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.

- I Separation of Rates for Chemical Reaction, Heat Transfer, and Mass Transfer
- I Particle Temperature Measurements Using FT-IR E/T Spectroscopy
- I Functional Group Description of Coal, Char, and Tar
- I Tar Formation Mechanisms
- I Char Formation Mechanisms
- I Intraparticle Transport
- I Pyrolysis of Volatiles and Soot Formation
- I Secondary Reaction of Tar
- I Particle Ignition
- I Ash Chemistry and Physics
- I 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; (C) completed.

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

I.E. SUMMARY OF SIXTH QUARTER PROGRESS

The second semi-annual review meeting for the project was held at Brigham Young University in Provo, Utah on March 22 and 23, 1988. The program for the meeting is listed in Table I.E-I. As a result of that meeting, the following action items were defined:

<u>1. Subtask 2a</u> - AFR will write a version of FG-DVC using a percolation theory approximation as an alternative to the Monte Carlo calculation for the lattice statistics to increase computational speed. The FG-DVC chemistry and transport will remain as in the original version. The two versions of the code will be compared to test the accuracy of the percolation theory approximation.

<u>2. Subtask 2b</u> - It was agreed that the five coals being studied under this task will be from the Argonne Premium Sample Bank. The apparatus construction schedule will be watched to insure that the required data are obtained.

<u>3. Subtasks 2g and 2h</u>

a. Under Subtask 2h, measurements will be made of sulfur capture. For validation of the sulfur capture model development (Subtask 2g), input parameters to PCGC-2 will be required for the coals being studied in 2h (Illinois #6 and Utah bituminous). These two coals, plus two others for which gasification data has already been obtained (North Dakota lignite and Wyoming subbituminous), will be sent to AFR for characterization to obtain the model parameters.

b. It was decided to add temperature measurements in Subtask 2h. Thermocouple and/or suction pyrometer probes will be added above and below the sorbent injection ports. Also, an attempt will be made to do FT-IR measurements in the reactor. Tentative plans were made for AFR to bring out an FT-IR during a one or two-week period in August 1988 to make the tests.

c. Consideration will be given to running gasification tests on one or two more coals in the reactor being used in Subtask 2h. A Pittsburgh Seam bituminous and an Upper Freeport will be considered to supplement the data already available on the four lower-rank coals. Consideration will also be given to obtaining some mild gasification data. These possibilities will depend on time and budget constraints.

Table I.E-1

AGENDA FOR JOINT AFR/BYU CONTRACT REVIEW MEETING

<u>TUESDAY, MARCH 22</u>

8:30-8:50	**Introduction and Overview (Dr. B. Scott Brewster, Research Associate, BYU)**
8:50-9:50	**AFR Presentation (Dr. Peter R. Solomon, President, and Dr. David G. Hamblen, Vice President, AFR)**
	AFR provide details
10:20-11:00	**Subtask 2h Presentation and Discussion**
9:50-10:00	Introduction (Dr. Paul O. Hedman, Professor of Chemical Engineering, BYU)
10:00-10:15	Sorbent mixing fluid mechanics (Mr. David Braithwaite, M.S. Candidate, BYU)
10:15-10:30	Laboratory-scale reactor modifications and space-resolved sulfur and nitrogen pollutant measurements (Mr. Aaron Huber, M.S. Candidate, BYU)
10:30-10:40	Discussion
10:40-11:00	**Break**
11:00-12:00	**Subtask 2b Presentation and Discussion**
11:00-11:10	Introduction (Dr. Geoffrey R. Germane, Associate Professor of Mechanical Engineering, BYU)
11:10-11:20	Char preparation (Dr. Angus U. Blackham, Professor of Chemistry, BYU/Mr. Gary Pehrson, Undergraduate, Dept. of Chemistry, BYU)
11:20-11:40	High-pressure reactor design and fabrication (Mr. Charles Monson, Ph.D. Candidate, BYU)
11:40-11:50	Discussion
11:50-1:00	**Lunch (Private room, Wilkinson Center)**

Table I.E-1 (continued)

AGENDA FOR JOINT AFR/BYU CONTRACT REVIEW MEETING

1:00-2:00	**Tour of Experimental Facilities**
1:00-1:20	Cold-flow facility (Mr. David Braithwaite)
1:20-1:40	High-pressure gasifier (Mr. Aaron Huber)
1:40-2:00	High-pressure reactor for detailed kinetics measurements (Mr. Charles Monson)
2:00-2:30	**Subtask 2g Presentation and Discussion**
2:00-2:05	Introduction (Dr. Scott Brewster)
2:05-2:25	Thermal NO_x model (Mr. Richard Boardman, Ph.D. Candidate, BYU)
2:25-2:35	Discussion
2:35-3:35	**Subtask 3a Presentation and Discussion**
2:35-2:45	Introduction (Dr. Scott Brewster)
2:45-3:05	Devolatilization models (Mr. Mike Hobbs, Ph.D. Candidate, BYU
3:05-3:25	Multiple solids progress variables (Dr. Scott Brewster)
3:25-3:35	Discussion
3:35-3:55	**Break**
3:55-4:50	**Subtask 3b Presentation and Discussion**
3:55-4:05	Introduction (Dr. Scott Brewster)
4:05-4:25	Simplified fixed-bed model (Dr. Sung-Chul Yi, Post-Doctoral Research Associate, BYU)
4:25-4:40	Fixed-bed technology (Dr. Mike Radulovic, Post-Doctoral Research Associate, BYU)
4:40-4:50	Discussion
4:50-5:00	**Wrapup Discussion**
	Friday's agenda

Table LE-1 (continued)

AGENDA FOR JOINT AFR/BYU CONTRACT REVIEW MEETING

FRIDAY, MARCH 25

8:30-8:45	**Welcome and Overview (Dean L. Douglas Smoot, College of Engineering and Technology, BYU)**
8:45-10:10	**Discussion of Fixed-Bed Technical Issues (Dean Smoot, Dr. Peter Solomon, Dr. Scott Brewster, Dr. David Hamblen, Dr. Sung-Chul Yi, Dr. Mike Radulovic)**
	Large particle submodel and interface with comprehensive code
	Datasets (cases to model)
10:10-10:30	**Break**
10:30-12:00	**Discussion of Entrained-Bed Technical Issues (Dean Smoot, Dr. Peter Solomon, Dr. Scott Brewster, Dr. David Hamblen, Mr. Michael Hobbs)**
	Interface between FG/DVC model and PCGC-2
	Integration responsibilities
	Code transfer
	Code version
	Datasets (cases to model)
	Comparison of devolatilization models
12:00-1:00	**Lunch**
1:00-3:00	**Discussion of Administrative Issues (Dean Smoot, Dr. Peter Solomon, Dr. David Hamblen, Dr. Scott Brewster)**
	Budget
	Plans for METC Gasification Contractor's Conference
	Date and plans for Fall contract review meeting
3:00	**Final Wrapup and Adjournment**

d. Consideration will be given to obtaining NO_x data in the transparent wall reactor at AFR to provide a validation data set for the NO_x submodel.

4. Subtask 3a

a. It was decided that the 1987 version of PCGC-2 will be the basic code into which FG/DVC will be integrated.

b. BYU will integrate FG/DVC into 87-PCGC-2, as modified to treat two solids progress variables.

c. BYU will develop a laminar version of PCGC-2 to allow simulation of AFR's laboratory experiments. Comparisons with AFR's data will be used to provide validation of the integrated code.

d. BYU will use the two progress variable version of PCGC-2 to test the integrated code.

The progress on the various subtasks during the past quarter is summarized below.

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

In order to further understand the role played by ion-exchangeable cations on char reactivity, samples of demineralized Zap coal were subjected to ion-exchange with Mg and Ca. Chars were prepared by heating in a TGA at 30°C/min to 900°C or 1000°C and reactivity measurements were done in both air and CO_2. In both gases, the loading of sufficient amounts of Mg or Ca produced a char which was equal or more reactive than chars produced from the raw coal.

Char samples obtained from drop tube experiments done with Pittsburgh Seam coal were prepared for SEM analysis by potting and polishing. The SEM photographs were taken and were analyzed to obtain quantitative information, such as bubble size and wall thickness, which can be used for validation of the viscosity and swelling models. Our preliminary analysis indicates that maceral effects may be important.

Work resumed on the viscosity model. Previously fits were made to the data of Fong and coworkers at MIT. However, the parameter values for the viscosity model needed to be changed significantly from the values used for polymers by van Krevelen, whose model served as the basis for our model. The reasons for this are being investigated.

Work continued on using the FG-DVC model to model the baseline pyrolysis data obtained for the 10 coals from the EFR and TG-FTIR reactors, as well as from FIMS analysis at SRI, International. It was also decided to simulate the available literature data for the Pittsburgh Seam coal, since a lot of work has been done on this coal. Some refinements were made to the treatment of internal and external transport in the model. Work was also done on comparing the FG-DVC model to the statistical model of Pugmire and Grant at the University of Utah which is based on percolation theory.

Entrained flow reactor experiments continued with three coals (Montana Rosebud, Beulah Zap, and Indian Head Zap) at 700, 1100, and 1400°C. The only coal of the set of 10 which has not been run at all is Illinois No. 6, which was recently received. Additional FIMS analysis experiments were done at SRI.

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

Char samples were prepared in the simple hot-tube reactor and in the BYU gasifier. Seven char samples were analyzed along with a sample of Utah bituminous coal. Construction of the high-pressure, controlled-profile reactor continued. Improvements were made in the reactor design to reduce cost and increase reliability. A program was developed to test and characterize the reactor.

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

Data collection was temporarily suspended under this subtask as the FT-IR spectrometer was needed for a different project.

Subtask 2.d. Ash Physics and Chemistry Submodel

SEM/dispersive x-ray analysis was performed on individual ash spheres that were recovered from the eight stages of a cascade impactor for experiments in the Transparent Wall Reactor (TWR) with Zap lignite coal. It was determined that the small particle sizes collected in the impactor may not give quantitative analysis results in our x-ray system. It was decided to modify the instrument conditions and use some pure mineral oxide standards in the appropriate size ranges for calibration.

Subtask 2.e. Large Particle Submodels

The design of the fixed bed reactor system was completed during the past quarter, parts were ordered and construction was begun. This reactor will have on-line analysis of evolved volatile products, functional group composition, and particle temperatures.

Subtask 2.g. SO_x-NO_x Submodel Development

Predictions of thermal NO in the integrated submodel were physically unrealistic. The literature on chemistry/turbulence interactions was reviewed. A new approach at calculating pollutant concentrations with chemistry/turbulence interactions was developed. A sorbent chemistry submodel was evaluated and compared with recent data at short residence time under independent funding at The University of Utah. The chemistry of sulfur in flames was reviewed from the literature.

Subtask 2.h. NO_x/SO_x Submodel Evaluation

Modifications of the cold-flow facility were completed and tests were initiated. Three injection jets for sorbent were found to be more effective than one. Work on modifying the gasifier for sorbent injection tests was continued. Modifications are being made to insert thermocouples and to make FT-IR measurements.

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

Work continued on incorporating the FG-DVC submodel under the SSPV and MSPV methods. Converged solutions were obtained for a combustion case and a gasification case with two progress variables tracking coal offgas. The approaches of tracking volatiles and char oxidation offgas separately and of tracking hydrogen separately from all other elements were both investigated. Results showed that variability in offgas composition, offgas enthalpy, or both, is important. For a swirling combustion case, the use of two progress variables decreased the size and severity of the fuel-rich region. Burnout and gas composition were both significantly affected. The FG-DVC submodel was delivered by AFR to BYU. The comparison of the FG-DVC with other coal reaction submodels continued. Work also continued under independent funding on the development of improved numerical methods and the incorporation into PCGC-2 of a sorbent injection submodel with subsequent chemical interaction with the gas.

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

Equations for an improved fixed-bed model were developed and coding is now approximately 80 percent completed. Physical property and transport correlations applicable to fixed beds were reviewed and documented. Sources of fixed-bed gasifier data were also reviewed and summarized.

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

Work was completed on preparing a version of the FG-DVC model for transfer from AFR to BYU. The time for the combined programs to run varied from 4.5 to 5.5 hours depending on the coal and conditions.

Subtask 4.b. Application of Fixed-Bed Code

No work was scheduled.