SECTION II. TASK 2. SUBMODEL DEVELOPMENT AND EVALUATION

Objectives

The objectives of this task are to develop or adapt advanced physics and chemistry submodels for the reactions of coal in an entrained-bed and a fixed-bed reactor and to validate the submodels by comparison with laboratory scale experiments.

Task Outline

The development of advanced submodels for the entrained-bed and fixed-bed reactor models will be organized into the following categories: a) Coal Chemistry (including coal pyrolysis chemistry, char formation, particle mass transfer, particle thermal properties, and particle physical behavior); b) Char Reaction Chemistry at high pressure; c) Secondary Reactions of Pyrolysis Products (including gas-phase cracking, soot formation, ignition, char burnout, sulfur capture, and tar/gas reactions); d) Ash Physics and Chemistry (including mineral characterization, evolution of volatile, molten and dry particle components, and ash fusion behavior); e) Large Coal Particle Effects (including temperature, composition, and pressure gradients and secondary reactions within the particle, and the physical effects of melting, agglomeration, bubble formation and bubble transport; f) Large Char Particle Effects (including oxidation); g) SO_x-NO_x Submodel Development (including the evolution and oxidation of sulfur and nitrogen species); and h) SO_x and NO_x Model Evaluation.

II.A. SUBTASK 2.a. - COAL TO CHAR CHEMISTRY SUBMODEL DEVELOPMENT AND EVALUATION

Senior Investigators - David G. Hamblen and Michael A. Serio
Advanced Fuel Research, Inc.
87 Church Street, East. Hartford, CT 06108
(203) 528-9806

Objective

The objective of this subtask is to develop and evaluate, by comparison with laboratory experiments, an integrated and compatible submodel to describe the organic chemistry and physical changes occurring during the transformation from coal to char in coal conversion processes.

Accomplishments

Work continued on the coal viscosity (fluidity) model. During the past quarter, the effects of different maceral groups on viscosity were addressed. The sensitivity of the model to the activation energy for the temperature dependence of the viscosity was also investigated. A value of about 80 kcal/mole was being used. However, we recently became aware of data from the literature on pitch carbonization where a value of 50 kcal/mole was used. We have also obtained additional fluidity data on coals in the Exxon sample bank which will be used to test the model.

In view of the importance of macromolecular network models to the accurate predictions of coal processing behavior, we have assessed the assumptions and limitations of the proposed models. A comparison was made of the FG-DVC model and two other network decomposition models, namely the DISARAY model of Niksa and Kerstein and the CPD model of Grant and coworkers, both of which employ percolation theory. We are considering using percolation theory instead of Monte Carlo methods as the basis of our network decomposition model in order to reduce the computation time for running the FG-DVC model.

An independent investigation was made of the rank dependence of the pyrolysis kinetics by doing experiments in a TG-FTIR reactor over a series of heating rates (3, 30, 50, 100°C/min) with three coals (Pocahontas, Pittsburgh,

No. 8, and Zap lignite, from the Argonne set. A comparison was done of the rank dependence of the rate constants for bridge breaking, tar evolution and CH_4 evolution at 450°C, determined from analyzing the TG-FTIR data at several heating rates and from fitting the FG-DVC model to fluidity, weight loss and methane evolution data at a single heating rate (3°C/min). The results indicated that the rates for tar evolution or bridge breaking vary by about a factor of 10 if the Pocahontas coal is excluded, which is consistent with previous results for coals from the same range of ranks. This corresponds to a difference in T_{max} for tar evolution of - 40°C at a heating rate of 30°C/min. If the Pocahontas coal is included, the rank variation for the tar evolution/bridge breaking rate is about a factor of 50. This corresponds to a difference in T_{max} for tar evolution of - 65°C at a heating rate of 30°C/min. The rates for tar evolution are consistent with those obtained by Burnham and coworkers at LLNL.

Work also began on adding the polymethylene species to the FG-DVC model. These are long chain aliphatic species which are important components of the tar in low rank coals. These will decompose by a free radical chain reaction rather that the depolymerization/crosslinking reactions which are characteristic of the primary coal network.

Viscosity Model

The previous modeling had been done by assuming that the coal was pure vitrinite. However, the data reported by van Krevelen indicated a significantly higher fluidity (lower viscosity) for exinite. The model was able to predict the higher fluidity for exinite and its variation with rank by making two changes in the coal composition file and one change in the model. The first change in the coal composition files was to reduce the average monomer molecule weight in the case of exinite. The second was to increase the hydrogen content from about 5.5% in the case of vitrinite to about 7% in the case of exinite. These changes made the average molecular weight in the liquid phase smaller. A change in a model parameter was necessary in order to make it more sensitive to molecular weight in order to match the available fluidity data.

We have also investigated the sensitivity of the model to the activation energy for the temperature dependence of the viscosity. A value of about 80 kcal/mole was being used. However, we recently became aware of data from the

literature on pitch carbonization where a value of 50 kcal/mole was used. We have also obtained additional fluidity data on coals in the Exxon sample bank which will be used to test the model.

Percolation Theory

In view of the importance of macromolecular network models to the accurate predictions of coal processing behavior, we have assessed the assumptions and limitations of the proposed models (Solomon et al., 1989a). A comparison was made of the FG-DVC model and two other network decomposition models, namely the DISARAY model of Niksa and Kerstein (1987) and the CPD model of Grant and coworkers (1989), both of which employ percolation theory. It appears that the way one performs the statistics (Monte Carlo, percolation theory, or other statistical methods) makes little difference. For example, we have substituted percolation theory methods for Monte Carlo calculations in the FG-DVC model and obtained comparable predictions for appropriately restricted cases. The important differences among models are in the assumptions for: 1) the network geometry; 2) the chemistry of bond breaking; 3) the chemistry of crosslink formation; 4) hydrogen utilization; and 5) mass transport. A paper was written which compares the models and considers how the assumed network properties relate to behavior observed for coal (Solomon et al., 1989a). This paper titled "Network Models of Coal Thermal Decomposition" is included as Appendix A.

Our current interest is in using percolation theory instead of Monte Carlo methods as the basis of our network decomposition model in order to reduce the computation time for running the FG-DVC model. This aspect of the work is described below.

General Properties of Networks - Figures II.A-1 and II.A-2 present the networks employed in the FG-DVC Monte Carlo calculations and percolation theory, respectively. For the FG-DVC Monte Carlo calculation, oligomers of ℓ clusters of a molecular weight distribution defined by M_{avg} and deviation (shown as the horizontal chains of clusters) are linked by m_0 crosslinks per monomer (shown as the vertical double lines) (Solomon et al., 1987,1988). The crosslinks are the branch points in the network where more than two bridges connect a cluster. During thermal decomposition, bridges break, crosslinks are added and the molecular weight of the oligomers is calculated by randomly distributing these changes.
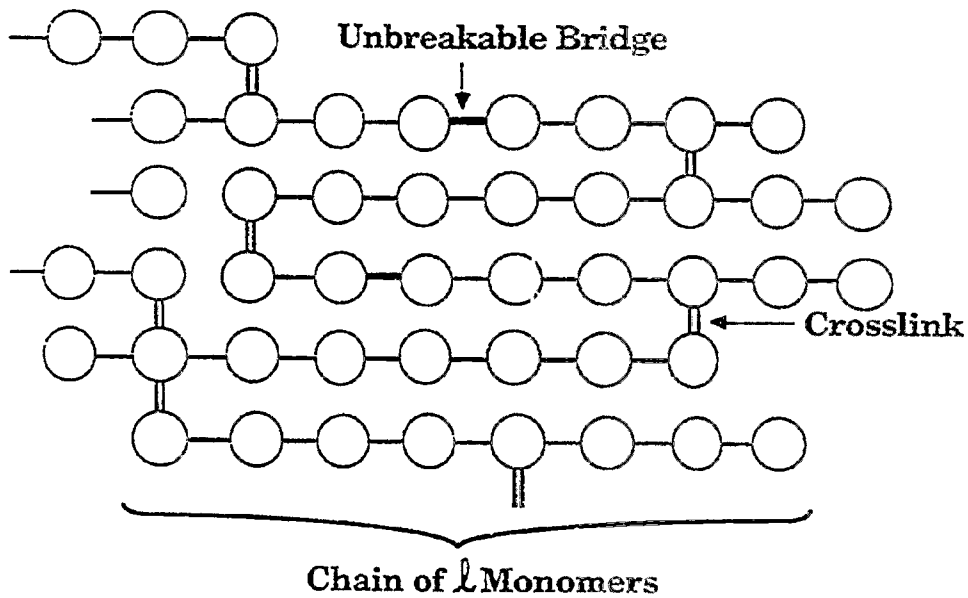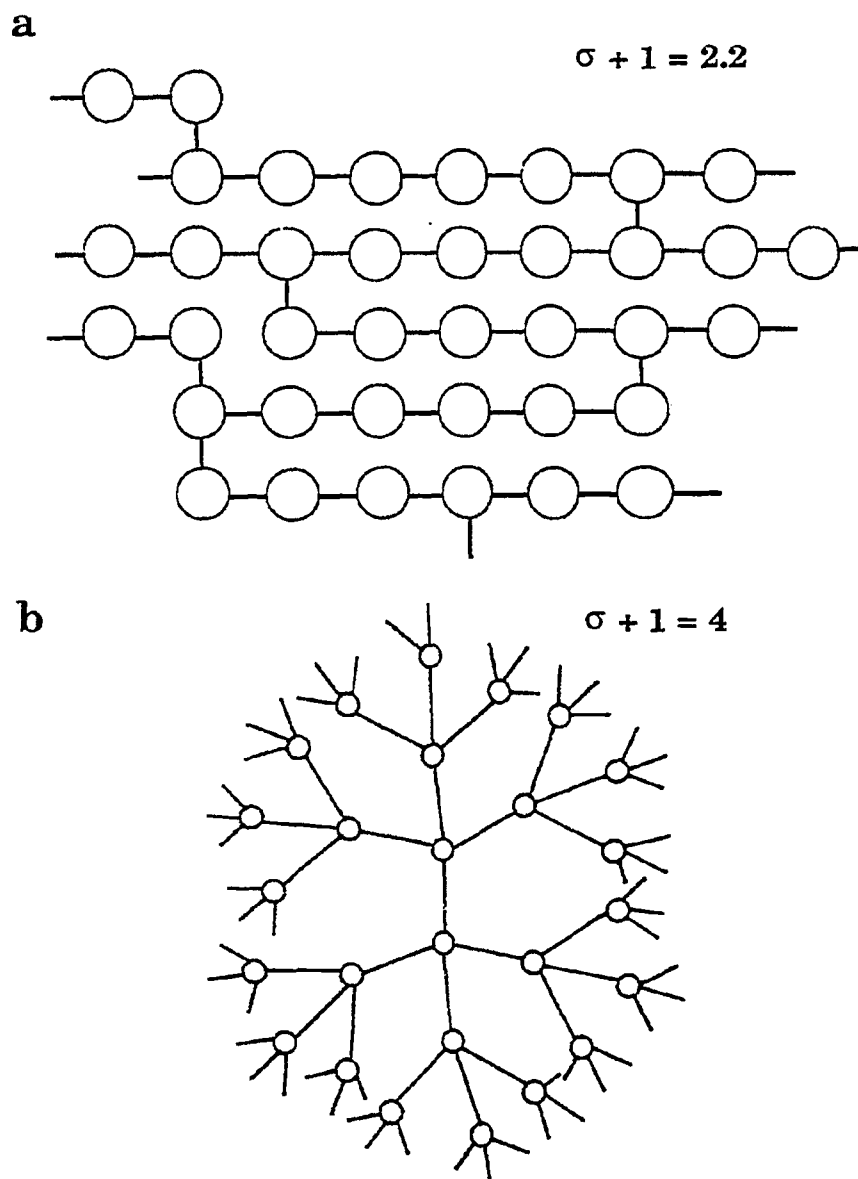
Figure II.A-1. Macromolecular Network Used in Monte Carlo Simulation.

a

$\sigma + 1 = 2.2$

b

$\sigma + 1 = 4$

Figure II.A-2. Bethe Lattice for a) Coordination Number 2.2 and b) Coordination Number 4.

For the percolation theory, a Bethe lattice is employed (Niksa and Kerstein, 1987; Grant et al., 1989; Fisher and Essam, 1961). Lattices are characterized by the coordination number $(\sigma + 1)$, which is the number of possible bridges per cluster. Figure 2 shows lattices for $\sigma + 1 = 2.2$ and $\sigma + 1 = 4$. The Bethe lattice has no loops, but it has been demonstrated that this lattice is a good approximation to a lattice of equivalent coordination number containing loops (Fisher and Essam, 1961).

The loop free geometry of the Bethe lattice allows for the number of free oligomers to be analytically expressed as a function of σ and the probability p of bonds being unbroken. This is the feature which makes the percolation theory so attractive from the standpoint of computer efficiency and for understanding the behavior of networks under conditions of varying bridge populations. In Fig. II.A-3, we present calculations using percolation theory for three values of $\sigma + 1$ for the monomer, the sum of oligomers up to 3, up to 10, and the sum of all free oligomers as a function of the number of unbroken bonds per ring cluster α, where $\alpha = 1/2\, p\, (\sigma + 1)$. If σ remains constant during pyrolysis, the molecular weight distribution is a single valued function of α. For ring clusters of molecular weight 300 amu, the sum of 1 to 3 oligomers corresponds roughly to the potential tar fraction (up to 900 amu), the sum of 1-10 corresponds to the extractable fraction (up to 3000 amu), and the sum of all oligomers corresponds to the liquids fraction (all free oligomers). It can be seen that with increasing σ, more broken bonds are required to achieve equivalent fractions of free oligomers. Also the relative amounts of tar, extracts, and liquids vary with σ.

<u>Comparison of Monte Carlo Calculation with Percolation Theory</u> - To further illustrate some of the differences between the FG-DVC Monte Carlo model and percolation theory calculations, the extract yield calculated for a case with tar evolution not permitted is plotted in Fig. II.A-4 along with the predictions of percolation theory for several values of α. The FG-DVC Monte Carlo predictions are not a single valued function of α. As pyrolysis proceeds, the increase in extract yield follows $\sigma + 1 \approx 2.2$ while the decrease in extract yield follows $\sigma + 1 \approx 4$.

It is important to know whether this result is an artifact of the Monte Carlo calculation or a real feature of pyrolysis. Based on what is happening
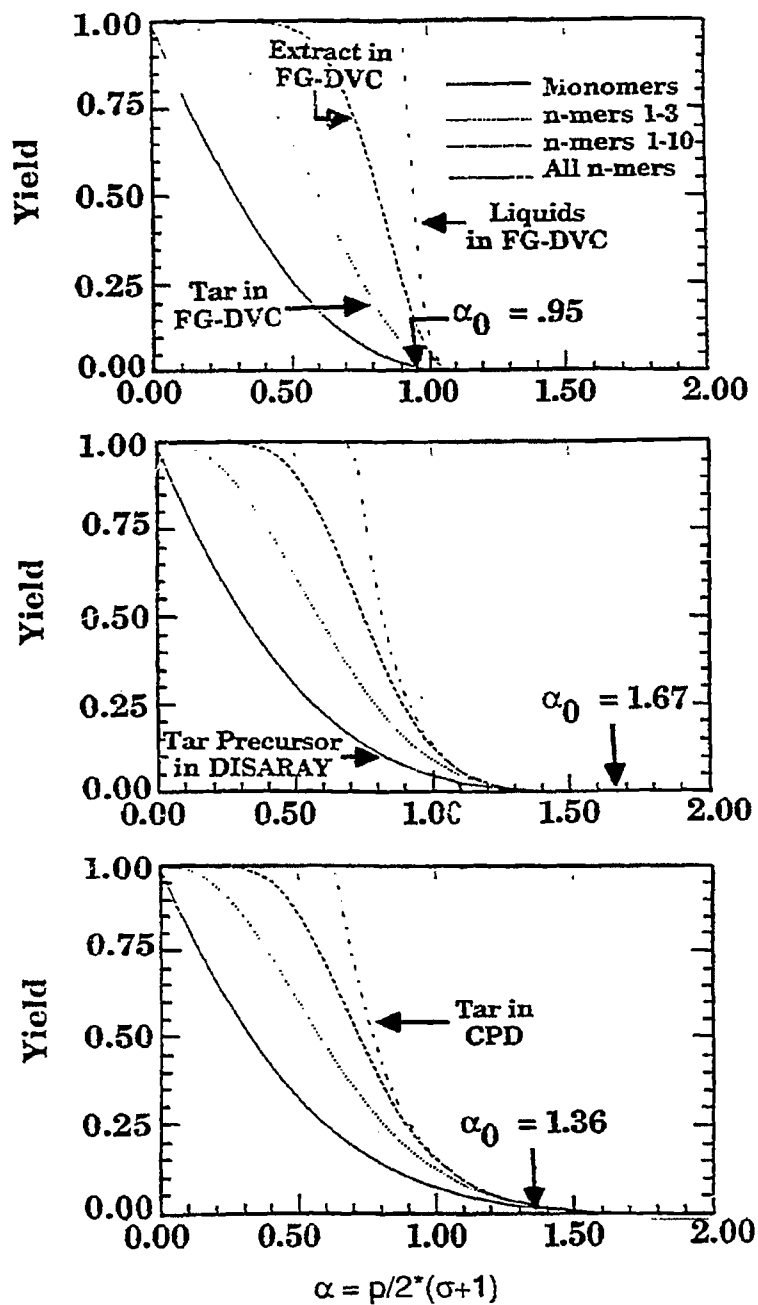
Figure II.A-3. Percolation Theory Predictions for Pyrolysis Products (monomers, tar, extracts and total liquids) for Three Values of the Coordination Number $(\sigma + 1)$. a) $\sigma + 1 = 2.2$, b) $\sigma + 1 = 3.25$ and c) $\sigma + 1 = 4.6$.

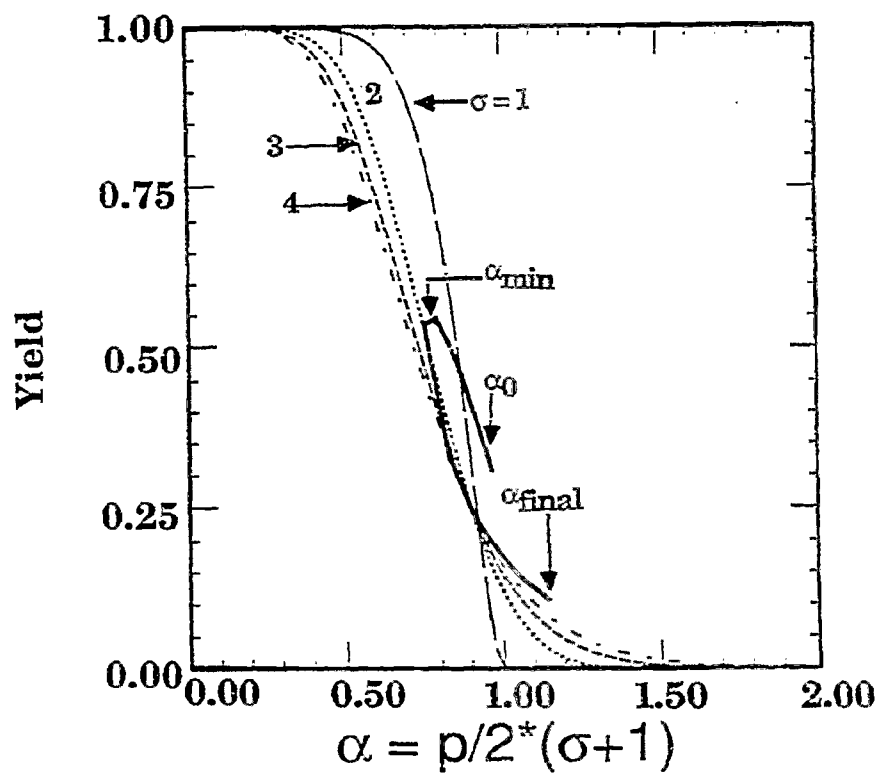**Figure II.A-4.** Extract Yield for a Lignite Predicted by the FG-DVC Model. a) Extract Yield vs. α and b) Variation in α with Time Heating at 450°C/min to 936K.

in pyrolysis, the result does make sense. For a bituminous coal, the initial process occurring in pyrolysis is bond breaking. This occurs by breaking bridges in the network described by $\sigma + 1$ between 2.1 and 2.5. No crosslinking is occurring initially as the solvent swelling ratio is observed to increase during this period (Deshpande et al., 1988). Eventually crosslinks start forming, resulting in an increase in the coordination number and in α. The network thus cannot adequately be described by a single coordination number. There is a coordination number for labile bridges and a separate coordination for crosslinks. This observation motivated the development of a more general percolation network with two coordination numbers discussed below.

Two σ Percolation Theory Method - In order to deal with a structure with a time dependent coordination number, we consider a Bethe lattice with two types of bonds, with coordination numbers and probabilities of occupation given by $\sigma_1 + 1$, p and $\sigma_2 + 1$, q for the two types, respectively. Such a lattice for $\sigma_1 = \sigma_2 = 1$ is illustrated in Fig. II.A-5. The analysis can be carried through using the same procedures as Fisher and Essam (1961) or Grant et al. (1989), but with extensions to deal with the extra variables as discussed in Solomon et al. (1989a).

Figure II.A-6 presents a comparison of the prediction for pyrolysis assuming the FG-DVC chemistry using: a) the Monte Carlo calculation, b) the two-σ percolation calculations ($\sigma_1 = 1$, $\sigma_2 = 1$) and c and d) two cases of the one-σ percolation calculation ($\sigma = 2.2$ and $\sigma = 3.2$). The calculations are made under the assumption that no tar is evolved. The tar values in Fig. II.A-6 are the sum of 1-3 n-mers remaining in the char. The Monte Carlo calculation in Fig. II.A-6a is matched best by the two-σ model if liquids are assumed to be the sum of the first 100 n-mers (i.e., up to 300,000 amu). The two-σ model has a reasonable value for the initial extract yield but predicts slightly more initial tar. Neither of the one-σ cases is a good match. Use of $\sigma = 2.2$ is good at low temperature but overpredicts the maximum values of extracts and liquids. Use of $\sigma = 3.2$ does a much better job on predicting the maximum values but the initial ratio of tar to extract is not consistent with what is observed for coal and the rate of increase of n-mers is too slow. It thus appears that the two-σ model can be used instead of the Monte Carlo calculations when no tar is evolved, while one-σ calculations are less accurate.
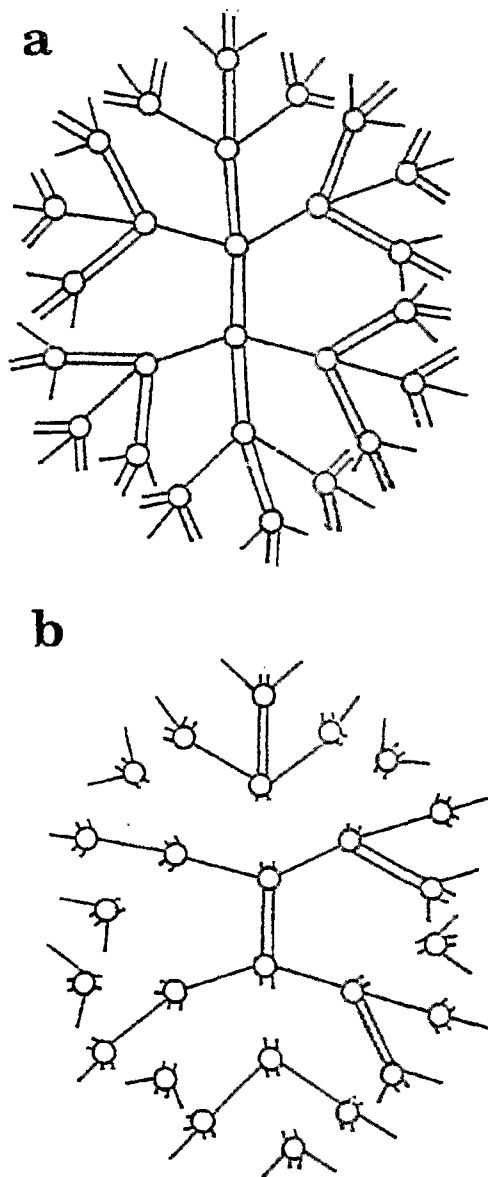
Figure II.A-5. Bethe Lattice for Two-σ Model with $\sigma_1 = 1$ (shown as single bonds) and $\sigma_2 = 1$ (shown as double bonds). a) Fully Linked Case (p= q = 1) is Like One-σ Model with $\sigma = 3$. b) With Most Double Bands Representing the Crosslinks Not Yet Formed to Represent the Starting Coal. The Lattice is Like a One-σ Model with $\sigma = 1$, Linear Chains.
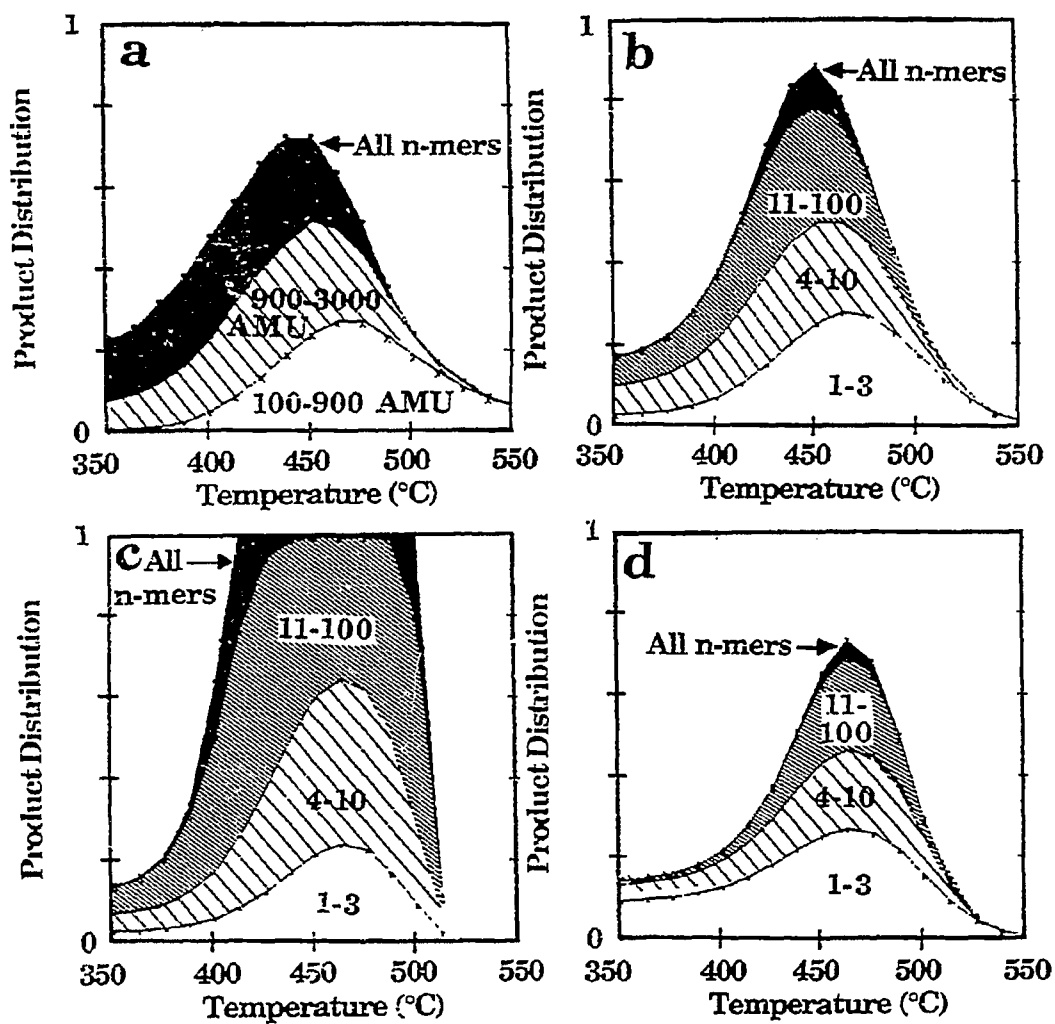
Figure II.A-6. Comparison of Distribution of n-mers for Pyrolysis at 450°C/sec to 936K. a) Monte Carlo Calculation, b) Two-σ Model ($\sigma_1 = 1$, $\sigma_2 = 1$), c) One-σ Model ($\sigma = 1.2$) and d) One-σ Model, $\sigma = 2.2$.

The real test, however, is how well the models fit the data for coal. A comparison of tar yield is not a sufficient test since α_o and $\Delta\alpha$ can always be selected in conjunction with the network geometry to fit the data. A critical test requires a careful comparison of how α_o and $\alpha(t)$ match with measurement of functional group changes in the char (e.g., the transformation of hydrogen functional groups and bridges), solvent swelling behavior (i.e., crosslink density), and the complete molecular weight distribution as reflected in the amounts of tar, extracts, and fluidity. This work remains to be done.

Rank Dependent Kinetic Rates

A recent paper reported the development of a network model for coal fluidity based on the FG-DVC model and its application to predict fluidity data for a wide range of coals (Solomon, et al., 1989b). In order to fit both the fluidity data and species evolution data, the bridge breaking and methane kinetic rates were adjusted from those used in the original model which were rank independent (Serio et al., 1987,1988; Solomon et al., 1988). An independent investigation was made of the rank dependence of the pyrolysis kinetics by doing experiments in a TG-FTIR reactor over a series of heating rates (3, 30, 50, 100°C/min) with three coals (Pocahontas, Pittsburgh, No. 8, and Zap lignite) which are at the extremes and midpoint of the rank range for the Argonne set. A comparison of the rank dependence of the rate constants for bridge breaking, tar evolution and CH_4 evolution at 450°C determined from analyzing the TG-FTIR data at several heating rates and from fitting the FG-DVC model to fluidity, weight loss and methane evolution data at a single heating rate (3°C/min) is shown in Fig. II.A-7.

The rates for tar evolution are lower than those used in the FG-DVC model for bridge breaking. This makes sense since the latter does not include transport. The rates for tar evolution or bridge breaking vary by about a factor of 10 if the Pocahontas coal is excluded, which is consistent with previous results for coals from the same range of ranks (Solomon and Hamblen, 1985). If the Pocahontas is included, the rank variation for the tar evolution or bridge breaking rates is about a factor of 50. The rates for tar evolution are consistent with those obtained by Burnham et al. (1989) for total hydrocarbon evolution from Rock Eval analysis of the same coals. This data is also shown in Fig. II.A-7.
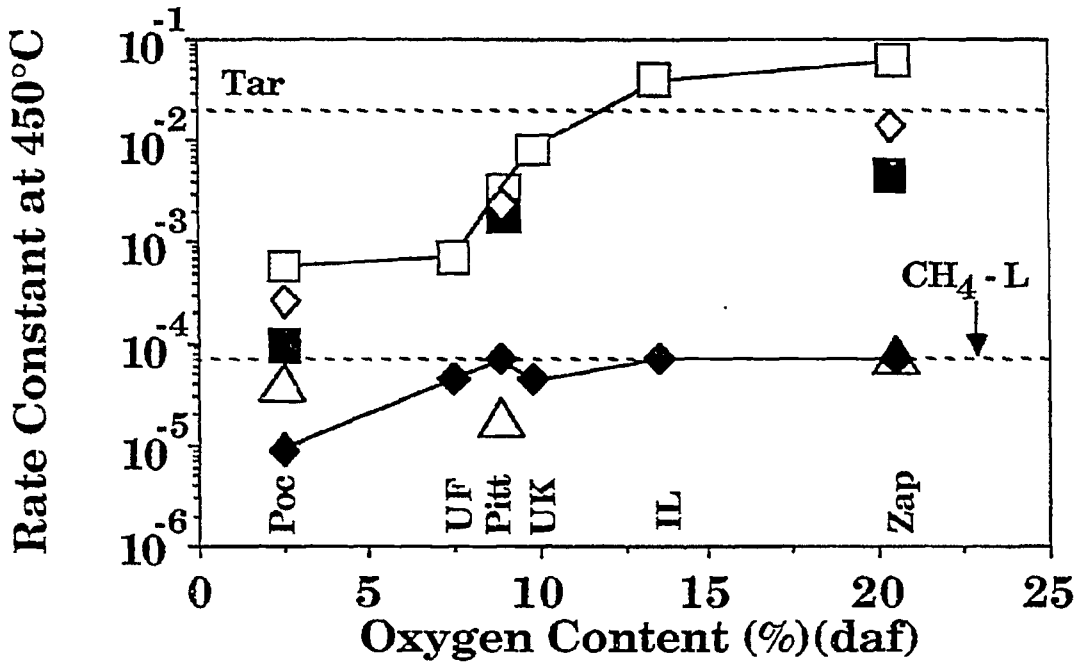
Figure II.A-7. Comparison of Kinetic Rates at 450°C for Bridge Breaking (BB), Tar Formation, and Methane-Loose (CH₄-L) Formation. (■) BB, (△) CH₄-L from FG-DVC Model Fits; (□) Tar, (◆) CH₄-L from TG-FTIR Data; (◇) Tar from Burnham et al. (1989). Dashed Lines are Rank Independent Parameters.

The kinetic parameters determined by either method for methane (loose) evolution are similar and show a much lower rank dependence. Finally, the rank independent parameters used in the original FG model are shown as horizontal dashed lines. These are in better agreement with results from the lower rank coals, which was expected since the set of coals used to obtain those parameters did not include the higher rank coals (Serio et al., 1987).

Polymethylenes

There is present in coals varying amounts (typically 0-9%, but in some cases as high as 18%) of long-chain aliphatics (polymethylenes). These have recently been reported in pyrolysis products by Nelson (1987) and by Calkins and coworkers (1984a,b,c,1985) and references quoted therein. The chains appear alone and attached to aromatic nuclei. During devolatilization, the smaller molecules may be released without bond breaking and the heavier molecules with bond breaking to contribute to the tar. The presence of these polymethylenes makes the tar more aliphatic than the parent coal. Further cracking of this material under more severe devolatilization conditions produces ethylene, propylene, and butadiene from which the concentration of polymethylenes may be determined (Calkins, 1985). Presently, the polymethylenes are included in the FG model as part of the aliphatic functional group pool, which is assumed to decompose to produce gas products, not tar. This leads to an error in determining the H/C ratio in the tar which can be important for low rank coals (Freihaut et al., 1988). If the amount of heavy polymethylenes is determined, these can be computed as a separate functional group pool with an appropriate release rate and added to the tar. However, strictly speaking, the polymethylenes should also be included as a type of oligomer so that the smaller species can vaporize directly, without bondbreaking. This would also allow the polymethylenes to be included in the extractable species.

The problem of vaporizing the small polymethylenes and including them in the extract yield are related. For most coals, there is a low temperature tar peak which is polymethylene-rich but also includes aromatic tars. Currently, the FG-DVC model uses an interactive procedure at the beginning of a simulation which adjusts the oligomer length to match the experimental pyridine extract yield with the molecular configuration in the computer. The model considers extract to be those molecules which are less than 3000 in molecular weight.

However, this does not produce tar molecules which are light enough to vaporize at low temperatures. A possible route to achieving the desired bimodal tar molecular weight distribution is to start out with a large oligomer length and allow the coal to undergo pre-pyrolysis using geological time-temperature profile. A second possibility is to use a distribution of oligomer sizes.

A literature review was done on the occurrence of polymethylenes in coals in order to help formulate a strategy to address the problem. This is included in Appendix B. This information can be summarized as follows:

1.   Polymethylenes, $(CH_2)_n$, are present in coals at a level of 0 – 18 wt.% depending on rank.

2.   Very high rank coals (anthracites) contain very little $(CH_2)_n$ while low rank coals (lignites) generally contain at least 10 wt.%. The amounts for coals of intermediate rank are highly variable and depend on geochemical factors.

3.   Exinite macerals are high in polymethylenes, followed by vintrinite and then inertinite.

4.   A significant fraction of the $(CH_2)_n$ are attached to aromatic structures in the coal and are not readily extractable.

5.   The $(CH_2)_n$ are the precursors for the ethylene, propylene, and butadiene produced from high temperature pyrolysis of coal. They are not precursors for methane, benzene or other light aromatic compounds.

6.   The $(CH_2)_n$ appear to play an important role in donating hydrogen to stabilize the reactive aromatic fragments.

7.   The $(CH_2)_n$ appear to decompose by a free radical chain reaction which is different than that observed for pure $(CH_2)_n$ in the gas phase. They also decompose differently than the main coal structure.

8.   Some of the $(CH_2)_n$ are light enough to vaporize directly without bond breaking. The low temperature tars which evolve prior to the main decomposition peak and the low temperature extracts from coal are enriched in $(CH_2)_n$.

9.   The vaporization laws which apply to $(CH_2)_n$ will be different than those which apply to the aromatic tars. For a given molecular weight, aliphatic compounds are more volatile than aromatic compounds.

10. The $(CH_2)_n$ will not participate in crosslinking reactions in the same way as the rest of the (aromatic) tar molecules.

All of these factors must be addressed to correctly deal with the occurrence of polymethylenes. However, some can be neglected in the first generation model.

Plans

Complete work on viscosity model. Continue work on refinement of rank dependent kinetic parameters. Continue investigation of the use of percolation theory to increase the FG-DVC code efficiency. Complete work on addition of polymethylenes to FG-DVC model. Complete work on pore transport model. Begin work on swelling model and on refinement of tar mass transport model.

II.B.   SUBTASK 2.B. - FUNDAMENTAL HIGH-PRESSURE REACTION
RATE DATA

Senior Investigators - Geoffrey J. Germane and Angus U. Blackham
Brigham Young University
Provo, Utah 84602
(801) 378-2355 and 6536

Student Research Assistants - Chuck Monson, Russell Daines,
and Gary Pehrson

Objectives

The overall objectives of this subtask are 1) to measure and correlate reaction rate coefficients for pulverized-coal char particles as a function of char burnout in oxygen at high temperature and pressure and 2) to provide kinetic rate measurements of sulfur species with sorbents for a range of stoichiometries under laminar, high-pressure conditions.

Accomplishments

Work continued during the last quarter on the testing of the high-pressure, controlled-profile (HPCP) reactor, the preparation and characterization of char, and the kinetics of char oxidation at high pressure.

High-Pressure Reactor Design and Fabrication

During the reporting period, modifications were performed on the feeder and the preheater. Plugging of the small, stainless-steel feed tubes with particles from sticky coal occurred during initial feeder tests. The tubes were replaced with tubes of a larger inner diameter to eliminate the plugging. The feed rate was also reduced with a 20:1 gear reducer, allowing slower feed rates without plugging.

Initial testing also led to changes in the preheater design. It was found that the cast alumina tube that surrounds the heating element was not large enough to allow sufficient heater movement. Because of thermal stresses during heating, the lower portion of the element spread and bent to one side as operating temperatures were reached. During testing, the heating element came into contact with the surrounding tube, resulting in breakage of both the

element and the tube. The preheater is currently configured without the surrounding tube or the packed bed and provides sufficient heat to the secondary flow at low pressure. The packed bed and a larger tube will be added, if needed, for high-pressure, high-flow operation.

Initial testing showed unacceptably high temperatures in the heater access port of the reactor. This temperature must remain below 300 degrees Centigrade to prevent overheating of the heater ends. A radiation shield consisting of a ceramic blanket was added which substantially reduced the port temperature. During subsequent tests the temperature has not exceeded 150 degrees.

The gas flow system that will control and measure the flows entering and exiting the reactor is being assembled. Completion of this system will allow the reactor to be operated at full design pressure. Delays in delivery of needed components have prevented completion of the reactor flow instrumentation.

Instrumentation/Optics - A microcomputer was obtained for use with the instrumentation system. An eight-channel, 12-bit analog-to-digital converter (A/D) board, a multiplexer, and a six channel, 12-bit digital-to-analog converter (D/A) board have been ordered for the microcomputer. The multiplexer has sixteen channels with cold-junction compensation for thermocouple temperature measurements. All thermocouples will be connected through the multiplexer to one channel of the A/D board. The remaining input channels will be used to record gas flows and pressure. Four channels of the D/A board will provide control signals to the heater controllers. The other output channels will be used in the future if the flow meters are converted to flow controllers.

The possibility of using a video microscope system to obtain in-situ particle size information is being examined. Such systems have been successfully used in combustion studies (Glass and Zygourakis, 1988; McCollor et al., 1987). The particle-imaging system being assembled for this project will provide particle temperature and velocity with reasonable accuracy. A measurement of the particle height as it falls through the optical volume can also be obtained, but no information on the aspect ratio of the particle can be extracted. A video system which views the particle stream orthogonally to the imaging system's view would provide the height and width of the particle as well as information on particle spacing.

Char/Tar Separation - The cyclone separator was modified this quarter under separate funding to more readily allow the removal of collected particles when the reactor was operating at pressures above atmospheric. The collection area is connected to a porous metal filter through an in-line valve. A valve was also installed to release the filter pressure after the in-line valve was closed. This system allows a stream of gas to scavenge the walls of the cyclone just before the sample is collected to ensure that all the particles move to the collection area.

The cyclone and impactor were tested this quarter with 10-μm-mass-mean-diameter, powdered limestone. Using the results from the cyclone tests in conjunction with a correlation suggested by Parker, et al. (1981) for cyclones operating at high temperatures and/or pressures, it was found that the 90-percent-cut diameter (the particle diameter at which 90 percent of the particles that size will be collected) will be below 15 μm for all runs, indicating that most of the char particle mass will be collected in the cyclone. The tar collected in initial coal devolatilization tests supports this observation. Using the SEM, only very fine char particles were found in the tar. Also, there was virtually no recoverable tar on the cyclone surfaces, so it is likely that there is almost no tar condensing on the char. The tests on the impactor indicate that the observed 50-percent-cut diameter is approximately the target design point of 5 μm; almost all particles larger than 10 μm go into the impactor's char collection probe. Overall efficiency of the collection system, configured for either char oxidation or coal devolatilization, should be high.

Char Preparation at High Temperature and Pressure

Plan - The main objective of the char preparation aspect of this study is to prepare char by three different methods: 1) a simple, hot-tube reactor at atmospheric and elevated pressure, 2) the BYU high-pressure, entrained-flow gasifier, and 3) the high-pressure, controlled-profile (HPCP) reactor that has been fabricated for this subtask. Some char samples have been prepared in the HPCP to serve as reference chars to which other char samples from the simple hot-tube reactor and the gasifier can be compared. The purpose of this comparison will be to determine how closely the properties of the chars prepared with the simple reactor and the gasifier compare to the properties of the chars prepared by the HPCP reactor. If the properties are sufficiently close for similar temperatures, pressures, heating rates and residence times,

then confidence will be established in the measured values of the oxidation kinetics of the chars prepared with the simple hot-tube reactor.

It is planned that chars will be prepared from five different coals: 1) Utah bituminous, 2) North Dakota lignite, 3) Wyoming subbituminous, 4) Illinois No. 6 bituminous, and 5) Pittsburgh No. 8 bituminous. A few kinetic runs will be made with premium samples from the Argonne coal bank. Additional runs will be made with bulk samples available at the BYU Combustion Laboratory.

Literature Survey - A recent paper by Oh, Peters and Howard (1989) describes the formation of bubbles and their transport within the coal particle during pyrolysis. It was found that as the coal reaches a critical temperature (the softening point), the bitumens melt and the coal becomes more plastic. As the coal becomes fluid, viscous flow of material blocks pores, reducing the open pore structure of the coal. Volatiles diffuse either to the particle surface or to the bubbles dispersed throughout the molten coal. Evidence of such bubble formation in Pittsburgh No. 8 coal has been found with SEM micrographs taken of the chars produced in this laboratory.

Char Properties for Kinetic Tests - Over the course of this study, a number of samples of small quantities of char have been prepared in the simple, hot-tube reactor at various temperatures, pressures, residence times and heating rates from Utah bituminous coal and Pittsburgh No. 8 bituminous coal. Data for some of these chars were given in the 10th Quarterly Report (Solomon et al., 1989). Eight chars were produced from Pittsburgh No. 8 coal at up to 1530 K and nearly 10 atm in the HPCP and hot-tube (HT) reactors during the reporting period. The preparation temperatures, pressures and residence times for these chars are summarized in Table II.B-1.

A large quantity of sample P8-15 was prepared from size-fractionated (64-75 microns) Pittsburgh No. 8 coal in the simple hot-tube reactor for char oxidation kinetic tests in the HPCP reactor. Because of the swelling nature of this coal, the required large quantities of char for the oxidation tests were prepared by a two-pass procedure to avoid plugging of the reaction tube. The first pass was through a large-diameter, ceramic tube (22 mm inside diameter) at a short residence time to separate some of the tar from the char. The intermediate char was then passed through a smaller ceramic tube (8 mm inside diameter) at 1530 K, 1 atm.

TABLE II.B-1.

PITTSBURGH NO. 8 CHAR PREPARATION SUMMARY

Sample	Reactor	Size[1]	Temp.	Press.	Res.Time	Quant.	Oxidized?	Crit.Temp.[3]	SEM
-	-	μm	K	atm	ms	gm	-	K	no.
P8-10	HT	64-75	1370	1	26	0.1	N	827	0
P8-11	HT	38-43	1300	1	25	0.5	N	-	0
P8-12	HT	64-75	1275	1	17	1.5	N	-	5
P8-13	HT	64-75	1530	9.5	70	0.1	N	-	1
P8-14	HT	64-75	1530	5.1	37	0.1	N	-	2
P8-15	HT	64-75	1530	1	80	18.5	Y	850	4
P8-16	HPCP	64-75	1380	3	257	1.0	N	817	2
P8-17	HPCP	64-75	1380	1	91	1.0	N	827	2

1 Parent coal size fraction
2 Char used for oxidation tests (Yes/No)
3 From TGA

Char samples P8-16 and P8-17 were prepared in the HPCP reactor. Runs were made with Pittsburgh No. 8 coal at 1380 K and at 1 and 3 atm. The water-cooled injection probe was used to introduce the coal into the reaction tube. The preheated secondary flow of nitrogen and the hot reaction tube walls brought the sample up to temperature. A cold nitrogen quench in the collection probe prevented further devolatilization. The cyclone was used to collect the char. Slight plugging occurred at the tip of the water-cooled injection probe after about 6 grams of coal were fed, but no other problems were encountered.

Table II.B-1 also lists TGA critical temperatures for several of the chars produced. The critical temperatures for chars prepared in the two reactors under similar temperatures and pressures agree very well, though the residence time in the hot-tube reactor was about one-third of that in the HPCP reactor. The determination of other properties for characterizing these chars is in progress but has not yet been completed due to problems with the CHN analyzer.

SEM micrographs have been taken of the char samples, including the oxidized char samples obtained from the HPCP reactor. The detailed analysis of the micrographs is also in progress; however, preliminary observations are given below.

Initial studies of the SEM's of the Pittsburgh No. 8 char samples P8-12 through P8-17 show an effect of residence time on porosity. As the residence time increases from 17 to 80 ms, the porosity of the particles apparently increases, though less than for the Utah bituminous coal. The porous particles in the Pittsburgh No. 8 char could be due to the fact that volatile evolution comes about by bubbles. These bubbles seem to exit through the particle wall and leave a large circular hole and some small circular holes. The porosity found in the Utah bituminous char did not show many circular holes but rather a honeycomb-shaped pore structure on the surface of the particles.

Also, chars for which C, H and N analyses are available show a trend of decreasing hydrogen content in the char with increasing residence time (Solomon et al., 1989). For chars prepared at 1340 K and 1 atm., the mass of hydrogen in the Pittsburgh No. 8 char decreased from 2.4 to 1.3 percent as the

residence time increased from 31 to 92 ms. This previously reported trend was also shown for the Utah char.

Kinetics of Char-Oxygen Reactions at High Pressure

Oxidation tests of the Pittsburgh No. 8 bituminous coal char sample P8-15 were conducted in air at atmospheric pressure in the HPCP reactor. The cooled injection probe was positioned to obtain particle residence times of about 50 and 100 ms. Reactor wall temperature was varied from 1173 to 1461 K. The test conditions are shown in Table II.B-2.

Gas temperatures were measured before each test with a Type-S thermocouple that was inserted through the injection probe and moved along the axis of the reaction tube. The 1-mm-diameter thermocouple bead was nested against a 3-mm ceramic tube that sheathed the thermocouple leads. Temperature measurement errors due to radiation from the reaction tube wall were neglected because of the small size and low emissivity (<0.1) of the thermocouple bead. Particle temperature was calculated using an energy balance that has been shown to give results consistent with pyrometry measurements (Ayling and Smith, 1972).

The breakdown of the CHN analyzer has temporarily delayed the determination of reactivities or kinetic parameters for samples collected from the oxidation tests. The analyses of unoxidized char titanium content will also be completed for independent determination of char burnout.

Other Activities

Continued discussions on char and tar preparation and analysis were held with other researchers in the Advanced Combustion Engineering Research Center. Meetings were held to review the status of analytical and test equipment and to discuss specific arrangements for sharing analytical capabilities. A member of the research team attended the ACERC First Symposium on Advances in Coal Spectroscopy at Salt Lake City, Utah in June, 1989.

Plans

Additional kinetic tests with Pittsburgh No. 8 bituminous coal char, and detailed CHN, TGA and SEM analyses will be completed during the next quarter. Tests with other coals will be initiated. The HPCP reactor instrumentation

TABLE II.B-2.

PITTSBURGH NO. 8 CHAR OXIDATION CONDITIONS

Sample	Size[1]	Quant.	Wall Temp.	Gas Temp.	Res. Time	%O₂	%Ti
-	μm	gm.	K	K	ms.	-	-
P8-15-1	64-75	2.0	1173	880	62	0.21	0.0760
-2			1173	960	114	0.21	0.0650
-3			1277	955	57	0.21	0.0665
-4			1277	1031	106	0.21	0.0625
-5			1370	975	56	0.21	0.0631
-6			1461	1239	89	0.21	0.0655

[1]Char size fraction.

and control system will be completed. and assembly of the optical system will continue. Signal conditioning and input/output boards will be installed in the microcomputer. and the development of control algorithms for heater and flow control will continue. The installation of all necessary instrumentation. such as flowmeters. pressure gauges. and thermocouples. will be completed.

II.C.   SUBTASK 2.c. - SECONDARY REACTION OF PYROLYSIS PRODUCTS AND CHAR BURNOUT SUBMODEL DEVELOPMENT AND EVALUATION

Senior Investigator - Michael A. Serio
Advanced Fuel Research, Inc.
87 Church Street, East Hartford, CT 06108
(203) 528-906

Objective

The objective of this subtask is to develop and evaluate by comparison with laboratory experiments, an integrated and compatible submodel to describe the secondary reactions of volatile pyrolysis products and char burnout during coal conversion processes. Experiments on tar cracking, soot formation, tar/gas reaction, char burnout, and ignition will continue during Phase II to allow validation of submodels in Phase II.

Accomplishments

Discussions continued with BYU on the modeling of the Transparent Wall Reactor (TWR) experiments with the Montana Rosebud Coal. This work is being reported under subtask 3.a.

Work was also done to modify the TWR experiment to do pyrolysis and combustion experiments with FT-IR measurements of particle temperatures. During the past quarter, a series of pyrolysis experiments was done with Zap lignite and Pittsburgh seam bituminous coal. These experiments included FT-IR gas and particle temperature measurements, thermocouple measurements of the gas temperature and collection of char samples with a probe at six different heights. The particle temperature measurements were used to reconstruct the particle temperature-time history. The pyrolysis yields were then simulated with the FG-DVC model and the results were consistent with the kinetic rates measured previously at high heating rates at AFR and Sandia for experiments where particle temperature measurements were made.

In-Situ FT-IR Diagnostics in TWR

Introduction - In the literature, there are orders of magnitude discrepancies in the reported rates for coal pyrolysis weight loss or tar loss. The conflict in values and the reasons for the conflict have been discussed previously (Solomon and Hamblen, 1985; Solomon and Serio, 1986). These studies concluded that inaccurate knowledge of coal particle temperatures was the chief cause of the variations.

To improve the knowledge of particle temperatures, a new method was developed which employs a Fourier Transform Infrared (FT-IR) spectrometer to measure the emission and transmission (E/T) in a reacting particle stream (Solomon and Hamblen, 1985; Serio et al., 1987). This technique has been applied to measure the temperature of coal particles in an entrained flow reactor (EFR) (Best et al., 1986; Solomon et al., 1987) and a heated tube reactor (HTR) (Solomon et al., 1986a). The kinetic rates, determined from these experiments for a number of coals and lignites (8.6×10^{14} exp(-228,500/RT)sec^{-1} for tar loss or approximately half this value for weight loss) was the highest ever reported at temperatures above 600°C. There were, however, some limitations to these experiments. The EFR experiments only allowed optical access for temperature measurement at one position and the HTR was limited to non-swelling coals. Recent experiments by Fletcher (1989) in an apparatus which does not have these limitations and which employs temperature measurements by 2-color pyrometry have confirmed these high rates within a factor of 2 for both low and high rank coals.

During the eleventh quarter, kinetic rate measurements were made on a Zap North Dakota lignite and a Pittsburgh Seam bituminous coal in a transparent wall reactor (TWR) which does not have the limitations of the HTR or EFR. The temperature measurements were made with the FT-IR E/T technique. This reactor, with the in situ FT-IR diagnostics, will be used under this subtask to make spatially resolved measurements on coal flames using a tomographic technique. These measurements will provide fundamental data on the processes of ignition, soot formation, and char burnout. The pyrolysis experiments allow a test of the experimental and optical systems for a simpler set of conditions.

Experimental - The measurement of particle temperatures from the particle's emitted radiation is difficult if the pyrolysis reactor has hot walls. In this

case, wall radiation scattered by the particles interferes with the emitted radiation. To overcome this problem, the pyrolysis experiments in this study were performed in a reactor with relatively cold walls. The apparatus is a transparent wall reactor (TWR) which has been previously described (Solomon et al., 1989). Nitrogen is passed through a heat exchanger and enters a reaction section at approximately 850°C. Coal entrained in cold nitrogen carrier gas is injected through a co-axial 7 mm diameter tube into the preheated stream. An octagonal glass enclosure shields the pyrolyzing stream from room air currents. The glass enclosure has movable KBr windows to allow access to the flame for radiation measurements. Particle velocities were measured using a video camera under slightly oxidizing conditions which allowed a small percentage of the particle to ignite.

To measure temperatures of pyrolyzing coal particles, several other problems had to be overcome. Because pyrolysis in this reactor occurs at relatively low temperatures (600-800°C), the measurements are made in the mid-infrared where sufficient energy is emitted. In addition, coal is not a gray-body and its emissivity changes during pyrolysis. To overcome this problem, the temperature has been measured using the amplitude of the radiated energy in a frequency range where the emissivity is close to one and independent of the extent of pyrolysis. The transmission is used to determine the emitting surface area of the particles. Finally, soot radiation can make the particle temperature appear much higher than it really is. Measurements have been made with a gas temperature of 850°C so soot formation did not occur.

The coals studied in this work were a dried Zap North Dakota lignite and a Pittsburgh Seam bituminous coal. The ultimate analyses are approximately those reported in Serio et al. (1987). Both samples were sized to 200 x 325 mesh. Weight loss was determined from captured char particles, by ash tracer analysis, using a Perkin Elmer TGA.

Results and Discussion - The emission spectra for the pyrolyzing particles at 15 cm above the injector are presented in Fig. II.C-1. The spectra are normalized by the emitting surface area using the measured attenuation at 3500
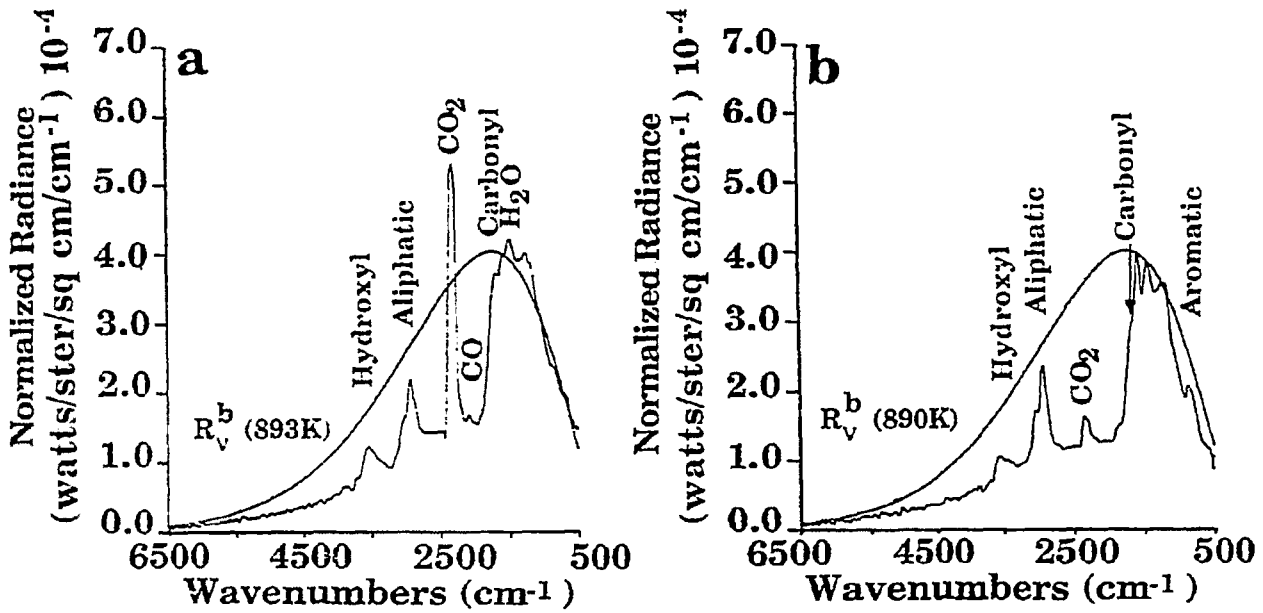
Figure II.C-1. Normalized Emission Spectra of Pyrolyzing
Coal Particles at 15 cm above the Nozzle and Theoretical
Black-Body Curve. a) Zap and b) Pittsburgh.

cm^{-1} assuming a total extinction efficiency of 1.2. The spectra are not gray-body. They reveal the infrared absorption bands in the char. Notice the higher hydroxyl and carbonyl bands in the lignite and the higher aliphatic and aromatic C-H bands in the bituminous coal. Bands for pyrolysis water, CO_2, and CO are also apparent. Also shown are theoretical black-body curves. Particle temperatures were determined by matching the theoretical curves to the radiance at 1600 cm^{-1}, where the emissivity is approximately 1.0 (Best et al., 1986).

Spectra such as these were obtained for both coals at positions between 5 and 40 cm. In addition, char samples were captured at a number of locations. The results for the Zap lignite are summarized in Fig. II.C-2. Figure II.C-2a shows the temperature measurement in the reactor made using a thermocouple and the FT-IR E/T technique to determine both particle and CO_2 temperatures (Solomon et al., 1987,1989). The CO_2 and particle temperatures agree to within 100°C. The thermocouple temperature measurements averaged across the estimated width of the particle stream are also in reasonable agreement except early in the reaction when the particle are heating and late when the gas is cooling. The particle's heating rate is about 5000°C/sec.

Figure II.C-2b shows the weight loss determined by ash tracer analysis. These are compared to predictions of the FG-DVC model (Solomon et al., 1988). The kinetic rates for bond breaking used in the FG-DVC model is
$k_B = 8.6 \times 10^{14} \exp(-228,500/RT) \sec^{-1}$. The predictions using 10 and 0.1 times this rate are also shown. The agreement is best with the highest of the three rates.

The results for the Pittsburgh Seam coal are presented in Fig. II.C-3. These results also agree best for $k_B \times 10$. Consequently, the high heating rate data do not show much of a rank variation. However, these measurements are not as sensitive to factors of 10 difference in rate.

Conclusions - The high kinetics rates for tar evolution or weight loss recently reported by Solomon et al. (1985,1986a), Serio et al. (1987) and Fletcher (1989) have been confirmed. At high heating rates, significant
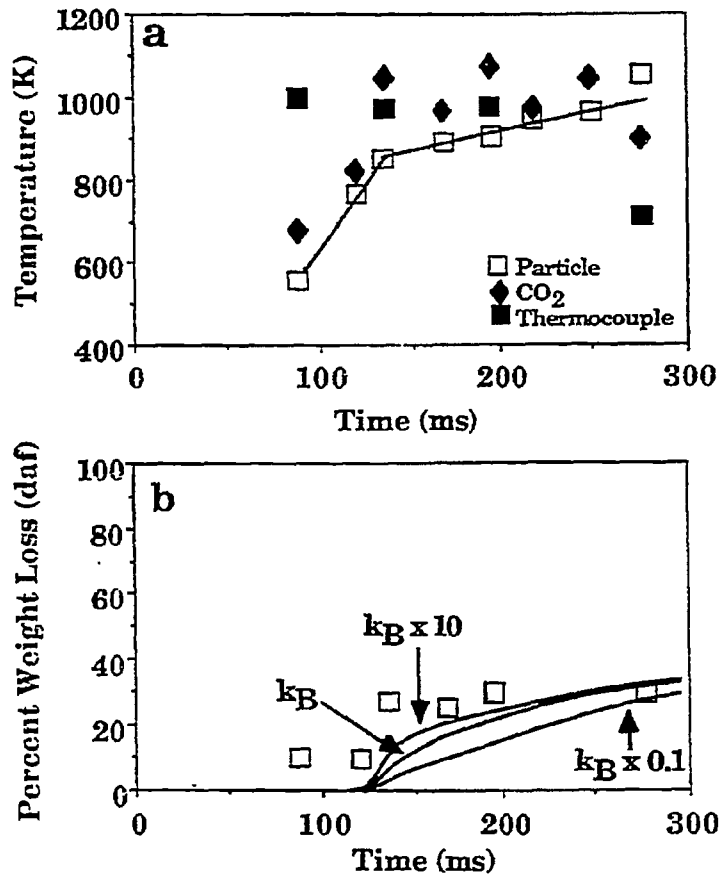
Figure II.C-2. Pyrolysis Results for Zap North Dakota Lignite. a) Temperatures and b) Weight Loss.
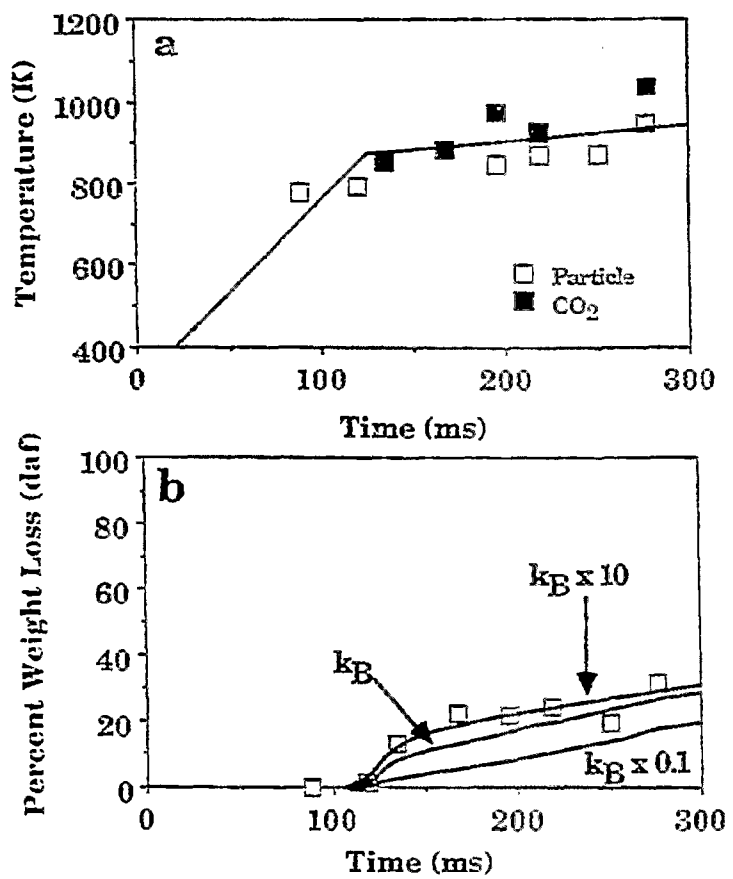
Figure II.C-3. Pyrolysis Results for Pittsburgh Seam Bituminous Coal. a) Temperatures and b) Weight Loss.

pyrolysis occurs within 100 ms at temperatures between 700 and 1000 K for both a lignite and a bituminous coal.

Plans

Modify TWR apparatus to make the flame more stable. Continue work with BYU on simulation of the TWR data.

II.D. SUBTASK 2.d - ASH PHYSICS AND CHEMISTRY SUBMODEL

Senior Investigator - James Markham
Advanced Fuel Research, Inc.
87 Church Street, East Hartford, CT 06108
(203) 528-906

Objective

The objective of this task is to develop and validate, by comparison with laboratory experiments, an integrated and compatible submodel to describe the ash physics and chemistry during coal conversion processes. AFR will provide the submodel to BYU together with assistance for its implementation into the BYU PCGC-2 comprehensive code.

To accomplish the overall objective, the following specific objectives are: 1) to develop an understanding of the mineral matter phase transformation during ashing and slagging in coal conversion; 2) To investigate the catalytic effect of mineral matter on coal conversion processes. Data acquisition will be focused on: 1) design and implementation of an ash sample collection system; 2) developing methods for mineral characterization in ash particles; 3) developing methods for studying the catalytic effect of minerals on coal gasification.

Accomplishments

Work continued on improving the collection of ash from the entrained flow reactor experiments with the eight Argonne coals. It appears that most of the problem for the Upper Freeport coal, where low collections were obtained, was due to particles and ash sticking in the collection probe. This appears to be solved by rinsing the probe with acetone.

SEM/X-ray analysis was done on the extracted material and compared to that collected in the cyclone. It was found that there was some differentiation. The former material was higher in iron and sulfur, lower in aluminum and silicon and about the same in alkali content.

Work on the effects of minerals on char reactivity continued. As discussed in the previous quarterly, a particular area of interest is the investigation of the effects of Na on the reactivity of demineralized Zap coal. It was observed that a loading of 0.5 wt.% Na significantly increased the reactivity of a char produced at 900°C in a TGA but that a loading of 2.0 wt.% Na significantly reduced the reactivity of a char produced under the same conditions. In both cases, a comparison is being made to char produced from the demineralized Zap coal. Surface area analyses were done of the chars during the past quarter. It appears that a significant reduction in the CO_2 surface area can explain the low reactivity of the 2.0 wt.% Na char. The reason for this has not yet been determined. SEM photographs do not reveal anything unusual about the char morphology.

Ash Collection

The material balance problem in the entrained flow reactor appears to have been solved. Material adhering to the interior of the extractor was not being removed physically, but has been removed by additionally employing an acetone rinse step. X-ray analysis of the extractor material has shown it to be enriched in iron and sulfur and depleted in aluminum and silicon as compared to the material deposited in the cyclone. The alkali contents of the material are virtually identical. The SEM photomicrographs (Figures II.D-1 thru II.D-5) of the materials show the extractor material to have a fused surface with adhering particles, while the cyclone collected particles tend to be more individual. The particles which appear to be adhering to the extractor material do not show the wide range of morphologies of the cyclone collected particles.

Experiments have shown that the helium quenching tends to increase the fouling of the extractor, as shown in Table II.D-1. It is unclear whether this is due to forcing material against the cold extractor walls or some other effect. X-ray analyses of extractor and cyclone collections with and without helium quenching have shown no appreciable differences between the extractor collections or between the cyclone collections, as shown in Table II.D-2. However, the extractor collection made with the helium quench off is higher in sulfur than that made with the helium on. The SEM photomicrographs appear to show a greater number of particles adhering to the fused framework with the helium quench off.

TABLE II.D-1 - ASH DISTRIBUTION FOR UPPER FREEPORT ENTRAINED FLOW REACTOR RUNS

	With He (Low Gas Velocity)	Without He (Low Gas Velocity)	1 m/s Without He (High Gas Velocity)
Cyclone	39.8%	78.4%	76.5%
Cas. Imp.	3.7%	2.6%	2.2%
Extractor	2.2%	0.0%	0.1%
Ext. Wash	50.1%	9.8%	12.9%
Cyc. Wash	3.8%	8.9%	6.8%
C.I. Wash	0.4%	0.3%	1.4%

TABLE II.D-2 - ELEMENTAL ANALYSIS OF UPPER FREEPORT ENTRAINED FLOW REACTOR ASHES

Element*	Raw Coal	Open Crucible Ash	Cyclone**	100% Burn-Out He-Quench ON		100% Burn-Out He-Quench OFF	
				Cyclone	Extractor	Cyclone	Extractor
Na	0.58	0.00	0.14	0.00	0.00	0.00	0.00
Mg	0.34	0.00	0.27	0.00	0.00	0.00	0.00
Al	14.11	12.83	12.63	16.60	10.38	12.97	5.96
Si	21.23	18.33	20.49	24.50	17.01	27.99	10.56
K	1.76	2.16	1.43	2.16	1.80	2.54	1.22
Ca	3.08	2.83	6.62	3.08	3.03	3.16	4.38
Ti	0.71	1.64	0.74	1.30	1.29	1.62	0.95
S(o)	9.05	0.24	0.33	0.62	0.67	0.29	2.69
S(m)	4.64	0.58	0.94	1.07	1.42	0.31	7.35
Fe	4.79	18.72	10.38	4.94	22.31	8.92	28.42

*   All values are weight % with ash normalized to 100%.
    Fe values are weight % Fe in oxide form only.

** No extract wash or mechanical cleaning of extractor.

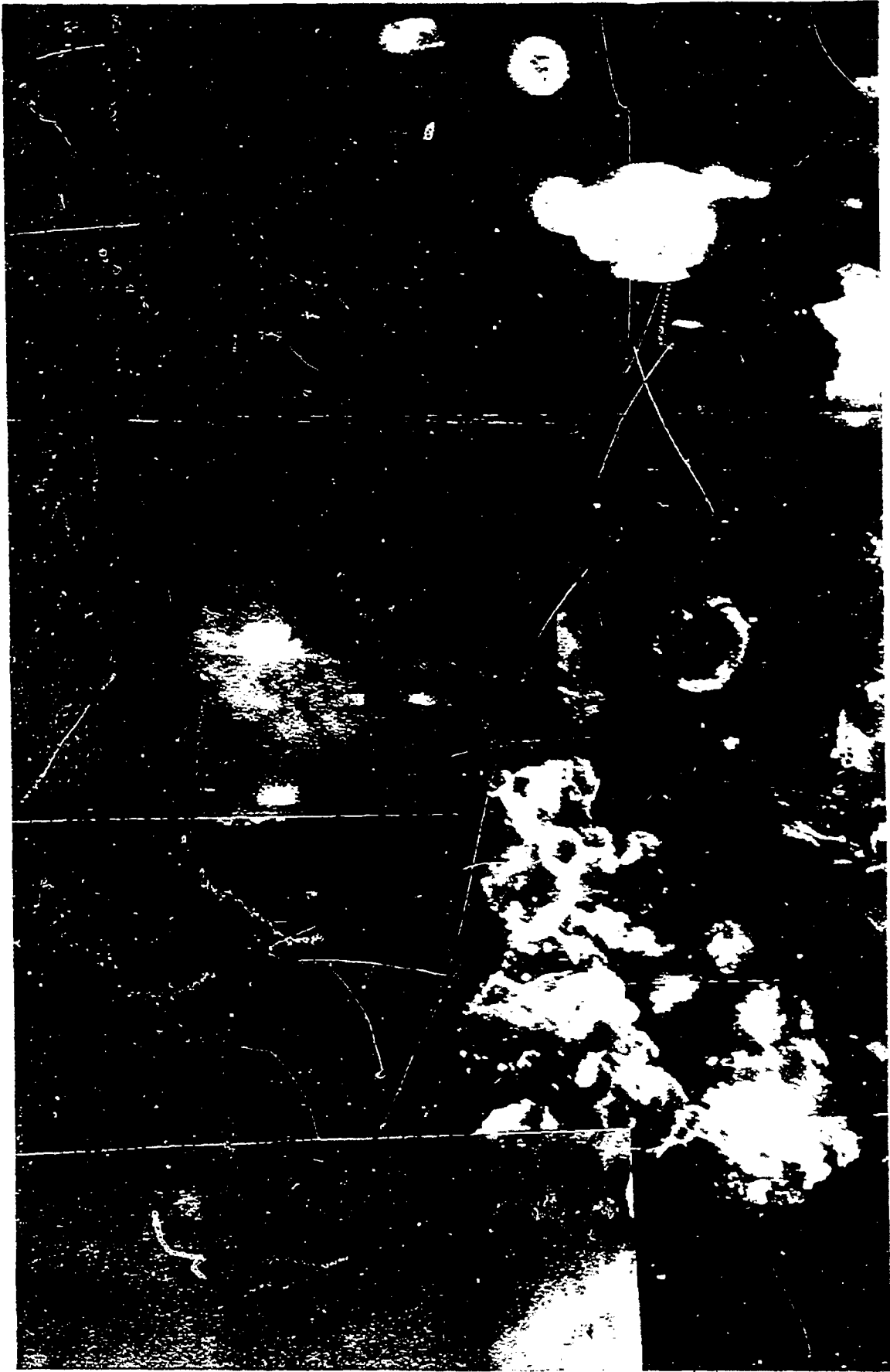$\longrightarrow$ $\Vert$ $\longleftarrow$ 10µm

Figure II.D-1. Cyclone Collection. Upper Freeport 100% Burn-out with He-Quench On.

→| |←—10μm

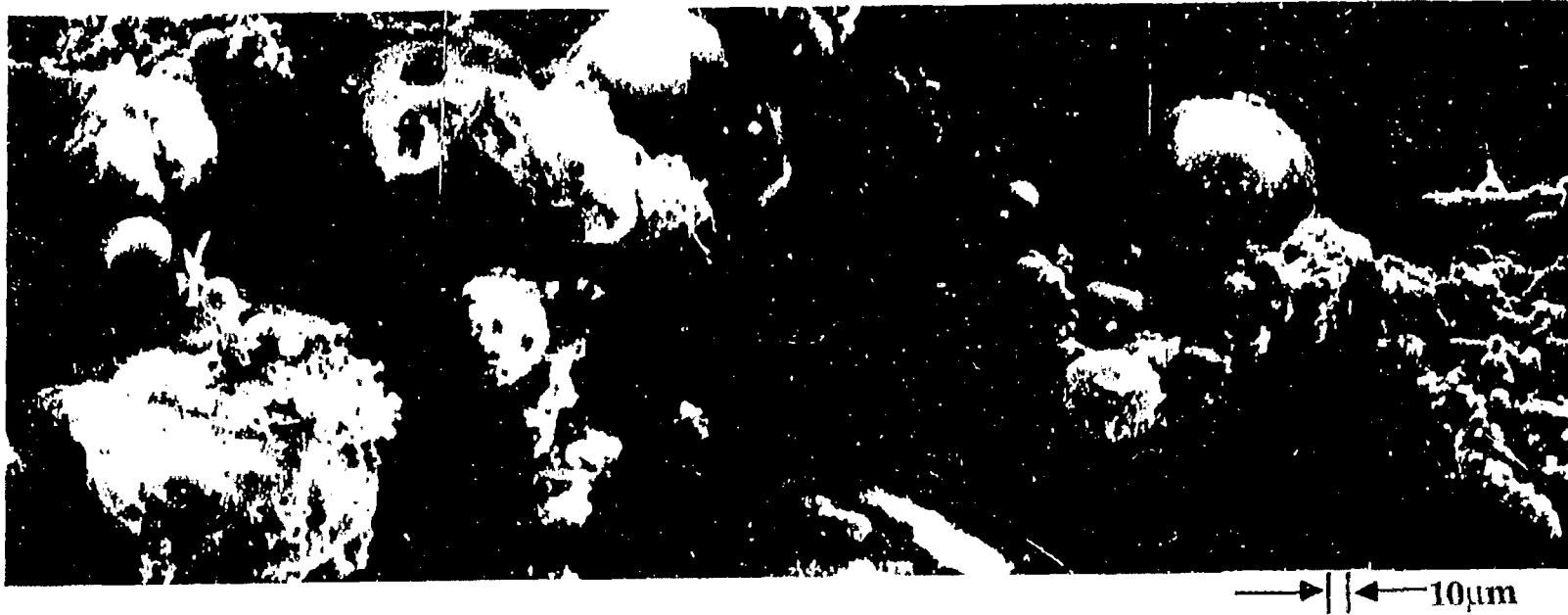**Figure II.D-2.** Extractor Washings, Upper Freeport 100% Burn-out, He-Quench On.

→| |← 10μm

Figure II.D-3. Cyclone Collection, Upper Freeport 100% Burn-out, He-Quench Off.

→| |←—10μm

Figure II.D-4. Extractor Washings, Upper Freeport 100% Burn-out, He-Quench Off.
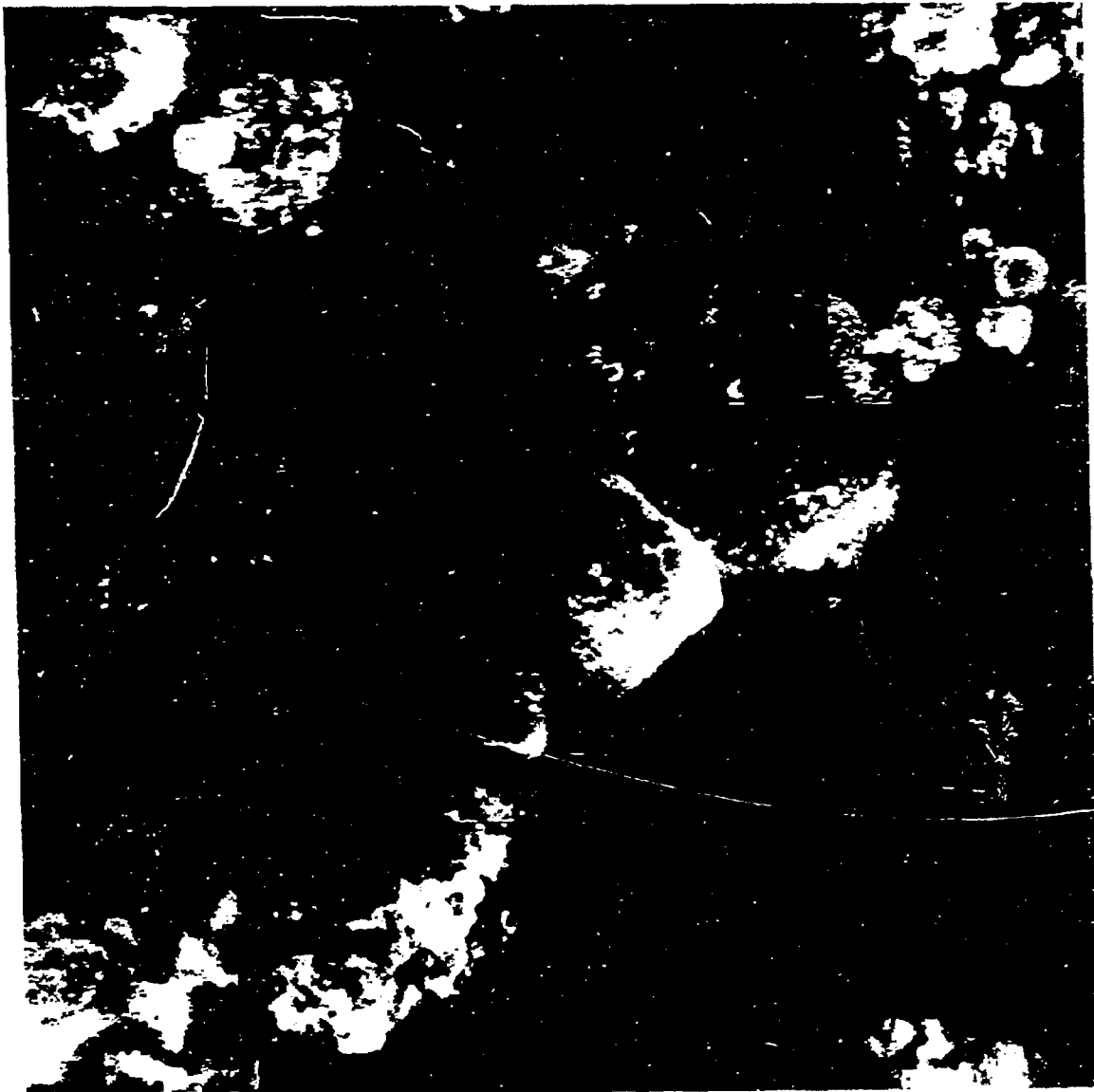
→| |←——10μm

Figure II.D-5. Cyclone Collection, Upper Freeport 100% Burn-out, He-Quench Off. No Extractor Clearing.

Char Reactivity

Work on the effects of minerals on char reactivity continued. As discussed in the previous quarterly, a particular area of interest is the investigation of the effects of Na on the reactivity of demineralized Zap coal. It was observed that a loading of 0.5 wt.% Na significantly increased the reactivity of a char produced at 900°C in a TGA but that a loading of 2.0 wt.% Na significantly reduced the reactivity of a char produced under the same conditions. In both cases, a comparison is being made to char produced from the demineralized Zap coal.

When surface area measurements were made on these chars, the results were rather surprising. The CO_2 BET surface areas for the chars from demineralized Zap, 0.5 wt.% Na and 2.0 wt.% Na chars were 274, 259, and 0.5 m^2/g, respectively. The N_2 BET surfaces areas for the same set of chars were 287, 19.5, and 0.9 m^2/g, respectively. The results would suggest that, at high loadings, a complex is formed which drastically reduces the surface area during pyrolysis of the loaded coal. It appears that the significant reduction in the CO_2 surface area can explain the low reactivity of the 2.0 wt.% Na char. The reason for this has not yet been determined. SEM photographs do not reveal anything unusual about the char morphology.

Plans

Continue study of mineral effects on the reactivity of low and high rank coals. Continue work on x-ray and SEM analyses of the separate ash collections, continue ash collections in the entrained flow reactor and study the possibilities of using the entrained flow reactor's extractor to measure fouling properties of coals.

II.E. SUBTASK 2.e. - LARGE PARTICLE SUBMODELS

Senior Investigator - Michael A. Serio
Advanced Fuel Research, Inc.
87 Church Street
East Hartford, CT 06108
(203) 528-9806

Objective

The objectives of this task are to develop or adapt advanced physics and chemistry submodels for the reactions of "large" coal particles (i.e., particles with significant heat and/or mass transport limitations) and to validate the submodels by comparison with laboratory scale experiments. The result will be coal chemistry and physics submodels which can be integrated into the fixed-bed (or moving-bed) gasifier code to be developed by BYU in Subtask 3.b. Consequently, this task will be closely coordinated with Subtask 3.b.

Accomplishments

The main modeling activity during the past quarter was to develop a revised version of the FG-DVC model which does not have a lot of extraneous variables which have accumulated over many years of development. This new version will be used by BYU in the Fixed-Bed Reactor Model and will eventually replace the version which is now in the Entrained Bed Model (PCGC-2). During the past quarter, discussions were held with BYU to reach an agreement on the features of the new version of the model. These discussions were completed and work on the new version began late in the quarter.

Work continued on testing the AFR fixed-bed reactor system. Some preliminary coal pyrolysis experiments were done with Zap lignite coal. The system appears to function properly except for an air leak that needs to be fixed.

Single Particle Model

The main modeling activity during the past quarter was to develop a revised version of the FG-DVC model which does not have a lot of extraneous variables which have accumulated over many years of development. This code will also be better documented and will be better organized in terms of the input and output. This new version will be used by BYU in the Fixed-Bed Reactor Model and will eventually replace the version which is now in the Entrained Bed Model (PCGC-2). Our goal is to have one version of the code which will be used in both reactor models and is functional either as an integrated or standalone version. This strategy will simplify the incorporation of additional improvements and submodels.

During the past quarter, discussions were held with BYU to reach an agreement on the features of the new version of the model. These discussions were completed and work on the new version began late in the quarter, and it was completed early in the twelfth quarter. This will be described in the Third Annual Report.

AFR Fixed-Bed Reactor

Work continued on testing the AFR fixed-bed reactor system. Some preliminary coal pyrolysis experiments were done with Zap lignite coal. The system appears to function properly except for an air leak that needs to be fixed.

Comparisons have been made between experiments with a single lump of Zap coal (10x10x4 mm) and the same amount of coal divided into 20 pieces of approximately 5.0 mm in diameter. Some significant differences were observed in the evolution profiles of the oxygenated species CO_2 and SO_2, although this was probably related to the different sensitivity of the samples to the air leak in the system. For the hydrocarbon species, the evolution profiles were similar, although the peaks were delayed to higher temperatures in the case of the large lump, as expected.

A comparison of the evolution profiles for the two particle sizes of Zap lignite for CH_4 and Tar Plus Aliphatics is shown in Figure II.E-1. It appears
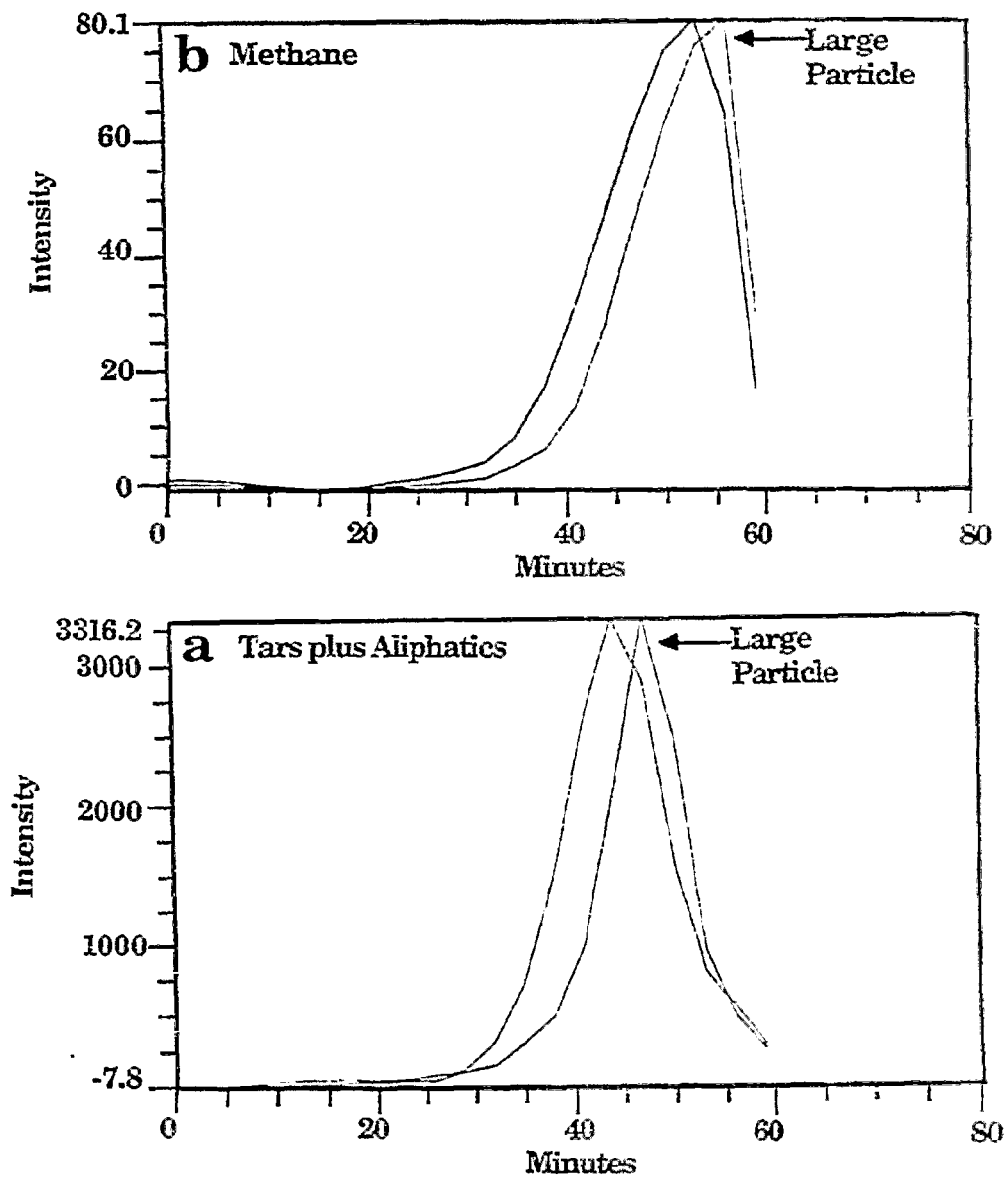
Figure II-E-1. Comparison of Evolution Profiles for Large and Small Pieces of Zap Lignite Coal Heated at 10°C/min in the Fixed-Bed Reactor. (see text). a) Tars plus Aliphatics; b) Methane.

that the reactor system will allow the evaluation of particle size effects on pyrolysis rates, as planned.

Plans

Continue development of single particle model. Complete testing of experimental apparatus and begin experiments. Begin work on tar repolymerization model.

II.F. SUBTASK 2.F. - LARGE CHAR PARTICLE OXIDATION AT HIGH PRESSURES

Senior Investigator - Angus U. Blackham
Brigham Young University
Provo, Utah 84602
(801) 378-2355

Objectives

Provide data for the reaction rates of large char particles of interest to fixed-bed coal gasification systems operating at pressure.

Accomplishments

Work has not been initiated on this subtask.

Plans

Consideration will be given to initiating this subtask during the next quarter.

II.G. SUBTASK 2.G. — SO$_x$/NO$_x$ SUBMODEL DEVELOPMENT

Senior Investigator - L. Douglas Smoot
Brigham Young University
Provo, Utah 84602
(801) 378-4326

Graduate Research Assistant - Richard D. Boardman

Objectives

The objectives of this subtask are 1) to extend an existing pollutant submodel in PCGC-2 for predicting NO$_x$ formation and destruction to include thermal NO, 2) to extend the submodel to include SO$_x$ reactions and SO$_x$-sorbent reactions (effects of SO$_3$ non-equilibrium in the gas phase will be considered), and 3) to consider the effects of fuel-rich conditions and high-pressure on sulfur and nitrogen chemistry in pulverized-fuel systems.

Accomplishments

NO$_x$ Submodel Development

The key focus of work during the past quarter has been the acquisition of thermal NO data to be used in evaluating the submodel. An experimental test program is being conducted at BYU with independent funding to obtain well-characterized data in a laboratory-scale reactor. A laboratory representative was also sent (under independent funding) to visit facilities in Karlsruhe and Heidelberg, West Germany, and to identify and compile thermal NO$_x$ data. One set of thermal NO$_x$ has been obtained from West Germany.

Details of the experimental work being conducted at BYU under independent funding were discussed previously in the 9th Quarterly Report (Solomon et al., 1988). Exit concentrations and temperature are being measured for natural gas tests with variation in swirl number, stoichiometric ratio, and wall temperature. Stoichiometric ratio is being varied from 1.0 to 1.15. Over this range, prompt NO formation is minimal due to fuel-lean operation, and N$_2$O formation is negligible. A full reactor map will be measured at a specified stoichiometric ratio and swirl number to provide spatial resolution of thermal NO$_x$.

The data which were obtained at Karlsruhe University (Kolb, 1989) also look promising for evaluating the thermal NO mechanism. They are, however, limited to effluent NO_x concentration and temperature. None of the major species were reported and because the natural gas composition varied diversely during the experimental program, the composition of the feed is not exactly known. In this study, fuel heating rate, stoichiometric ratio and swirl number were parametrically varied. These data will provide a qualitative reference for model evaluation and will complement the comparisons that will be made with the data collected in the BYU reactor.

A first model prediction was made using the joint thermal and fuel NO mechanism of Mitchell and Tarbell (1982) as discussed in the 9th Quarterly Report. Figures II.G-1a and 1b compare NO and HCN concentrations for this alternative mechanism with previous predictions made using the revised NO_x submodel and also experimental data. For this first case, the mechanism of Mitchell and Tarbell (1982) predicts NO_x concentrations well above both the measured values and the profile predicted by the fuel NO mechanism of Smith et al. (1982). HCN concentrations are closely predicted by both mechanisms. Interpretation of these predictions will be made. Also, additional predictions will be made for low-rank coals and gasification conditions where the NH_3 concentrations are substantially higher and the original NO_x model has not successfully predicted NO_x concentrations.

SO_x-Sorbent Reactions Submodel Development

Plans to make equilibrium SO_x predictions have been completed for coal combustion cases and have been reported previously in the 9th Quarterly Report. Predictions for gasification conditions are awaiting improvements in PCGC-2 to solve the full energy equation for fuel-rich conditions, and to provide for solid-particle flows in all inlet streams. Progress is being made under Subtask 3.a to improve the robustness of the code for converging gasification simulations. Once this is completed, an increased emphasis will be made in completing the SO_x-sorbent reactions submodel.

Plans

The test program for measuring thermal NO in an ACERC reactor will be completed. Efforts will then focus on testing and validating the revised NO_x

■ ● Measured (Asay, 1982)
······ Original Model
—— Revised-fuel only
— — Revised-fuel and thermal
— — — Revised-fuel and thermal
      optional rate expression
—··— Revised. Alternative
      Global mechanism (Mitchell
   and Tarbell, 1982)

a)

NOx (ppm)

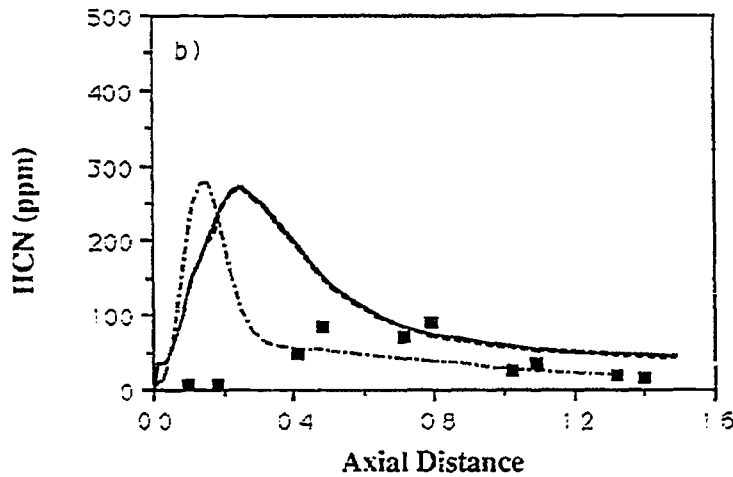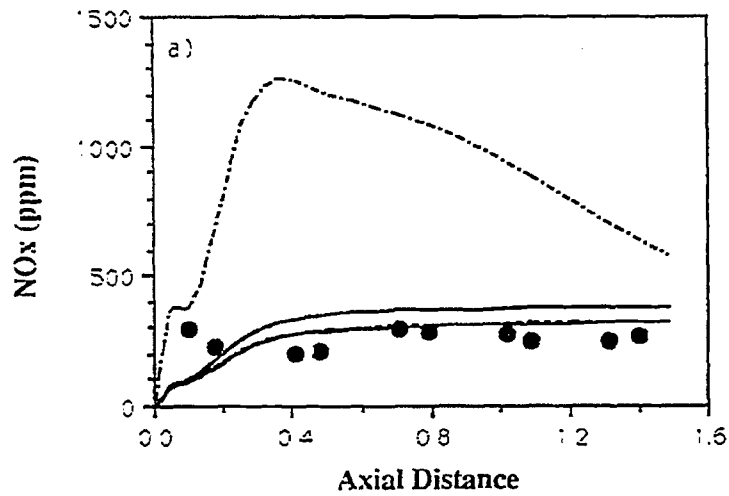Axial Distance

b)

HCN (ppm)

Axial Distance

Figure II.G-1. Comparison of measured and predicted a) NOx and
      b) HCN concentration using the original
      submodel and the revised submodel.

submodel using the experimental data. Predictions will be also be made using the alternative fuel NO mechanism and compared with the existing fuel NO mechanism for low-rank (lignite) coal.

II.H SUBTASK 2.H -- SO$_X$/NO$_X$ SUBMODEL EVALUATION

Senior Investigator - Paul O. Hedman
Brigham Young University
Provo, Utah 84602
(801) 378-6238

Student Investigators - David Braithwaite, Aaron Huber,
Laren Huntsman, Gregg Shipp

Objectives

The objectives of this subtask are 1) to obtain detailed turbulence measurements for radial, cross-jet injection of sorbent particles in a cold-flow facility designed to replicate the geometry of a 2-D combustor/gasifier, 2) obtain concentration profile data for sulfur and nitrogen pollutant species from laboratory-scale, coal reaction tests at atmospheric and elevated pressure with and without the presence of sorbents, and 3) to investigate the effect of pressure on the effectiveness of sorbent injection in capturing sulfur pollutants.

Accomplishments

This subtask has been completed and reported in previous quarterly and annual reports. No work was planned during this quarter.

Plans

No further work is planned for this subtask.