reactor (FBR) system continued. It includes two independently heated stages. The reactor system was assembled and tested and is now being used for lignin pyrolysis experiments under independent funding. It appears to work as planned. A redesign of the upper reactor chamber was required in order to eliminate a tar deposition problem. As expected, the quantitation of gas and tar is much better than in the old system and a wider range of sample sizes and flow rates can be used. Some problems were encountered with the software used to quantify the IR data, but these appear to have been resolved.

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

For this subtask, the decision was made previously to construct an experimental facility that would connect to the HPCP reactor of Subtask 2b. Of the two experimental approaches considered in the previous reports, the decision has been made to develop the "cantilever beam insert." In this approach the sample will be mounted horizontally to one or two of the optical access ports of the HPCP reactor. A summary of the design of this facility was prepared and sent to a few principal investigators active in fields of closely related research for their comments and criticisms. The suggestions received have been included in the details for the design of this facility. Construction of this "cantilever beam insert" will start during this next quarter. Analytical procedures for monitoring rates of oxidation of large particles continue to be evaluated. Further data analysis of large particle oxidation in air in platinum crucibles shows a marked dependence of mass reactivity on the initial mass of the large particles. This is in contrast to a dependance on temperature, which was expected.

Subtask 2.g. SO_x-NO_x Submodel Development

During the past quarter, the method used to determine atomic oxygen concentrations in the NO_x submodel was revisited. Further insight into the best quasi-equilibrium expression to use for predicting atomic oxygen concentrations in lean, swirling-flow, natural gas flames was gained. Work continued on the integration and evaluation of a SO_x/sorbent reaction computerized submodel. This submodel has been integrated into PCGC-2 and is currently being evaluated. Experimental data are being sought to determine H_2S capture rates to use in an H_2S sulfation subroutine.

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

Work continued on code evaluation and user-friendliness. Data from four reactors were identified for code evaluation. Simulations were performed for a natural gas flame in the BYU controlled-profile reactor and for the near-burner field of a full-scale industrial boiler. Two-dimensional combustor data were requested from Imperial College. The graphical user interface for editing input files was extended to particle combustion. Diagnostic messages were added to the code to help users detect errors in code input. A set of minimum specifications for a foundational, entrained-bed code that will satisfy the terms of the contract was identified. These specifications were documented in a letter to AFR and METC. Additional features that would enhance code performance were also identified. Two menu-driven post-processors were developed for converting PCGC-2 plotting files for gas and particle properties into a format that can be used by spreadsheet programs.

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

During the last quarter, work continued on developing and evaluating the one-dimensional fixed-bed model. The model response to variations in operating conditions was validated by simulating several such test cases. Predicted temperature profiles were compared to measurements for the atmospheric, air-blown Wellman-Galusha gasifier fired with Elkhorn bituminous, Jetson bituminous, Leucite Hills subituminous, and Utah Blind Canyon bituminous coals. These test cases included temperature profiles at different operating conditions. Discussions with AFR, about the single particle FG-DVC submodel for integration into the fixed-bed code, continued. Development of the user's manual for the fixed-bed code was initiated. The first draft of the manual was prepared. A progress report on fixed-bed model development was presented at the Peer Review Meeting in Pittsburgh and the Project Review Meeting in Morgantown. An article on fixed-bed model development was prepared and published in ACERC's Burning Issues.

Subtask 3.c. Generalized Fuels Feedstock Submodel

PCGC-2 was modified to allow sorbent injection in the primary stream.

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

Potential application cases for demonstrating the entrained-bed code were identified. A post-doctoral research associate was recruited to work on this subtask.

Subtask 4.b. Application of Fixed-Bed Code

Work continued on collecting fixed-bed design and test data from the open literature as well as by direct contact of the individuals and the organizations active in the field. No new data sets have been obtained. No new test cases were identified or simulated.