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Fossil Fuel Conversion - Measurement and Modeling

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"FOSSIL FUEL CONVERSION - MEASUREMENT AND MODELING"
Contract No. DE-AC21-93MC30040

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1. EXECUTIVE SUMMARY

1.1. PROGRAM BACKGROUND AND DESCRIPTION

Direct utilization of coal, i.e., coal combustion, currently dominates the industrial and utility applications but advanced technologies, based on coal gasification, are emerging as clean and cost competitive alternatives. It was stated in the EPRI Journal recently (J. Douglas, Vol. 15, 4-11 1990): "Coal combustion has provided the bulk of the nation's electric power for over a hundred years. But conventional coal technology based primarily on the use of steam turbines, is nearing its theoretical efficiency limit - - the so-called Rankine barrier. To increase performance further, coal power plants will have to move progressively away from steam-based systems toward advanced generation cycles. A new line of integrated gasification power plants incorporating advanced gas turbines or molten carbonate fuel cells is expected to boost efficiency well beyond today's level of around 37% - efficiency may approach 60% by the year 2020. When fully realized, these advanced plants will co-produce electricity and such valuable chemicals as hydrogen, methanol, and gasoline, while nearly eliminating air emissions and solid wastes."

The DOE Clean Coal Technology (CCT) demonstration program, currently has several demonstration projects on coal conversion technologies. These demonstration projects include a variety of system configurations based on fixed-, fluidized-, and entrained-bed gasifiers with hot and cold gas cleanup processes and pressurized and circulating fluidized-bed combustors. In addition, the Federal Energy Technology Center in Morgantown, WV has supported the construction of a test facility at Wilsonville, AL which employs a transport reactor (circulating fluidized bed) for the gasification and combustion of coal. FETC had also proposed the construction of a Gasification Product Improvement Facility (GPIF) at the Fort Martin Power Plant, Monongalia County, West Virginia. The GPIF would have included an innovative air-blown, dry-bottom, pressurized, fixed-bed coal gasifier. However, that project was ultimately cancelled due to funding constraints.

The previous project, "Measurement and Modeling of Advanced Coal Conversion Processes" (MMACCP), funded by DOE/FETC (Contract #DE-AC21-86MC23075) and also done jointly by AFR and BYU, advanced the state of the art in coal conversion, in general, and in entrained and fixed-bed coal gasification, in particular. Computer aided reactor design software based on that contract is already available. An advanced one-dimensional model of fixed-bed coal gasification, FBED-1, was developed, evaluated, and applied to a number of test cases. Many advances were made: a coal-general devolatilization submodel (FG-DVC), generalized gas phase chemistry, coal-general char reactivity model, equilibrium SO_x/NO_x , variable and overlapping coal reaction zones, variable bed porosity and solid velocity, ash layer effects, and tar production. A methodology was established to determine all the required kinetic and composition parameters for coal using routine laboratory experiments. The first fixed-bed devolatilization submodel was developed and the first large particle oxidation rates at

high pressure were measured. Comprehensive comparisons of temperature and pressure profiles with experimental data were also made.

An advanced version of PCGC-2, a two-dimensional entrained-bed gasification code, which incorporates FG-DVC was also developed. The advanced version has new submodels for laminar flow, turbulence with laminarization, coal devolatilization, char reactivity, char viscosity and swelling, thermal NO_x , sorbent injection, and sorbent/sulfur reactions. Improvements were also made in many existing submodels, most notably the energy equation option for predicting external heat loss, the fuel NO_x submodel, and the radiation submodel. Code predictions were compared with data from several laboratory-scale reactors, and the code was applied to practical-scale processes of interest to FETC.

In order to make these codes more versatile for wider application, further research is needed on a number of issues. These issues include: large-particle devolatilization in fixed-bed reactors; large-particle combustion and gasification in fixed-bed reactors; mixing, heat transfer, and caking in transport reactors; fresh coal and recycle char gasification and sulfur capture in transport reactors; development of an advanced fixed-bed coal gasification model to treat a variety of configurations and modes of operation; development of an advanced transport reactor coal gasification model which is valid for dense flows.

Computer modeling of natural gas combustors is receiving increased attention lately and designers of these combustors are beginning to rely on computer modeling as much as on more traditional tools such as well-established correlations and experiments. BYU has two comprehensive computer codes, PCGC-2 and PCGC-3, that may be considered as starting points for developing a multi-dimensional combustion code. Both codes have been developed primarily to simulate pulverized coal combustion processes. PCGC-2 is axisymmetric and two-dimensional, while PCGC-3 is Cartesian and three-dimensional. Because of the three-dimensional nature of typical gas combustors, PCGC-3 has been selected as a starting point.

In addition, there are a wide variety of commercial processes based on fluidized-bed technology. These reactors take on a variety of forms and bed densities, depending on the velocity of the fluidizing medium. Fluidized beds have several advantages over more conventional technology; fuel flexibility, high combustion efficiency, high heat release rate, good load following capabilities, efficient SO_2 capture, and low NO_x emissions. Many of the previously developed advanced submodels for the chemical and physical behavior of coal during conversion (pyrolysis, viscosity, char combustion, char gasification, etc.) are applicable to fluidized-bed processes. However, the heat and mass transfer processes that are unique to fluidized beds cannot be described by the existing PCGC-2 or FBED-1 codes into which these advanced submodels have been integrated. Consequently, there is a need to upgrade existing fluidized bed codes with these submodels.

1.2. OBJECTIVES

The original objectives of this research project were:

- to provide experimental data on critical processes such as large-particle devolatilization, gasification, and combustion in fixed-bed reactors as well as fresh coal and recycle char gasification and sulfur capture in transport reactors;
- to correlate these data and develop appropriate advanced submodels;
- to develop advanced, more generalized codes for fixed-bed gasification, transport reactor gasification or combustion, fluidized-bed combustion, which will include these submodels;
- to develop an advanced methodology for modeling fuel gas combustion and incorporate the methodology into an advanced code for gas turbine combustors being developed under an independent DOE-funded project;
- to evaluate the advanced codes by comparison with experimental data;
- to apply the advanced codes to systems of interest to FETC;
- to install the 3 advanced reactor codes (fixed-bed, transport, fluid-bed) at FETC and train METC personnel in their use.

1.3. TECHNICAL APPROACH

First, it should be stated that the overall objective of the work was the development of technology to predict fossil fuel conversion behavior in advanced systems. To do this, Advanced Fuel Research, Inc. (AFR) and Brigham Young University (BYU) built on the foundation of models (FG-DVC, PCGC-2 and FBED-1) which were generated under contract DE-AC21-86MC23075, "Measurement and Modeling of Advanced Coal Conversion Processes." This prior project resulted in models which generally predict the results of laboratory and pilot scale conversion reactors. The present project applied these models to reactors to interest to FETC. This required adding increased generality to the fixed bed model (FBED-1) and an extension of the entrained bed model (PCGC-2) to higher solid loadings. In addition, the program enhanced a 3-D gas combustion code, PCGC-3, developed by the NSF Advanced Combustion Engineering Research Center (ACERC), which is based at BYU, and an existing fluidized bed code, MFIX, was selected for integration of advanced submodels. The project focused initially on two reactor systems being supported by FETC, the GPIF reactor to be constructed at the Fort Martin Power Plant and the Transport Reactor to be constructed at Wilsonville. When the GPIF project was cancelled, more emphasis was placed on the Hague Coal Combustor at the Kennebunk Test Facility, however, the project goals are consistent with the modeling of many other fuel conversion systems, including fuel gas

combustors and pressurized fluidized bed coal combustors.

The reactors that were modeled, such as the GPIF, Transport Reactor and Hague Combustor, are extremely complex physical, chemical and heat transfer systems. However, the models were developed for these systems from an established foundation. The FG-DVC model of coal conversion gives an accurate description of the volatile evolution and fluidity of a coal during pyrolysis. This is complemented by a model of temperature and coal-dependent char reactivity. PCGC-2 with FG-DVC provides a good description of the combined coal conversion process under dilute particle loading and FBED-1 with FG-DVC provides a reliable description of fixed-bed coal conversion in one dimensional counter current flow. To model the GPIF and Transport Reactors, we modified the existing codes to extend their range of applications. In the case of PCGC-2, the code was modified to treat the more dense solids loadings of transport reactors, and for the FBED-1 we included co-current solids and gas flow.

PCGC-3 has been subjected to an extensive amount of validation using gas phase combustion data. This code development has been supported by over \$2 million dollars in annual funding by NSF and private companies for the past five years. The MFIX code for fluidized beds has been developed and tested for several years at FETC-Morgantown.

1.4. CRITICAL TECHNICAL ISSUES

To achieve the goals of the project, the computer models must provide accurate and reliable descriptions of fixed-bed, transport reactor, fluidized-bed and gas combustor processes. This required the reduction of very complicated and interrelated chemical and physical processes to mathematical descriptions and subsequently to operational computer codes. To accomplish this objective, a number of critical technical issues were identified in the project work plan:

- large coal particle devolatilization rates;
- large coal particle oxidation and gasification rates at high pressure;
- heat and mass transport limitations of large coal particle devolatilization, oxidation, and gasification rates;
- rates for tar cracking;
- numerical methods for stiff, non-linear problems;
- mixing, heating, and caking processes of coal injected into the transport reactor;
- gasification chemistry of fresh and recirculated char in the transport reactor;

- sulfur capture in the transport reactor;
- validation of the advanced fixed-bed gasification model;
- validation of the advanced 2-D transport reactor gasification model;
- turbulent gas-phase chemistry with an emphasis on predicting CO and NO_x emissions in lean, premixed combustion;
- streamlining the submodels so they can be used efficiently in the 2-D and 3-D fluidized-bed codes;
- validation of the improved fluidized-bed code.

1.5. SUMMARY OF ACCOMPLISHMENTS

Because the funding for this project was significantly curtailed compared to the original contract, not all of the above issues could be addressed. However, there were many significant accomplishments, as outlined below.

Subtask 2.1 – Fixed Bed Devolatilization Processes

The work in this subtask was concentrated on developing a 1-D large particle devolatilization model which integrated our FG-DVC code with a heat transfer code and physical property submodels. Such a model could be used for integration into the Fixed-Bed Gasifier code being developed at BYU, FBED-1, and the Fluidized-Bed Gasifier Code, being developed at FETC, MFIX. Based on a literature review, a standalone heat transfer model for large spherical coal particles was developed first. This numerical model was validated by comparing its predictions of the spatial temperature distribution inside a particle with the exact solutions for simple boundary conditions.

A second step was the simplification of our FG-DVC model for integration with the large particle model. Several options were outlined which had different levels of simplification of the full FG-DVC model and were sent to BYU and FETC-WV for consideration. These options represented a compromise between the predictive capability desired and the corresponding computational complexity. The third step was integration of the heat transfer model and the simplified coal devolatilization model. The fourth step was to also integrate the full FG-DVC model with the heat transfer model, so that comparisons could be made.

The simplified coal devolatilization model, called FG-DVC Reduced Equation Set (RES) was successfully integrated into both the FBED-1 model and MFIX models, but without the heat transfer model. The integration with FBED-1 is discussed under subtask 2.5, while the integration with MFIX is discussed under task 4.

Work was also done on characterization of the coals that would be used in the PyGas™ gasifier and on formulation of a tar cracking submodel that would describe the transformation of tar into soot in fixed bed gasifiers. The three PyGas™ coals (Mettiki, Mapco, Consol) were pyrolyzed at high heating rates in an Entrained Flow Reactor (EFR) and at low heating rates in a TG-FTIR apparatus. The latter experiments revealed a significant effect of particle size on the yields of volatile nitrogen species (NH₃, HCN).

Subtask 2.2 - Fixed-Bed Combustion And Gasification Processes

Experimental data collected in our previous project were analyzed and the results of these analyses were published. A high-pressure controlled profile reactor was modified and improved. Oxidation rates were measured for coals of interest to the PyGas™ project as well as for coals of more general interest. Extensive experiments were performed with char samples at atmospheric and elevated pressures. The results were presented in detail in a thesis; a summary is given in this report. A high-pressure thermogravimetric analyzer was acquired and installed, principally with independent funding.

Subtask 2.3 – Physical Processes in Transport Reactors

Data for turbulent particle dispersion were collected from the literature and used to develop a particle dispersion model. The work on heat transfer was not completed and caking was not addressed.

Subtask 2.4 – Chemical Processes in Transport Reactors

A literature review, survey of ongoing projects and reactor modifications were completed. The experimental work and submodel development were not completed due to funding constraints.

Subtask 2.5. - Advanced Fixed-Bed Model Development And Evaluation

During the period of this contract, work was initiated to improve the existing fixed-bed code, FBED-1 for industrial applications. Additional sensitivity analyses of the FBED-1 model were performed to study the effects of the available submodel options. The effects of the devolatilization submodels, the oxidation and gasification submodels, and the gas phase chemistry options were studied. The governing equations were rederived starting from first principles. Modifications were made in the routines used to evaluate the derivatives to make them consistent with the LSODE solver. The fixed-bed model was extended to handle a cocurrent flow configuration. This modified model was used to simulate the cocurrent and countercurrent sections of the staged PyGas gasifier of the Gasification Product Improvement Facility project; see Subtask 5.1 of this report. The CHEMKIN-II and CHEMKIN-RG packages were obtained from Sandia National Laboratories and the University of Iowa, respectively, and were studied as stand-alone packages.

An additional area of effort during the period of this contract has been the incorporation of a reduced coal devolatilization model, FG-DVC-RES into the FBED-1 computer program. The reasons for incorporation of the reduced model include faster overall execution time and enhanced robustness of the numerical method. Incorporation of FG-DVC-RES into FBED-1 has required extensive modifications to the existing code. Rather than utilizing the detailed description of devolatilization based on the solution of 153 coupled ordinary differential equations, the FG-DVC-RES model uses a description of the volatile mass released, based on the solution of a single ordinary differential equation. All the necessary information (e.g., gas species composition), which would be provided from the full devolatilization model, is then obtained from correlation of the volatile mass released with the results of a previous FG-DVC simulation. Thus, all the parts of the FBED-1 computer code that utilize the functional-group description of coal devolatilization must necessarily be rewritten to accept the format of the reduced model. This resulted in the need to rewrite and restructure significant portions of the FBED-1 code. However, the resulting version, based on the reduced model, is substantially simpler in its coding and requires significantly less CPU time to run.

Subtask 2.6 - Advanced Two-Dimensional Transport Reactor Model Development And Evaluation

A cold flow version of the 2-D transport reactor model was completed and validated against existing data. The hot flow version for reacting particles was not fully developed and validation data from UNDEERC or Wilsonville was unavailable because of Kellogg's proprietary concerns.

Task 3 - Modeling of Gas Phase Combustion

A new, axisymmetric turbulent combustion submodel was developed for lean, premixed combustion in gas turbines. Two reduced mechanisms for methane combustion were evaluated and implemented in the submodel. The submodel was integrated into a comprehensive combustion flow code, and preliminary comparisons were made between predictions and laboratory-scale data.

Task 4 - Modeling of Fluidized Bed Systems

A streamlined version of AFR's FG-DVC model was prepared and sent to FETC-WV for integration into the FETC MFIX code. The initial integration was complete but subsequent testing and evaluation at FETC were incomplete.

Subtask 5.1 - Advanced Fixed-Bed Code Application And Implementation

The FBED-1 code, modified under Subtask 2.5 to include the cocurrent option, was applied to the PyGas™ gasifier. The PyGas™ gasifier was to be tested under the Gasification Product Improvement Facility (GPIF) project.

Subtask 5.2 - Advanced Two-Dimensional Transport Gasification Code Applications and Implementation

Work was begun on applying the code to the UNDEERC and Wilsonville reactors but was stopped because of lack of access to the data. The User's Manual and Code Installation at FETC were not completed since only a cold flow version of the code was validated.

Subtask 5.4 - Modeling of Fluidized-Bed System Applications and Implementation

This task was not completed since Task 4 was also incomplete. The FG-DVC model was integrated in the MFIX Code at FETC by FETC personnel with assistance from AFR. However, further training, application of the combined code and the User's Manual was not completed, since the integrated code development was not complete.

Subtask 5.5 - Applications Of ACERC Combustion And Gasification Codes And AFR Diagnostic Capabilities To Systems Of Interest To METC

The PCGC-3 code was applied to the Hague Coal Combustor. The Hague coal combustor was to be tested under the Externally-Fired Combined Cycle (EFCC) project.

SUBTASK 2.1 FIXED-BED DEVOLATILIZATION PROCESSES

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Objectives

The original objective of this subtask was to correlate and model the effects of temperature and concentration gradients in coal and char particles during pyrolysis (especially of large particles, ≥ 1 cm) and gasification (especially through an ash layer) under conditions typical of fixed-bed coal gasifiers. Selected experimental measurements were to be made to fill in gaps in the available literature data.

Accomplishments

The work in this subtask was concentrated on developing a 1-D large particle devolatilization model which integrated our FG-DVC code with a heat transfer code and physical property submodels. Such a model could be used for integration into the Fixed-Bed Gasifier code being developed at BYU, FBED-1, and the Fluidized-Bed Gasifier Code, being developed at FETC, MFIX. Based on a literature review, a standalone heat transfer model for large spherical coal particles was developed first. This numerical model was validated by comparing its predictions of the spatial temperature distribution inside a particle with the exact solutions for simple boundary conditions.

A second step was the simplification of our FG-DVC model for integration with the large particle model. Several options were outlined which had different levels of simplification of the full FG-DVC model and were sent to BYU and FETC-WV for consideration. These options represented a compromise between the predictive capability desired and the corresponding computational complexity. The third step was integration of the heat transfer model and the simplified coal devolatilization model. The fourth step was to also integrate the full FG-DVC model with the heat transfer model, so that comparisons could be made.

The simplified coal devolatilization model, called FG-DVC Reduced Equation Set (RES) was successfully integrated into both the FBED-1 model and MFIX models, but without the heat transfer model. The integration with FBED-1 is discussed under subtask 2.5, while the integration with MFIX is discussed under task 4.

Work was also done on characterization of the coals that would be used in the PyGas™ gasifier and on formulation of a tar cracking submodel that would describe the transformation of tar into

soot in fixed bed gasifiers. The three PyGas™ coals (Mettiki, Mapco, Consol) were pyrolyzed at high heating rates in an Entrained Flow Reactor (EFR) and at low heating rates in a TG-FTIR apparatus. The latter experiments revealed a significant effect of particle size on the yields of volatile nitrogen species (NH_3 , HCN).

Heat Transfer Model

Heat transfer in a large spherical coal particle model has been studied by a number of investigators (Agarwal et. al, 1983, 1986; Agarwal, 1986; Hajaligol et al., 1988). The mathematical expression of the physical process is as follows:

$$\begin{cases} \rho c \frac{\partial T}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \alpha \frac{\partial T}{\partial r} \right) + H \frac{dp}{dt} \\ -\alpha \frac{\partial T}{\partial r} \Big|_{r=R} = h(T|_{r=R} - T_g) \\ \frac{\partial T}{\partial r} \Big|_{r=0} = 0 \\ T(r, 0) = T^0 \end{cases} \quad (2.1-1)$$

where T is the temperature, c , α , and ρ are the specific heat, the thermal conductivity and the density of the coal, respectively, H is the heat of pyrolysis, h is the surface heat transfer coefficient, r is the radial coordinate, t is the time, and R is the radius of the particle. The initial coal temperature is T^0 , and the gas temperature is T_g . In the absence of pyrolysis, i.e., $H=0$, and with constant α , ρ , and c , Eq. 2.1-1 has an analytical solution given by Jakob (1959). The rate of pyrolysis needs to be provided by a coal devolatilization model which will be addressed later.

Work started with constructing a numerical model of Eq. 2.1-1 with conditions:

$$H=0, \alpha, \rho, \text{ and } c \text{ constant} \quad (2.1-2)$$

so that the numerical solution can be compared with the exact solution. Using the Crank-Nicholson finite difference discretization, we have

$$\begin{aligned} \rho_j^n c \frac{T_j^{n+1} - T_j^n}{\Delta t} &= \frac{\alpha}{r_j^2 \Delta x} \left(r_{j+1/2}^2 \frac{T_{j+1}^{n+1} - T_j^{n+1}}{\Delta t} - r_{j-1/2}^2 \frac{T_j^{n+1} - T_{j-1}^{n+1}}{\Delta t} \right) + H_j k_j (\rho_f - \rho_j^n) \\ &= \frac{\alpha}{r_j^2 (\Delta x)^2} \left[r_{j+1/2}^2 T_{j+1}^{n+1} - (r_{j+1/2}^2 + r_{j-1/2}^2) T_j^{n+1} + r_{j-1/2}^2 T_{j-1}^{n+1} \right] + H_j k_j (\rho_f - \rho_j^n) \end{aligned} \quad (2.1-3)$$

A numerical computer code was developed based on Eq. 2.1-3 and condition 2.1-2. Numerical solutions of Eq. 2.1-1 are compared with the exact solution in Figure 2.1-1. The numerical solution used 50 nodes along the particle radial direction. The computation time on a SPARC-2 workstation is minimal. $Bi=2hR/a$ is the Biot number and can be estimated from the Nusselt number, $Nu=2hR/\alpha_g$, where α_g is the thermal conductivity of the gas phase. In a fluidized bed, Kothari (1967) has correlated Nu to the bed conditions as

$$Nu = 0.03 Re_p^{1.3} \quad \text{for} \quad Re_p < 100 \quad (2.1-4)$$

and for $Re_p < 100$

$$\begin{aligned} Nu &= 2.0 + 0.6 Re_p^{1/2} Pr^{1/3} && \text{(for single particles)} \\ Nu &= 2.0 + 1.8 Re_p^{1/2} Pr^{1/3} && \text{(for fixed beds)} \end{aligned} \quad (2.1-5)$$

where $Re_p = 2Ru\rho_g/\mu_g$ is the particle Reynolds number, $Pr=c\mu_g/\alpha_g$ is the Prandtl number, u is the superficial gas velocity, and μ_g is the gas viscosity.

The numerical solutions with condition 2.1-2 provided a good starting point. Temperature dependent coal properties were eventually incorporated into the code based on Merrick's thermal physical coal model (Merrick, 1983).

FG-DVC Reduced Equation Set (RES) Coal Devolatilization Model

In order to solve Eq. 2.1-1 numerically with Eq. 2.1-2, it is required that the rate equations of coal devolatilization be appropriately expressed and solved along with the heat transfer equation. It is well known that coal devolatilization is a complicated process, and cannot easily be modeled with a single rate equation, especially when the compositions of char, gas, and tar and the amounts of the gas species are desirable. The full FG-DVC model was implemented in the current version of FBED-1 in the previous contract, with which only small isothermal particles can be modeled. Incorporating an intra-particle heat transfer model will require a substantial simplification of the FG-DVC model, in order to reduce the computational burden.

After a careful re-examination of the FG-DVC model, a number of model simplification options were proposed as outlined in Table 2.1-1. These options were constructed based on the following considerations:

1. Devolatilization of individual gas species occurs independently (except for NH_3 , HCN) in the model.
2. Tar and gas evolutions are coupled.
3. Tar evolution is influenced by pressure and heating rates. In order to model the pressure and heating rate dependence, the tar submodel in FG-DVC

Table 2.1-1 Options for Coal Devolatilization Submodel Integration with FBED-1

	Number of equations to solve	Features	Drawbacks
Option 1	1	The total weight loss equation is solved. Other process variables (tar amount, gas species, char composition, rates, etc.) as a function of time are obtained from correlation with the total weight loss.	Needs the standalone FG-DVC to estimate the total weight loss and tar yield at a nominal heating rate and pressure. The correlation is calculated at a given heating rate and pressure. Some error will be introduced when heating rates and pressure change significantly. The evolution of nitrogen gases is especially sensitive to changes in heating rate and pressure in our current model.
Option 2	15	The equations for total gas evolution, tar amount and its molecular weight distribution are solved. Other process variables (gas species, char composition, rates, etc.) as a function of time are obtained from correlation with the total weight loss.	Nitrogen gases are not modeled appropriately (see above).
Option 3	17	The equations for total gas evolution, tar amount and its molecular weight distribution, and nitrogen gases are solved. Other process variables (gas species, char composition, rates, etc.) as a function of time are obtained from correlation with the total weight loss.	
Option 4 Full FG-DVC			Too many equations to solve.

Figure 2.1-1. Temperature distribution inside a coal particle.

must be retained. However, this can be implemented in a pre-processing step, so that the computational burden is not unduly increased.

It was therefore assumed that:

1. The total light gas evolution can be modeled using a single rate equation with a distributed activation energy accounting for multiple gas species contributions.
2. When the tar evolution amount is known from a pre-processing step, it can be treated as another "gas species" in addition to the light gas evolution, so the total volatile evolution can be modeled with a single rate equation.
3. Alternatively, the tar submodel can be solved along with the light gas species model, but it adds an additional computational burden.
4. The amounts of individual gas species can be recovered from correlation with the total volatile or total light gas amounts. This correlation is provided by the full FG-DVC model calculation which is run in a pre-processing step.

In summary, the light gas species can be modeled with a simplified model since these evolve independently, but the tar submodel cannot be easily simplified since the evolution depends on the process conditions (heating rate, pressure). With option 1 in Table 2.1-1, the tar amount is estimated from the preprocessing step with FG-DVC based a nominal heating rate and bed pressure. Tar is then lumped into the total volatile equation and its contribution is modeled via its share in the activation energy distribution. Figure 2.1-2 shows a comparison of the predictions on the instantaneous gas elemental composition by the simplified one-equation model and the full FG-DVC calculation. In the one-equation model, the gas elemental composition is correlated with the total weight loss. The correlation is given by a standalone FG-DVC calculation and is an input to the one-equation model. The comparison is generally quite good. A standalone version of FG-DVC with a Reduced Equation Set (RES) was coded and was tested by comparing the predictions with data and with the predictions of the complete model.

A package containing the FG-DVC-RES source code along with the standalone FG-DVC code and its companion program, COALS, was sent to our colleagues at BYU for testing and integration with FBED-1. It provides two options in obtaining the rates of individual gas species and tar from the rate and the amount of the overall weight loss, which is modeled with one first-order rate equation using a distributed activation energy model. Option number 1 (called the INTERCO subroutine) assumes a constant partition based on the final gas species composition predicted by FG-DVC. Option number 2 (called the INTERC subroutine) uses correlation functions to predict variable gas evolution rates which are also given by a standard FG-DVC calculation. The COALS program is used to interpolate the input files for unknown coals based on those for a set of reference coals based on a method developed by Zhao et al. (1994).

Figure 2.1-2. Instantaneous gas composition predicted by (—) full FG-DVC and (---) one-equation FG-DVC models for Pittsburgh #8 coal heated at 10,000°C/s.

In either case, FG-DVC-RES input files must be generated with FG-DVC calculations at a pre-determined nominal heating rate and pressure. FG-DVC-RES can be used to model coal pyrolysis at similar conditions. However, the nominal conditions provide only an approximate description of the physical conditions under which a coal is pyrolyzed in a reactor, and it is possible that the estimation of the nominal condition may not be accurate. Given such variations, the input files generated at one condition have to remain valid for a range of conditions. This range must be large enough to cover the variations expected in a reactor. Figures 2.1-3 to 2.1-5 present a set of test calculations with FG-DVC-RES and FG-DVC. The FG-DVC-RES input files generated at 5000°C/s and 1 atm were used to simulate pyrolysis of a Pittsburgh seam coal at 1000°C/s, 5000°C/s and 10000°C/s. The results are compared with calculations with the full FG-DVC model at the respective heating rates in Figs. 2.1-3 to 2.1-5. The comparisons are very good at all three heating rates. These results demonstrate that the input files generated at 5000°C/s are valid under pyrolysis conditions which deviate significantly from the nominal conditions. Of course, it is also possible to iterate on the estimation of the nominal conditions until convergence is obtained.

The version of FG-DVC-RES which has been developed requires two input files, a composition file containing composition information and a kinetics file with a distribution function of the activation energy for the total weight loss. The composition file is created by the pre-calculation of the complete FG-DVC model with nominal pyrolysis conditions. A computer code was developed to generate the FG-DVC-RES kinetics file by fitting the weight loss curve generated by the FG-DVC model. This kinetic input file contains the discrete distribution density function of the activation energy for the total coal devolatilization weight loss. A computer code, DAEG (distributed activation energy generator), has been written to generate this file to fit a weight loss curve from either an experimental measurement or a FG-DVC model calculation.

Fig. 2.1-6 displays the fits by DAEG with weight loss curves of eight Argonne coals from our TG-FTIR measurements at 30 °C/min. With DAEG, FG-DVC-RES can now fit almost perfectly the TG-FTIR data or FG-DVC weight loss curves. Fig. 2.1-7 is the discrete distribution function of the activation energy (E/R) used by FG-DVC-RES to produce the fit for the Pittsburgh Seam coal in Fig. 2.1-6. The center of the distribution is at about 27,500 Kelvin, which is consistent with our previous estimations of coal devolatilization kinetics for this coal. This distribution is obviously of a non-Gaussian type, with more fractions appearing in the higher energy portion. The initial version of the DAEG had an option to use a Gaussian distribution, but these generally yield poor fits to the overall weight loss curves.

Fig. 2.1-8 shows a comparison of weight loss curves calculated by FG-DVC-RES with the activation energy distribution in Fig. 2.1-7 and a benchmark FG-DVC calculation for pyrolysis of Pittsburgh Seam coal at 5000 °C/s. The goodness of the fit demonstrates the heating rate independence of the distributed activation energy model. A distribution

Figure 2.1-3. Comparison of predictions by FG-DVC and FG-DVC-RES, 1000°C/s.

Figure 2.1-4. Comparison of predictions by FG-DVC and FG-DVC-RES, 5000°C/s.

Figure 2.1-5. Comparison of predictions by FG-DVC and FG-DVC-RES, 10,000°C/s.

Fig. 2.1-6 Fits produced by DAEG for weight loss curves of eight Argonne Coals (○) TG-FTIR data; (—) Fits.

Fig. 2.1-7 Distribution of the activation energy of Pittsburgh Seam Coal.

Fig. 2.1-8 Weight loss curves calculated with FG-DVC and FG-DVC-RES.

produced at a given heating rate with DAEG can be safely extrapolated to other heating rate conditions.

Figure 2.1-9 shows a comparison of TG-FTIR pyrolysis data obtained at 30 °C/min for the same Pittsburgh No. 8 coal and the predictions of FG-DVC and FG-DVC-RES. In general, the agreement of the two versions for the individual gas species and tar is good and both compare well with the data. The exceptions are the high temperature CO₂ peak, due to carbonate decomposition and the low temperature H₂O peak, which is due to moisture.

A detailed comparison of the INTERC0 and INTERC options of the FG-DVC-RES model was made at BYU and is discussed in detail under subtask 2.5. Both routines were compared with the standalone FG-DVC model at a nominal heating rate of 5000 K/s, which is high for a fixed-bed gasifier and more representative of devolatilization in a fluidized-bed gasifier or combustor. However, these conditions were used to provide a severe test for the model. In general, it was found that, while INTERC0 allows for correct predictions of the total species yields, the early transient behavior shows discrepancies with the standalone model. The opposite result was found with INTERC, i.e., the transient behavior is captured, but the total yields do not always agree.

Another problem that was identified was the noisiness of the evolution rate curves predicted with the INTERC option. When the INTERC option is invoked, it produces several spikes on the rates curves for high heating rate runs, which would cause numerical difficulties when it is integrated with a code like FBED-1. Investigation into this problem has indicated two major sources for the spikes: 1) very rapid changes of the rate of weight loss and 2) the spikes from the tar evolution curves by the FG-DVC model. The weight loss may not be the best choice for being a reference process when modeling high heating rate experiments. A better candidate may be the total gas yield.

The predictions of the FBED-1 model integrated with FG-DVC-RES were compared to the predictions of the standalone FBED-1 model (with full FG-DVC) and the results were found to be in general agreement. There were small differences as discussed under subtask 2.5, but the benefits of the FG-DVC-RES model in terms of simplifying the overall role and reducing the computation time were thought to be significant. Additional work to iron out the problems that were identified with FG-DVC-RES was not possible due to the reduction in funding for this contract.

Integration of the Heat Transfer and the Coal Devolatilization Models

Under this subtask, work was also done to develop a standalone large coal particle devolatilization model (LCPD). The initial version of LCPD (v0.2) was coded by integrating the FG-DVC-RES with the heat transfer model discussed above. This version assumed constant coal physical properties (heat capacity and heat conductivity) and zero heat of pyrolysis, except that the density of the coal was correlated with the pyrolysis weight loss. The results of a sample calculation for 5 mm coal particles and a

Fig. 2.1-9 Comparison of predictions and TG-FTIR data for FG-DVC and FG-DVC-RES.

constant gas temperature of 1000 K are illustrated in Fig. 2.1-10. The coal pyrolysis kinetics are given by FG-DVC based on the Consol #2 coal provided by Riley-Stoker. Figures 2.1-10a-c and f evaluate the effect of the density coupling on the overall pyrolysis process by comparing the results of two calculations, one of which is density coupled (solid lines) and the other which has density decoupled (dashed lines). These calculations indicate that the density variations do not significantly affect the pyrolysis process for a single large coal particle. In Figs. 2.1-10d and 2.1-10e, the pyrolysis rates and temperatures as a function of time are plotted for the surface, the middle layer and the center of the particle, for the density coupled case. In Fig. 2.1-10d, rates are also compared with the average rate of the particle. Fig. 2.1-10a shows the average density vs. time which is equivalent to the weight loss curve. It is evident from both Fig. 2.1-10a and d that these particles lose most of their weight at a constant devolatilization rate. This phenomenon results from the propagating temperature wave toward the center of the particles. The pyrolysis time scale is clearly controlled by the time scale of the heat transfer and, as a result, the rate curve of the weight loss is not characteristically determined by the pyrolysis kinetics. Some small fluctuations in the average rate curve in Fig. 2.1-10d are due to numerical problems, which need to be fixed. Constant coal physical properties were assumed in these calculations.

It is clear that the material at and immediately underneath the surface is exposed to a much higher heating rate than the interior portion of the particle. This variation in heating rate may exceed the range over which the FG-DVC-RES input files are valid. For this reason, the LCPD code was also integrated with our complete FG-DVC model in order to provide a reliable standalone code as a test bed for investigating the phenomenon of large coal particle devolatilization. The integration required that the FG-DVC model be implemented in a differential-equation (DE) form. This formulation and coding of a DE version of FG-DVC proceeded along the lines of a previous DE version developed for the FBED-1 code. This implementation includes all the reactions modeled by our algebraic version of FG-DVC. To model the distributed activation energies for the gas pools, a truncated Gaussian approach is used in the DE version. This approach is similar to the one reported in the FG-DVC section of the FBED-1 user's manual (Solomon, et al, 1993). These two FG-DVC implementations give slightly different results, because of the use of two different approaches for modeling the distributed activation energy. The differences are small and they give comparable predictions when compared with our TG-FTIR data.

The integration of our heat transfer model and the full FG-DVC model was completed, as indicated above. The new code is named LCPD-FGDVC. The LCPD-FGDVC predictions for the pyrolysis of a 5 mm Consol #2 coal particle are presented in Fig. 2.1-11. The heat capacity and thermal conductivity of the coal were variable and were calculated with a model given by Merrick (1983, 1987). The external heat transfer coefficient was estimated with a correlation by Kothari (1967) and was based on the conditions specified for the PyGas reactor. The number was about 10 times smaller than the value we used in the previous simulation (Fig. 2.1-10). Merrick's model also predicts a lower thermal conductivity. These new values should give a more realistic

Fig. 2.1-10 Pyrolysis of a 5 mm Consol #2 particle predicted by LCPD-RES model. The gas temperature was 1000 K (727°C).

Fig. 2.1-11 Pyrolysis of a 5 mm Consol #2 particle predicted by LCPD-FGDVC. The gas temperature was 900°C.

description of the pyrolysis conditions and properties of the coal particles in PyGas. The gas temperature was 900°C and the gas pressure was 600 psi. Because of the small external heat transfer coefficient, the surface heat-up is not as fast as in the previous simulation (Fig. 2.1-10) and the pyrolysis rates at the surface and in the center show only small differences (Fig. 2.1-11d). Once again, the total pyrolysis rate of the particle has a "flat" shape and is controlled by the heat transfer. Within the 20 second residence time, the pyrolysis of the particle is almost completed.

To integrate the large coal particle submodel into FBED-1, the submodel must be numerically simple while retaining reasonable physical sophistication. It is expected that the submodel will use an average particle temperature passed from FBED-1. It is not clear at this point how FBED-1 will model the internal heat transfer of large particles. With the current FBED-1 model, there is no intra-particle temperature gradient calculated and coal particles are assumed to be isothermal. If this approach remains, we will have an average particle temperature such as that in Fig. 2.1-11f, which will be passed to the submodel to predict the pyrolysis of the large particles. It is important to identify the extent to which this approach will affect the predictions for large particle devolatilization. As a test, the average particle temperature in Fig. 2.1-11f was used to simulate the pyrolysis of this 5mm particle with FG-DVC. The total weight loss curve (normalized average density) of this simulation was plotted in Fig. 2.1-11a to be compared with the result of LCPD-FGDVC. At the end of the 20 second residence time, both calculations gave almost the identical total weight loss. However, Fig. 2.1-11a indicates a difference in the instantaneous pyrolysis rates predicted by the two calculations. It is concluded that, if FBED-1 provides an accurate estimate of average particle temperature, FG-DVC or FG-DVC-RES are still applicable submodels, although modifications to the submodels may be necessary to match the rates calculated by LCPD-FGDVC.

It is also of interest to investigate the effect of variable coal physical properties, as specified by Merrick's model, on the particle pyrolysis. Figure 2.1-12 plots the total weight loss curves by LCPD-FGDVC with Merrick's model and other four sets of constant properties which are listed in Table 2.1-2. It is evident that coal physical properties play an important role in large particle pyrolysis. In all the calculations reported here, the heat of pyrolysis was assumed to be zero.

Table 2.1-2. Coal physical properties used in Figure 2.1-12.

Case	Thermal Conductivity, W/Km	Cp, J/kgK
1	0.677	2380
2	0.324	2536
3	0.677	2536
4	0.677	1500

Fig. 2.1-12 Pyrolysis weight loss of a Consol #2 coal. Gas temperature 900°C.

Predictions for the LPCD-FGDVC model predictions were compared with experimental data in the literature for model verification. Morris and Keairns (1979) studied three American coals at high pressure (10 atm) in a laboratory small scale fluidized-bed facility with inert fluidizing gas. They reported 50% and 95% methane devolatilization times, corrected for in-bed gas dispersion, for an Indiana coal. Fig. 2.1-13 compares the model predictions with data on the variation of the methane devolatilization time with mean particle size. The model predicts quite well the 50% methane devolatilization time. The slight under-prediction of the 95% time is believed to be caused by the fact that coal particles used in the experiment had a range of particle sizes, which is not accurately described by an arithmetic mean particle size. This is more clearly shown when the in-bed methane concentration is predicted and compared with the uncorrected off-gas data in Fig. 2.1-14. The time lag between the predicted and measured curves could arise from gas dispersion between the bed and the outlet. However, the contribution from larger particles in the size range could also lead to longer devolatilization times. Morris and Keairns measured the dispersion time with a tracer method, and showed that the minimum dispersion time is 3 seconds. Since their off-gas data in Fig. 2.1-14 indicate that methane starts to be collected at the outlet as early as 1 second after coal addition, it is not clear how this information can be used to correct the off-gas data to derive the in-bed concentration. Given these uncertainties, the model predicts well both the evolution rate and the ultimate yield of methane of the large particles.

The heat transfer rates to coal particles in fixed and fluidized bed are difficult to model accurately. Many investigators have reported correlations to calculate Nusselt numbers from particle Reynolds numbers. The heat transfer coefficients given in the literature vary by several orders of magnitude. Gunn (1978) summarized those data and proposed a more generalized correlation which was implemented in our model.

The LPCD-FGDVC model predictions were also compared with data by Stubington and Sumaryono (1984). The predictions are in good agreement with data at 950 °C. However, the model predictions have large discrepancies with data at 740 °C and 850 °C. On the other hand, the temperature variation of the devolatilization time given by Morris and Keairns (1979) is correctly predicted by our model. The reason for the discrepancy with the former data set is not clear and needs to be further investigated. This may result from the difficulty in accurately specifying the heat transfer coefficient.

The heat transfer from hot bed materials to the cold coal particles also needs to be considered. This type of heat transfer has not been properly accounted in the heat transfer coefficients in the literature. These coefficients deal with the heat transfer between the gas and solid phases in these beds, both of which are assumed to be isothermal and homogeneous. This assumption is not necessarily true in fluidized beds due to the extensive mixing of not only gas and solids but also solids and solids. The cold, newly added solids are mixed quickly with hot, already-in-bed solids and therefore particles at the same location in the bed can have different temperatures. This is especially the situation in the experiments of Morris and Keairns (1979) and Stubington

Fig. 2.1-13 Predicted and measured CH_4 devolatilization times as a function of particle size.

Fig. 2.1-14 In-Bed CH_4 concentration in a fluidized bed with an Indiana HVC coal. Particle diameter = 1.55 mm. Data from Morris and Kearns (1979).

and Sumaryono (1984), in which a small number of coal particles were added into fluidized beds with controlled temperatures. In order to model this effect, we used an effective pressure in evaluating the heat transfer coefficient:

$$P_{\text{eff}} = P + 10 \text{ (atm)} \quad (2.1-6)$$

where P is the actual gas pressure in the bed. This approach is crude and more rigorous treatments are needed. Solids-to-solids heat transfer in a bed involves both radiation and conduction. The radiation is governed by the Stefan-Boltzmann law and can be readily modeled.

The LCPD-FGDVC model in its final form incorporated many improvements over the initial version, discussed above. It uses a more accurate correlation for convective surface heat transfer in fixed and fluidized-bed conditions. It also considers, in addition to convective heat transfer, the radiative heat transfer to coal particles, which appears to be not negligible. The model was validated with data from large coal particle devolatilization experiments which have been collected from the literature. The data used for validation are of three types, 1) particle center temperatures measured with a fine thermocouple, 2) total weight loss measured with a TGA, and 3) individual gas concentrations from devolatilization in a fluidized bed. The so-called 95% or 90% devolatilization time, frequently reported in the literature in studies of large coal particles, was found to be of little value in our task because of the difficulty in its determination.

Fig. 2.1-15 compares the measured and predicted particle center temperatures for an Arkwright coal of three particle sizes. As can be seen in the figure, the predictions match very well the measured data. The upward turn of the measured temperature that occurs in the later stages of devolatilization is due to the contraction of the coal particles. This type of contraction has, however, not been observed in fixed and fluidized beds, and is believed to be related to the features of this experiment, in which a coal particle was held by the fine thermocouple inserted into the particle. The measured and predicted total weight loss of a coal particle during pyrolysis are compared in Fig. 2.1-16.

In making the predictions shown above, we have used a consistent set of parameters. The coal elemental composition, coal particle size, reactor gas temperature and pressure are the only inputs required by the model. A coal database is used to construct the input files necessary for the FG-DVC model. The LCPD-FGDVC model is described in the paper by Zhao et al., (1996).

Characterization of PyGas™ Coals

A study of coal pyrolysis and gasification behavior relevant to the PyGas™-reactor operation was also done. Samples of three coals were received from the Riley-Stoker Corporation for which elemental analysis was available. Initial experiments involving

d=16 mm

d=13.5 mm

d=10.2 mm

Fig. 2.1-15 Particle temperature of an Arkwright coal particle heated in a Tubular Reactor (non-radiative). Reactor Temperature = 650°C. Data from Adesanya and Pham (1995).

Fig. 2.1-16 Weight loss of a coal particle (weight ≈ 12.6 g) at 900°C (Gas Temperature). Data from Peeler and Poynton (1992).

low heating rate pyrolysis were completed using a TG-FTIR system. Moisture and ash contents as well as char reactivity experiments were done for all of the coals.

A number of pyrolysis runs were carried out in an entrained-flow reactor (EFR) using the coals provided by Riley. Material balance closure was found to be poor, which led to a thorough examination of the system. The reactor was completely disassembled and several ceramic parts had to be replaced. In addition to the repairs of refractory parts, two important changes were made. During the disassembling procedure, it was observed that there was a large dead volume (about 100 liters) that was not easily purged. It was also observed that the temperature measurement was performed by a thermocouple that was exposed directly to the heaters. Thus, during the repair these two problems were corrected. An additional purge line for the dead volume was installed. Two additional thermocouples were added to the system; one was embedded in the alumina chips in the preheater and the other one was placed in contact with the test tube in such a manner so that it would not be directly exposed to either the heaters or the preheater.

Five Entrained Flow Reactor (EFR) runs were carried out in the rebuilt system with the three coals supplied by Riley. The mass balances indicated an excess of water, and the reactor was re-examined to identify the problem. It was found that the water-cooled char collector was leaking, and that part of the system was sent to a mechanical shop for repair. Although the collected EFR data are not completely reliable, the observed trends in the pyrolysis yields were found to be similar to those obtained for Argonne Premium coals of the same rank. Using low heating rate pyrolysis data from TG-FTIR experiments, FG-DVC input files were created for the Consol, Mapco, and Mettiki coals. The code was then run for the conditions similar to those of the EFR experiments, and the results for the Mapco coal are shown in Fig. 2.1-17. It can be seen that, as expected, the FG-DVC model predicts a higher tar yield for the high heating rate conditions. The EFR experimental data show that the actual tar yield is appreciably lower, whereas the yield of gas is higher than the model predictions. This can be interpreted as a result of secondary-pyrolysis reactions (tar cracking), which certainly occur during the EFR runs, and which are not yet completely described by the FG-DVC model.

A study of the effect of particle size on pyrolysis yields and on the evolution of nitrogenous species (HCN and NH_3) was initiated. Pyrolysis of Mettiki coal was carried out in the TG-FTIR apparatus using small and large particle sizes ($d_p < 150 \mu\text{m}$ and $d_p \sim 5 \text{ mm}$). The results of these runs are presented in Figs. 2.1-18 to 2.1-23. They show a somewhat larger char yield for the large particles at the expense of a lower gas yield. This may be due to retrograde reactions, although the effect is rather small.

In contrast, a strong influence of particle size on nitrogen evolution from Mettiki coal has been observed. In Fig. 2.1-23a, HCN and NH_3 evolution curves are shown for the particle-size range $0\text{-}150 \mu\text{m}$. As in the previous study of nitrogen release (Bassilakis

Fig. 2.1-17 Comparison of product yields for slow (TG-FTIR) and high (EFR) heating rate pyrolysis (Mapco coal). The FG-DVC model predictions are for a particle temperature of 850°C and heating rate of $5,000^{\circ}\text{C/s}$.

Fig. 2.1-18 TG-FTIR pyrolysis data for major species for Mettiki coal, $d_p < 150 \mu\text{m}$ (wt.% as received basis, heating rate $30^\circ\text{C}/\text{min}$, moisture content 1.5%, and ash content 9.9%).

Fig. 2.1-19 TG-FTIR pyrolysis data for minor species for Mettiki coal, $d_p < 150 \mu\text{m}$ (wt.% as received basis, heating rate $30^\circ\text{C}/\text{min}$, moisture content 1.5%, and ash content 9.9%).

Fig. 2.1-20 TG-FTIR pyrolysis data for major species for Mettiki coal, $d_p \approx 5$ mm (wt.% as-received basis, heating rate $30^\circ\text{C}/\text{min}$, moisture content 0.07%, and ash content 12.9%).

Fig. 2.1-21 TG-FTIR pyrolysis data for minor species for Mettiki coal, $d_p \approx 5$ mm (wt.% as-received basis, heating rate $30^\circ\text{C}/\text{min}$, moisture content 0.07%, and ash content 12.9%).

Fig. 2.1-22 The effect of particle size on product yields during slow heating rate pyrolysis at $30^{\circ}\text{C}/\text{min}$ for Mettiki coal.

Fig. 2.1-23 Comparison of nitrogen evolution patterns for different size particles during pyrolysis of Mettiki coal: (a) $d_p < 150 \mu\text{m}$; (b) $d_p \approx 5 \text{ mm}$.

et al., 1993), a bimodal NH_3 evolution pattern can be seen. This was hypothesized to correspond to the primary and secondary ammonia release, as illustrated in Fig. 2.1-24. According to the proposed model (Bassilakis et al., 1993), coal-bound nitrogen (coal-N) is first released as HCN and (primary) ammonia, and this stage is followed by HCN hydrogenation on the char surface to form secondary ammonia as a product. If this mechanism is correct, then an increase in particle size, and thus also in gas residence time within the particle, would lead to an increase in secondary- NH_3 release at the expense of the HCN peak. The primary ammonia peak should remain unchanged as it is not affected by an increase in the gas diffusion path length within the particle. This is precisely what is seen in Fig. 2.1-23b. It should also be noted that the release of secondary- NH_3 and HCN occurs at the same time, which further supports the proposed mechanism. The heterogeneous HCN-to- NH_3 conversion scheme is in contrast to the gas-phase HCN hydrogenation mechanism suggested by Baumann and Möller (1991). If the HCN-to- NH_3 conversion were a gas-phase reaction, then it would be difficult to justify its particle-size dependence, unless H_2 evolution happens to be particle size dependent. The collected data certainly provide strong evidence in favor of the heterogeneous scheme.

In order to help confirm this conclusion, pyrolysis of the Mapco and Consol coals was also carried out in the TG-FTIR apparatus using both small and large particle sizes ($d_p < 150 \mu\text{m}$ and $d_p \gg 5 \text{ mm}$). In addition, runs involving somewhat larger samples of small-size particles were also carried out ($d_p < 150 \mu\text{m}$; $m_s = 57\text{-}59 \text{ mg}$ versus the standard $18\text{-}22 \text{ mg}$) because of the relatively low sensitivity of the detector for HCN and also so that the particle size effects could be examined on an equal sample size basis. The results of these runs are presented in Figs. 2.1-25 to 2.1-38, and are summarized in Table 2.1-3 (the table includes the Mettiki-coal data collected in the previous reporting period).

The strongest effect of particle size has been found for the evolution of nitrogen (NH_3 and HCN). The experiments carried out using Mapco and Consol coals confirmed the data collected with Mettiki coal (see the previous monthly report). In Figs. 2.1-37 and 2.1-38, HCN and NH_3 evolution curves are shown for the particle-size range $0\text{-}150 \mu\text{m}$, and for a five-millimeter coal particle. As in the case of the Mettiki coal and in the previous study of nitrogen release (Bassilakis et al., 1993), a bimodal NH_3 evolution pattern was found. This is attributable to the primary and secondary ammonia release (the low- and high-temperature NH_3 peaks, respectively), as discussed above. The peaks shown in Figs. 2.1-37 and 2.1-38 show that the release of secondary- NH_3 and HCN occurs at the same time, which is in agreement with the proposed mechanism. Data presented in Figs. 2.1-37 and 2.1-38, as well as those in Fig. 2.1-23 show that an increase in particle size, and thus also in gas residence time within the particle, leads to an increase in secondary- NH_3 release at the expense of the HCN peak. The primary NH_3 peak remains unchanged as it is not affected by an increase in the gas diffusion path length within the particle. For five-millimeter particles, the slight shift in the peak positions towards higher temperatures is a result of heat-transfer effects. The collected

Table 2.1-3. TG-FTIR pyrolysis data.

	Mapco			Consol			Metiki		
d _p (mm)	< 0.150	< 0.150	~ 5	< 0.150	< 0.150	~ 5	< 0.150	< 0.150	~ 5
m _s (mg)	21.63	57.33	53.61	18.31	58.08	46.2	16.32	60.49	54.12
T _{crit} (°C) (11 wt%/min)	560			629			662		
pyrolysis product	Yield (wt% coal, daf)			Yield (wt% coal, daf)			Yield (wt% coal, daf)		
moisture*	3.2	0.86	2.8	1.1	0.98	0.05	1.5	0.81	0.07
ash*	9.1	10.9	2.0	11.3	11.5	11.9	9.9	11.2	12.9
char	59.7	61.8	60.5	59.8	62.4	62.3	73.8	77.5	79.7
tar	21.1	20.5	24.2	24.9	13.4	22.2	10.7	10.6	9.7
total gas	18.3	17.0	15.5	15.3	24.2	15.1	13.8	11.8	9.6
CH ₄	3.4	2.9	3.5	4.2	3.65	3.9	4.1	3.6	3.9
H ₂ O (pyr.)	6.6	8.0	7.4	4.7	5.4	8.0	4.4	4.0	3.7
CO ₂	2.4	1.5	1.05	2.2	1.4	0.89	1.6	1.2	0.48
CO	5.2	3.9	2.9	3.3	2.3	1.9	2.8	1.9	1.1
SO ₂	0	0.07	0	0.21	0	0	0.46	0.49	0
C ₂ H ₄	0.43	0.35	0.28	0.33	0.31	0.19	0.36	0.35	0.21
NH ₃	0.14	0.14	0.18	0.10 [†]	0.16	0.17	0.07 [†]	0.08	0.11
HCN	n.d.	0.09	0.06	n.d.	0.07	0.05	n.d.	0.05	0.02
COS	0.13	0.06	0.08	0.26	0.11	0.06	0	0.13	0.11

* as received

† noisy signal

Fig. 2.1-24 Model for nitrogen evolution from coal during pyrolysis.

Fig. 2.1-25 TG-FTIR pyrolysis data for major products for Mapco coal, $d_p < 150 \mu\text{m}$, (wt.% as – received basis; $m_s = 21.63 \text{ mg}$, heating rate 30°C/min , moisture content 3.2%, and ash content 9.1% as received).

Fig. 2.1-26 TG-FTIR pyrolysis data for minor products for Mapco coal, $d_p < 150 \mu\text{m}$, (wt.% as – received basis; $m_s = 21.63 \text{ mg}$, heating rate 30°C/min , moisture content 3.2%, and ash content 9.1% as received).

Fig. 2.1-27 TG-FTIR pyrolysis data for major products for Mapco coal, $d_p < 150 \mu\text{m}$, (wt.% as - received basis; $m_s = 57.33 \text{ mg}$, heating rate 30°C/min , moisture content 0.86% , and ash content 10.9% as received).

Fig. 2.1-28 TG-FTIR pyrolysis data for minor products for Mapco coal, $d_p < 150 \mu\text{m}$, (wt.% as-received basis; $m_s = 57.33 \text{ mg}$, heating rate 30°C/min , moisture content 0.86% , and ash content 10.9% as received).

Fig. 2.1-29 TG-FTIR pyrolysis data for major products for Mapco coal, $d_p \approx 5$ mm, (wt. % as-received basis; $m_s = 53.61$ mg, heating rate $30^\circ\text{C}/\text{min}$, moisture content 2.8%, and ash content 2.0% as received).

Fig. 2.1-30 TG-FTIR pyrolysis data for minor products for Mapco coal, $d_p \approx 5$ mm, (wt.% as-received basis; $m_s = 53.61$ mg, heating rate $30^\circ\text{C}/\text{min}$, moisture content 2.8%, and ash content 2.0% as-received).

Fig. 2.1-31 TG-FTIR pyrolysis data for major products for Consol coal, $d_p < 150 \mu\text{m}$, (wt.% as-received basis; $m_s = 18.31 \text{ mg}$, heating rate 30°C/min , moisture content 1.1%, and ash content 11.3% as received).

Fig. 2.1-32 TG-FTIR pyrolysis data for minor products for Consol coal, $d_p < 150 \mu\text{m}$, (wt.% as-received basis; $m_s = 18.31 \text{ mg}$, heating rate 30°C/min , moisture content 1.1%, and ash content 11.3% as received).

Fig. 2.1-33 TG-FTIR pyrolysis data for major products for Consol coal, $d_p < 150 \mu\text{m}$, (wt.% as-received basis; $m_s = 58.08 \text{ mg}$, heating rate 30°C/min , moisture content 0.98%, and ash content 11.5% as received).

Fig. 2.1-34 TG-FTIR pyrolysis data for minor products for Consol coal, $d_p < 150 \mu\text{m}$, (wt.% as-received basis; $m_s = 58.08 \text{ mg}$, heating rate 30°C/min , moisture content 0.98%, and ash content 11.5% as received).

Fig. 2.1-35 TG-FTIR pyrolysis data for major products for Consol coal, $d_p \approx 5$ mm, (wt.% as-received basis; $m_s = 46.2$ mg, heating rate $30^\circ\text{C}/\text{min}$, moisture content 0.05%, and ash content 11.9% as received).

Fig. 2.1-36 TG-FTIR pyrolysis data for minor products for Consol coal, $d_p \approx 5$ mm, (wt.% as-received basis; $m_s = 46.2$ mg, heating rate $30^\circ\text{C}/\text{min}$, moisture content 0.05%, and ash content 11.9% as received).

Fig. 2.1-37 Comparison of nitrogen evolution patterns for different size particles during pyrolysis of Mapco coal: (a) $d_p < 150 \mu\text{m}$; (b) $d_p \approx 5 \text{ mm}$.

Fig. 2.1-38 Comparison of nitrogen evolution patterns for different size particles during pyrolysis of Consol coal: (a) $d_p < 150 \mu\text{m}$; (b) $d_p \approx 5 \text{ mm}$.

data provide strong evidence in favor of the heterogeneous scheme of secondary NH_3 formation from HCN.

As part of the investigation of the mechanisms for the formation of NO_x pollutant precursors (HCN and NH_3) during coal devolatilization, TG-FTIR data for 19 coal samples have been analyzed. The coals investigated included 8 Argonne coals, 3 coals that were scheduled to be used in the PyGas gasifier (Consol, Mettisei, Mapco), and 4 Australian coals. The data were collected at $30^\circ/\text{min}$ to 900°C (holding for 4 minutes) under atmospheric pressure and helium sweep gas. The tested samples were all particle size fractions which were -200 mesh.

The nitrogen contents of the coals are plotted as a function of carbon content in Fig. 2.1-39. There appears to be a relationship between nitrogen content and coal rank. The nitrogen content increases with rank to a maximum for coals with about 88-85% carbon and decreases with a further increase of rank. The gaseous nitrogen, excluding tar nitrogen, consists of mainly HCN and NH_3 . The amount of atomic nitrogen, N_2 , is believed to be negligible and is ignored in our analysis. The amount of gaseous nitrogen measured for each coal is normalized by the corresponding coal nitrogen content and is plotted against carbon content in Fig. 2.1-40. The data show that the percentage of nitrogen liberated during devolatilization has a decreasing trend with increased rank. It is consistent with our previous conclusion based on the Argonne coals. Figure 2.1-41 illustrates the variation of the normalized amount of nitrogen evolved as HCN with coal rank. The data are scattered, although the amounts tend to be lower for higher rank coals. The normalized amount of nitrogen in NH_3 , however, has a very regular variation with coal rank, as shown in Fig. 2.1-42. Coals with higher ranks release less NH_3 in devolatilization under our experimental conditions.

As discussed above, we have postulated a coal nitrogen release model that attributes a major portion of NH_3 to a secondary reaction of HCN with hydrogen on the char internal pore surface. We have also shown good agreement of our own data and literature data with the model. Based on this model, one would expect a correlation between the yields of HCN and NH_3 . For the coals we studied here, there is a generally a consistent coal-to-coal variation in the yields of HCN and NH_3 , as shown in Figs. 2.1-40 to 2.1-42. But the trends shown in Figs. 2.1-41 and 2.1-42 also indicate that there exist additional factors limiting the formation of NH_3 .

TG-FTIR data on nitrogen evolution from coal during pyrolysis were examined to see whether HCN and NH_3 release patterns could be related to coal rank or nitrogen functionality. Information on nitrogen speciation in the parent coal as determined by X-ray Photoelectron Spectroscopy (pyrrolic, pyridinic, and quaternary nitrogen) has been obtained from Kelemen et al. (1994) and Nelson et al. (1992). Fifteen coals were examined, and the data are presented in Table 2.1-4. The dependence of nitrogen functionality on coal rank is shown in Fig. 2.1-43. It can be seen that the predominant functional form of nitrogen in coal is pyrrolic-N, and that its dependence on coal rank is

Table 2.1-4. TG-FTIR data on nitrogen evolution from coal during low heating rate pyrolysis (wt % coal, daf, unless stated otherwise).

Coal	Elemental Analysis								Nitrogen Functionality (%)			Amount of Gas-N Released during Pyrolysis (g N/ g original coal, daf)			
	Moisture ^a	Ash ^b	VM ^b	C	H	N	S	O ^c	N-5	N-6	N-Q	HCN	NH ₃ (1)	NH ₃ (2)	HCN + NH ₃
Beulah-Zap	32.24	9.72	44.94	72.94	4.83	1.15	0.70	20.34	59	25	16	0.057	0.047	0.068	0.172
Wyodak-Anderson	28.09	8.77	44.73	75.01	5.35	1.12	0.47	18.02	60	25	15	0.053	0.048	0.059	0.160
Illinois #6	7.97	15.48	40.05	77.67	5.00	1.37	2.38	13.51	62	26	12	0.043	0.033	0.091	0.167
Blind Canyon	4.63	4.71	45.84	80.69	5.76	1.57	0.37	11.58	55	31	14	0.057	0.032	0.100	0.189
Lewiston-Stockton	2.42	19.84	30.17	82.58	5.25	1.56	0.65	9.83	60	31	9	0.034	0.030	0.094	0.158
Pittsburgh #8	1.65	9.25	37.82	83.20	5.32	1.64	0.89	8.83	61	32	7	0.022	0.035	0.097	0.154
Upper Freeport	1.13	13.18	27.45	85.50	4.70	1.55	0.74	7.51	65	28	7	0.017	0.022	0.085	0.124
Pocahontas #3	0.63	4.77	18.60	91.05	4.44	1.33	0.50	2.47	64	33	3	0.019	0.012	0.046	0.077
Bayswater	2.49	12.08	39.8	83.59	5.35	1.88	1.10	8.08	54	29	17	0.093	0.022	0.102	0.217
Bulli	0.84	13.57	23.8	87.43	4.63	1.71	0.32	5.91				0.067	0.045	0.070	0.182
Curragh	0.93	11.16	20.3	88.54	4.67	1.85	0.48	4.46				0.083	0.020	0.071	0.174
Scotts Creek	1.46	12.98	16	88.66	4.57	2.05	0.57	4.15				0.052	0.026	0.081	0.159
Consol #2	5.8	11.2	35.8	84.8	5.65	1.49	2.00	6.06				0.036	0.026	0.106	0.168
Mapco #2	5.9	8.3	37.8	83.2	5.45	1.49	0.78	9.08				0.047	0.020	0.095	0.162
Mettiki #2	4.6	13.8	18.8	89.56	4.76	1.37	1.97	2.34				0.026	0.021	0.045	0.092

^a as-received basis

^b dry basis

^c by difference

Notation:

N-5 percentage of pyrrolic nitrogen
N-6 percentage of pyridinic nitrogen
N-Q percentage of quaternary nitrogen
NH₃ (1) primary ammonia (low-temperature NH₃ peak)
NH₃ (2) secondary ammonia (high-temperature NH₃ peak)

TG-FTIR Experimental Conditions:

particle size: < 75 μ m (- 200 mesh)
sample size: 15-80 μ g
purge gas: helium at 250 ml/min.
heating rate: 30 °C
maximum temperature: 900 °C
hold time: 4 min.

Fig. 2.1-39 Relationship between coal nitrogen and carbon contents.

Fig. 2.1-40 Variation of gaseous nitrogen as a function of coal carbon content.

Fig. 2.1-41 Variation of HCN yield as a function of coal carbon content.

Fig. 2.1-42 Variation of NH₃ yield as a function of coal carbon content.

Fig. 2.1-43 Nitrogen functionality versus coal rank.

rather weak. Pyridinic nitrogen seems to increase as coal rank increases, whereas the percentage of quaternary nitrogen strongly declines with increasing rank.

In Figure 2.1-44, the evolution of HCN and NH_3 during coal pyrolysis is shown as a function of coal rank. As expected, the amounts of both species decrease as coal rank increases. The scatter of data in the carbon-content range of 83–89% is caused mainly by unusually high HCN levels observed in the case of four Australian coals (Bayswater, Bulli, Curragh, and Scotts Creek). Primary and secondary ammonia ($\text{NH}_3(1)$ and $\text{NH}_3(2)$, respectively) exhibit similar decreasing trends with coal rank (Fig. 2.1-45). The scatter in the $\text{NH}_3(2)$ data could be explained by our hypothesis that secondary ammonia is formed by heterogeneous hydrogenation of HCN, and thus depends on both HCN evolution and the inventory of active hydrogen sites on the char surface.

No clear trends in HCN and NH_3 evolution patterns were observed as a function of the percentage of pyrrolic or pyridinic forms, but HCN and NH_3 seem to correlate with quaternary nitrogen (Fig. 2.1-46). It is not clear, however, whether this is an inherent trend, or just a result of the correlation between quaternary-N and coal rank (see Figs. 2.1-43, 2.1-44, and 2.1-46).

A paper entitled "Predictive modeling of the evolution of NO_x precursors from coal" was presented at an Engineering Foundation conference *The Economic and Environmental Aspects of Coal Utilization VI* in Santa Barbara, CA, 29 January - 3 February, 1995 (Wójtowicz et. al., 1995a). Another paper, "Modeling of HCN and NH_3 released during coal pyrolysis," was accepted for presentation at the 8th International Conference on Coal Science that was held in Oviedo, Spain, in September 1995 (Wójtowicz et. al., 1995b).

Modeling of Tar Cracking

In order to help formulate a tar cracking submodel, data for tar and gas yields from moving-bed gasifiers compiled in an EPRI report (Thimsen and Maurer, 1990), together with data from pyrolysis in the TG-FTIR apparatus, were analyzed. The TG-FTIR data was obtained under an inert atmosphere (helium) at a heating rate of $30^\circ\text{C}/\text{min}$. In the case of the gasifiers, atmospheric and high pressure data were available. In addition, a range of oxidant/coal and steam/coal ratios had been used, leading to a spread in experimental values. These data are shown in Fig. 2.1-47.

For coals of carbon content 79-83 %, a significant decrease in tar (~ 11 -16 % on a dry ash free coal basis, dafc) is observed between the TG-FTIR results and data from atmospheric pressure gasifiers, and an additional decrease (~ 7 -11 % dafc) is observed between the atmospheric and the pressurized gasifier conditions. The variations for lower rank coals (~ 70 -77 % carbon) are lower, not exceeding 10 % dafc between the TG-FTIR tar yields and the atmospheric pressure gasifier tar yields, and being almost nil between the atmospheric and pressurized gasifier tar. Based on a previous study (Solomon, et. al., 1993), it was concluded that the reduction in tar can come from

Fig. 2.1-44 Evolution of HCN and NH₃ during slow heating rate pyrolysis (TG-FTIR data).

Fig. 2.1-45 Evolution of primary ammonia (NH_3 (1)) and secondary ammonia (NH_3 (2)) during slow heating rate pyrolysis (TG-FTIR data).

Fig. 2.1-46 Evolution of HCN and NH₃ during slow heating rate pyrolysis as a function of the percentage of quaternary nitrogen in coal (TG-FTIR data).

No recycled tar data included

Fig. 2.1-47 Tar yields as a function of coal carbon content for atmospheric gasifiers, high pressure gasifiers, and TG-FTIR apparatus.

several processes: 1) tar cracking, 2) tar repolymerization, 3) tar gasification, 4) in-situ oxidation of the coal leading to low tar yields. Tar cracking has been shown to occur between 800 and 1000°C. Extraparticle tar repolymerization as an explanation was not supported by experiments where tar was recondensed in a colder coal bed and observed to be easily and completely revaporized. Tar gasification was not observed to a significant extent for gas temperatures between 800 and 1000 °C (for a residence time of a few seconds). The possible occurrence of in-situ oxidation needs further study.

As an attempt to identify the tar destruction processes, a comparison of the gas yields obtained under the various experimental conditions was performed, and the carbon mass balance was determined. The following yields were obtained for coals containing ~ 80 % carbon. As discussed above, the tar yield reductions between the TG-FTIR conditions and the atmospheric pressure gasifier conditions are ~ 11-16 % dafc. The TG-FTIR and atmospheric pressure gasifier values for the methane yields are not significantly different, the latter being slightly higher (+ 0.7 % dafc). Yields of light hydrocarbon gases are very similar, within less than 0.3 % dafc. Finally, in the case of the atmospheric pressure gasifier, the dust (soot) yields fall in the range 0-3 % dafc, with a few data points at ~ 8 % dafc. This is to be compared to the corresponding dust yields for the TG-FTIR experiment which are zero. This implies that some cracking occurs under the atmospheric pressure gasifier conditions, but may not be significant under all conditions. The carbon mass balance can be closed by analyzing the data given by the CO and CO₂ yields. These yields include the gases formed during pyrolysis as well as the gases from combustion and gasification. The amount of carbon contained in these gases can be compared to an estimation of a similar yield from the TG-FTIR data. The latter value can be obtained by adding the carbon yields of pyrolysis CO and CO₂ to the carbon contained in the char. After doing these calculations, it is observed that more carbon (+ 10 % dafc for coals containing 80 % carbon) is gasified in the atmospheric pressure gasifier than is expected from the estimations based on the TG-FTIR data. This indicates that some of the carbon which was released in the tar during TG-FTIR experiments is being gasified in the atmospheric gasifier. More quantitatively, considering that the tar composition is ~ 80 % carbon, the carbon amount corresponding to the tar decrease is 9-13 % dafc. This is roughly compensated by the increase in dust, methane carbon (CO + CO₂) and gasified carbon (total: ~ 10.5-13.5 % dafc), indicating that the mass balance is closed. This analysis however does not allow the identification of the mode of retention of the tar in the char, i.e., repolymerization, lower amount of tar formation, or homogeneous cracking or gasification of the tar. It is likely that more than one mechanism contributes to the loss of tar.

In the case of pressurized gasifiers, and again for coals containing ~ 80 % carbon, the yields of tar are approximately 7-11 % dafc lower than in the case of the atmospheric gasifiers. Conversely, the yields of methane are significantly higher than in the case of the atmospheric gasifiers for all coal ranks, by ~ 4 % dafc for low rank coals (70 % C), and for medium rank coals (80 % C), by ~ 5-7 % dafc. Considering that an increased

methane yield occurs for all coal ranks, this result suggests that the gasification reaction $C + 2H_2 \rightarrow CH_4$ is more important at higher pressures. However, the methane yield is even higher in coals of medium rank (80 % C), where tar yields are usually high, suggesting that tar cracking also makes an important contribution at high pressures. For coals containing 80 % carbon, the yields of carbon gasified, obtained from the yields of CO and CO₂, are slightly higher in the case of the pressurized gasifier than for the atmospheric gasifier by ~ 2-3 % daf, while the dust yields are roughly the same. These numbers suggest that the carbon amount corresponding to the reduction in tar from the atmospheric to the pressurized case, which is 5.5-9 % daf (assuming ~ 80 % carbon in the tar), is roughly compensated by the increase in carbon in methane and in CO and CO₂, which amounts to 5.5-8.5 % daf. In this case, the mass balance is also closed.

In conclusion, this analysis suggests that: 1) tar cracking occurs in both atmospheric and pressurized gasifiers, and may be more important in the high pressure gasifiers, but in any case is not extensive and cannot account for the whole reduction in tar yield, and 2) the remaining carbon which was released in the tar during the TG-FTIR experiments is being gasified in the atmospheric and pressurized gasifiers as CH₄, CO or CO₂.

Because of funding constraints, little additional progress was made on formulation of a tar cracking submodel.

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SUBTASK 2.2 - FIXED-BED COMBUSTION AND GASIFICATION PROCESSES

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Objectives

The original objectives of this subtask were to measure, correlate, and model oxidation and gasification processes for large coal particles. Due to incomplete funding, the subtask was only partially completed.

Accomplishments

Experimental data collected in our previous project were analyzed and the results of these analyses were published. A high-pressure controlled profile reactor was modified and improved. Oxidation rates were measured for coals of interest to the PyGas™ project as well as for coals of more general interest. Extensive experiments were performed with char samples at atmospheric and elevated pressures. The results were presented in detail in a thesis (Mathias, 1996); a summary is given in this report. A high-pressure thermogravimetric analyzer was acquired and installed, principally with independent funding.

Analysis of Previously Collected Data

Under our previous project, "Measurement and Modeling of Advanced Coal Conversion Processes," oxidation rates were measured for large char particles from six coals of different ranks (Solomon et al., 1993). The experiments were conducted in a muffle furnace, with a Meker burner, and in a High-Pressure Controlled Profile (HPCP) reactor. The effect of coal rank, oxidation temperature, and initial mass of char particle were studied. The cube root of mass declined linearly with time for all coals, consistent with a thick ash-layer model, until the very end of burnout. Ash layers formed and usually remained in place around the char particles. Average mass reactivities increased with decreasing initial char mass and possibly with decreasing char ash percentage. Temperature had little effect on char reactivity except at lower temperatures.

Under our present project, "Fossil Fuel Conversion-Measurements and Modeling," these previously collected data on oxidation rates of large coal/char particles were further analyzed and the results of these analyses were presented in several papers (Blackham et al., 1994; Bateman et al., 1995a; Bateman et al., 1995b; Eatough and

Smoot, 1996). Several papers were also published on oxidation rates of small coal/char particles (Monson and Germane, 1993; Cope et al., 1994; Monson et al., 1995). These efforts helped to disseminate our experimental results and provided a foundation for our new experimental efforts.

Improvement of High-Pressure Facility

Under our previous project, a unique experimental facility was also constructed for measuring oxidation rates for large particles at high temperatures and high pressures. It consists of a Cantilever Balance Attachment (CBA) for the BYU High-Pressure Controlled Profile (HPCP) reactor. The balance unit measures the mass loss of stationary particles as they oxidize in the HPCP reactor. It includes a force transducer, a ceramic cantilever beam and a platinum wire-mesh sample basket. The basket is secured to the cantilever beam and extends into the reactor tube through one of the optical access ports of the HPCP reactor. This facility permits measurements of the oxidation and gasification rates of the coal/char particles at pressures up to 15 atm and temperatures up to 1700 K.

The experimental facility was redesigned under our present project. A pre-test uncertainty analysis revealed substantial uncertainty in mass measurements particularly for small samples. The redesign of the facility, mostly of the CBA, reduced this uncertainty by more than half.

Measurement of Oxidation Rates of Large Coal and Char Particles

Preliminary experiments were conducted with three coals of interest to the PyGasTM project i.e. Consol #2, Mapco #2, and Mettiki #2. The coal samples were obtained from Riley Stoker Corporation. Final experiments were conducted with three coals of more general interest i.e., Pittsburgh (hvAb), Utah Blind Canyon (hvBb), and Wyodak - Anderson (subC). These coals of different ranks belong to the ANL Premium Coal Bank and are included in the ACERC suite of commonly used research coals. The coal samples were obtained from the Argonne National Laboratory's Premium Coal Bank.

Following the redesign of the experimental facility, the oxidation rates were measured for large particles of these three coals at atmospheric pressure. It was found that devolatilization conditions substantially affected oxidation reactivities. In order to separate this effect from the effects of other variables, the remaining experiments were performed with char prepared at constant conditions.

The experiments were conducted with Pittsburgh char at atmospheric and elevated pressures. The oxidation rate increased substantially as the oxygen partial pressure increased while the total pressure remained constant, Figure 2.2-1 A and B. On the other hand, the oxidation rate decreased also substantially as the total pressure increased while the partial pressure of oxygen remained approximately constant, Figure 2.2-1 C and D. However, the oxidation rate changed only slightly when the total

Figure 2.2-1. Char oxidation rates vs. time (A,C,E) and conversion (B,D,F).
 (A,B) Oxygen partial pressure 6.0, 12.1, and 18.1 kPa, total pressure 86.1 kPa;
 (C,D) Oxygen partial pressure ~21.3 kPa, total pressure 86.1, 304.0 and 506.6 kPa;
 (E,F) Oxygen partial pressure 18.1, 63.8, 106.4 kPa, total pressure 86.1, 304.0 and 506.6 kPa;

pressure increased using air and thus increasing the oxygen partial pressure in the same ratio, Figure 2.2-1 E and F. In this set of experiments the mole fraction of oxygen remained constant indicating that the mole fraction may be a more appropriate variable than the oxygen partial pressure to describe these results. These experimental results also indicate that a Langmuir-type correlation may be appropriate, as also suggested by Essenhig and Meschner (1996). The effects of other variables such as particle mass, number of particles, gas temperature, and gas velocity were also investigated.

The results were presented in a thesis (Mathias, 1996) and two papers (Solomon et al., 1994 and Solomon et al., 1995).

Acquisition of High - Pressure Thermogravimetric Analyzer

The HPCP reactor is limited to less than 15 bar while some important coal conversion technologies operate at substantially higher pressures. To extend the experimental capability to higher pressures and also to secure accuracy and convenience of thermogravimetric measurements, a High - Pressure Thermogravimetric (HPTG) analyzer was purchased from DMT in Germany, principally with independent funding. The HPTG analyzer can operate at pressures up to 100 bar and temperatures up to 1400K. The analyzer was installed and some preliminary experiments with large coal and char particles were performed. However, due to reduction in total project funding, no further tests with the HPTG analyzer were performed.

Summary and Conclusions

The experimental data collected in our previous project were further analyzed and the results of these analysis were presented in a number of papers. The high-pressure controlled profile reactor and the cantilever balance attachment were redesigned, reducing the measurement uncertainty by more than half. Preliminary experiments were conducted with three coals of interest to the PyGasTM project i.e. Consol #2, Mapco #2, and Mettiki #2. The final experiments were performed with three coals of more general interest i.e. Pittsburgh, Utah Blind Canyon, and Wyodak-Anderson at atmospheric pressure. The experiments were also conducted with Pittsburgh char at atmospheric and elevated pressures. It was found that the oxidation rate increased substantially as the oxygen partial pressure increased while the total pressure remained constant. The results were presented in a thesis and two papers. The high-pressure thermogravimetric analyzer was also acquired in order to expand the pressure range and to secure the accuracy and convenience of thermogravimetric measurements.

The experimental data from this project and from other sources should be used to develop an advanced model for oxidation processes of large coal/char particles at high pressures. The mole fraction may be an appropriate variable and a Langmuir-type correlation is suggested as a basis for data correlation.

Acknowledgments

The samples of three coals of interest to the PyGas™ project, Consol #2, Mapco #2, and Mettiki #2 were provided by Mr. Vijay Dixit of Riley Stoker Corporation. The samples of the three coals of more general interest, Pittsburgh, Utah Blind Canyon, and Wyodak-Anderson, were provided by Mr. Kenneth Anderson of the Argonne National laboratory. This is gratefully acknowledged.

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SUBTASK 2.3 PHYSICAL PROCESSES IN TRANSPORT REACTORS

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Objectives

The original objective of this subtask was to correlate and model the mixing, heat transfer and caking processes occurring in a transport reactor under conditions typical of gasification.

Accomplishments

Data for turbulent particle dispersion were collected from the literature and used to develop a particle dispersion model. The work on heat transfer was not completed and caking was not addressed.

Turbulent Particle Dispersion Model

A literature review was done to collect data on physical processes in transport reactors. Contact was also made with participants in ongoing related work at Kellogg, UNDEERC, CCNY, and FETC. A new particle dispersion model is being input into PCGC-2 in order to use it to describe transport reactors (See subtask 2.6). A number of data sets on the particle dispersion in turbulent flow were collected and used for verification of the particle dispersion model developed under subtask 2.6. These data encompass various types of gas flow, including grid generated turbulent flow, confined jet flow, and flow in circulating fluidized beds.

SUBTASK 2.4 CHEMICAL PROCESSES IN TRANSPORT REACTORS

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Objectives

The original objective of this subtask was to correlate and model the process of gasification of fresh coal and recycle char, and of sulfur capture in a transport reactor.

Accomplishments

A literature review, survey of ongoing projects and reactor modifications were completed. The experimental work and submodel development were not completed due to funding constraints.

Literature Review and Project Summary

As in subtask 2.3, a literature review was done and contact was made with those involved in related work in order to design the test matrix. One of the first requirements was to identify and locate samples of coal for testing. Contact was made with Gunnar Henningsen of M.W. Kellogg. He indicated that they were very interested in cooperating with us and in sharing some of their data from the unit at Wilsonville. Only one transport reactor is being built there and it will be alternated between gasification and combustion runs. They were planning to use Illinois No. 6 coal and dolomite. We also made contact with those involved with the companion study at the University of North Dakota Energy and Environmental Research Center (UNDEERC). Because of delays in the startup of the unit at Wilsonville, as time went on we began to focus on using the pilot scale data from UNDEERC. However, since the approval of M.W. Kellogg was required to use this information, long delays were experienced in getting approval and these efforts were abandoned when the project funding was curtailed.

Laboratory Studies at AFR

A test matrix for the subtask was developed and several reactor designs were considered for the experiments. The critical issue was the determination of the effect of the heat carrier on product yields and composition. Reference runs (i.e., those without a heat carrier) would be carried out in a heated-tube reactor (HTR), as described in the Research Plan (Solomon and Smoot, 1993). One of the options considered was the introduction of the heat carrier (e.g., quartz sand and/or char) with coal particles into the HTR and comparing the results with the reference case. It was not clear, however, whether the concentration of heat-carrier particles would be sufficient to reflect the

particle-particle and gas-particle interactions characteristic of transport reactors. Another experimental option was the design and construction of a small-scale circulating fluidized-bed reactor that could be operated with and without the heat carrier. The difficulty associated with this alternative was a high gas flow rate that the product collection system needs to handle. Direct measurement of the gas composition using an FTIR analyzer, and possibly also a gas chromatograph, was contemplated for this option.

Ultimately, a decision was made to pursue experiments in a modified heated-tube reactor (HTR). The rationale behind this choice was a better defined flow field and gas-solid interface. Data collected in such a system will be more suitable for kinetic analysis than those collected in a circulating fluidized bed where the effect of turbulence would obscure intrinsic kinetics. Intrinsic kinetic expressions determined in this study could then be incorporated into a flow model that accounts for turbulence, particle-particle interactions, etc. In order to facilitate the study of the heat carrier effect on product yields, composition and char reactivity, with minimum modification of the existing HTR set-up, a new coal feeder was designed and constructed.

It was envisioned that the modified coal feeder will serve as a feeder for a mixture of coal and sand. However, it was observed that the feeding process separated coal from the sand. An additional feeder was installed so the coal and sand could be fed separately and mixed right before the reactor entrance. The combined feeder was checked for feeding uniformity, calibrated and integrated with the reactor.

New tubes were purchased for the heated-tube reactor and the system was tested for high-temperature operation (up to 900 °C). The testing included the determination of wall-temperature profiles along the reactor, as shown in Fig. 2.4-1. Due to the possibility of thermal damage to the heated-tube reactor at the high temperatures envisaged for this work, it was decided that the existing stainless-steel tubes should be replaced with those made of a high-temperature alloy. This was done, and the high-temperature performance of the reactor system was tested for several hours.

Once it became clear that the funding for this project would be significantly curtailed, the experimental efforts under this subtask were abandoned and the focus shifted to trying to complete the development of the transport reactor code under subtask 2.6, based on existing data.

Reference for Subtask 2.4

Solomon, P.R. and Smoot, L.D., Research Plan, Contract No. DE-AC21-93MC30040 (December 23, 1993).

Fig. 2.4-1 Temperature profiles along the heated-tube reactor. (tests #1, #3 and #4: N_2 , 5ℓ/min; test #2: N_2 , 11.9ℓ/min; test #5: steam 1 atm; test #6: steam, 5 atm; tests #2-4: an extra layer of insulation between the top of the reactor and the second thermocouple was used).

SUBTASK 2.5. - ADVANCED FIXED-BED MODEL DEVELOPMENT AND EVALUATION

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Objective

The objective of this subtask was to develop an advanced fixed-bed model incorporating the advanced submodels developed in Subtasks 2.1 and 2.2 and to evaluate the model by comparing its predictions with the experimental data available from the literature. Due to incomplete funding, this subtask was only partially completed.

Accomplishments

During the period of this contract, work was initiated to improve the existing fixed-bed code, FBED-1 for industrial applications. Additional sensitivity analyses of the FBED-1 model were performed to study the effects of the available submodel options. The effects of the devolatilization submodels, the oxidation and gasification submodels, and the gas phase chemistry options were studied. The governing equations were rederived starting from first principles. Modifications were made in the routines used to evaluate the derivatives to make them consistent with the LSODE solver. The fixed-bed model was extended to handle a cocurrent flow configuration. This modified model was used to simulate the cocurrent and countercurrent sections of the staged PyGas gasifier of the Gasification Product Improvement Facility project; see Subtask 5.1 of this report. The CHEMKIN-II and CHEMKIN-RG packages were obtained from Sandia National Laboratories and the University of Iowa, respectively, and were studied as stand-alone packages.

An additional area of effort during the period of this contract has been the incorporation of a reduced coal devolatilization model, FG-DVC-RES into the FBED-1 computer program. The reasons for incorporation of the reduced model include faster overall execution time and enhanced robustness of the numerical method. Incorporation of FG-DVC-RES into FBED-1 has required extensive modifications to the existing code. Rather than utilizing the detailed description of devolatilization based on the solution of 153 coupled ordinary differential equations, the FG-DVC-RES model uses a description of the volatile mass released, based on the solution of a single ordinary differential equation. All the necessary information (e.g., gas species composition), which would be provided from the full devolatilization model, is then obtained from correlation of the volatile mass released with the results of a previous FG-DVC simulation. Thus, all the parts of the FBED-1 computer code that utilize the

functional-group description of coal devolatilization must necessarily be rewritten to accept the format of the reduced model. This resulted in the need to rewrite and restructure significant portions of the FBED-1 code. However, the resulting version, based on the reduced model, is substantially simpler in its coding and requires significantly less CPU time to run.

Publications

One paper has been published (Radulovic et al., 1995) and another is in press (Ghani et al., 1996). Several posters have been presented, including: (Radulovic et al., 1994), presented at the Twenty-Fifth Symposium (International) on Combustion in Irvine, California; (Solomon et al., 1994), presented at the Coal-Fired Power Systems '94 Meeting; and (Solomon et al., 1995), presented at the Advanced Coal-Fired Power Systems '95 Review Meeting.

Section Outline

The remainder of this section is split into five general sections. The first is a brief description of the fixed-bed process itself, in reference to the Wellman-Galusha gasifier. The second section is used to present the basic equations used to model the fixed-bed gasifier and to provide brief descriptions about some of the methods used to compute important rates and compositions. The third section is used to present some important findings that resulted from the sensitivity study. In the fourth section, details of the effort to integrate FG-DVC-RES into the FBED-1 code are presented. And finally, a discussion and some recommendations for future work are offered.

Combustion and Gasification Processes

Fixed bed systems are simple and reliable, have high thermal efficiency, and require minimal pretreatment of feed coal. Combustion and gasification of coal in fixed or slowly moving beds of packed coal particles are of commercial interest. Such beds can be operated at high pressure, providing opportunity for increased power generation efficiency through combined cycle processes. Fixed beds are also a popular choice for mild gasification since, by their countercurrent nature, the liquids can be quickly removed before being altered by substantial reaction. A schematic of a typical atmospheric fixed-bed gasifier is shown in Figure 2.5-1.

The coal is fed to the top of the reactor and moves downward under gravity, countercurrent to the rising gas stream. The dry or slagging ash is removed at the bottom of the reactor. The feed gas is commonly composed of air or oxygen and steam. The excess steam is supplied to the gasifier to control the ash temperature. As the coal slowly descends, the hot gases produced in the gasification and combustion zones exchange energy with the colder solid. The water vapor and, subsequently, the volatile matter are released when the coal reaches sufficiently high temperatures. After the drying and devolatilization zones, the char enters the gasification zone, where carbon reacts with steam, carbon dioxide, and hydrogen. The endothermic reactions in this

Figure 2.5-1. Schematic of the atmospheric pressure, air-blown, dry-ash, Wellman-Galusha gasifier.

section produce carbon monoxide and hydrogen. The slightly exothermic reaction of hydrogen with carbon produces methane. Differentiation between the "combustion zone" and the "gasification zone" is based on the presence or absence of free oxygen. Combustion and gasification reactions can occur simultaneously in the "combustion zone." Combustible gases such as carbon monoxide or hydrogen may react with oxygen. The exothermic combustion reactions provide the necessary energy for the endothermic gasification reactions and drying. The blast gas, which is composed of steam and air (or oxygen), is preheated by the hot ash.

The solid residence time in the drying, devolatilization, gasification and oxidation zones may be on the order of several hours. The residence time in the ash zone may be even higher, depending on the thickness of this zone. The gas residence time is on the order of seconds. The solid and gas temperature gradients are highest in the devolatilization and oxidation zones.

Fixed-bed combustion and gasification processes and technologies are treated in more detail in our previous reports (Solomon et al., 1987, 1988), in our contribution to a book on coal combustion (Radulovic and Smoot, 1993) and in our review article (Hobbs et al., 1993).

Basic Equations

Conservation Equations

The conservation equations for the one-dimensional, fixed-bed model, FBED-1, are listed in Table 2.5-1. The governing system of equations for the model consists of 191 highly non-linear, coupled, first order, differential equations. Table 2.5-1 shows only the 38 conservation equations for gas and solid phase. Remaining equations are related to the devolatilization and tar cracking submodels and are presented elsewhere (Solomon et al., 1987, 1988). The equations presented in Table 2.5-1 are the gas and solid overall continuity equations, gas and solid energy equations, and gas and solid species as well as elemental continuity equations. The constitutive relations for solids flow and the submodels of solids flow in fixed-beds have been proposed only recently and are in development stage (Gray et al., 1988, 1991). No solution of these equations has been attempted so far. Plug flow is assumed for both the gas and solid phases. Therefore, momentum transport equations are not considered and only differential equations for continuity and energy are treated in the model described herein. The equations presented here are, perhaps, deceptively simple since they are formulated as balance equations. The complexity of these equations lies in the right hand side which involves heterogeneous reactions of char as well as homogeneous reactions in the gas phase.

Overall Gas and Solid Continuity Equations

The overall gas and solid continuity equations are given by Equations 1 and 2 in Table 2.5-1. The summation is over all processes and heterogeneous reactions which

consume the coal. These include drying, devolatilization, char gasification by CO_2 , H_2O and H_2 , and char oxidation. Reaction rates are expressed as the volumetric rate of mass addition to the gas phase. Thus, a positive rate corresponds to a source of mass for the gas phase and a sink for the particle phase. The submodels used to determine these rates are as follows:

Table 2.5-1. Conservation Equations for FBED-1

$$\text{Overall Gas Continuity} \quad \frac{dm_g}{dz} = A \sum_{i=1}^6 r_i \quad (1)$$

$$\text{Overall Solid Continuity} \quad \frac{dm_s}{dz} = -A \sum_{i=1}^6 r_i \quad (2)$$

$$\text{Gas Phase Energy} \quad \frac{d(m_g h_g)}{dz} = A \left(Q_{sg} - Q_{gw} + \sum_{i=1}^6 r_i h_{g,i} \right) \quad (3)$$

$$\text{Solid Phase Energy} \quad \frac{d(m_s h_s)}{dz} = A \left(-Q_{sg} - Q_{sw} - \sum_{i=1}^6 r_i h_{g,i} \right) \quad (4)$$

$$\text{Gas Phase Species Continuity} \quad \frac{dm_{g,l}}{dz} = A \sum_{i=1}^6 r_{i,l}^{gas} \quad (5-26)$$

$$\text{Gas Phase Elemental Continuity} \quad \frac{dm_{g,j}}{dz} = A \sum_{i=1}^6 r_{i,j}^{gas} \quad (27-31)$$

$$\text{Overall Tar Continuity} \quad \frac{dm_{tar}}{dz} = A r_d^{tar} \quad (32)$$

Tar Elemental Continuity

$$\frac{dm_{tar,j}}{dz} = Ar_{d,j}^{tar} \quad (33-37)$$

Moisture Continuity

$$\frac{dm_{moisture}}{dz} = -Ar_{drying} \quad (38)$$

1. Equations 39-164 describe the FG-DVC devolatilization submodel.
2. Equations 165-191 describe the lower bound of the distribution function for the gas phase tar cracking reactions and follow the FG-DVC formulation.
3. Equations 5-26 are solved only when the gas phase is not considered to be in chemical equilibrium.
4. $i=1-6$ represents drying, devolatilization, CO_2 , H_2 , H_2O gasification, and oxidation reactions respectively.
5. $j=1-5$ represents elements C, H, O, N, and S respectively.
6. $l=1-22$ represents 22 gaseous species considered in FBED-1.

Drying - The volumetric rate of drying of coal is based on the diffusion-limited vaporization of moisture from the coal particle, as described by Smoot and Smith (1979).

$$r_{drying} = C_g M_w d_p \eta_p D_{wg} (X_{wp} - X_{wg}) \quad (2.5-1)$$

Hobbs et al. (1992a) showed that blowing or transpiration effects influenced the rates by less than 5% for large particles at operating conditions typical of fixed-bed coal gasifiers. These effects are, therefore, assumed negligible.

Devolatilization - Devolatilization is based on the FG-DVC submodel. The details of the governing equations for the FG-DVC submodel are presented by Solomon et al. (1988). The evolution of light gaseous species is computed from the FG portion and the evolution of tar is computed from the DVC (Solomon et al., 1987) portion of the submodel, respectively. The tar may also be allowed to convert to the light gaseous species within the char matrix. This option is exercised by selecting the value of 1 in Eqs. 2.5-2 and 2.5-3. The evolution rates for the light gaseous species and tar are given by

$$\frac{dY_i(gas)}{dt} = \langle k_i \rangle \cdot \left[Y_i(char) + Y_i(tar) \cdot \begin{bmatrix} 0 \\ 1 \end{bmatrix} \right] \quad (2.5-2)$$

$$\frac{dY_i(tar)}{dt} = \left(\frac{dY(tar)}{dt} \right)_{DVC} \cdot \left(\frac{Y_i(char)}{\sum_i Y_i(char)} \right) - \langle k_i \rangle \cdot Y_i(tar) \cdot \begin{bmatrix} 0 \\ 1 \end{bmatrix} \quad (2.5-3)$$

The net decomposition rate of the individual functional groups in the char can then be determined by

$$\frac{dY_i(char)}{dt} = -\frac{dY_i(gas)}{dt} - \frac{dY_i(tar)}{dt} \quad (2.5-4)$$

The above equation presents decomposition of char functional groups by the devolatilization reactions only. The kinetic parameters for the devolatilization submodel are coal dependent. The functional group composition data are published for the eight Argonne Premium coals and can be estimated for other coals. These data can be adjusted to match the ultimate composition of the feed coal following the procedure outlined by Ghani et al. (1993). The rates computed by the above expressions are per unit mass of initial char and can readily be converted to the overall coal devolatilization rates using the following expression:

$$r_i = \rho_{sm}^o (1 - \varepsilon) (1 - \Omega_{ash}^o - \Omega_{moisture}^o) \frac{dY_i(gas, tar, char)}{dt} \quad (2.5-5)$$

Oxidation and Gasification - The char functional groups are also consumed by the heterogeneous oxidation and gasification reactions. In FBED-1, two submodels are provided for char consumption by heterogeneous oxidation and gasifications reactions following the formulation of Hobbs et al. (1992a). These are the Shell Progressive (SP) submodel and the Ash Segregation (AS) submodel. Hobbs et al. (1992a) allowed the oxidation and gasification reactions to consume only the non-volatile carbon and organic sulfur functional groups. No mechanism was provided to consume other functional groups by the heterogeneous gasification and oxidation reactions. In the present formulation, these reactions act on all functional groups. This provides an improved mechanism for the simultaneous conversion of char by drying, devolatilization, and heterogeneous oxidation and gasification reactions. The volumetric rate of char consumption by oxidation and gasification reactions is given by:

$$r_i^{o,g} = \frac{A_p \eta_p v_p Mw_p C_{ig}}{\frac{1}{k_{r5}} + \frac{1}{k_m} + \frac{1}{k_{eff}}} \quad (2.5-6)$$

The expressions for the particle diameter and particle number density for the SP submodel as given by Hobbs et al. (1992a) are

$$d_p = \left[(1 - \Omega_{ash}^0) d_u^3 + \Omega_{ash}^0 d_0^3 \right]^{1/3} \quad (2.5-7)$$

$$\eta_p = \frac{6(1 - \varepsilon)}{\pi d_p^3} \quad (2.5-8)$$

Gas and Solid Energy Equations

The gas and solid energy equations are given by Equations 3 and 4 in Table 2.5-1. The expressions for the calculation of Q_{sg} , Q_{gw} , and Q_{sw} have been discussed by Hobbs et al. (1992a) and are presented below

$$Q_{sg} = \zeta h_{sg} \pi d_p^2 \eta_p (T_s - T_g) \quad (2.5-9)$$

The adjustable factor ζ to account for the reactive nature of the fixed bed may have a value in the range 0.02 to 1.0 (Lowry, 1963). Dzhaphyev et al. (1986) attributed the observed decrease in heat transfer rates to unsteady effects. A value of 0.05 was determined by comparison with data from commercial gasifiers and used in the simulations.

The volumetric wall heat losses from the solid and the gas phase, Q_{gw} and Q_{sw} , are calculated as follows:

$$Q_{gw} = \frac{4h_{gw}}{D} (T_g - T_{wall}) \quad (2.5-10)$$

$$Q_{sw} = \frac{4h_{sw}}{D} (T_s - T_{wall}) \quad (2.5-11)$$

The gas-wall and solid-wall heat transfer coefficients, used in the above equations, include the contributions of conduction, convection and radiation. The equations used to compute these coefficients are presented in detail by Hobbs et al. (1992a) and Ghani et al. (1993).

The last term in the energy equations represents the energy exchange due to the coal decomposition processes i.e., drying, devolatilization, and heterogeneous reactions of char with CO_2 , H_2 , H_2O and O_2 . A discussion of these heat effects is presented next.

Heat of Vaporization - The heat of vaporization accounts for the energy exchange due to drying of the feed coal. This term is calculated as

$$h_{total}^{vap} = h_f^o + h_{vap}(T_s) + h_s(T_s) \quad (2.5-12)$$

Heat of Devolatilization - Since devolatilization is a coal dependent process the heat of devolatilization can not be computed directly. However, the computation of energy exchange due to devolatilization is possible. In FBED-1, the energy exchange due to devolatilization is computed following the model proposed by Merrick (1983). Merrick's model, which considers 9 species, including tar, was extended to accommodate 27 functional groups of the FG-DVC devolatilization submodel. The resulting equations are

$$r_{devol} h_{devol} = \sum_{k=1}^{nfg+1} \frac{\partial q}{\partial m_k} \frac{dm_k}{dt} \quad (2.5-13)$$

where

$$\frac{\partial q}{\partial m_k} = \sum_{j=1}^5 A_{jk} \left(\lambda_j - \Phi_j + \frac{f(\bar{T})}{\mu_i} \right) - h_k \quad (2.5-14)$$

$$\frac{dm_k}{dt} = r_{d,k}^{gas} \quad (k = 1, \dots, nfg) \quad (2.5-15)$$

$$\frac{dm_{nfg+1}}{dt} = \sum_{k=1}^{nfg} r_{d,k}^{tar} \quad (2.5-16)$$

Heat of Reactions - The heats of reaction for the gasification and oxidation reactions of char are calculated by performing an energy balance around the particle-gas interface. The products of heterogeneous reactions are assumed to leave the char particle at the particle temperature. A sample calculation for the heat of reaction associated with the oxidation reaction of char is provided by Ghani et al. (1993). The heats of reactions for the gasification reactions can be calculated in a similar manner.

Gas Phase Species Continuity Equations

The composition and temperature of the gas phase were determined in MBED-1 by total or partial equilibrium submodels. In the total equilibrium submodel, all gaseous species, including tar, were assumed to be in chemical and thermal equilibrium. For the partial equilibrium option, tar was held out of chemical equilibrium. In this case, the remaining gaseous species were taken to be in equilibrium. The predicted product gas composition using the above approaches did not compare well with the experimental

data. In order to improve on these predictions, an additional option is provided in FBED-1. In this option, the gases are prevented from reacting to equilibrium below a user-specified temperature. This option is mainly exercised during drying and devolatilization when the gas phase temperature is low. Gas phase kinetics would be required to hold certain gas species out of equilibrium in the high temperature region. For all these options, all species, including tar, are considered to be in thermal equilibrium. Equations 5-26 in Table 2.5-1 are solved only when the gas phase is assumed to be out of chemical equilibrium. Otherwise, the gas phase species concentrations are computed from the equilibrium submodel.

Gas Phase Elemental Continuity Equations

The mass rate of change of each reactive element in the gas phase is given by Equations 27-31 in Table 2.5-1. These elements include C, H, O, N, and S. Elements related to inert species such as Argon do not take part in any reaction, thus eliminating the need for a differential equation. The term $r_{i,j}^{gas}$ represents the volumetric evolution rate of the j -th element contributed by the i -th reaction. These reactions include drying, devolatilization, and heterogeneous oxidation and gasification reactions of char, and have been discussed previously. It should be noted that tar is treated as a pseudospecies in the gas phase; therefore, the gas phase elemental continuity equations, shown in Table 2.5-1, include the contribution of tar.

Tar Overall and Elemental Continuity Equations

Tar, which is part of the gas phase, is treated as a pseudospecies in FBED-1. The use of the advanced devolatilization submodel makes tracking of tar throughout the reactor bed possible. Tar can be either assumed to be nonreactive in the gas phase, which would classify the one-dimensional model as a partial equilibrium model, or assumed to react to completion in the gas phase. The evolution of tar is based on the FG-DVC submodel as discussed previously. The overall tar continuity is given by Equation 32; its elemental continuity is given by Equations 33-37 of Table 2.5-1. The tar yield predicted by MBED-1 was consistently higher for all the coals simulated. This was attributed to the lack of tar repolymerization mechanism and gas phase decomposition of tar. The fixed-bed model, FBED-1, was, therefore, extended to account for the decomposition of tar in the gas phase. The tar cracking submodel is based on the following assumptions (Serio, 1992): 1) the k -th functional group in tar evolves to the k -th functional group in gas, 2) the decomposition of tar follows the same kinetics as that of gas evolution from the char, and 3) the evolution of gas from tar takes place at the gas temperature.

Solid Species Continuity Equations

The solid particle is represented as being composed of moisture, ash, and organic functional groups. The coal particles are assumed to be of uniform size; size distribution effects are not considered. Ash is considered inert and does not require a

differential equation. Moisture is released during the drying of the coal particles; the equation governing the drying process has been discussed previously. The composition of the char is updated from the instantaneous functional group composition of the char. The functional groups are depleted by devolatilization as well as by gasification and oxidation reactions.

Auxiliary Equations

The set of auxiliary equations for FBED-1 is essentially the same as that for MBED-1 (Table 2, Hobbs et al. (1992a)). Since plug flow is assumed for both the solid and the gas phase, gas phase momentum equation is solved only to calculate the gas phase pressure drop. Ergun's equation is used to calculate the friction factor and the bed void fraction is assumed to vary linearly between the feed coal and the product ash void fractions. At temperatures higher than the user-specified value, usually 1200 K, the gas phase is assumed to be in chemical and thermal equilibrium and its composition and temperature are computed by Gibbs free energy minimization. The option to keep tar either in or out of chemical equilibrium is preserved in FBED-1. The calculation of heat and mass transfer coefficients and transport and thermodynamic properties of gas and tar phases are based on the same correlations as used in MBED-1 and presented by Hobbs et al. (1992a).

Sensitivity Analysis

The effects of submodel options for devolatilization, and oxidation and gasification processes, three options for the gas phase chemistry, and five model parameters on the predictions of FBED-1 have been studied. The submodel options and gas phase chemistry options have been enumerated previously. The model parameters include solid-gas heat transfer coefficient, diffusion through the ash layer, oxidation and gasification kinetic rates, wall heat loss, and switch temperature for gas phase equilibrium. The effect of feed gas temperature has also been studied. The sensitivity to the submodel options, gas phase chemistry options, and model parameters is demonstrated by simulating the atmospheric-pressure, air-blown, dry-ash, Wellman-Galusha gasifier, fired with the Jetson bituminous coal (Thimsen et al., 1984-85). The changes in the gas and solid temperature fields and the product gas composition of major species are analyzed to understand the effect of the submodel options and the model parameters. The sensitivity analysis reported by Hobbs et al. (1992a), using the earlier version of the model, MBED-1, was only qualitative, since some of the boundary conditions were not satisfied in those simulations. The sensitivity analysis presented here is quantitative since the boundary conditions for both the feed coal and the feed gas streams are fully satisfied. The variations in the model parameters were explored over wide ranges. However, the results presented here are only for the values which yielded converged solutions. This resulted in a narrow range for some parameters, especially for gas-solid heat transfer coefficient and oxidation and gasification kinetic rates.

The recommended options for the FBED-1 model are the FG-DVC submodel for devolatilization, the SP submodel for oxidation and gasification, and the partial chemical equilibrium option for the gas phase. The partial equilibrium option is exercised by keeping tar non-reactive and gases non-reactive below the switch temperature but both in thermal equilibrium. The base case with the recommended options has been discussed in detail by Radulovic et al. (1995). The effects of the submodel options and model parameters on the predictions of FBED-1 model are shown and compared with the results for the base case (Radulovic, 1995).

Devolatilization Submodel

The major difference between the FG-DVC and the FG-SET devolatilization submodels is in the computation of tar evolution. The FG-SET submodel uses the semi-empirical correlation of Ko et al. (1988), to compute the potential tar forming fraction, which is the dry, ash-free mass fraction of the coal that can evolve as tar in the devolatilization process. The potential tar forming fraction of the coal evolves to tar following a first order Arrhenius-type kinetic rate. The derivation of the equations for the FG-SET model are given by Hobbs (1990). The more fundamental FG-DVC submodel computes tar evolution based on the coal structure. The reader is referred to Solomon et al. (1988) for complete details. The FBED-1 predictions with the FG-SET submodel, as presented here, use 27 functional groups and coal dependent-kinetics as used for gas evolution by FG-DVC. This is different from the MBED-1 (1992a) model which used 19 functional groups and coal-independent kinetics for the FG-SET submodel. The use of 27 functional groups and rank-dependent kinetics allows the comparison of both devolatilization submodels on consistent basis. The calculated results are shown in Figure 2.5-2. The tar evolution rate predicted by FG-SET submodel is higher which leads to a higher peak for the net devolatilization rate. The FG-SET submodel also predicts secondary peaks due to evolution of tightly bound gaseous species. This may be attributed to the difference in the computation of kinetic rates. Both submodels use a distributed activation energy which follows a Gaussian distribution. The FG-SET submodel uses a fixed, time-independent distribution whereas the FG-DVC submodel uses a distribution which has a time-dependent, lower cut-off limit. This probably smooths out any secondary peaks due to lower rates. The product gas temperature predicted by the FG-SET submodel is lower which leads to a longer devolatilization zone and lower temperatures in the devolatilization zone. As a result, the gasification rates are also lower and longer gasifier length is needed for complete conversion of char. The product gas composition, however, is comparable for both options.

Ash Segregation Submodel

The effect of char consumption rates using the ash segregation (AS) submodel for char oxidation and gasification reactions is shown in Figure 2.5-3. The results show a dramatic impact on the temperatures and char consumption rates by oxidation and gasification reactions. The predicted solid temperature using the AS model shows a very sharp peak and very fast burnout in the oxidation zone. The shell progressive

Figure 2.5-2. Effect of devolatilization submodel on FBED-1 predictions.

Figure 2.5-3. Effect of oxidation and gasification submodel on FBED-1 predictions.

(SP) model results in a more gradual burnout of the char and change in particle diameter is not as steep as for the AS submodel. In addition, the predicted peak solid temperature is much higher when using the AS submodel. This is as expected since the diffusional resistance due to the presence of ash layer in the SP submodel tends to reduce the reaction rate and hence the peak temperature. The higher temperatures and reaction rates in the AS submodel result in shorter reactive zones. The product gas composition does not show any significant changes. These results suggest that the SP submodel is more appropriate for the fixed-bed combustion and gasification of coal.

Gas Phase Chemistry Options

The effects of various options on the product gas composition, as predicted by FBED-1, are shown in Figure 2.5-4A. As more mass is allowed to react to equilibrium, the predicted gas composition deviates more from the experimental values. This is specifically true for H_2O and suggests that, for high moisture coals, the gas phase composition computed assuming total equilibrium will predict results which may be in gross error. The predicted results using the partial equilibrium option keeping tar non-reactive and gases non-reactive below the user-specified switch temperature compare best with the experimental values (Thimsen et al., 1984). The switch temperature for these simulations was determined, by comparisons of the predicted and experimental values, to be 1200 K. This value, however, is not a universal value since it has not been tested for high moisture coals. For comparison, the results of the MBED-0 (Hobbs et al., 1992b) predictions are shown in Figure 2.5-4B. FBED-1 results show significant improvement in product gas composition over the results of MBED-0. It should be noted that Hobbs et al. (1992b) reported the results on dry, CH_x -free basis. The values reported here are wet, CH_x -included basis. Improvements in the FBED-1 predictions are also due, in part, to the split, back-and-forth, shooting technique which satisfies the boundary conditions for the feed gas. Thus, one-dimensional computations are indeed needed to adequately predict the product gas composition.

Solid-gas heat transfer coefficient

Figures 2.5-5A, 2.5-6A, and 2.5-7A show the effects of solid-gas heat transfer coefficient on solid and gas temperatures and product gas composition. VonFredersdorf and Elliott (1963) reported that the solid-gas heat transfer in a reacting system may be up to fifty times lower than that of a non-reacting system. In FBED-1, this is accounted for by correcting the heat transfer coefficient for non-reacting systems, multiplying by an adjustable factor. Results for the base case are shown for a value of 0.05 which was determined by comparison of the predicted and experimental temperature profiles for the solid phase. A decrease in this factor to 0.0475 lowers the solid temperature which results in lower gasification and oxidation rates. This leads to a longer reaction zone. An increase in the value of this factor to 0.055 increases the solid temperature and the gasification and oxidation rates and therefore leads to a shorter reaction zone. Gas temperature profiles (Figure 2.5-6A) show a similar trend since

Figure 2.5-4. Effect of gas phase chemistry options on FBED-1 predictions

Figure 2.5-5. Predicted sensitivity of solids temperature to model parameters and operational variables.

Figure 2.5-6. Predicted sensitivity of gas temperature to model parameters and operational variables.

Figure 2.5-7. Predicted sensitivity of product gas composition to model parameters and operational variables.

these profiles are coupled with the solid phase fields. No significant effect on the product gas composition (Figure 2.5-7A) is observed.

Diffusion through Ash Layer

The effect of diffusion of the oxidation and gasification reactants through the ash layer on solid temperature, gas temperature and product gas composition is shown in Figures 2.5-5B, 2.5-6B, and 2.5-7B. The effective diffusivity of the reactants through the ash layer depends on the porosity of the developing ash layer and is estimated by the following expression:

$$D_{eff} = \phi D_{im}$$

where D_{im} is the molecular diffusivity of species i through the mixture and is calculated using the Chapman-Enskog theory for gaseous mixtures (Bird et al., 1960). The coefficient, ϕ , accounts for the porosity of the developing ash layer and is estimated by dividing the ash porosity by tortuosity squared, which is taken to be 2 (Laurendeau, 1978). In absence of any available experimental data, Hobbs et al. (1992a) recommended a value of 0.5 for the coefficient, ϕ . This value was taken to be the base value of the sensitivity analysis presented here. A decrease around the base value of 0.5 show a longer reaction zone. The peak solid temperature for a lower value of ϕ , 0.45, slightly increases while the peak gas temperature slightly decreases. Both the peak solid and gas temperatures show small decreases for a higher value, 0.6. No significant effect is observed on the product gas composition.

Oxidation and Gasification Kinetic Rates

The base conditions for these parameters are the rank-independent kinetic parameters for oxidation and gasification reactions. These parameters were based on the data of Field et al. (1967) and Goetz et al. (1982), and were correlated by Hobbs et al. (1992a). A change in the oxidation and gasification kinetic parameters changes the relative contribution of the exothermic and endothermic reactions. This affects the temperature profiles as well as the product gas distribution due to char consumption by heterogeneous reactions. By doubling the oxidation and gasification kinetic rates, the endothermic reactions become relatively more important and reduce the peak temperatures as shown in Figures 2.5-5C and 2.5-6C. In addition, the char consumption during the gasification reactions increases leaving much less carbon available for the exothermic oxidation reaction which also contributes to the lower peak temperatures. A slight decrease in oxidation and gasification kinetic rates also leads to a shorter reaction zone but the peak solid temperature remains unchanged. Both a decrease and an increase in the kinetic rates yield slightly higher CO and H₂, and slightly lower amounts of CO₂, CH₄, and H₂O as shown in Figure 2.5-7C.

Wall Heat Loss

The effect of wall heat loss is shown in Figures 2.5-5D, 2.5-6D, and 2.5-7D. A 10% decrease in the wall heat transfer coefficient decreases the heat loss by 14%. The product gas temperature increases by 6 K. This leads to a shorter reaction zone due to the additional available energy. Similarly, a 10% increase in the wall heat transfer coefficient increases the wall heat loss by about 10% showing a non-linear behavior. The product gas temperature is also lowered by 10 K. This results in a longer reaction zone and a shorter ash zone. The observed non-linear behavior is due to the effective lengths and temperatures of various reactive zones and the ash zone. A longer ash zone, which has low temperature, results in lower wall heat loss. The peak solid temperatures do not show any significant deviations from the base case. Higher product gas temperature yields higher amounts of CO and H₂, and lower amounts of CO₂, CH₄, and H₂O.

Switch Temperature

The switch temperature above which the gas phase is considered to be in chemical equilibrium as well as in thermal equilibrium shows a significant effect on solid and gas temperatures as well as on product gas composition. A lower switch temperature yields significantly lower amounts of CH₄ and H₂O, and higher quantities of H₂ as shown in Figure 2.5-5E. The amount of CO₂ in the product gas also increases. The effluent gas temperature decreases as the switch temperature is lowered, as shown in Figure 2.5-6E, leading to an extended reaction zone. These results are consistent with the observed behavior for the wall heat loss. Furthermore, these results indicate that the product gas is not in chemical equilibrium at the low effluent temperatures. This is especially true for high moisture coals which yield much higher quantities of H₂ and CH₄ and lower quantities of H₂O when the gases are allowed to react to equilibrium. Additional simulations, with coals of varying ranks, should be performed to obtain a value of switch temperature with more general applicability. An option for full gas phase chemical kinetics should also be considered.

Feed Gas Temperature

The effects of feed gas temperature are shown in Figures 2.5-5F, 2.5-6F, and 2.5-7F. The lower feed gas temperature results in lower gas peak temperature. The solid peak temperature, on the other hand, does not show any significant change. The effect of lowering the feed gas temperature by 10K is more pronounced than increasing the temperature by 10K. This is attributed to much lower product gas temperature resulting from lower feed gas temperature. The product gas composition does not show any significant change.

Reduced Devolatilization Model Integration

The reasons for integrating FG-DVC-RES into the FBED-1 code arise primarily from the desire to reduce the current CPU time required for fixed-bed simulations; this

reason is especially important for future plans that include extending the code to two- and three-dimensional simulations. Further reasons include, however, the desire to reduce programming complexity and the investigation into full back-and-forth integration techniques.

This section discusses the efforts toward integrating the reduced devolatilization model, FG-DVC-RES into the FBED-1 computer program. The section is split into three parts. In the first part the model is presented and discussed. The second part discusses our efforts toward verifying that the reduced model does in fact reproduce the results of a full FG-DVC simulation. In the third part details of the integration are discussed and some results, comparing output produced by FBED-1 and FBED-1-RES, are presented. FBED-1-RES is the name of the final fixed-bed code that utilizes the reduced devolatilization mechanism.

The Reduced Devolatilization Model, FG-DVC-RES

The current version of FG-DVC-RES models the volatile mass released, m_v with a single ordinary differential equation as follows:

$$\frac{dm_v(t)}{dt} = k[m_{v,f} - m_v(t)] \quad (2.5-17)$$

where m_v is the instantaneous amount of volatiles released per unit weight of dry ash-free coal and $m_{v,f}$ is the total amount of volatiles available for release. The reaction rate, k is calculated from

$$k = k_o \int_{E_t}^{E_{max}} \exp\left(\frac{-E}{RT}\right) f(E) dE \quad (2.5-18)$$

where k_o is the pre-exponential factor, E_t is the lower bound of the integration, E_{max} is the upper bound of the integration, and $f(E)$ is the distribution function of the activation energy. This simple model is based on the assumption that at a given nominal pressure and heating rate condition, the total weight loss from coal devolatilization can be modeled with one ordinary differential equation with distributed activation energy.

FG-DVC-RES models the volatile mass released only. In order to recover the complete devolatilization information provided by FG-DVC, e.g. yields, rates and compositions, a correlation is provided with $m_v(t)$ and $dm_v(t)/dt$. For a more complete description of the reduced devolatilization model, refer to Subtask 2.1 of this report.

Comparison of FG-DVC and FG-DVC-RES

Significant time and effort was expended making detailed comparisons between the FG-DVC-RES model and the FG-DVC-stand-alone model. The motivation for this

effort was to establish the capability of the reduced model, not only to reproduce the global features of the devolatilization process, e.g. char weight loss, but to reproduce the details of the process as well. At the beginning of this investigation it was discovered that although the weight loss history of a coal particle undergoing devolatilization could be accurately reproduced, some of the rates of production of gaseous species and elemental composition of gas, tar, and char were not as accurately reproduced. This report summarizes our findings and includes some of the more pertinent comparisons.

Included are two sets of results, presented in Figures 2.5-8 to 2.5-15 and Figures 2.5-16 to 2.5-23. Both of these sets of results compare predictions of gaseous species concentrations, total gas, tar and char weight fractions, and gas, tar and char elemental compositions, all as a function of time. The results presented in Figures 2.5-8 to 2.5-15 are based on the INTERC0 subroutine (constant rates) and the results presented in Figures 2.5-16 to 2.5-23 are based on the INTERC subroutine (variable rates). Both sets of results are presented to assess the capability of FG-DVC-RES to reproduce the details of an FG-DVC-stand-alone simulation for a given heating rate and final temperature; the heating rate and final temperature used in the simulations are 5000 K/sec and 1273 K, respectively. The coal type is Jetson bituminous.

Figures 2.5-8 to 2.5-9 and 2.5-16 to 2.5-17 show comparisons of gas species yields, normalized per unit mass of coal, between the stand-alone and RES models. Note that while use of INTERC0 allows correct prediction of total species yields, the early transient behavior shows discrepancies with the stand-alone model. This behavior is opposite to that produced by INTERC, the transient is correct but the total yields do not agree; the total yields with both models should agree.

Figures 2.5-10 to 2.5-11 and 2.5-18 to 2.5-19 show comparisons of the rates of production of the same gaseous species shown in Figures 2.5-8 to 2.5-9 and 2.5-16 to 2.5-17. Note that the rates computed using the INTERC0 subroutine and shown in Figures 2.5-10 to 2.5-11 display different peak values and are shifted to the left of the stand-alone peaks, although the integrated areas under the rate curves is identical as the total yields are identical. In Figures 2.5-18 to 2.5-19 the shape of the rate curves, computed using the INTERC subroutine, are close to the stand-alone rate curves except for the appearance of jaggedness, especially for CO₂, and sharp spikes. It is expected that this jaggedness and the presence of spikes will cause numerical difficulties in integration.

Figures 2.5-12 and 2.5-20 show the total gas production, total tar production and char weight loss for the INTERC0 and INTERC models, respectively. It is interesting that even though the values of gas and tar production disagree with the stand-alone model in the transient portion of the results presented in Figure 2.5-12, their sum permits close agreement with the char weight loss predicted by the stand-alone model.

Figures 2.5-13 to 2.5-15 and 2.5-21 to 2.5-23 show instantaneous elemental

Figure 2.5-8. Evolution of major gaseous species predicted by INTERCO (—) and standalone FG-DVC model (⊕).

Figure 2.5-9. Evolution of minor gaseous species predicted by INTERCO (—) and standalone FG-DVC model (⊕).

Figure 2.5-10. Evolution rate of major gaseous species predicted by INTERCO (—) and standalone FG-DVC model (—○—).

Figure 2.5-11. Evolution rate of minor gaseous species predicted by INTERCO and standalone FG-DVC model ($\circ$).

Figure 2.5-12. Evolution of gas, tar and char predicted by INTERCO (—) and standalone FG-DVC model (—○—).

Figure 2.5-13. Elemental composition of gas predicted by INTERCO (—) and standalone FG-DVC model (—○—).

Figure 2.5-14. Elemental composition of tar predicted by INTERCO and standalone FG-DVC (results coincide).

Figure 2.5-15. Elemental composition of char predicted by INTERCO (—) and standalone FG-DVC model (—○—).

Figure 2.5-16. Evolution of gaseous species predicted by INTERC (—) and standalone FG-DVC model (—○—).

Figure 2.5-17. Evolution of gaseous species predicted by INTERC (—) and standalone FG-DVC model (—○—).

Figure 2.5-18. Evolution rate of gaseous species predicted by INTERC (jagged line) and standalone FG-DVC model (smooth line).

Figure 2.5-19. Evolution rate of gaseous species predicted by INTERC (jagged line) and standalone FG-DVC model (smooth line).

Figure 2.5-20. Evolution of gas, tar and char predicted by INTERC and standalone FG-DVC model (results coincide).

Figure 2.5-21. Elemental composition of gas predicted by INTERC (—) and standalone FG-DVC model(⊖).

Figure 2.5-22. Elemental composition of tar predicted by INTERC and standalone FG-DVC model (results coincide).

Figure 2.5-23. Elemental composition of char predicted by INTERC (—) and standalone FG-DVC model (○).

composition of gas, tar and char, computed using the INTERC0 and INTERC subroutines, respectively. Although both of the reduced models permit reasonable comparisons with the stand-alone model, the INTERC0 model produces a kinked behavior in the gas composition at approximately 0.85 seconds.

It should be noted that the devolatilization conditions selected for this comparison are severe in that the heating rate is relatively high compared to that typically encountered in a fixed-bed reactor. It is expected that comparisons based on a heating rate of 1-2 degrees Kelvin per second will be better.

Integration of FG-DVC-RES into FBED-1

The actual integration of the reduced devolatilization model into FBED-1 is relatively straight forward. First, the set of 153 equations which comprise the FG-DVC devolatilization model are removed. In place of these 153 equations that describe devolatilization is put a single ordinary differential equation that describes volatile mass release. This single equation is the basis for the FG-DVC-RES model. Given instantaneous values of solid temperature and volatile weight loss, the model returns an instantaneous volatile mass release rate as well as values for instantaneous rates of gaseous species and tar production, and elemental compositions of gas, tar, and char. These values are all determined through a correlation of the instantaneous value of the volatile mass released with the results of an *a priori* FG-DVC simulation.

The second part of the integration requires removal of all functional-group descriptions within FBED-1 and replacement of these descriptions with appropriate values obtained from the correlation mentioned above. For example, the mass fraction of all devolatilization gases in the base FBED-1 code are obtained by summing all the like functional groups of each particular gaseous specie at any instant of time during the devolatilization process; the same applies for gaseous rates of devolatilization. With FG-DVC-RES, however, there are no functional group descriptions for devolatilization, only the gaseous species compositions and rates themselves, as well as tar and char rates and compositions. Thus, proper integration of the gas, tar and char compositions and rates, computed using the FG-DVC-RES model, requires removal of all functional group descriptions, followed by recoding of each gas, tar and char component description.

Aside from greatly reduced computational demands, the integration of FG-DVC-RES into FBED-1 results in far less bookkeeping. The 153 variables required to integrate FG-DVC are replaced with a single volatile mass release variable for integration of a single equation, plus variables that contain gaseous species rates and tar and char elemental composition. As mentioned, these latter variables are obtained through correlation of the single volatile mass release variable with an *a priori* FG-DVC simulation. The drawback to this simplification in the operation of FBED-1 is the need to perform *a priori* FG-DVC simulations and the restrictions this imposes on the permissible devolatilization conditions.

Comparison of FBED-1 and FBED-1-RES

To enable evaluation of the FBED-1-RES code, results of a fixed-bed simulation are presented for both the FBED-1 and the FBED-1-RES codes. The simulation is based on the experimental operation of the Wellman-Galusha gasifier. Details of the physical gasifier may be found in Thimsen et al. (1984-85), and of the FBED-1 simulation in Radulovic et al. (1995).

Profile results for temperature, pressure, major and minor gaseous species, and particle diameter may be found for both simulations in Figures 2.5-24 and 2.5-25. Also found in these figures are results for devolatilization, drying, oxidation and gasification rates. The most noticeable difference between the simulations is the shift toward the right of the location of the steep gradient in gas and solid temperatures produced with the FBED-1-RES model. The other noticeable difference in the simulation results is the shape of the devolatilization rate curve; it is narrower and has a higher peak in the FBED-1-RES simulation. Some minor differences may also be found in the gaseous species compositions.

Qualitatively, the comparison between the simulations is excellent. The only differences are related to the location of the steep temperature and concentration gradients. Quantitatively, there are some differences, but these are small and may be attributable to the differences in the devolatilization submodels themselves. It should be noted in this discussion that the FG-DVC-RES model that was integrated into the existing FBED-1 code to produce FBED-1-RES code, and the FG-DVC model that resides in the existing FBED-1 code exhibit differences in devolatilization predictions, even for the same coal and devolatilization conditions. The FG-DVC-RES model in use here is based on a more recent FG-DVC model than the one that resides in the existing FBED-1 code. The new FG-DVC model is algebraic in nature, while the old one that resides in the existing FBED-1 code is differential. Furthermore, additional gaseous devolatilization species are included in the new FG-DVC model. Thus, a more representative comparison would be between the new FBED-1-RES code and an FBED-1 code that is based on the new FG-DVC model. This is because the new FG-DVC model is currently used to create the input files for FG-DVC-RES model.

Back and Forth Integration

Aside from the desire to reduce CPU time and programming complexity, a further reason for incorporating FG-DVC-RES into the FBED-1 code is the desire to integrate the FBED-1 system of equations using a full back-and-forth integration strategy. Currently, the system of equations is integrated using a split back-and-forth technique whereby the full set of equations is integrated in the downward pass and only the set of equations referring to the gas quantities is integrated in the upward pass; the solid phase quantities are held fixed from the previous downward integration pass. It is felt that a simplified devolatilization model, such as FG-DVC-RES, may facilitate this goal.

Figure 2.5-24. FBED-1 predictions for the atmospheric pressure, air-blown, dry-ash, Wellman-Galusha gasifier, fired with the Jetson bituminous coal.

Figure 2.5-25. FBED-1-RES predictions for the atmospheric pressure, air-blown, dry-ash, Wellman-Galusha gasifier, fired with the Jetson bituminous coal.

The full back-and-forth integration of FBED-1 has not been completed, nor has it been fully determined that it is even possible. But toward this end, a reverse integration of the reduced devolatilization model has been performed. It was found that FG-DVC-RES could be integrated in reverse provided that accurate boundary conditions, obtained from a forward integration, were used. In other words, a forward integration of FG-DVC-RES needs to be performed to generate a $m_v(t)$ vs. time curve, given an input temperature vs. time curve. From this forward integration information, m_v and T are selected at some point in time near the end of devolatilization and used as boundary conditions for the reverse integration; m_v is used as a boundary condition for the ODE and T is used to compute a reverse temperature vs. time history. Provided that the normalized value of m_v is greater than approximately 0.01, the reverse integration works fairly well.

The difficulty in integrating FBED-1 in reverse is that the boundary condition for a reverse integration of FG-DVC-RES can not be established *a priori*. Trials on the reverse integration of FG-DVC-RES in a stand-alone fashion suggest that not only does the boundary condition for m_v have to be selected with care, but the reverse temperature vs. time history has to match that used in the forward integration. If these values are not chosen with care, then the reverse integration is not successful.

Figure 2.5-26 shows the results of a test of the reverse integration of FG-DVC-RES compared with the result of a forward integration. The forward integration result is the uppermost curve at $t=0$ seconds. It starts at 42.5 grams of volatile mass at $t=0$ seconds and finishes at 0 grams of volatile mass at t equal approximately 750 seconds. There are four reverse integration curves presented in the graph in addition to the forward integration curve, although only three can be clearly seen. Each reverse integration curve starts at a point on the forward integration curve equal to 10, 1, .1, and .01 percent of $m_{v,f}$. The curve that starts at 10 percent $m_{v,f}$ follows the forward integration result exactly and ends up with a final value of m_v equal to 42.5 grams. The curve that starts at 1 percent follows the forward integration curve closely, initially, but ends up with a final value just below the forward integration result. The curve that starts at .1 percent also follows closely in the beginning, but ends up with a final value just above 40 grams. The curve that starts at .01 percent follows the forward integration result closely in the beginning, but goes unstable and shoots to infinity at around $t=500$ seconds.

The heating rate and final temperature used in the above test case are 1 K/s and 1500 K, respectively. The coal description is based on Jetson bituminous, with the distributed activation energy curve being approximated with a Gaussian distribution. It should be noted that no reverse integration could be successfully performed using the distributed activation energy input file that accompanies FG-DVC-RES.

Discussion and Recommendations for Future Work

An improved, comprehensive, one-dimensional model, FBED-1, for

Figure 2.5-26. Comparison of reverse integration results with the forward integration results.

countercurrent combustion and gasification of coal in fixed beds has been developed and evaluated. The advances achieved by this model include integration of a coal-dependent devolatilization submodel, FG-DVC (Solomon et al., 1987 and 1988), an improved treatment of the heat effects associated with devolatilization, an improved treatment of the simultaneous drying, devolatilization, oxidation and gasification reactions, an option to keep the gas phase out of chemical equilibrium below a specified temperature, and a split, back-and-forth, shooting method that satisfies the boundary conditions for both the feed coal and the feed gas streams. The model predictions have been compared with the experimental data for two coals, the Jetson bituminous coal and the Rosebud subbituminous coal, in the atmospheric-pressure, air-blown, dry-ash, Wellman-Galusha gasifier. The agreement with the experimental data for the product gas composition, the product tar flow rate, the wall heat loss, and the pressure profile is quite good (Radulovic et al., 1995). The FBED-1 predictions show marked improvements when compared with the results of the MBED-1 model. The predicted temperature profiles, while overpredicting the peak temperatures, properly simulate the trends and various zones encountered in fixed bed combustion and gasification of coal.

An illustrative simulation showing the axial profiles for major and minor species, the char consumption rates by the drying, devolatilization, and heterogeneous reactions and the particle burnout profiles has been presented in Radulovic et al. (1995). The results show a number of uncertainties in the model predictions. The predicted overall burnout is always close to unity as the currently available kinetic parameters for the heterogeneous reactions depend only on the gas phase concentration of the oxidation or gasification agents. This also leads to very steep change in temperature in the oxidation zone. Additional research is needed to study the effect of available char mass on the oxidation and gasification kinetics. The kinetic parameters for the oxidation and gasification reactions used in this model were obtained from small particle experiments at atmospheric pressure. Recent research conducted at this laboratory shows a significant effect of particle size and gas pressure on the kinetic parameters for char oxidation. The research is continuing to study the effects of pressure on oxidation and gasification of large char particles and will result in improved kinetic parameters. Incorporation of these kinetic parameters for the oxidation and gasification of large particles will lead to improved predictions of the solid and gas temperatures and associated heat effects in fixed bed processes. There is also a need to provide an improved treatment of extinction of the gasification and oxidation reactions. Such treatment may significantly reduce numerical difficulties in integration of the system of equations from the bottom to the top of gasifier and may lead to improved simulation of the ash zone.

The predicted profiles for the sulfur and nitrogen pollutants show only H_2S and HCN in the product gas. The amounts of NO and SO_2 are significant only in the high temperature, oxidizing equilibrium zone. This indicates a need for a detailed pollutants submodel to properly predict the emissions of nitrogen and sulfur species. Several submodels are currently available to predict the emissions of sulfur and nitrogen

pollutants. These submodels can be integrated in the FBED-1 model and in conjunction with the advanced devolatilization submodel, FG-DVC, can yield accurate predictions for the emissions of these pollutant species.

The treatment of heat and mass transfer in the reactive fixed beds should also be improved. In the FBED-1 model, the effect of the reactive nature of the fixed bed on heat transfer is accounted for by correcting the non-reactive, solid-to-gas heat transfer coefficient using a constant factor. A value of 0.05 has been used in the simulations but this should not be considered a universal factor. Additional experiments must be performed on reactive fixed-beds to study the effect of reactions on the interphase heat and mass transfer.

Incorporation of a solids flow model may also significantly improve the predictions of the FBED-1 model. The plug flow assumption does not provide a realistic description of the solids flow in the fixed-bed systems. As the coal particles devolatilize and undergo gasification and oxidation, they change in size and settle. This significantly affects their residence time which may be quite different from the values computed by the plug flow assumption. Submodels for solids flow are, currently, in development stage and should be integrated when they become available.

The present option to switch between non-equilibrium calculations and equilibrium calculations leads to discontinuity in the gas phase composition during the downward integration pass. An option should be provided for full treatment of gas phase kinetics. This option, coupled with the heterogeneous char reactions, should yield improved predictions for the gas phase composition and eliminate any inconsistency due to the arbitrarily selected switch temperature. Finally, the initial guess for the FBED-1 model must be such that complete conversion of coal takes place during the first downward integration pass. Once, this condition is satisfied, the predictions of the FBED-1 model are locally convergent. However, the question of global convergence has not been resolved. The code may, perhaps, be made globally convergent by incorporating a full, back-and-forth integration scheme as it will remove any inconsistencies between the downward and the upward integration passes. However, due to the highly non-linear nature of the problem such an implementation may be difficult. This difficulty has been partly addressed by implementing the reduced devolatilization submodel, FG-DVC-RES, but difficulties still remain.

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Nomenclature

Symbol	Definition and Units
A	Cross sectional area of gasifier, m^2
A	Particle surface area, m^2
A_{jk}	Mass fraction of element j in pseudospecies tar or functional group k

C	Molar concentration, kmol/m^3
D	Diffusivity, m^2/s
D	Gasifier diameter, m
d	Particle diameter, m
F	Fraction of original carbon
f	Enthalpy function for char
h	Enthalpy, J/Kg
h	Heat transfer coefficient, $\text{J}/\text{m}^2\text{sK}$
k	Arrhenius rate constant, m/s or $1/\text{s}$
k	Mass transfer coefficient, m/s
m	Volatile mass released, kg
$\dot{m}$	Mass flow rate, kg/s
M_w	Molecular weight, kg/kmol
q	Heat release for daf coal, J/kg
Q	Heat loss, J/s
r	Volumetric reaction rate, $\text{kg}/\text{m}^3\text{s}$
t	Time, s
T	Temperature, K
X	Mole fraction, kmol/kmol
Y	Functional group mass fraction, kg/kg initial char
z	Axial distance, m
ε	Bed void fraction, void volume/bed volume
Φ	Heat of combustion of elements, J/kg
ϕ	Interaction parameter

η	Particle number density, $1/m^3$
λ	Stoichiometric coefficient, <i>mole/mole</i>
μ	Atomic weight, <i>kg/katom</i>
ν	Stoichiometric coefficient, <i>mole/mole</i>
ρ	Density, <i>kg/m³</i>
Ω	Dry, ash-free mass fraction
ζ	Particle area factor to account for internal surface burning
ζ	Adjustable factor for solid-to-gas heat transfer coefficient

<i>Subscripts</i>	<i>Definition</i>
<i>ash</i>	Ash
<i>devol</i>	Devolatilization
<i>drying</i>	Drying
<i>eff</i>	Effective
<i>f</i>	Formation
<i>FG</i>	Functional group
<i>g</i>	Gas
<i>gw</i>	Gas-to-wall
<i>i</i>	Integer counter used to keep track of elements, species, or reactions
<i>i</i>	index for drying, devolatilization, gasification and oxidation reactions
<i>i, k</i>	index for functional groups
<i>j</i>	index for elements C, H, O, N, and S
<i>m</i>	mass transport
<i>nfg</i>	Number of functional groups used in the devolatilization submodel

<i>p</i>	Particle
<i>r</i>	Reaction
<i>s</i>	Sensible
<i>s</i>	Solid
<i>sg</i>	Solid-to-gas
<i>sm</i>	Solid measured (refers to the apparent density)
<i>sw</i>	Solid-to-wall
<i>t</i>	Tar
<i>total</i>	Total
<i>vap</i>	Vaporization
<i>w</i>	Wall
<i>w</i>	Water
<i>wg</i>	Water in the bulk gas phase
<i>wp</i>	Water at the particle surface

Superscripts Definition

<i>g</i>	Gasification
<i>o</i>	Initial
<i>o</i>	Oxidation
<i>s</i>	Sensible
<i>vap</i>	Vaporization

SUBTASK 2.6 ADVANCED TWO-DIMENSIONAL TRANSPORT REACTOR MODEL DEVELOPMENT AND EVALUATION

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Objectives

The original objective of this subtask was to develop and evaluate a 2-D transport reactor model incorporating advanced submodels developed in subtasks 2.3 and 2.4.

Accomplishments

A cold flow version of the 2-D transport reactor model was completed and validated against existing data. The hot flow version for reacting particles was not fully developed and validation data from UNDEERC or Wilsonville was unavailable because of Kellogg's proprietary concerns.

Stochastic Turbulence Particle Dispersion (STPD) Model

Work began by modifying the particle trajectory model in PCGC-2. The particle model in PCGC-2 uses an empirical approach to model the turbulence effects on the coal particle motion, and can not be extended to model the transport reactor situation. We replaced the current particle model with a true stochastic turbulence particle dispersion (STPD) model, which considers various effects, including gas turbulence, particle number density distribution, and particle-particle interactions. This model is an extension of one developed previously at AFR (Zhao et. al., 1993; Solomon, et. al, 1996). Of particular importance for the case of transport reactors is an empirical expression which incorporates the effect of the fluctuating particle number density on the drag force. Data on particle dispersion in controlled turbulent flow were collected from the literature for comparison with the model.

The initial work was focused on developing and verifying a stochastic turbulence particle dispersion (STPD) model for dense flows. This turbulence particle dispersion model uses the following equations to model the motion of a coal particle (the pyrolysis weight loss is ignored for the moment):

(2.6-1)

$$\begin{cases} dV'_x - \beta V'_x dt + \sqrt{\frac{4\beta k}{3}} dW_1(t) \\ dV'_y = -\beta V'_y dt + \sqrt{\frac{4\beta k}{3}} dW_2(t) \\ dU_x = \Gamma(\bar{V}_x + V'_x - U_x)dt \\ dU_y = \Gamma(\bar{V}_y + V'_y - U_y)dt \\ dX = U_x dt \\ dY = U_y dt \end{cases}$$

where V and U are the velocities of gas and the particle, respectively, x and y are the particle spatial coordinates, W_1 and W_2 are two independent Wiener stochastic processes, k is the gas turbulence kinetic energy, and b is the inverse of the turbulent time scale or particle-eddy interaction time, whichever is smaller. Variables in upper case are random variables (stochastic processes). A mean value is indicated by $\bar{}$ and $'$ indicates the fluctuation component.

This model uses the first two expressions in Eq. 2.6-1 to simulate the turbulent component of the gas velocity. It has been demonstrated that the turbulence generated has the exact values of k and the time scale given by the k - ε model. This is the advantage of our model in comparison with those of Gosman and Ioannides (1981), and Shuen et al. (1983). Their models used a direct Monte Carlo method to alter the local gas velocity and these numerical schemes will not necessarily give the correct values of k and ε . There are in-depth discussions on the numerical solution of Eq. 2.6-1 by Kloeden and Platen (1982). Truncated Fourier series with independent Gaussian random coefficients were also used to simulate the gas turbulence (for example, Wang and Stock (1992)), but computing a truncated Fourier series consumes large amount of computer time. Our model is much more efficient.

In order to verify our model, predictions of particle dispersion need to be compared with existing data. One such comparison has been made with data in grid generated turbulence by Snyder and Lumley (1971). It was found that our model under-predicts the data. Shuen et al. (1983) indicated that their model was calibrated with Snyder and Lumley's data (1971), but the nature of this calibration is not clear. We agree with Shuen et al. (1983) that it may be due to the arbitrary estimation of the time and length scales of the turbulence. It is true that, although the Eulerian integration time and length scales do present the scales in which the turbulence develops, they may not be quantitative enough to be used in the turbulence particle dispersion model. Our model is clearly limited by the state-of-the-art in understanding gas turbulence phenomenon. Although this is a fast advancing field, the k - ε description was still the most commonly accepted model. Examining other turbulence models is beyond the scope of this contract. In order to fit Snyder and Lumley's data (1971), the time scale given needs to

be increased by a factor of 2.7. The model predictions after the calibration and the data are plotted in Figure 2.6-1.

Work was also carried out to calculate the Eulerian particle properties, such as the mean velocity and the particle number density, from the stochastic particle model. Obtaining statistically meaningful values requires a large number of particle trajectories. The distributions of particle number density, mean velocities, and mean square velocities are plotted in Figs. 2.6-2 and 2.6-3 with 500 and 5,000 particle trajectory calculations, respectively. The calculation was based on Snyder and Lumley's fluid data mentioned above and particles were injected from a point source up-stream. It is clear that, while the two calculations resulted in the same distributions, the distributions in Figure 2.6-2 are much smoother than those in Fig. 2.6-3. The insufficient number of trajectories which resulted in the noisy signals in Fig. 2.6-2, would cause severe convergence problem in the gas phase calculation, especially at high particle loadings. Since practical inlet pipes have finite diameters, model calculations have to inject particles from multiple positions throughout this diameter. Calculating 5,000 particle trajectories at each injection point imposes a heavy computational load on the code. We have to calculate only the number of trajectories, that is practically possible and look for ways to smooth the noisy distributions.

Interface of STPD Model with PCGC-2 Code

An interface of the model with PCGC-2 needed to be developed so that it could take the flow field information passed by PCGC-2, calculate the particle dispersion and return the required source terms back to PCGC-2 for updating the flow field. Associated with the new particle trajectory model, there were extensive modifications of the PCGC-2 code including the calculations of source terms for the mass, momentum, and turbulence equations. Another required development was a user graphic interface for the particle dispersion submodel. A set of C subroutines were written to invoke an X-window graphic interface to plot both the particle trajectories being modeled and any desired fluid field contours. This development enhanced the debugging efficiency and made the code more user friendly. When coding the SPTD model for PCGC-2, we have taken particular care to insure the portability of the code, so that its integration with other computational fluid dynamics codes, such as PCGC-3, will be straightforward.

Figure 2.6-4 compares the particle number densities in a coal combustor predicted by the stochastic model and the deterministic model currently used in PCGC-2. The major difference in the prediction is the particle number density near the reactor wall. The stochastic model predicts more realistic particle dispersions, which shows that there is a high particle concentration near the wall region. Particles are driven toward to the wall by the high turbulence along the center line. The accumulation of particles near the wall is due to the low gas velocity in that region, which leads to low particle movability. It also predicts the recirculation of particles. Conversely, the deterministic model shows no indication of particle impingement with the wall and no particles reaching the region

Figure 2.6-1 Prediction of particle dispersion compared with data of Snyder and Lumley (1971).

Figure 2.6-2 Predictions of Eulerian particle properties for AFR dispersion model and fluid data of Snyder and Lumley (1971). a) Particle number density; b) Mean particle axial velocity; c) Mean square particle axial velocity; d) Mean particle radial velocity; e) Mean square particles radial velocity. Number of particles calculated = 500; particle diameter = $46.5\mu\text{m}$; particle density = 260 kg/m^3 .

Figure 2.6-3 Predictions of Eulerian particle properties for AFR dispersion model and fluid data of Snyder and Lumley (1971). a) Particle number density; b) Mean particle axial velocity; c) Mean square particle axial velocity; d) Mean particle radial velocity; e) Mean square particles radial velocity. Number of particles calculated = 5000; particle diameter = $46.5\mu\text{m}$; particle density = 260 kg/m^3 .

Particle Number Density

Stochastic Model

Deterministic Model

Figure 2.6-4 Particle number density predicted by Stochastic Model and Deterministic Model.

near the wall. This comparison demonstrated that the stochastic model is able to predict more precisely the particle trajectories and the fine structure of the particle distribution. Such abilities are crucially important in modeling the transport reactors in which the particle motion plays a key role.

We have studied using PCGC-2 a number of cases with a geometries typical to transport reactors, but with dilute particle loadings. The converged flow field was used for the SPTD model to test the numerical behavior and compatibility of the model. A model development effort on particle-particle interactions was also initiated.

A characteristic of transport reactors that has been difficult to explain is the distribution of particle number density in the reactor. Measurements have shown a unique flow pattern with a dilute core and a dense annulus. Flow is positive upward in the core while downward in the annulus, thus forming an internal recirculation. There is a general agreement that the downward flow in the annulus is caused by the high particle number density in that region. The gas flow is unable to push particles upward at this density and the falling particle cloud will eventually change the flow direction in that region. However, there is no explanation on what drives particles to the wall.

We have speculated that the gas turbulence is the main reason, and have been working with this hypothesis. As discussed above, we had reported initial success in modeling the particle dispersion in transport reactors. We have seen that particles tend to accumulate in the wall region driven by the turbulence. In this project, we have added to our model a key element, which explicitly includes the effect of turbulence on the particle motion.

The following are the equations of motion for a particle in a gas flow. The set is given in a cylindrical coordinate system. Both the gas and particle velocities are instantaneous values, not average values.

$$\begin{cases} m_p \frac{du_z}{dt} = \Gamma(v_z - u_z) \\ m_p \frac{du_r}{dt} = \Gamma(v_r - u_r) + \frac{1}{r} u_\theta^2 \\ m_p \frac{du_\theta}{dt} = \Gamma(v_\theta - u_\theta) \end{cases} \quad (2.6-2)$$

Where u and v are the velocities of gas and the particle, respectively; subscripts z , r , and θ denote the axial, radial and tangential components of the velocities; m_p is the mass of the particle and Γ is the drag coefficient.

If we average the velocities on both sides of the equations, most of the fluctuating velocity components will diminish. But, the fluctuating tangential velocity, which represents the centrifugal force remains, as given in Eq. 2-6-3 where a bar above a

variable denotes its mean value and a prime denotes the fluctuation component. This term which is missing from the formulation in PCGC-2, will unambiguously drive particles to the wall. In Eq. 2-6-3, we assume no swirl, e.g., the tangential gas velocity as well as tangential particle velocity has a zero mean value.

$$\begin{cases} m_p \frac{d\bar{u}_z}{dt} = \Gamma(\bar{v}_z - \bar{u}_z) \\ m_p \frac{d\bar{u}_r}{dt} = \Gamma(\bar{v}_r - \bar{u}_r) + \frac{1}{r} \langle u_\theta^2 \rangle \\ \frac{d\bar{u}_\theta}{dt} = 0 \end{cases} \quad (2.6-3)$$

This discovery has led us to model the particles in three dimensional space. We have subsequently modified our model to include the tangential velocity. This modification increases the computational burden of the model, but it appears to be our only choice at this stage.

Fig. 2.6-5 is a contour plot of particle number density in a transport reactor calculated with our modified particle turbulence dispersion model. It shows clearly the high concentration of particles near the reactor wall.

With the high solids loading in transport reactors, there are two effects which predominantly control the flow field, 1) damping and/or enhancing of turbulence by the solid phase and 2) the strong momentum exchange between the gas and solid phases, which leads to a large pressure drop along the center line of the reactor.

In order to account for the first effect, PCGC-2 uses a model proposed by Melville and Bray (1979), in which particles moderately damp the turbulence by decreasing the turbulence viscosity of the gas,

$$v_{tg,particle} = \frac{v_{tg,noparticle}}{(1 + \rho_b / \rho_g)^n} \quad (2.6-4)$$

Where the v 's are the gas turbulence viscosities and ρ_b and ρ_g are the bulk densities of particle and gas respectively. The n suggested by Melville and Bray is 0.5. We found it is necessary to reduce this damping effect in order to maintain an adequate turbulence level in the transport reactor.

When the momentum exchange is ignored and if $n=0.05$ in Eq. 2.6.4, we are able to get a converged solution with PCGC-2. The solution compares well with the data collected at the City College of New York (CCNY). The downward gas flow at the reactor wall is predicted and the radial variations of both the gas and solid velocities are in good

Stochastic Model

Figure 2.6-5. Particle number density.

agreement with the data. However, ignoring the momentum exchange cannot be reasonably justified.

The strong momentum exchange imposes a challenge to PCGC-2, which was developed originally for dilute solids loadings. At high solids loadings, we have had difficulty in converging the solution for the gas phase. We found that this is partially due to the grid used in our modeling of the CCNY transport reactor. This reactor is about 28 feet tall and has a 6 inch diameter. We used a grid with 40 grid nodes along the axial direction and 21 nodes in radial direction. This was to ensure that the numerical model is solvable with our computational power. However, this grid has an unreasonable aspect ratio which caused significant numerical instabilities. Realizing this problem, we constructed another grid which has 300 nodal points along the axial direction. This solves the numerical instability problem, but the size of the problem is much larger than before, and therefore, the convergence rate is very slow.

A converged solution was obtained, although the convergence criterion had to be relaxed due to reasons discussed below. Fig. 2.6-6 shows a particle trajectories plot composed of more than 100 trajectories. Colors are used to distinguish the particle starting positions. Particles are constantly changing directions under the influence of gas turbulence in the reactor, as they are injected from the bottom and conveyed to the exit at the top. There are more particles close to the wall than along the center line. This is more clearly demonstrated in Fig. 2.6-7, in which the radial distributions of void fraction at different heights are plotted. These distributions are in good agreement with data collected at CCNY. Fig. 2.6-8 is the radial distribution of axial gas velocity at 2/3 height of the reactor. The gas velocity is high in the core region and low near the wall, due to both the friction of the wall and high solid concentration at the wall indicated in Fig. 2.6-7. However, the model is not yet able to predict the correct flow pattern, with a reverse flow near the wall as indicated by the data, even though the model correctly predicts the solids distribution.

It was discovered that we must relax the convergence criterion for the transport reactor modeling. The high solid loading leads to strong momentum exchange between the gas and solid phases. The source terms in the momentum finite difference equations are large and dominantly control the flow field. The original convergence criterion may need modification. A more serious problem is the large pressure gradient (pressure drop), which causes numerical difficulties for the SIMPLE based methods used in PCGC-2. The SIMPLE method solves the modified continuity equation for pressure and then uses the pressure difference to solve the momentum equation for velocity. The calculation of the pressure difference introduces a round-off error, which is not severe in most cases where there is no large pressure variation in the reactor, but it becomes a problem in modeling transport reactors.

We have compared our modeling results with measurement data on 1) axial gas velocity, 2) void fraction and 3) pressure drop. Fig. 2.6-9 compares the calculated and measured radial variation of the void fraction in the CCNY transport reactor at 1/2 of the

Figure 2.6-6. Predicted particle trajectories in CCNY transport reactor.

Figure 2.6-7. Predicted void fraction distributions in CCNY transport reactor.

Figure 2.6-8 The radial distribution of axial gas velocity at $L/H=2/3$.

Radial Variation of Void Fraction in Transport Reactor
Data Collected at CCNY
superficial gas velocity = 3m/s, solid flow rate = 50 kg/m²s, L/H=0.5

Figure 2.6-9. Comparison of calculated and measured void fraction distribution in a transport reactor.

height, and shows a very good agreement. Unfortunately, there are no data points close to the wall, probably due to the difficulty of measuring the near-wall void fraction.

Fig. 2.6-10 plots the axial pressure variation in the entire length of the reactor. The pressure drop at 1/2 of the height can be derived from the plot and is 270 N/M^3 . Compared to 236 N/M^3 , the measured value of the CCNY unit, our model prediction is quite satisfactory. It is known that the pressure drop in the transport reactor is largely due to the solids loading. The gas momentum lost to conveying the solids has to be compensated by an increase in pressure at the inlet. Assuming the correctness of the SIMPLE algorithm used in PCGC-2 for the pressure-to-momentum coupling, pressure drop is accurately modeled only if the model predicts the gas-to-solid momentum exchange and solid volume fraction (or void fraction) correctly. The fact that we have come close in predicting the pressure drop suggests a robust performance of the model in this regard.

The next focus of the work was on extending our transport reactor code to model coal gasification and combustion. In order to identify the main problems that need to be solved, one test case was modeled with a reactor wall temperature of 500°C , starting from a converged solution of a "cold" case. The computational time for one gas phase iteration is from 30 minutes to 1 hour on our Pentium 100 PC. It is tolerable, although this is about 5 times longer than that for the "cold" case. However, the computational time for one particle phase calculation is intolerably long, which is typically one day (24 hours). Therefore, a need was identified for a major reworking of the coding for the particle phase reactions.

An investigation was conducted on the original PCGC-2 subroutines to determine what kind of modifications need to be made. In the coal solid combustion part of the PCGC-2 code, there is a section which performs calculations on coal/water slurry combustion, which is an unnecessary residue from the early versions of PCGC-2. For CFB applications, modeling slurry combustion will not be necessary, so this option can be dropped to increase code efficiency. The particle temperature calculation can also be improved to help computation speed. The biggest gain in speed, however, may come from the ordinary differential equation solver. PCGC-2 has a predictor-corrector solver with step size control to solve the particle entropy equation. This should not be necessary now, since the particle motion is governed by stochastic equations and the stochastic equation solver controls the overall precision. It was determined that some of the particle subroutines need to be completely rewritten.

An investigation was conducted to profile the code to identify the subroutines that consume most of the CPU time. Several of the subroutines were found to be the biggest consumers, some of which could be called less frequently to reduce CPU time without causing significant loss of accuracy. Code changes were made and tests indicated a big improvement in the run speed. Some preliminary work with a hot flow version of the model is discussed under subtask 5.2.

Pressure Variation in CCNY Transport Reactor

superficial gas velocity = 3m/s, solid flow rate = 50 kg/m²s

Average Pressure Drop = 332 N/m³
Pressure Drop at 1/2 height = 270 N/m³

Figure 2.6-10. Model prediction of the pressure variation in CCNY transport reactor.

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TASK 3 - MODELING OF GAS PHASE COMBUSTION

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Objectives

The original objectives of this task were to develop, refine, and expand advanced submodels for gaseous combustion and NO_x emission applicable to lean, premixed combustion of natural gas in gas turbines, and to integrate the submodels into a comprehensive combustor flow model. Due to incomplete funding, the task was only partially completed.

Accomplishments

A new, axisymmetric turbulent combustion submodel was developed for lean, premixed combustion in gas turbines. Two reduced mechanisms for methane combustion were evaluated and implemented in the submodel. The submodel was integrated into a comprehensive combustion flow code, and preliminary comparisons were made between predictions and laboratory-scale data.

Turbulent Combustion Submodel

The new turbulent combustion submodel is based on the velocity-scalar Monte Carlo PDF method. Monte Carlo PDF methods are compared with other approaches in Table 3-1 and the velocity-scalar PDF method is compared with other PDF methods in Table 3-2. PDF methods are general and treat the reaction term exactly, without further approximation beyond the instantaneous kinetic expression. Monte Carlo PDF methods are efficient and scale linearly with the number of independent variables. The velocity-scalar PDF method is the simplest PDF method that treats the turbulence/chemistry interactions in sufficient detail for premixed flames.

An existing velocity-scalar PDF code, PDF2DS, was used as the starting point for the submodel development. PDF2DS was developed by Dr. Stephen Pope and co-workers at Cornell University (Pope, 1995; Correa and Pope, 1992; Anand et al., 1989) and licensed from BEAM Technologies (Ithaca, NY). It was extended under this task to be applicable to swirling, axisymmetric flows and to include chemical reaction, and the resulting submodel was integrated into a comprehensive, combustion fluid dynamics code, PCGC-3, for two-dimensional, axisymmetric calculations. The relationship between the new PDF submodel and PCGC-3 is illustrated in Figure 3-1. PCGC-3 was used to calculate the mean velocity field and turbulence properties. The PDF submodel provided the density field, incorporating the effects of complex chemical reactions and

Table 3-1. Modeling Approaches for Turbulent Combustion with Kinetics.

Method	Advantages	Disadvantages
EDC (Magnussen and Hjertager, 1976; Magnussen, 1990).	Complex chemistry Simple to add to CFD codes based on laminar chemistry	Empirically based (Bilger, 1989, 1993a; Williams, 1993) Difficult to use with realistic multistep kinetics (Bilger, 1993a) Limited to wrinkled flames (Borghi, 1990) Assumes gradient diffusion Can produce spurious peaks in mean temperature in reaction zone (Hsu et al., 1996) Multiple solutions possible; application to premixed flames not straight-forward (Gran, 1994)
Assumed PDF (Correa et al., 1988; Champion 1980; Spalding, 1971; Lockwood and Naguib, 1975; Bilger, 1980; Janicka and Kollman, 1978; Correa and Gulati, 1992; Correa et al., 1984; Bockhorn, 1989)	Simpler than Monte Carlo PDF methods	Limited to binary mixing (Fox, 1995) Limited to 2 or 3 reactive scalars (Lau, 1995) Usually assumes statistical independence Assumes gradient diffusion PDF shape must be assumed Complex phenomena such as extinction and differential diffusion precluded Small errors in PDF shape may result in large errors in mean reaction rate (Goldin and Menon, 1996) Does not account rigorously for interactions between turbulence and chemistry (Lau, 1995)
Flamelet (Peters, 1984; Abd Al-Masseeh et al., 1990; Duclos et al., 1993)	Complex chemistry	Only valid in thin flamelet regime (Bilger, 1988, 1989, 1992, 1993a) Advanced versions require strain history of the flow (Bilger, 1993) Limited to binary mixing (Fox, 1995) Has difficulty dealing with backmixing (Fox, 1995)
Conditional moment closure (Bilger, 1993a, 1993b; Klimenko, 1990)	Allows use of full kinetic mechanisms (Bilger, 1993) Inexpensive (Smith et al., 1992) Eulerian formulation; can be readily added to existing CFD codes (Fox, 1995)	Scalar fluctuations about conditional mean assumed small (Correa et al., 1994; Fox, 1995) Results for multi-step chemistry and inhomogeneous flows have not been reported (Fox, 1995) Shape of the PDF must be assumed (Smith et al., 1992)
Monte Carlo PDF (Dopazo, 1994; Pope, 1981b, 1985; Correa and Pope, 1992; Haworth and El Tahry, 1991; Anand et al., 1989)	PDF shape calculated (Hsu et al., 1996) Reaction treated exactly (Hsu et al., 1996) Amenable to parallel processing (Hsu et al., 1996)	Expensive Currently affordable only for reduced chemistry (Pope, 1996; Bilger, 1993a) Molecular transport and transport due to the fluctuating pressure gradient must be modeled (Bilger, 1993a; Haworth and El Tahry, 1991)
Linear eddy (Kerstein, 1988)	Distinguishes among effects of turbulent mixing, molecular diffusion, and chemical reaction at all scales of the flow (McMurtry et al., 1993) Detailed parametric studies are economically feasible (McMurtry et al., 1993)	Practical application still in early stages of development (McMurtry et al., 1993) High computational requirements (Fox, 1995)
Local integral moment (Dahm and Tryggvason, 1995; Dahm et al., 1996; Suresh et al., 1994; Chang et al., 1991)	Economical Complex flows; predicts large-scale structure Complex chemistry	Requires mixture fraction gradients; not yet applied to premixed combustion where reaction kinetics dominate

Table 3-2. Comparison of Monte Carlo PDF Methods.

Method	Advantages	Disadvantages
Node-based composition PDF (Chen et al., 1990; Chen and Kollman, 1992; Hsu et al., 1994a, 1994b, 1994c)	Simplest PDF method No. of particles in each cell is constant No particle sorting to determine cell location	Same as distributed-particle composition PDF method plus: Randomness in the implementation of convection leading to statistical error (Pope, 1994b) For non-orthogonal grids, may be difficult to compute effective cell flowrates (Fox, 1995) Difficult to choose proper time step (Fox, 1995)
Distributed-particle composition PDF	Convection is deterministic resulting in decreased statistical error (Pope, 1994b) Time step can be made arbitrarily small (Fox, 1995) Particle equation of motion is grid independent (Fox, 1995)	Same as velocity-composition PDF method plus: Convection by turbulent velocity modeled by gradient diffusion (Anand et al., 1993) Randomness in the implementation of turbulent diffusion, i.e., by random walk (Pope, 1994b) Neglects effects of density fluctuations on velocity field
Velocity-composition PDF	Turbulent diffusion exact (Borghi, 1990) Variable density effects (i.e., fluctuations) exact (Anand et al., 1996)	Contains no information on the time or length scales of the turbulent motions (Anand et al., 1993) Molecular mixing must be modeled (Norris and Pope, 1991a) Particles must be sorted to determine cell location at each time step, a computationally intensive task No. of particles per cell varies randomly
Velocity-composition-dissipation PDF (Anand et al., 1993; Anand et al., 1996; Norris and Pope, 1995; Pope, 1991)	Provides complete closure; stand-alone method (Pope and Chen, 1990; Norris and Pope, 1991b) Allows for multiple time scales, accounts for internal intermittency, has potential to account for large scale structures, and better accounts for particle history effects on local turbulent structure (Anand et al., 1993)	Needs a robust algorithm for calculating the mean pressure field; recently developed pressure algorithm needs more development (Anand et al., 1996)

Figure 3.1. Relationship between PCGC-3 and velocity-scalar PDF submodel.

their interactions with the turbulence. This sequence was repeated until mutual convergence of the flow and combustion calculations was obtained.

Joint PDF Transport Equation — The PDF submodel solves the transport equation for the joint PDF of velocity and composition scalars:

$$\begin{aligned} & \rho(\underline{\psi}) \frac{\partial f}{\partial t} + \rho(\underline{\psi}) V_j \frac{\partial f}{\partial x_j} + \underbrace{\frac{\partial}{\partial \psi_\alpha} [\rho(\underline{\psi}) S_\alpha(\underline{\psi}) f]}_{\alpha=h} + \left(\rho(\underline{\psi}) g_j - \frac{\partial \langle p \rangle}{\partial x_j} \right) \frac{\partial f}{\partial V_j} \\ & = \frac{\partial}{\partial V_j} \left[\left\langle -\frac{\partial \tau_{ij}}{\partial x_i} + \frac{\partial p'}{\partial x_j} \right| \underline{V}, \underline{\psi} \right] f + \frac{\partial}{\partial \psi_\alpha} \left[\left\langle \frac{\partial J_i^\alpha}{\partial x_i} \right| \underline{V}, \underline{\psi} \right] f - \frac{\partial}{\partial \psi_h} \left[\langle \nabla \cdot \underline{q} \rangle \right] f \end{aligned} \quad (3-1)$$

Hence, the method is also referred to as a *velocity-composition* PDF method. Equation 3-1 can be derived from the general equations for conservation of mass, momentum, energy, and species for low-Mach-number flow (Pope, 1985). Here, f represents the local one-point, one-time, joint velocity-composition PDF, ρ is the density, V is the velocity, ψ_α is the α -dimensional composition scalar, S_α is the reaction source term, g_j is the body force, p is the pressure, p' is the pressure fluctuation (due to turbulence), τ_{ij} is the stress tensor, J_i^α is the diffusive flux, ψ_h is the specific enthalpy, and $\nabla \cdot \underline{q}$ is the specific enthalpy source term (due to radiation). Equation 3-1 illustrates the capability of the velocity-composition PDF method to completely describe the important chemical kinetic and convective transport effects in reacting, turbulent flows. These effects are described by the underlined terms in Equation 3-1 and appear in closed form. The terms on the right-hand side required modeling since the required information for computing the conditional expectations (indicated by the angle brackets) is not available from the single-point, joint PDF.

The first term on the right-hand side of Equation 3-1 represents transport of the PDF in velocity space by the viscous stress and fluctuating pressure gradient. This term is described with a simplified Langevin model (Pope, 1994a). The second term represents transport in composition space by the diffusive flux and is described by an interaction-by-exchange-with-the-mean (IEM) model (Pope, 1990; Correa, 1993; Correa and Braaten, 1993; Dutta and Tarbell, 1989; Leonard and Hill, 1991; Pope, 1985; Correa and Pope, 1992). The k - ϵ model is used to provide the mixing frequency (ϵ/k) to both of these models. The mean radiation flux divergence is provided by the discrete ordinates radiation model (Fiveland, 1988; Jamaluddin and Smith, 1988). A spectral-line weighted-sum-of-gray-gases model (Denison and Webb, 1995) provides gas emissivity.

Monte Carlo Solution — Because of the large dimensionality of the velocity-composition PDF ($7+\alpha$), Equation 3-1 is not amenable to conventional solution with finite differences. It is, however, efficiently solved indirectly with a Monte Carlo method (Carmen and Feikema, 1995; Chen and Kollmann, 1988; Correa, Gulati, and Pope,

1988; Haworth and Pope, 1987; Nguyen and Pope, 1984; Pope, 1981a; Pope, 1993; Roekaerts, 1991; Dopazo, 1994; Correa and Pope, 1992). A large number of Lagrangian fluid particles evolving in time are used to represent the joint velocity-composition statistics. Each particle may be thought of as coming from a different realization of the flow (Pope, 1994a).

The time step for the Lagrangian solution is determined from the minimum of all local residence and mixing times in the reactor. A time-splitting technique (Pope, 1994b) is used to sequentially calculate the change in particle properties due to the simultaneous processes of mixing, etc. Here, the term "particle" refers to a fluid element. The particles are first convected for half of a time step. The changes in particle properties due to mixing, reaction, and radiation are then calculated for the full time step. Finally, the particles are convected to their final positions for the time step.

In addition to performing the reaction and mixing calculations at the half-time-step position, these calculations are performed sequentially for several smaller time steps in order to minimize the error due to the coupling between mixing and reaction. In his velocity-composition PDF predictions of a premixed flame, Gran (1994) observed that the mean reaction rate was apparently under-predicted and inferred that this under-prediction may be due to coupling between reaction and diffusion that is not accounted for in the time-splitting Lagrangian approach. The size of the reduced time step was determined from partially stirred reactor (PaSR) calculations where it was gradually reduced until it was not affecting the results. In the limit of an infinite number of particles and an infinitely small time step, the Monte Carlo method provides an exact solution to Equation 3-1 (Haworth and El Tahry, 1991).

Fluid particle velocities evolve in the PDF submodel according to the simplified Langevin model (Haworth and Pope, 1986) and are also adjusted to maintain consistency with the mean velocity and kinetic energy fields provided by the Eulerian flow code (Pope, 1993). This consistency ensures that the no-slip condition is satisfied at the walls (Correa et al., 1994; Dopazo, 1994). Convective heat loss is calculated based on the law of the wall (Launder and Spalding, 1974).

An unstructured grid is used to store mean values of particle properties. The mean fields for velocity, pressure gradient, and turbulence (ϵ/k) are passed to the PDF submodel and fluid particles are then allowed to evolve for one reactor residence time or a specified fraction thereof. Overall convergence requires a statistical steady-state in the PDF calculation and simultaneous satisfaction of the Navier-Stokes equations. Overall mass and energy balances are used to help determine convergence. One macro-iteration for a 3-D case involving approximately 3500 nodes, 1.5×10^4 tetrahedral cells, and 1.5×10^6 particles requires approximately two hours of CPU time on an HP-735 workstation. A macro-iteration consists of converging the Navier-Stokes equations and then performing Lagrangian PDF calculations for the specified length of time, which in this case was 20 percent of the reactor residence time.

Combustion Chemistry

The most complete mechanism for natural gas combustion may be the GRI-Mech 2.11 (Bowman et al., 1996), which consists of 277 elementary reactions and 49 species. Although Monte Carlo PDF methods are capable of treating arbitrarily complex chemistry, full mechanisms are beyond the practical range of present-day computers for turbulent flows. Therefore, reduced mechanisms are needed to represent the combustion chemistry. Two reduced mechanisms, a two-step mechanism and a four-step mechanism, were evaluated by comparing predictions in a partially stirred reactor model with the full GRI mechanism. Both reduced mechanisms were then implemented in the turbulent combustion submodel for detailed reacting flow calculations.

Two-Step Mechanism — The following two-step, five-species mechanism was proposed by Dryer and Glassman (1973) for combustion of methane:

This mechanism is based on the empirical observation that CO is formed very quickly in a thin primary zone, where the methane is consumed and most of the heat is liberated, and is then converted to CO₂ in a much thicker secondary zone (Westenberg, 1971). CH_x radicals generated by the methane-consuming reactions are more reactive than CO and apparently consume the available oxygen. It is only after these radicals have disappeared that CO can oxidize at an appreciable rate (Correa, 1992). With optimized rate parameters, Westbrook and Dryer (1981) used the above mechanism to predict lean and rich flammability limits as well as the dependence of flame speed on pressure and equivalence ratio.

The above two-step mechanism requires two reactive scalars to define the chemical state in adiabatic, premixed combustion. If the system is non-adiabatic, enthalpy is additionally required, and if the system is non-premixed, the mixture fraction is required. Mixture fraction is a passive (e.g., conserved) scalar.

Four-Step Mechanism — Several studies have emphasized the role of hydrogen-containing free radicals such as H and OH in predicting CO (Chen et al., 1993; Correa et al., 1994). The following four-step, five-species mechanism was proposed by Seshadri and Peters (1990) and includes H radicals:

This mechanism was derived from a skeletal mechanism consisting of 25 elementary reactions and 16 species (Smooke and Giovangigli, 1991). Steady-state assumptions were applied to OH, O, HO₂, CH₃, CH₂O, CHO, CH₃O and H₂O₂, and some of the resulting algebraic relationships were truncated. Several of the simplifications are valid only at high temperature (Peters, 1991). Seshadri and Peters (1990) used the above mechanism to analyze the inner structure of a methane-air premixed flame and obtained reasonable predictions of flame velocity at pressures varying from 1 to 80 atm.

Evaluation of Reduced Mechanisms — Predictions with the two- and four-step mechanisms were compared with the full GRI-Mech 2.11 mechanism in a partially stirred reactor (PaSR) model. In the PaSR, the contents of the reactor are not completely mixed on a molecular level, even though the reactor is homogeneous (Chen, 1993; Correa, 1993). A finite rate of molecular mixing is specified via a mixing frequency. Mixing is required, even in a premixed flame, in order to bring the reactants to reaction temperature. Without sufficiently rapid mixing, ignition will not occur and reactions cannot be sustained. Thus, the PaSR provides an excellent means of evaluating the ability of reduced chemical mechanisms to simulate ignition phenomena. In addition, the ability of the reduced mechanisms to predict post-ignition combustion phenomena, such as pollutant formation and CO/CO₂ conversion, is better evaluated in the context of turbulent mixing where a wider variety of conditions is encountered, than in a perfectly stirred or plug-flow reactor model which have no stochastic behavior and where the conditions are more uniform.

The PaSR can be thought of as a zero-dimensional, composition PDF model. Indeed, the governing equation for the PaSR can be obtained by integrating the composition PDF transport equation over three-dimensional space. It is conveniently solved with the Monte Carlo method. The reactor is assumed to be filled with a large number (e.g., 1000) of fluid particles to represent the statistics. At each time step, the fluid particles undergo mixing, chemical reaction, and throughput (mass addition and removal). Mixing is accomplished between randomly selected pairs of particles (Curl, 1963; Dopazo, 1979) or by relaxing the properties of all of the particles deterministically toward the ensemble mean values. The deterministic approach is referred to as the interaction-by-exchange-with-the-mean (IEM) model (Meyers and O'Brien, 1981; Borghi, 1988). Throughput is accomplished by adding fresh, unreacted particles and randomly removing an equal number of particles at each time step. When the IEM model is used, it is this random removal process that gives the PaSR model its stochastic nature. In the case of premixed combustion, the fresh fluid particles consist of both fuel and air.

PaSR predictions for atmospheric LPC were made with both reduced mechanisms and with GRI-Mech 2.11 (Frenklach et al., 1995, 1996). The statistics were represented by 650 particles. The equivalence ratio was 0.8, the mixing frequency was 5000 Hz, the inlet temperature was 300 K, and the reactor residence time was 2 ms. Rather than integrate the rate equations numerically for each particle, a table of reaction rates as functions of the reaction scalars (e.g., for the two-step mechanism) was generated in a

pre-processing phase for efficiency. Reaction rates were then obtained during the simulation phase by table look-up rather than by direct integration. In the PaSR, it is practical to integrate the equations directly, during the simulation phase, but in a real combustor simulation, direct integration would be impractical. Therefore, the PaSR provided a means of developing and validating the table look-up procedure as well as evaluating the two reduced mechanisms. Of course, table look-up is impractical for the full mechanism, due to the large number of reaction scalars, and direct integration was used in this case.

Details of the reaction rate table for the two-step mechanism are as follows: Changes in the two scalar quantities ($\text{kmol CH}_4/\text{kg}$ and $\text{kmol CO}/\text{kg}$) due to chemical reaction for a time increment of 10^{-6} sec were tabulated over the allowable composition space, for an equivalence ratio of 0.8, an inlet temperature of 300 K, and 1 atm pressure. Predicted mean temperature and species predictions using the look-up table were compared with direct integration. A non-uniform table, heavily weighted toward low values of methane concentration, was required in order to obtain accurate predictions.

Figure 3-2 shows the evolution of ensemble mean temperature, CO mole fraction, and CH_4 mole fraction as functions of non-dimensional time (actual time normalized by the reactor residence time). The predictions evolve from the assumed initial condition of equilibrium to a stochastic steady-state. The four-step mechanism overpredicts the steady-state, mean temperature (relative to the full mechanism) by 25 K, whereas the two-step model overpredicts it by more than 100 K. The higher temperature obtained with the reduced mechanisms is probably due to the lesser degree of dissociation that is allowed relative to the full mechanism. The four-step mechanism allows for more dissociation (e.g., H atoms) than the two-step mechanism.

For CO, the four-step mechanism underpredicted the full mechanism by about 12 percent. The assumption of partial equilibrium for OH in the four-step mechanism may have contributed to this discrepancy. The significant underprediction of CO by the two-step mechanism shows the importance of including hydrogen chemistry.

For CH_4 , both reduced mechanisms gave similar results, overpredicting the full mechanism by about 16 percent. One might have expected the four-step mechanism to do better because hydrocarbon fuel breakup reactions are strongly influenced by H and OH radicals (Peters and Kee, 1987). Apparently, the partial equilibrium assumption for OH or the truncations in the steady-state relationships negate any improvement that might have been achieved with the inclusion of H. Similar work that has been conducted under independent funding (Hedman et al., 1994-1997), has shown that a similar mechanism that does not truncate the steady-state relationships deviates from the full mechanism on CH_4 by only about 8 percent. Work on this project was terminated due to lack of funding. However, further work in this general area has been continued at this Center with independent funding (Hedman et al., 1994-97).

Figure 3.2. Evolution of mean temperature, CO mole fraction, and CH_4 mole fraction predicted by the PaSR model for the reduced and full mechanisms.

Model Predictions

Validation of the new turbulent combustion submodel integrated into the comprehensive, CFD-based combustion code PCGC-3 was initiated by simulating an atmospheric-pressure, laboratory-scale gas turbine combustor (LSGTC) and comparing initial predictions with preliminary, detailed measurements of LPC of natural gas (Cannon et al., 1997; Schmidt, 1995). Details of the combustor are given by Flores and Hedman (1996). It was originally designed at Pratt & Whitney Aircraft Co. (Sturgess et al., 1990) to reproduce the flow and combustion characteristics which are found in a modern annular aeroengine combustor. This combustor has been subsequently modified and fitted with a newly designed premixer and injector for LPC of natural gas (Hedman et al., 1994-97). The combustor was designed to be axisymmetric, with a diameter of approximately 150 mm. Flat quartz windows, 60 mm wide, were located on the sides of the chamber to allow for the use of laser-based diagnostic equipment.

The LSGTC was simulated at conditions of 0.74 swirl number, 0.8 equivalence ratio, 1 atm and 300 K inlet temperature, assuming axisymmetric geometry. A grid consisting of 1276 nodes and 2365 triangular elements was generated using the GeoMesh (Fluent, Inc., 1994a) and TGrid (Fluent, Inc., 1994b) software packages. The joint PDF was represented by 1.7×10^5 fluid particles. Measured velocity profiles were used as inlet conditions. The inlet air flow rate was 500 slpm. Both convective and radiative heat losses were considered. A uniform wall temperature of 700 K was assumed. The total CPU time was about 264 hours on an HP-735 workstation.

Model predictions with the two-step mechanism are compared with measurements in Figure 3-3. The two-step mechanism was used initially because of its simplicity. Figures 3-3a through 3-3c show the measured and predicted components of velocity. The mean axial velocity predictions in Figure 3-3a show the internal (IRZ) and external (ERZ) recirculation zones. The predicted IRZ is longer and wider than measured. This discrepancy is probably due to the assumption of isotropic turbulent viscosity in the $k-\epsilon$ model. Similar results were obtained by Benim (1990) for finite element analysis of non-reacting, confined, turbulent swirling flow. It must be emphasized that these are the first predictions that were obtained with this model for this reactor and are, therefore, very preliminary in nature. Due to lack of funding, work on this project was terminated before the effects of assumed inlet conditions, turbulence modeling options, etc., could be investigated.

The mean radial velocity field in Figure 3-3b is similar to the measured field. Both the predicted penetration of the maximum radial velocity and the entrainment in the ERZ are similar to the measured results. The predicted and measured mean tangential velocities in Figure 3-3c have similar maximum values, but a faster decay in the tangential velocity field was predicted at downstream axial locations (> 50 mm). At the centerline, the measured radial and tangential velocities are not zero, indicating that the

Figure 3-3. Experimental data of Hedman and coworkers (Cannon et al., 1997; Schmidt, 1995) and predictions for swirling (swirl no. = 0.74), premixed, lean (equivalence ratio = 0.8) combustion of natural gas and air in the BYU laboratory-scale gas turbine combustor (LSGTC).

flow is not perfectly axisymmetric, or that the axis of flow symmetry does not correspond exactly with the centerline of the combustor.

Figure 3-3d shows the measured and predicted temperature fields. The length of the penetration zone, indicated by the region of cold unburned fluid, was similar for the measurements and predictions. Also a similar maximum temperature of about 1750 K was observed in both predictions and measurements. Work on this project was terminated due to lack of funding, but related work was continued under independent funding (Hedman et al., 1994-97).

Summary and Conclusions

A new turbulent combustion submodel applicable to axisymmetric LPC in gas turbine combustors has been developed and implemented in a comprehensive combustor model. The model has been used to simulate LPC in a laboratory-scale gas turbine combustor and preliminary results were encouraging. The new submodel is based on the velocity-scalar PDF method, which was selected as the best available method for incorporating complex chemistry and the interactions with turbulence into a complex CFD calculation. A partially stirred reactor model has been used to evaluate reduced chemical mechanisms and has been shown to be a valuable tool for doing so. In order to develop a useful model for practical gas turbine combustors, the submodel must be extended to three-dimensional flow, it must be incorporated into a combustor flow model with a more flexible (e.g., unstructured) grid capable of treating the complex geometries of practical gas turbine combustors, and a reduced chemical mechanism capable of predicting NO_x in LPC must be implemented. The model must also be validated with detailed experimental data.

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TASK 4 MODELING OF FLUIDIZED BED SYSTEMS

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Objectives

The original objective of this subtask was to integrate general submodels for coal pyrolysis, char oxidation, char gasification and coal properties into an existing model for fluidized-bed systems.

Accomplishments

A streamlined version of AFR's FG-DVC model was prepared and sent to FETC-WV for integration into the FETC MFIX code. The initial integration was complete but subsequent testing and evaluation at FETC were incomplete.

Integration of FG-DVC Submodel with Fluidized-Bed Code

Work was done on the development of a coal devolatilization submodel for a fluidized bed code. A fluidized bed model under development at FETC, MFIX, was chosen for code development. As with the fixed bed code development, several options were outlined and were sent to Tom O'Brien at FETC-WV for consideration. These options have different levels of simplifications of the full FG-DVC, as discussed under subtask 2.1 (see Table 2.1-1). After discussions with our colleague at FETC, option 1 was selected. In its standalone format, this is the same model that was developed under subtask 2.1 for integration into the FBED-1 code.

The objective was to allow AFR's advanced coal pyrolysis model, FG-DVC to be applied to the modeling of the fluidized-bed section of the PyGas™ gasifier. The computational efficiency of the FG-DVC-RES model ensures that this goal can be achieved without adding a further computational burden to the MFIX model. After the development of the standalone version of FG-DVC-RES, it was sent to FETC for integration with MFIX, for testing of code compatibility. This version uses either a constant partitioning of coal, or a time dependent partition, as discussed under subtask 2.1.

Samples of three coals to be used in the PyGas system were received from Riley Stoker Corporation, and were analyzed with TG-FTIR in our lab, as discussed under subtask 2.1. Model input files of these coals for both FG-DVC and FG-DVC-RES were generated.

While the initial integration of the two codes was completed at AFR, the subsequent testing and evaluation at FETC were not completed, apparently due to funding constraints.

SUBTASK 5.1 - ADVANCED FIXED-BED CODE APPLICATION AND IMPLEMENTATION

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Objectives

The original objectives of this subtask were to apply the advanced fixed-bed code to the gasifiers of interest to METC, such as the GPIF gasifier, to install the code at METC, and to train METC personnel in its use. Due to incomplete funding, the subtask was only partially completed.

Accomplishments

The FBED-1 code, modified under Subtask 2.5 to include the cocurrent option, was applied to the PyGas™ gasifier. The PyGas™ gasifier was to be tested under the Gasification Product Improvement Facility (GPIF) project.

PyGas™ Gasification Process

The existing fixed-bed technology is not well suited for caking coals due to agglomeration problems which lead to low conversion efficiencies. To facilitate the handling and gasification of caking coals, a new process, the PyGas™ gasification process, has been developed (Brown and Sadowsky, 1991). A schematic of the PyGas™ gasifier is shown in Figure 5.1-1. The process is carried out in four stages:

- (1) The coal is rapidly pyrolyzed in a central transport or bubbling, fluidized-bed section of the gasifier. The heating rates in the pyrolyzer are such that the tars are liberated in gaseous rather than liquid form. This eliminates agglomeration of the coal particles initiated by coating of the particle surfaces by liquid tar.
- (2) The gas and the char are separated in the freeboard zone by gravity. Additional air is added to the freeboard zone to cause gas-phase cracking of the tar and the higher hydrocarbons generated in the pyrolyzer. The amount of additional air is adjusted to attain temperatures high enough to initiate gasification of char.
- (3) The char is then gasified in a cocurrent fixed-bed section of the gasifier. Only part of the char is converted by the endothermic gasification reaction during this stage. This cools the gas stream and diminishes the gasification reactions.

Figure 5.1-1. Schematic of the PyGas™ gasifier.

- (4) Finally, the char is gasified and burnt completely in a countercurrent fixed-bed section. Additional quantities of air and steam are added at the bottom of this section. The final product gas is the combined stream from the exits of the cocurrent and the countercurrent stages of the gasification process.

The PyGasTM gasifier was to be tested under the GPIF project of the Morgantown Energy Technology Center.

PyGasTM Gasifier Simulations

FBED-1 Code and Assumptions- Under our previous project, "Measurement and Modeling of Advanced Coal Conversion Processes," a simulation of the PyGasTM gasifier was attempted using the fixed-bed code, FBED-1 (Solomon et al., 1993). The attempt indicated that the existing FBED-1 model was not sufficient to simulate the emerging configurations involving combined beds and different flow patterns.

Under our present project, "Fossil Fuel Conversion - Measurement and Modeling," the fixed-bed code, FBED-1, was extended to handle a cocurrent flow pattern. This work was described under Subtask 2.5.

The modified FBED-1 code with the cocurrent flow option was then successfully applied to simulate the PyGasTM gasifier using the preliminary input data provided by METC and the final design geometry and input data provided by Riley Stoker Corporation. The geometry of the gasifier required separate simulations of five flow regions, with the results of one region being used as the input for the following region. Several assumptions were made for the simulation of the PyGasTM gasifier:

- (1) The solid residence time in the pyrolyzer is long enough to allow complete devolatilization of the coal.
- (2) The amount of supplementary air fed to the freeboard zone is adjusted to allow complete cracking of the tar and to raise the temperature of the gas phase to initiate gasification. The solid residence time in the freeboard zone is assumed to be too short to allow any significant heat transfer between the solid and the gas phases or heterogeneous reactions.
- (3) The char is assumed to be completely burnt in the countercurrent fixed-bed section of the gasifier. The flow rates of air and steam are adjusted to achieve complete conversion of char.

Coal Kinetic Parameters- At the time when these simulations were performed, Subtasks 2.1 and 2.2 had only started. The objectives of these subtasks were to measure, correlate, and model devolatilization, oxidation, and gasification processes for

large coal particles at high pressures. Thus, lacking the final results of these subtasks, the best available kinetic parameters were used for this task. The devolatilization kinetic parameters were for the small particles of the Pittsburgh coal at atmospheric pressure. The oxidation and gasification kinetic parameters were also for the small particles of the Pittsburgh coal but adjusted for high pressure. The adjustment for the PyGasTM pressure of 41 atmospheres was based on our previous high-pressure work (Monson et al., 1995 and Bateman et al., 1995). Monson et al. conducted experiments to study the effect of pressure on kinetic parameters for oxidation of small (40-70 μm) char particles at pressures up to 1520 kPa. Their results show that oxidation rates increase modestly as pressure increases from atmospheric pressure to 507 kPa and decrease as pressure increases further to 1520 kPa. Bateman et al. measured the effect of pressure on oxidation rates of large (5-8 mm) char particles at pressures up to 760 kPa. Their results indicate that the oxidation rates are significantly greater at pressures of 507 and 760 kPa than at atmospheric pressure. No significant differences in the rates are observed between 507 and 760 kPa. The adjustment of the rates was performed by assuming that the rates increase to 507 kPa, after Monson et al., and remain constant thereafter.

Simulations- The pyrolyzer was simulated by using the zero-dimensional submodel, FBED-0, of the fixed-bed code. The devolatilization was modeled by FG-DVC and the elemental compositions of the product tar and char were predicted. The gas composition was computed assuming partial equilibrium by specifying tar to be non-reactive. In the freeboard zone, the composition was computed by taking into account the supplementary air feed and allowing the tar to react to equilibrium. The cocurrent and the countercurrent fixed-bed sections were simulated by the one-dimensional fixed-bed code, FBED-1. The FBED-0 submodel was used to provide the initial guesses for the effluent gas composition and temperature. The input composition and flow rate of char to the lower fixed bed were adjusted to reflect the conversion in the previous stages of the gasifier.

The simulations were completed for the all-rank average oxidation and gasification kinetics at atmospheric pressure, for the Pittsburgh #8 kinetics at atmospheric pressure, and for the Pittsburgh #8 kinetics at 41 atmospheres. Only the simulation results for the final design geometry and input data with the Pittsburgh #8 kinetics at 41 atmospheres are presented here.

Results- The predicted flow rates and gas compositions at various stages of the PyGasTM gasifier are given in Table 5.1-1. The detailed profiles for the upper, cocurrent and the lower, countercurrent sections of the gasifier are shown in Figure 5.1-2. The coal conversion in the pyrolyzer is 36.2%; approximately 12.0% of the coal mass is released as tar. The pyrolyzer gas leaves at 1472 K. The addition of air and the reactions of tar and higher hydrocarbons in the freeboard zone increase the gas temperature. This increase is moderated by the addition of steam so that the gas temperature at the freeboard exit is 1508 K. The coal conversion in the upper, cocurrent section of the gasifier is only 3.6%; this conversion is due to gasification by

Table 5.1-1. Predicted flow rates and gas compositions at various stages of the PyGas™ gasifier.

Quantity	Pyrolyzer	Freeboard	Upper bed	Lower bed	Raw gas
Coal, kg/s	1.51	1.02	1.02	.97	---
T _{coal} , K	339.00	1036.00	1036.00	1376.00	---
Air, kg/s	1.80	1.20	---	3.10	---
T _{air} , K	533.00	533.00	---	533.00	---
Steam, kg/s	0.74	0.60	---	0.87	---
T _{steam} , K	525.00	644.00	---	644	---
Product gas, kg/s	2.85	4.83	4.88	4.71	9.59
Composition, vol.%					
Ar	0.48	0.48	0.48	0.53	0.50
CO	2.76	4.30	5.13	21.77	13.49
CO ₂	5.76	7.62	8.21	6.72	7.36
CH ₄	0.00	0.00	0.00	0.01	0.01
H ₂	8.58	8.68	11.09	16.14	13.73
H ₂ O	43.87	39.95	36.84	12.02	24.62
H ₂ S	0.00	0.12	0.14	0.50	0.32
N ₂	38.55	38.83	38.10	42.30	39.97
NH ₃	0.00	0.00	0.01	0.01	0.01
O ₂	0.00	0.00	0.00	0.00	0.00
T _{gas} , K	1472.00	1508.00	1382.00	1462.00	1418.00
T _{solid} , K	1036.00	1036.00	1376.00	563.00	---
Burnout ¹ , wt.%	36.20	0.00	3.60	60.20	---
Tar, kg/s	0.18	0.00	0.00	0.00	0.00

¹Burnout is given as wt.% with respect to coal feed

Figure 5.1-2. Predicted profiles for the cocurrent and countercurrent sections of the PyGas™ gasifier.

H₂O, CO₂ and H₂. The gasification rates are low because of the low solid temperature. The gas temperature at the cocurrent section exit is 1382 K. The coal conversion in the lower, countercurrent section of the gasifier is 60.2%; this is due to oxidation by O₂ and gasification by H₂O, CO₂, and H₂. The kinetic rates are much higher than in the upper, cocurrent section because of the higher solid temperatures. Large amounts of CO and H₂ are produced in this section. The product gas, which is the mixed stream from the cocurrent and countercurrent sections, is rich in CO and H₂ and has small amounts of CH₄; the product gas temperature is 1418 K.

Publications

The results of this subtask were presented in a poster (Radulovic et al., 1994) and three papers (Solomon et al., 1994, Solomon et al., 1995, and Ghani et al., 1996).

Summary and Conclusions

The existing fixed-bed technology is not well suited for caking coals due to agglomeration problems which lead to low conversion efficiencies. To facilitate the handling and gasification of caking coals, a new process, the PyGasTM gasification process, has been developed. The PyGasTM gasifier was tested under the GPIF project of the Morgantown Energy Technology Center.

The modified FBED-1 code with the cocurrent flow option, was applied to the PyGasTM gasifier using the preliminary input data provided by METC and the final design geometry and input data provided by Riley Stoker Corporation. The simulations were performed for the all-rank average oxidation and gasification kinetics at atmospheric pressure, for the Pittsburgh #8 kinetics at atmospheric pressure, and for the Pittsburgh #8 kinetics at 41 atmospheres.

The best kinetic parameters available at the time of simulations were used. The oxidation and gasification kinetic parameters were for the small particles of the Pittsburgh coal but adjusted for high pressure. The simulations with kinetic parameters for large coal/char particles at high pressures, resulting from our recent efforts, may yield different predictions.

The results were presented in a poster and three papers.

Acknowledgements

The preliminary design and input data for the PyGasTM gasifier by Mr. Lawrence J. Shadle of METC. The final design and input data were provided by Mr. Richard S. Sadowsky of CRS Sirrine Engines, Inc. and Vijay B. Dixit of Riley Stoker Corporation. This is gratefully acknowledged.

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SUBTASK 5.2 - ADVANCED TWO-DIMENSIONAL TRANSPORT GASIFICATION CODE APPLICATIONS AND IMPLEMENTATIONS

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Objectives

The original objective of this subtask was to install the transport reactor code at FETC, train FETC personnel in its use and apply the code to simulate one or more reactors of interest of FETC.

Accomplishments

Work was begun on applying the code to the UNDEERC and Wilsonville reactors but was stopped because of lack of access to the data. The User's Manual and Code Installation at FETC were not completed since only a cold flow version of the code was validated.

Application of Transport Reactor Code

Discussions were held with Dr. Jim Longanbach of FETC on using the transport reactor code developed under subtask 2.6 to model the Wilsonville and UNDEERC reactors. A set of input requirements and prediction capabilities was sent to FETC-WV. FETC completed a review of the model input requirements and predication capabilities and concluded that the modeling effort could be valuable for the work planned at both facilities.

While awaiting receipt of the data from UNDEERC, work continued on a sensitivity analysis using the existing AFR Transport Reactor Code, which was originally validated against cold flow data and was subsequently run at high temperatures for the non-reacting case. The results are illustrated in Figures 5.2-1 and 5.2-2.

In Figure 5.2-1, the void fractions at $H/L=0.5$ are plotted versus the radial distance. The conditions are the same as those used in the CUNY cold flow experiments, except for raising the reactor temperature. One can see similar behaviors of the void fractions at different temperatures, i.e., the void fractions do not vary much from the reactor center line until a short distance from the wall. Close to the wall, void fractions drop dramatically indicating large concentrations of solid particles. One may notice that, at the reactor wall, void fractions are always equal to 1 (no particles), this corresponds to the assumption that the particles do not stick to the wall. If we examine the decreases

Figure 5.2-1. Predicted void fraction for CUNY Transport Reactor with increasing reactor temperature.

Figure 5.2-2. Predicted pressure profiles for CUNY Transport Reactor with increasing reactor temperature.

of void fractions near the wall for different temperatures, we can see that void fractions decrease more for $T=600^{\circ}\text{C}$ than for $T=300^{\circ}\text{C}$. But these decreases are less for $T=900$ and 1200°C than for $T=600^{\circ}\text{C}$. This is a very interesting phenomenon that we can also observe from examining Figure 5.2-2, where predictions of the operating pressures along the reactor centerlines are given. The pressure drop is larger for $T=600^{\circ}\text{C}$ than that for $T=300^{\circ}\text{C}$, which may be due to the increase of gas viscosity. The pressure drops for $T=900$ and 1200°C are somewhere between those of $T=600^{\circ}\text{C}$ and $T=300^{\circ}\text{C}$, which may be caused by the decrease of gas density. There are two competing mechanisms that affect pressure drop with increasing temperatures: 1) increasing gas viscosity would increase pressure drop, while 2) decreasing gas density would decrease pressure drop. Additional work is required to investigate the effect of temperature on transport reactor operations and to include the effects of chemical reactions.

The work on direct modeling of the UNDEERC and Wilsonville transport reactors was abandoned because of the difficulty in getting appropriate data from UNDEERC or Wilsonville due to proprietary concerns on the part of Kellogg. Subsequently, discussions were held with Larry Shadle of FETC on how AFR and BYU could participate in supporting the FETC in-house dynamic modeling effort for transport reactors. Some information about this project was sent by Larry Shadle to AFR for review. However, this effort also had to be terminated due to the lack of funds.

SUBTASK 5.4 - MODELING OF FLUIDIZED-BED SYSTEM AND IMPLEMENTATION

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Objectives

The original objective of this subtask was to install at FETC the advanced pyrolysis and oxidation submodels integrated with a fluidized-code, train FETC personnel in its use and apply the code to fluidized-bed systems of interest to FETC.

Accomplishments

This task was not completed since Task 4 was also incomplete. The FG-DVC model was integrated in the MFI Code at FETC by FETC personnel with assistance from AFR. However, further training, application of the combined code and the User's Manual was not completed, since the integrated code development was not complete.

SUBTASK 5.5 - APPLICATIONS OF ACERC COMBUSTION AND GASIFICATION CODES AND AFR DIAGNOSTIC CAPABILITIES TO SYSTEMS OF INTEREST TO METC

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Objectives

The original objective of this subtask was to apply the appropriate existing ACERC combustion and gasification codes e.g., PCGC-3, PCGC-2, and FBED-1 to practical systems of interest to METC such as the Hague combustor. Due to incomplete funding, the subtask was only partially completed.

Accomplishments

The PCGC-3 code was applied to the Hague coal combustor. The Hague coal combustor was to be tested under the Externally-Fired Combined Cycle (EFCC) project.

Hague Coal Combustor

The Hague coal combustor is a part of the Kennebunk test facility, an externally-fired, combined cycle demonstration facility built by Hague International under funding from the Morgantown Energy Technology Center. This is an emerging technology for powering combined gas and steam turbine cycles with coal or other fuels containing ash (Orozco, 1993). The heat input to the gas turbine is supplied indirectly through a ceramic heat exchanger. The ceramic heat exchanger, coupled to the coal combustor and the slag screen, replaces the conventional gas turbine combustor. A schematic of the coal combustor, the slag screen, and the ceramic heat exchanger is shown in Figure 5.5-1.

The combustor is a two-stage, down-fired, pulverized coal combustor. A swirl burner brings the pulverized coal and the combustion air together. A collar divides the first stage from the second and also provides the access ports for the second stage air. The first stage operates fuel-rich to reduce NO_x emissions. To complete combustion, the remaining combustion air is added in the second stage. Successful operation of the downstream units, the slag screen and the ceramic heat exchanger, depends strongly on the performance of the combustor in maximizing carbon burnout and slag capture.

Figure 5.5-1. Schematic of the Hague coal combustor, slag and ceramic heat exchanger.

Simulations of Hague Coal Combustor

PCGC-3 Code- The performance of the combustor was predicted by a three-dimensional, steady-state coal combustion code, PCGC-3. The gas flow is solved in the Eulerian framework, using a finite-difference formulation of the Navier-Stokes equations coupled with the energy conservation equation. The particle transport is solved separately in the Lagrangian framework, and the two phases are coupled through various source terms. The turbulent, Reynolds stresses are approximated by an effective eddy viscosity. The conservation equations are closed by the Prandtl mixing length model, the standard $k-\epsilon$ model, or the nonlinear $k-\epsilon$ model. The gas phase reactions are assumed to be fast and limited by turbulent mixing rates only. Thus, the reaction rates are calculated using locally instantaneous equilibrium based on the degree of mixing of the relevant species. The extent of mixing between inlet gas streams is described by a conserved scalar variable, mixture fraction. The fluctuations of the mixture fraction are modeled by a probability density function. Particle reactions such as drying, devolatilization, oxidation, and gasification are included. Devolatilization is modeled by a single-step or a two-step model. Oxidation and gasification rates are determined from Arrhenius-type expressions. Radiative heat transfer between gases, particles, and walls is modeled by a discrete-ordinates method. Formation of thermal and fuel NO_x is included. The Zel'dovich mechanism is used for the thermal NO_x and global reaction rates based on the de Soëte rates are used for the NO_x . Formation and capture of SO_x species by a sorbent can also be modeled if needed. A more detailed description of PCGC-3 is provided by Smoot (1993).

Coal Kinetic Parameters- The preliminary simulations were conducted using the devolatilization and oxidation kinetic parameters for a hvAb coal similar to the coal fired at the Kennebunk test facility. Such a coal is Pittsburgh #8. The devolatilization kinetic constants for the Pittsburgh #8 coal were taken from Solomon et al. (1986) as:

$$E = 2.285 \times 10^8 \text{ J/kmol}$$

$$A = 4.28 \times 10^{14} \text{ 1/s}$$

where E and A were the activation energy and the pre-exponential factor, respectively, in the Arrhenius-type devolatilization rate equation. The devolatilization yield, Y , for the Kennebunk test coal¹ was estimated as:

$$Y = 0.406 \text{ of daf coal.}$$

The oxidation kinetic constants for the Pittsburgh #8 coal were taken from the ACERC data base as:

$$E = 8.4807 \times 10^7 \text{ J/kmol}$$

$$A = 2.26 \text{ m/K}^n\text{s}$$

$$n = 1$$

¹ Since no information was provided for the coal seam and mine of this coal, it was designated the Kennebunk test coal.

where E, A, and n were the activation energy, the pre-exponential factor, and the temperature exponent, respectively, in the Arrhenius-type oxidation rate equation.

The final simulations were performed with the devolatilization and oxidation kinetics measured for the Kennebunk test coal samples supplied by Hague International. The devolatilization rates were measured and the devolatilization kinetic parameters were determined by AFR as:

$$E = 2.285 \times 10^8 \text{ J/kmol}$$

$$A = 4.26 \times 10^{13} \text{ 1/s}$$

$$Y = 0.414 \text{ of daf coal.}$$

The oxidation rates were measured and the oxidation kinetic parameters were determined by ACERC for the Kennebunk test coal as shown in Table 5.5-1. The temperature exponent, n, was set to zero. The procedure was explained by Reade and Hecker (1994).

Table 5.5-1. Measured oxidation kinetic parameters for Kennebunk test coal.

d_p (μm)	E (J/kmol)	A (m/s)
6.	1.42×10^8	5.500×10^2
18.	1.14×10^8	1.190×10^3
35.	1.30×10^8	1.475×10^3
60.	1.17×10^8	2.670×10^3
100.	1.06×10^8	1.125×10^4
245.	9.55×10^7	1.560×10^4

As seen from Table 5.5-1, these global oxidation kinetic parameters provided were somewhat dependent on the particle size.

Round 1 Simulations- The simulations were conducted using the following options and parameters: the standard k- ϵ turbulence model, the single-step devolatilization model, the oxidation model, and the devolatilization and oxidation rate constants for a hvAb coal such as Pittsburgh #8. The particle absorption and scattering coefficients dependent on the particle size were determined and used in the simulations. The combustor design and input data were received from Hague International. The computational grid was constructed of 86,240 cells (110x28x28). Four runs were performed in Round 1. The typical CPU time for one run including 20 particle calculations with 150 gas iterations each, was around 46 hours on a HP 735 workstation. The mass balance closure was within 0.05% and the energy balance closure was within 6.66%. The maximum gas phase residual, for enthalpy, was 4.21. All of the other gas phase residuals were between 2.26 and 3.36. The maximum particle phase residual was 3.84.

The energy balance closure and the residuals indicated insufficient convergence. The difficulties were considered to be due to the ill-defined boundary conditions at the

combustor outlet. The combustor outlet is large and the boundary conditions at the outlet strongly influence the flow and the temperature fields in the combustor. The additional data about the combustor outlet and the slag screen, the first unit downstream from the combustor, were requested from Hague International. The additional data were also requested for the burner outlet velocities, the wall temperature distribution, and the devolatilization and oxidation kinetic rates.

Round 2 Simulations - The simulations were performed using the same options, parameters, design and input data as in Round 1 but with an updated version of the PCGC-3 code. The computational grid was still constructed of 86,240 cells (110x28x28). Twenty-one runs were performed in Round 2. The typical CPU time for one run including 10 particle calculations with 100 gas iterations each, was around 16 hours. The mass balance closure was within 0.01% and the energy balance closure was within 4.74%. The maximum gas phase residual, for enthalpy, was 3.46. The maximum particle phase residual was 3.40. The results were improved but were still not considered sufficiently converged.

Hague International responded to the request for the additional data by providing the combustor outlet geometry; the other data requested were not available. Thus, the burner outlet velocities were calculated using simplified, lumped mass and energy conservation equations for steady, frictionless, and uniform flow. The devolatilization and the oxidation kinetic rates were to be measured by AFR and BYU, respectively. Samples of the coal fired at the Kennebunk test facility were requested from Hague International.

Round 3 Simulations - The simulations were conducted using the same options, parameters, design and input data as in Rounds 1 and 2 except for the extended computational domain and the new burner outlet velocities. The computational domain was extended to include the combustor outlet duct; it consisted of 107,000 cells (100x37x28). The burner outlet velocities were set to the newly corrected values. Ten runs were performed in Round 3. The typical CPU time for one run was around 25 hours. The mass balance closure was within 0.004% and the energy balance closure was within 0.99%. The maximum gas phase residual, for enthalpy, was 2.90. The maximum particle phase residual was 2.91.

These results indicate good convergence, confirming the expected effect of the extended computational domain. The predicted gas velocities, particle trajectories, gas temperatures and compositions were realistic but the flow field in the first, upper combustor stage was strongly asymmetric. This asymmetry was to be checked by refining the computational grid.

The samples of the coal fired at the Kennebunk test facility were received from Hague International and the measurements of the devolatilization and oxidation kinetic rates were initiated by AFR and BYU, respectively.

Round 4 Simulations - The main objective of this round of simulation was to check the strong asymmetry of the flow field in the first, upper combustor stage. This was done by substantially refining the computational grid particularly in the burner region. The computational grid was constructed of 238,500 cells (100x53x45). Four runs were conducted in Round 4. The runs were not successful; the problem was related to the choke ring and the burner geometry and to the inlet velocities in the grid and the input data files. The problem was resolved and a new, final round of simulations was started.

Round 5 Simulations - The simulations were performed using the same options, parameters, design and input data as in Round 4 except for the corrected choke ring and burner geometries and the corrected inlet velocities in the grid and input data files. The estimates of the burner velocities were further improved by using the estimates of the flow friction and the empirical data on the burner swirl number (Beér and Chigier, 1972; Gupta et al., 1984). Fifteen runs were performed before satisfactory convergence was achieved. The typical CPU time for one run was 41 hours. The mass balance closure was essentially perfect and the energy balance closure was within 0.55%. The maximum gas phase residual, for enthalpy, was 1.27. The maximum particle phase residual was 2.56. For a computational problem of this size and complexity, the values of 1%, 2%, 3 and 3 respectively, are considered good. Therefore, these results indicated excellent convergence.

The questionable, strong asymmetry in the flow field of the first, upper combustor stage, found in the third round of simulations, was absent in these final simulations. The asymmetry was caused, in part, by an error in the inlet velocities and, in part, by a coarse grid.

The devolatilization and oxidation rate measurements for the Kennebunk test coal were completed and the kinetic constants were determined at this time. The newly measured kinetic rates were used in final runs. The devolatilization rate was independent but the oxidation rates were dependent on the particle size. Eight final runs were performed. The typical CPU time for these runs increased to 68 hours because the oxidation rates were dependent on the particle size. The mass and the energy balance closures and the gas and the particle phase residuals still indicated excellent convergence.

The simulations results were found to be relatively insensitive to the devolatilization rate but sensitive to the oxidation rates. The differences in the velocity field were still relatively small but the differences in the temperature field were significant. The maximum gas temperature was reduced from around 2200K to 1990K. The sensitivity to the change in the wall temperature between 800K and 1000K was also investigated and found to be relatively small.

Results

Because of the great volume of the results available from these simulations, only the selected results for Run 21 of Round 5 are presented here. Run 21 was the final run performed.

A vector plot of gas velocities at an axial section through the centerline of the Hague combustor is shown in Fig. 5.5-2. Fig. 5.5-3 is a vector plot of gas velocities at a cross section through the lower combustor stage. The velocity field is quite complex at the burner and in the lower combustor stage but fairly uniform in the upper combustor stage. A shaded color plot of gas temperatures at the axial section through the combustor centerline is shown in Fig. 5.5-4. The region of high temperatures is close to the burner. The reduction of gas temperatures by the second stage air nozzles is evident below the collar. Fig. 5.5-5 is a shaded color plot of NO_x mole fractions at the axial section through the combustion centerline. The zones of high NO_x mole fractions are similarly placed as the zones of high temperatures indicating the importance of thermal NO_x . At the time when these simulations were performed no measurement results were available and thus no comparison of predictions and measurements was possible.

Publications

The results of this subtask were presented in one publication (Solomon et al., 1995).

Summary and Conclusions

The Hague coal combustor is a part of the Kennebunk test facility, an externally-fired, combined cycle demonstration facility built by Hague International under funding from the Morgantown Energy Technology Center. This is an emerging technology for powering combined gas and steam turbine cycles with coal or other fuels containing ash.

The PCGC-3 code was applied to the Hague coal combustor using the design and input data provided by Hague International. The simulations were performed for the Pittsburgh #8 coal devolatilization and oxidation kinetic parameters as well as for the Kennebunk test coal kinetic parameters. The size of the computational grid ranged from 86,240 cells (110x28x28) to 238,500 cells (100x52x45). There were five rounds of simulations and 62 simulation runs. The typical CPU times for these runs ranged from 16 hours to 68 hours. Because of the great volume, only the selected results are presented in the report. The results of these simulations such as the vector plots of gas velocities, the shaded color plots of gas temperatures and NO_x mole fractions, and others, provided a wealth of data and a clear picture of this complex process.

ARROW LEGEND

8.97E-02

4.08E+01

Fig. 5.5-2. Gas velocity (m/s) vectors at the axial section through the centerline of the Hague combustor.

ARROW LEGEND

2.16E-01

9.93E+00

Fig. 5.5-3.

Gas velocity (m/s) vectors at the cross section through the lower stage of the Hague combustor.

LEGEND

1.99E+03

1.69E+03

1.39E+03

1.09E+03

7.88E+02

4.88E+02

Fig. 5.5-4. Gas temperatures (K) at the axial section through the centerline of the Hague combustor.

8.95E+02

7.16E+02

5.37E+02

3.58E+02

1.79E+02

0.00E+00

Fig. 5.5-5. NO_x mole fractions (ppm) at the axial section through the centerline of the Hague combustor.

The best coal kinetic parameters available at the time of these simulations were used. While the preliminary simulations were conducted using the available kinetic parameters for the Pittsburgh #8 coal, the final simulations were performed with the devolatilization and oxidation kinetics measured for the Kennebunk test coal samples. The devolatilization rates were determined by AFR; the oxidation rates were measured by ACERC.

The results were presented in one publication.

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APPENDIX A

List of Papers and Publications Resulting from this Contract

Advanced Fuel Research, Inc.

- Serio, M.A., Zhao, Y., Wójtowicz, M.A., Charpenay, S., Solomon, P.R. and Nelson, P.F., "Modeling of Coal Quality Effects Based on a Comprehensive Devolatilization Model," Fourth International Conference on the Effects of Coal Quality on Power Plants, EPRI, Charleston, S.C., (August 17-19, 1994).
- Serio, M.A., Wójtowicz, M.A., Bassilakis, R., Chen, Y., Charpenay, S. and Jensen, A., "Measurement and Modeling of Coal Quality Effects," Fifth International Conference on the Effects of Coal Quality on Power Plants, EPRI, Kansas City, KS, (1997, May 20-22).
- Wójtowicz, M.A., Zhao, Y., Serio, M.A., Bassilakis, R., Solomon, P.R. and Nelson, P.F., "Modeling of Hydrogen Cyanide and Ammonia Release During Coal Pyrolysis," Proceedings of the Eighth International Conference on Coal Science, Coal Science and Technology, Elsevier, Amsterdam, **24**, 771-774 (1995).
- Zhao, Y., Serio, M.A. and Solomon, P.R., "A Priori Simulation of Coal Pyrolysis Experiments Based on Coal Elemental Compositions," ACS Div. of Fuel Chem. Preprints, **39**, (2), 569 (1994).
- Zhao, Y., Serio, M.A., Bassilakis, R. and Solomon, P.R., "A Method of Predicting Coal Devolatilization Behavior Based on the Elemental Composition," 25th Symposium (Int.) on Combustion, The Combustion Institute, Pittsburgh, PA, pp. 553-560 (1994).
- Zhao, Y., Serio, M.A. and Solomon, P.R., "Modeling the Devolatilization of Large Coal Particles," Coal Science, (J.A. Pajares and M.D. Tascon), Elsevier Science, 833-833 (1995).
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Brigham Young University

Bateman, K.J., Germane, G.J., Smoot, L.D., and Eatough, C.N., "A Facility for High-Pressure Measurements of Reaction Rates of Millimeter-Sized Coal," Energy & Fuels 9(2) 295-301 (1995a).

Bateman, K.J., Germane, G.J., Smoot, L.D., Blackham, A.U., and Eatough, C.N., "Effect of pressure on oxidation rate of millimetre-sized char particles," Fuel 74(10) 1466-1474 (1995b).

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Eatough, C.N., and Smoot, L.D., "Devolatilization of large particles at high pressure," Fuel 75(13) 1601-1606 (1996).

Ghani, M.U., Radulovic, P.T., and Smoot, L.D., "An improved model for fixed-bed coal combustion and gasification: sensitivity analysis and application," Fuel 75(10) 1213-1226 (1996).

Mathias, J.A., "High Pressure Oxidation Rates for Large Coal and Char Particles," M.S. thesis, Department of Mechanical Engineering, Brigham Young University, Provo, UT, 144p (December, 1996).

Radulovic, P.T., Ghani, M.U., and Smoot, L.D., "An Improved Model for Fixed-Bed Coal Combustion and Gasification," Fuel 74 (4) 582-594 (1995).