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 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 included:

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
A 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 Coupling of Submodels with Comprehensive Codes
I Comprehensive Code Efficiency
I Turbulence
I SO_x and NO_x
I Generalized Fuels Models
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. FIFTH YEAR PROGRESS

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

During the past year, work was done 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). Simulations were also done 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. The main unresolved question was the choice of the ΔP parameter which is used in the tar transport model. It was decided that it was best to use this as an adjustable parameter of the model. The other choice was to develop a new external transport model for tar. This was not thought to be the best option at this stage of the contract.

The process of defining the deliverable FG-DVC submodels was completed during the past year. Under this subtask, submodels will be completed for swelling, sulfur and nitrogen evolution, char reactivity and optical properties. The swelling model is an extension of the recently completed fluidity model. A first draft of a manual was written for the stand-alone (percolation) version of FG-DVC. Copies of the manual were sent to BYU.

During the past year, work was also done on using the FG-DVC model to simulate mild gasification processes. The model was modified to include a hydrocarbon cracking routine which describes the cracking of long chain paraffin and olefin species down to smaller hydrocarbons (C_1-C_3's). The model was applied to data obtained from pyrolysis of Illinois No. 6 coal in the IGT mild gasification Process Research Unit (PRU) under essentially isothermal conditions.

Work continued on the swelling model. A single bubble version of the swelling model is now being developed for comparison to data on the Pocahontas coal, which is the most difficult coal to model with respect to the swelling behavior at high heating rates. A numerical problem which made the predictions sensitive to the size of the time step was fixed.

Work continued on the sulfur and nitrogen submodel. The first step was to run the series of Argonne coals in the TG-FTIR apparatus with the post-oxidizer attached. This allows detection of species that are not easily detected in the IR, such as H_2S (oxidizes to SO_2). Runs have been done with all eight Argonne coals. The preliminary data suggest that the ratio of NH_3/HCN is much higher than what is observed in pyrolysis at higher temperatures.

Work continued on the char reactivity submodel. After examination of several possible approaches, a decision was made to use the Random Pore Model of Bhatia and Perlmutter to describe the reaction under the kinetic control regime. Compared to other possible approaches, such as those of Gavalas or Simons, it is mathematically simpler (fewer parameters) and has been tested against a wider variety of data. It is able to describe the variation of surface area with conversion based on an analytical expression with a single adjustable parameter which describes the initial pore structure. The recent progress has been in fitting the reactivity model to both isothermal and non-isothermal data for chars produced from the Argonne coals and developing a set of values for the kinetic rate parameters (A, E_0, σ), the active site concentration (β) and the char structural parameter (Ψ) for the Random Pore Model. A relationship was developed to describe the functional form of the active site concentration, β, with respect to changes in coal rank, mineral content, and the degree of pyrolysis.

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

The high-pressure, controlled-profile (HPCP) reactor, including the char, tar and gas separation and collection system, has been successfully operated in coal devolatilization, char preparation and char oxidation experiments. The optical diagnostics for particle temperature, size and velocity were assembled and calibrated, and initial measurements of oxidizing char particles were successfully made. Coal particle classification continued throughout the reporting period with the objective of preparing carefully sized samples of the coals selected for study in two ranges of particle diameter. Carefully sized samples of four coals have been prepared and stored for the upcoming char preparation and oxidation 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.

Under this subtask, models for ignition and soot formation will be delivered. The essential ingredients of the ignition model are already in PCGC-2. What is needed is to refine the assumptions regarding the fraction of CO_2 formed at the surface, as opposed to the gas phase, and the amount of energy feedback to the particle from the oxidation reaction of CO. These are related questions. The soot formation model, to date, is a calculation of the equilibrium amount of condensed carbon. This does a good job of predicting the location of the soot maximum but not the magnitude or the burnout. What is needed is a kinetic model for soot formation and destruction.

During the past year, work was done on developing a radiative model for soot as part of the soot submodel and the results were sent to BYU. The inputs are the volume fraction of soot and the temperature. The output is the average soot emissivity. The main difficulty is to correct for the presence of CO_2 and H_2O. This work is being done jointly with BYU since the radiation model is an integral part of PCGC-2.

Subtask 2.d. Ash Physics and Chemistry Submodel

Under this subtask, a model for ash chemistry and physics was outlined. The inputs will be the starting mineral concentrations and size distributions while the outputs will be the composition and size distribution of the fly ash. Because of the complexity of this problem and the large amount of DOE and NSF supported work being done elsewhere, this submodel will primarily be an integration of work done outside AFR.

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 was used for lignin pyrolysis experiments under independent funding. It appears to work as planned.

Under this subtask, a model for the repolymerization of tar in fixed bed gasifiers is being developed. The relatively low yield of tar from these systems is believed to be the result of recondensation of tar in the top of the bed which carries the tars back into the bed where they can be repolymerized intc char or cracked into gas. A key parameter will be the gas exit temperature at the top of the bed. The model to be developed will be based on experimental data from the two-stage fixed-bed reactor system discussed above, as well as data from the literature. The model inputs will be the tar yield and tar molecular weight distribution (MWD) from the standard FG-DVC model). The outputs will be the actual tar yield, tar MWD, char yield and gas yield as a function of the bed conditions.

A compilation was made of literature data from laboratory reactors and full-scale moving bed gasifiers that can be used to help validate the model. The focus has been on data for the Pittsburgh seam coal which shows the change in tar yield and/or composition with variations ir heating rate ced depth, flow rate, pressure, particle size, and reactor type.

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

Construction of the balance unit for the large-particle insert was initiated. A series of sets of large particles was devolatilized and oxidized in platinum crucibles in air. A run was also made with a large particle pressed from pulverized coal. Smaller particles have a larger mass reactivity. North Dakota lignite and Wyoming subbituminous coal show results similar to Utah bituminous coal. However, Illinois #6 coal is distinctly lower in reactivity. For this coal, the developing ash particle maintained the same shape as the char particle while the burnout progressed, rather than crumbling as the others did.

Subtask 2.g. SO_x - NO_x Submodel Development

The NO_x and SO_x/sorbent reactions submodels were incorporated into the final product code versions. Additional insight into the thermal NO submodel was obtained. Evaluation of the SO_x/sorbent reactions submodel was initiated. A benchmark case was used to demonstrate the sorbent capture submodel and to investigate the effects of Ca/S ratio on SO_2 reduction efficiency. Code graphics routines were modified to include sorbent particles.

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

A new version of the FG-DVC submodel, with rank-dependent kinetics, was incorporated into PCGC-2. The effects of direct enthalpy feedback from volatiles flames to devolatilizing particles and heterogeneous CO_2 formation to oxidizing particles were investigated. Simulations for the base code (without FG-DVC) were performed for the BYU/ACERC controlled-profile reactor, the Imperial College reactor, the BYU gasifier, the ABB Combustion Engineering drop-tube reactor, and the Goudey plant of New York State Electricity and Gas. A sensitivity study of particle optical properties was performed. Code input was simplified. A graphical user interface for preparing code input was extended to include particle combustion data. Diagnostic messages were added to the code. Post-processing programs for plotting predictions and comparing with experimental data were consolidated into a single program with several options. Minimum specifications for a foundational, entrained-bed code that will satisfy the terms of the contract were identified.

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

Work continued on the fixed-bed model. The first version (MBED-1) was completed and evaluated. A user's manual was written, and the code and user's manual were submitted to METC. Minimum specifications for the final code product (FBED-1) were determined. A major improvement in FBED-1 is the inclusion of the FG-DVC submodel. Preliminary integration of FG-DVC was performed jointly by BYU and AFR, and necessitated restructuring of the code. The present version of FBED-1 includes the properly integrated FG-DVC percolation submodel, and was tested by simulating the Wellman-Galusha gasifier fired with Jetson bituminous coal. The results compare well with predictions from previous versions of the code.

Subtask 3.c. Generalized Fuels Feedstock Submodel

Modifications were completed to allow PCGC-2 to simulate coal and sorbent injection in additional (sidewall) inlets.

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

Letters were written to representatives of three Clean Coal Technology projects for information. Response was received from Coal Tech Corp., and their cyclone combustor was selected as an application case. The other application case will be the Texaco gasifier (Coolwater project).

Subtask 4.b. Application of Fixed-Bed Code

Two new cases of potential interest for code application were identified. Both are fixed-bed gasifiers integrated into gasification/combined-cycle systems.