5th Quarterly 1/88 WP#71

I.E. FIFTH QUARTER PROGRESS

The first annual review meeting for the project was held at Advanced Fuel Research, Inc. in East Hartford, CT on November 12 and 13, 1987. The program for the meeting is listed in Table I.E-I.

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

A review of internal pore transport models was prepared by Professor Eric Suuberg of Brown University. It was determined that differences in the pressure arops calculated by the Simons and Gavalas approaches to internal transport were primarily due to different assumptions regarding the pyrolysis rate. The geometry of the Simons approach makes it the easiest model to use in predicting swelling based on knowledge of the pressure inside pores and so it will be used in the future swelling model. However, the model will be modified to reflect the fact that transport in the finest pores needs to be described by an activation diffusion process. The review is presented in Appendix A.

Additional characterization of the coal samples for this program was performed by TG-FTIR and Field Ionization Mass Spectrometry (FIMS). To examine the effect of product evolution, char viscosity, and transport on the swelling of char, drop tube experiments have been done with a Pittsburgh coal at temperatures varying from 475-600°C in 25°C intervals. The chars collected from these experiments have been characterized for volatile content and reactivity in a TGA. Selected chars will be potted and polished for analysis of their morphology by SEM. Some samples have been examined under the SEM without polishing.

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

Utah bituminous coal was selected for the initial char oxidation studies. Preparations were continued to obtain char from the BYU gasifier. Samples were also prepared in a simple hot-tube reactor. The high pressure reactor design was completed, and construction was initiated. Orders have been placed for the reactor components. The literature review of sulfur capture by sorbents was continued.

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

Studies of ignition and soot formation in flames were continued in the transparent wall reactor (TWR). Attention is being focused on what controls

Table LE-L MEASUREMENT AND MODELING OF ADVANCED COAL **CONVERSION PROCESSES**

Contract No. DE-AC2I-85MC23075

Schedule

Thursday, November 12, 1987

S:30	Transportation	from Par	kview E	Lilton to .	AFR
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9:00 Introduction

9:30 - 12:1	.5 AFR Progr	am Overview	L. Douglas Smoot Peter R. Solomon Chairman
	9:30 - 9:50	Combined FG-DVC Model	David G. Hamblen
	9:50 - 10:20	Implementation of FG-DVC on Sun Workstation	Girish V. Deshpande
	10:20 - 10:40	Break	
	10:40 - 11:00	Viscosity Model	Philip E. Best
	11:00 - 11:20	Mass Transport in Pores	Eric M. Suuberg
	11:20 - 11:40	Mass and Heat Transport Limits and Large Particle Effects	Michael A. Serio
	11:40 - 12:00	Ignition, Soot Formation, Flame	Po-Liang Chien
	12:00 - 12:15	Char Reactivity	Michael A. Serio
12:15 - 1:15	Lunch in AF	R Lunchroom	
1:15 - 3:00	BYU Program Overview		L. Douglas Smoot Chairman
	115-1:30	Introduction First Year Objectives Personnel Overall Summary of Accomplishments 	L. Douglas Smoot
	1:30 - 1:45	Design of High Pressure Reactor	Scott Brewster
	1:45 - 2:00	Thermal NO _x Extension Validation for Fuel Rist/High Pressure	L. Douglas Smoot
	2:00 - 2:15	Cold Flow Modifications	Scott Brewster
	2:15 - 3:00	Entrained Flow Code • Single Solids Progress Variable (SSPV) Met • Multiple Solids Progress Variable (MSPV) 1 • Statistical Gas Dispersion (SGD) Method • Thermal Parameters	Scott Brewster hod Method
3:00 - 3:45	PCGC-2 Serio, 2	2 Demo (Scott Brewster, Mike Hobbs, Michael Then Zhong Yu)	David G. Hamblen Chairman

Peter R. Solomon

Table LE-1. (continued) MEASUREMENT AND MODELING OF ADVANCED COAL CONVERSION PROCESSES

Contract No. DE-AC21-85MC23075

<u>Schedule</u>

3:45 - 3:55	Break	
3:55 - 4:45	BYU Program Overview Continued	L. Douglas Smoot
3:	 55 - 4:35 Fixed Bed Code Review of Exhisting Codes Advanced Model Plan External Review Meeting 	L. Douglas Smoot/ Sung-Chul Yi
4:	35 - 4:45 Summary • Second Year Objectives	L. Douglas Smoot
4:45 - 5:30	Laboratory Tour, (James R. Markham-TWR, Kenneth Tarantul-LCF, Robert M. Carangelo-TG-FTIR, James R. Markham-HTR, Rosemary Bassilakis-SEM)	Michael A. Serio Chairman
5:30 - 6:00	Discussion	Peter R. Solomon
6:00	Transportation to Restaurant	
6:30 - 8:30	Dinner	
	Friday, November 13, 1987	
3 :00	Friday, November 13, 1987 Transportation from Parkview Hilton to AFR	
8:00 8:30 - 9:30	Friday, November 13, 1987 Transportation from Parkview Hilton to AFR Discussion of Data Sets to Model	Peter R. Solomon L. Douglas Smoot
8:00 8:30 - 9:30 9:30 - 11:00	Friday, November 13, 1987 Transportation from Parkview Hilton to AFR Discussion of Data Sets to Model Presentation of Fixed Bed Plan	Peter R. Solomon L. Douglas Smoot L. Douglas Smoot Chairman
8:00 8:30 - 9:30 9:30 - 11:00 11:00 - 12:00	Friday, November 13, 1987 Transportation from Parkview Hilton to AFR Discussion of Data Sets to Model Presentation of Fixed Bed Plan Discussion	Peter R. Solomon L. Douglas Smoot L. Douglas Smoot Chairman L. Douglas Smoot Chairman
8:00 8:30 - 9:30 9:30 - 11:00 11:00 - 12:00 12:00 - 1:00	Friday, November 13, 1987 Transportation from Parkview Hilton to AFR Discussion of Data Sets to Model Presentation of Fixed Bed Plan Discussion Lunch	Peter R. Solomon L. Douglas Smoot L. Douglas Smoot Chairman L. Douglas Smoot Chairman

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oth Quarterly 1/88 WP#71

ignition (heterogeneous or homogeneous oxidation) and soot formation. Seven additional samples have been completed in addition to the four reported in the Annual Report. Flame properties were compared with characteristics of the samples to determine the factors which control flame behavior. A comparison of the ignition of several samples suggests that the rate of ignition correlates with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars is heterogeneous; ignition of high rank coals is homogeneous; but low rank coals exhibit both homogeneous and heterogeneous contributions to ignition. Soot formation in combustion correlates well with tar yield in pyrolysis suggesting that tar is the chief precursor of soot.

Subtask 2.d. Ash Physics and Chemistry Submodel

During the fifth quarter, two sample collection probes were constructed that can be inserted into the transparent wall reactor (TWR) to allow for the collection of char with its transforming mineral matter from the flame at various stages of burnoff, and of fly ash from above the flame. Both probes result in no visual disruption of the stability, size or ignition delay time of the flames. Initial sample collections were performed.

Subtask 2.e. Large Particle Submodels

The literature review of heat and mass transport effects in coal pyrolysis was completed. A critical evaluation was made of two models from the literature that have been used to describe coupled reaction and transport in large particles.

A major effort was made on design of the fixed-bed reactor. This reactor will have on-line analysis of evolved volatile products and on-line measurement of weight loss, functional group composition and particle temperature.

Subtask 2.g. SO_x-NO_x Submodel Development

A revised NO_x submodel has been completed. Revisions to the previous model include simplification of the overall flow of subroutine calls and calculation procedures in order to facilitate transfer of the code to the Unix operating system. A literature survey of SO_x chemistry was initiated to determine the key reaction mechanism and identify the important aspects of predicting SO_x behavior. This effort will receive increased emphasis in the upcoming quarter. With the thermal NO_x rate of formation turned off, prediction of fuel NO_x by the revised

- 6 -

Dun Quarterly 1/00 WF#/1

model matched that of the former code for a swirling-flow, coal combustion case. Efforts are currently being made to validate predictions with chermal NO, included.

Subtask 2.h. NO_x/SO_x Submodel Evaluation

Work continued on the cold-flow study for turbulence and mixing measurements with cross-flow injection. Fabrication of the clear plastic flow chamber was completed. A new research team for the gasifier was organized, and training in gasifier operation was initiated. A sorbent particle feeder was designed and is being constructed.

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

Work continued on the Single Solids Progress Variable (SSPV) and Multiple Solids Progress Variables (MSPV) methods for incorporating the FG/DVC model into PCGC-2. Under the SSPV method, the existing particle model in the 1987 version of PCGC-2 was carefully reviewed, and an interface between the comprehensive code and the single particle model was proposed. Work is continuing to review an advanced research version of PCGC-2 (Baxter, 1987) before a final recommendation is made. Under the MSPV method, calculations were continued to investigate the effect of using two progress variables to track coal offgas. After locating and fixing several bugs in the code, a converged solution was obtained where the existing mixture fraction variables were used to separately track coal volatiles and heterogeneous oxidation offgas. Work is continuing to investigate the effects of separately tracking various elements and allowing coal offgas enthalpy to vary with extent of burnout. Other accomplishments include selection of the UNIRAS graphics software for examining code output. The advanced research version of PCGC-2 (Baxter, 1988) was installed and demonstrated on the Sun workstation at AFR. The FG/DVC model and a model developed at The University of Utah (Grant et al., 1988), based on percolation theory, are being reviewed and evaluated.

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

A research plan for developing an advanced fixed-bed model was prepared based on the written comments and recommendations of expert consultants. This plan was presented to AFR and METC at the annual contract review meeting. Data comparisons and a sensitivity analysis of the Washington University 2-D model were performed. Jun Quarcerty 1/00 W F/1

A plan for developing a simplified fixed-bed code with several of the advanced model features was formulated.

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

The FG/DVC model was successfully integrated with PCGC-2. The first generation code took 15 hours to run compared to less than 4 hours for running the PCGC-2 code alone. We analyzed the FG/DVC code to find ways of reducing the burden it placed on the combined code. A major area of investigation was to reduce the number of monomers in the model coal molecule created in the DVC routine. It was found that the number of monomers could safely be reduced by a factor of three without affecting the accuracy of the simulation. This change reduced the total CPU time for running the integrated code down to 6.5 hours. We examined reducing the number of calls to the FG/DVC subroutines. It was found that there were some redundant calls and we were able to further reduce the time to a little over four hours per simulation, in which the FG/DVC model takes less than 20% of the total time.

Subtask 4.b. Application of Fixed-Bed Code

No work was scheduled.

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 nigh 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 affects 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 Investigator - David G. Hamblen 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. Many of the data and some computer codes for this submodel are available, so it is expected that a complete integrated code will be developed during Phase I. Improvements in accuracy and efficiency will be pursued during Phase II.

Accomplishments

A review of internal pore transport models was prepared by Professor Eric Suuberg of Brown University. It was determined that differences in the pressure drops calculated by the Simons and Gavalas approaches to internal transport were primarily due to different assumptions regarding the pyrolysis rate. The geometry of the Simons approach makes it the easiest model to use in predicting swelling based on knowledge of the pressure inside pores and so it will be used in the future swelling model. However, the model will be modified to reflect the fact that transport in the finest pores needs to be described by an activated diffusion process. The review is presented in Appendix A.

Additional characterization of the coal samples for this program was performed by TG-FTIR and Field lonization Mass Spectrometry (FIMS).

To examine the effect of product evolution, char viscosity, and transport on the swelling of char, drop tube experiments have been done with a Pittsburgh coal at temperatures varying from 475-600°C in 25°C intervals. The chars collected from these experiments have been characterized for volatile content and reactivity in a TGA. Selected chars will be potted and polished for analysis of their morphology by SEM. Some samples have been examined under the SEM without polishing. SUI QUELLEITY 1/00 MFF/1

Work was done on developing a droptube furnace to study the morphology of individual char particles. Some preliminary low temperature chars of Pittsburgh #3 bituminous coal were made and characterized through SEM micrographs and by pyrolysis and char reactivity measurements in a TGA.

Coal Characterization

Additional characterization of the coal samples for this program was performed by TG-FTIR and Field Ionization Mass Spectrometry (FIMS).

TG-FTIR Analysis

This analysis consists of thermogravimetric analysis (TGA) with analysis of the evolved products by Fourier Transform Infrared (FT-IR) spectroscopy. The TG-FTIR consists of a sample suspended from a balance in a programmable furnace. The evolved products are swept into a gal cell for analysis by FT-IR. The FT-IR allows on-line measurements of the gas and tar concentration and composition. The apparatus has been described by Carangelo et al (1987) and Whelan et al (1988).

The results of monitoring the tar evolution for eight of the coal samples is presented in Fig. II.A-1. The temperature at which the peak evolution rate is reached is shown in parentheses for each coal. The temperatures vary from 450°C for the lignite to 500°C for the Pocahontas. As suggested in several previous papers (see Solomon and Hamblen, 1983) the kinetics for tar evolution are insensitive to coal rank. Similar insensitivity was observed for the other major species as well.

An interesting feature of the evolution curves is a low temperature evolution peak which is probably due to unattached guest molecules in the coal. These are most apparent in the Pittsburgh and Upper Freeport evolution curves. A comparison of the infrared spectra obtained at the low and high tellerature peaks is presented in Fig. II.A-2. The spectrum taken at the early peak (Fig. II.A-2b) has been scaled up to compare to the spectrum from the later peak (Fig. II.A-2c). The earlier peak appears to have a slightly higher aliphatic to aromatic content compared to the later peak. This would be consistent with the concept of some guest polymethylene in the coal, perhaps mixed with small molecules more representative of the coal's average organic structure.



Figure II.A-1. Evolution Rate for Tar from Eight Coals in a TG-FTIR at 0.5°C/sec. a) Upper Freeport, b) Wyodak, c) Illinois #6, d) Pittsburgh #8, e) Pocahontas #3, f) Utah Blind Canyon, g) Upper Knawha, h) Zap Lignite, and) Rosebud.



Figure II.A-2. Spectrum of Products Evolved in Pyrolysis. a) Rate for Tar Evolution showing two Peaks, b) Spectrum at First Peak and c) Spectrum at Second Peak.

5th Quarterly 1/88 WP∉71

FIMS Analysis

Molecular weight distributions of coals were obtained at SRI International using the Field Ionization Mass Spectrometry (FIMS) apparatus described by St. John et al. (1978). The coal samples were pyrolyzed directly in the FIMS apparatus. The FIMS technique produces little fragmentation of the evolved tars and so provides a good determination of the tar molecular weight distribution. Figures II.A-3 to II.A-8 present the weight loss of the sample heated in the FIMS apparatus at 0.05/sec.

The spectra show a distinct progression from low to high rank. The highest rank coals, Pocahontas (Fig. II.A-6) and Upper Freeport (Fig. II.A-3) both show low intensities at low molecular weights (100 - 200 amu). This suggests few one and two ring clusters. The intensity in the 200 - 600 amu range, however, suggests the presence of three, four and higher ring cluster sizes and dimers and trimers of these. The low yield for the Pocahontas is due to its higher bond energies (500°C tar peak in Fig. II.A-2) and lower number of small ring clusters capable of being volatilized.

The intermediate rank coals, Pittsburgh (Fig. II.A-5), Utah (Fig. II.A-7) and Upper Kanawha (Fig. II.A-8) all have similar molecular weight distributions showing substantial intensities in the 100 to 200 amu region indicative of one and two ring clusters as well as in the 200 to 600 amu range.

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The low rank coal, Wyodak (FIg. II.A-4) shows high intensity between 100 and 200 amu, but substantially lower intensity above 200 amu. This is typical of the Zap lignite also, and has been explained by extensive cross linking related carboxyl groups in low rank coals (Solomon et al. 1988).

In future work, these FIMS spectra will be simulated using the FG-DVC model.

Swelling Experiments

In this quarter, extensive work was done on developing a drop tube furnace in which individual char particles could be studied at various stages of pyrolysis. The apparatus is designed to drop a dilute sample of particles without carrier gas into a preheated furnace. This geometry will insure rapid heating of the individual particles to the furnace temperature.



Figure II.A-3. Results for Upper Freeport Coal Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/sec. a) Weight Loss vs. Temperature and b) Tar Molecular Weight Distribution.



Figure II.A-4. Results for Wyodak Coal Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/sec. a) Weight Loss vs. Temperature and b) Tar Molecular Weight Distribution.



Figure II.A-5. Results for Pittsburgh #8 Coal Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/sec. a) Weight Loss vs. Temperature and b) Tar Molecular Weight Distribution.



Figure II.A-6. Results for Pocahontas Coal Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/sec. a) Weight Loss vs. Temperature and b) Tar Molecular Weight Distribution.



Figure II.A-7. Results for Utah Blind Canyon Coal Pyrolyzed in the SRI FIMS Apparatus at 0.05°C/sec. a) Weight Loss vs. Temperature and b) Tar Molecular Weight Distribution.





5th Quarterly 1/88 WP#71

The coal samples subjected to pyrolysis were of the 200 x 325 mesh sieved fraction of Pittsburgh #8 bituminous coal.

Pyrolysis was performed in an electrically heated drop tube furnace (Fig. II.A-9). A thermolyne tube furnace was used to heat a vertically standing, 2" I.D. x 22" long vycor tube. Samples were dropped into the radiation cavity from a gas cooled vial having a 200 mesh screen as a cap. The 200 mesh screen limited the number of particles entering the cavity with each shake or injection and thus prevented agglomeration. Prior to particle injection, the system was purged with nitrogen through upper and lower inlets. Immediately before particle injection the lower gas flow was shut off to allow the particles to free-fall through the tube.

The chars were accumulated in a stainless steel collection chamber which was submerged in an ice bath to prevent further pyrolysis.

Typical SEM micrographs of the collected chars are shown in Figs. II.A-10-14. At 465°C most particles are still angular in shape although some early stages of surface flowing and swelling are present. At 508°C only a few particles still possess their angularity and cenospheres as large as 62 microns have formed. In some particles, bubble cells are observed. At 535°C particles have begun to collapse and in the 602°C and 682°C char cases the majority of particles have collapsed. The char particles must still be quite fluid at this point and must remain fluid as the gas inside the cenosphere cools. Cenosphere size cannot be determined at this point.

The collapsing of the cenospheres has not previously been observed. In previous studies the furnace temperature has been 700°C or higher. Under these conditions, the particle may go through its fluid phase and start to solidify prior to being cooled in the collector. The reason for the collapsing particles will be studied further.

The TGA was employed to describe the amount of volatiles remaining in each of the chars collected. All char _amples as well as the raw source coal were heated in nitrogen at 30°C/min to 900°C. Figures II.A-15a and 16a display the weight loss curves generated for the 465°C and 508°C char cases, while the percent volatiles released (DAF) in the TGA are plotted in Fig. II.A-17 as a function of drop tube temperature. This plot demonstrates a direct correlation between an increase in drop tube temperature and a decrease in volatiles released in the TGA.

- 21 -



Figure II.A-9. Schematic Diagram of the Drop Tube Furnace.



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Figure II.A-10. SEM Micrograph of a 465°C Drop Tube Char of Pittsburgh #8 Bituminous Coal. Magnification X400.



Figure II.A-11. SEM Micrograph of a 508°C Drop Tube Char of Pittsburgh #8 Bituminous Coal. Magnification X400.



Figure A-12. SEM Micrograph of a 535°C Drop Tube Char of Pittsburgh #8 Bituminous Coal. Magnification X400.



Figure II.A-13. SEM Micrograph of a 602°C Drop Tube Char of Pittsburgh #8 Bituminous Coal. Magnification X400.



Figure II.A-14. SEM Micrograph of a 682°C Drop Tube Char of Pittsburgh #8 Bituminous Coal. Magnification X400.



Figure II.A-15. . a) Pyrolysis of Pittsburgh #8 465°C Drop Tube Char in TGA at 30°C/min in N₂ b) Oxidation of the Further Pyrolyzed Pittsburgh #8 465°C Drop Tube Char in TGA at 30°C/min in Air.



Figure II.A-16. a) Pyrolysis of Pittsburgh #8 508°C Drop Tube Char in TGA at 30°C/min in N2. b) Oxidation of the Further Pyrolyzed Pittsburgh #8 508°C Drop Tube Char in TGA at 30°C/min in Air.





As determinations and oner reactivity measurements were also done in the TGA. After subjecting the collected char samples to pyrolysis in nitrogen as described above, the samples were neated in air at 30°C/min to 900°C. The weight loss curves for the 465°C and 508°C oner cases are displayed in Figs. II.A-15b and 16b.

Initial attempts were made to report the extent of pyrolysis by the percent char collected as determined by the ash tracer method of analysis. The percent char values on an ash free basis were plotted against the drop tube temperatures (Fig. II.A-18). Although there appears to be a linear correlation, the percent char values were unusually low (the ash values were unusually high) when compared to higher temperature pyrolysis data. There are two possibilities for this: 1) the presence of air in the drop tube system causing partial oxidation or 2) selective collection of heavier particles which contain more ash. The SEM micrographs provided no evidence of surface oxidation. During the experiment however, particles were observed just outside the drop tube inlet. TGA analysis shows this sample to contain half the ash value of the sample removed from the collection chamber suggesting that segregation is occurring.

Char reactivity measurements (Tcr) are plotted in Fig. II.A-19 as a function of drop tube temperature. This plot indicates that the collected chars produced at different drop tube temperatures are similar in reactivity after the treatment at 900°C. This result is expected. It is interesting to note however, that the drop tube chars proved to be more reactive (had a lower $T_{\rm Cr}$) than their source coal. It is possible that the rapid heating rate in the tube furnace resulted in either an increase in active site area or an increase in accessible surface area. This effect will be further studied.

In the 508°C (Figs. II.A-16b) char case as well as in the 535°C and 602°C char cases, a bump is apparent in curves just prior to oxidation. At approximately 280°C a gradual increase in wt3 occurs. This increase, which is probably the result of chemisorption of O_2 , reaches a maximum of 1 1/2 - 2 wt3 at 450°C. TG-FTIR analysis indicates that the drop in weight and the leveling off of the sample before weight loss from oxidation is due to the evolving oxidation products H₂O, SO₂, CO₂ and CO. This phenomenon will be further studied and evolution curves will be included in the next quarterly report.



Percent Char (DAF) Collected





Figure II.A-19. Variation of Char Reactivity with Drop Tube Temperature.

Plans

Obtain the missing FIMS spectra and push to higher temperatures (\sim 500°C) for the higher rank coals like Pocahontas. Finish the Entrained Flow reactor and TG-FTIR measurements on the 9 standard coals and initiate modeling with the FG-DVC model. Continue the study of melting and swelling of the Pittsburgh Seam coal. In the next quarter more low temperature pyrolysis runs will be done and char samples will be subjected to potting and polishing. Start the development of the swelling model; work on improvements in the viscosity 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 (801) 378-6536

Objectives

The overall objectives of this subtask are 1) to measure and correlate fundamental 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 fundamental kinetic rate measurements of sulfur species with sorbents for a range of stoichiometries under laminar, high-pressure conditions.

Specific objectives for the last quarter include:

- 1. Continue reactor fabrication and construction.
- Initiate preparation of the test cell to house the reactor and the optical instrumentation.
- 3. Begin preparation of test samples of char from Utah bituminous coal under atmospheric and greater than atmospheric pressures.
- 4. Continue development of the sorbent capture test plan.

Accomplishments

Four components of this subtask have been identified to accomplish the objectives outlined above: 1) char preparation at high temperature and high pressure, 2) determination of the kinetics of char-oxygen reactions at high pressure, 3) design and construction of a laminar-flow high pressure reactor, and 4) measurements of fundamental sulfur capture rates by sorbents. Most of the effort during the last quarter was focused on Components 1 and 3 in preparation for accomplishing the work identified by Components 2 and 4.

Component I -- Char Preparation at High Temperature and High Pressure

Utah bituminous coal has been selected as the first coal for study under this program because of the availability of this coal at the BYU Combustion Laboratory and its inclusion as one of the coals in the Argonne premium coal sample bank. Chars of this coal from at least three preparations will be compared for differences and similarities in properties. Differences or similarities will be correlated with the kinetics of oxidation of these chars to be determined in the high-pressure reactor under construction as indicated in Component 3 of this report. The reference char sample to which others will be compared will be prepared in the high-pressure reactor, at pressures up to 20 atmospheres. Meanwhile, preparation of two other char samples is in 1) a sample from the BYU high-pressure entrained-flow gasifier progress: which can operate at pressures up to 10 atmospheres and 2) samples from a simple hot-tube reactor, without optical access, designed to produce char at pressures up to 20 atmospheres.

During this quarter, preparations were continued for a run in the gasifier in which char produced at elevated pressure will be collected. A run in the gasifier has been made, but operation was not satisfactory for collecting a char sample. The gasifier run in which a sample is collected for this task component will be one of the runs in a planned series of preparatory runs for Subtask 2.h.

Char samples have been collected from a simple hot-tube reactor. The values for gas flows and temperatures at atmospheric pressure to give satisfactory char samples are being determined. Two preliminary runs have been made. The schematic of this reactor is shown in Figure II.B-1. A feeder and a receiver to operate at pressures above atmospheric are being designed which will be contained in small stainless steel bulbs.

The purpose of this reactor is to provide the means to prepare small samples of chars under a variety of experimental conditions to help determine which conditions will be selected for the high-pressure reactor (with optical access) when construction is completed.

Component 2 -- Kinetics of Char-Oxygen Reactions at High Pressure

No work was planned or conducted for this component.



Figure II.B-1. A simple hot tube reactor for preparation of small samples of char.

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Component 3 -- High-Pressure Reactor Design and Fabrication

Final Design -- The final detailed design for the reactor was performed during the quarter, and fabrication was initiated. Figure II.B-2 shows a vertical cross-sectional view of the reactor and preheater. Figure II.B-3 shows the main reactor shell in its final design configuration. The number of heaters was increased from 7 to 9 in order to increase the available amount of heat at the ends of the reactor where the greatest heat loss will occur. One of the additional heaters will be placed in the lower section of the reactor head to help the secondary gas remain at its preheated temperature upon entering the reaction tube.

The preheater was redesigned to increase gas temperature and to minimize the heat loss from the gases as they pass from the preheater to the reactor. The preheater shell will be constructed from the same size steel tube as the main reactor shell and will be welded to the reactor head at a 45 angle (see Figure II.B-2), allowing the exit of the preheater to be closer to the reaction tube inlet. The preheater will contain two, 20-in. Kanthal Super 33 elements in a bed of alumina spheres. The alumina spheres increase the heat transfer area for the gas flowing through the bed and provide support for the neating elements. A ceramic honeycomb section at the preheater exit will retain the alumina spheres while allowing the secondary gas to flow into the reactor. The preheater will be insulated with the same castable ceramic as the reactor.

The design allows the reaction tube to be removed or exchanged for a different size without disassembling any of the main sections; only the injector and collection probe end plates need to be removed to gain access to the reaction tube.

Figure II.B-4 shows two horizontal cross-sectional views of the reactor. The lower view shows a plane at the window centerline, and the upper view shows a plane a few inches above the windows. The heater access port that runs the entire length of the main section can be seen in Figures II.B-3 and II.B-4. The access port encloses the ends of the heaters which will protrude from the reactor shell. A removable access port cover plate provides

- 38 -


Figure II.B-2. Vertical cross sectional view of reactor and preheater.

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Figure II.B-3. Outer view of main reactor shell.

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Figure II.B-4. Two horizontal cross-sectional views of the reactor body.

structural support to the outer shell when the reactor is pressurized and allows access to the heaters and instrumentation for servicing. Two braces maintain reactor rigidity when the cover is removed. Power leads and instrument wires are fed into the port through Conax sealing glands. The reactor insulation is cast in place and is nonremovable except for the sections that hold the heaters and their respective thermocouple probes. These sections are removable, through the heater access port, for servicing or installation of new heaters or thermocouple probes (see Figure II.B-4). Smaller heater access ports are located at the lower part of the head and the top of the preheater for servicing the heating elements at these locations.

<u>Instrumentation</u> -- A search is in progress for high speed data acquisition boards for micro-computers to interface with the advanced optical instrumentation which requires data acquisition at a speed of 2 MHz. Hardware components capable of this speed have been identified for the IBM AT, but none have yet been found for the Macintosh II.

<u>Fabrication</u> -- Materials for the construction of the reactor shell and preheater have been obtained and fabrication has been started. The outer shell tubes have been cut to length and are ready to be machined for the sight and heater access ports and then welded to the flanges. The sight window flanges will be the final items to be welded to the main section and they will then be machined to ensure that opposite windows are parallel and that adjacent windows are perpendicular. The BYU Research Machine Shop and the Mechanical Engineering Shop will be utilized for the reactor construction.

A custom, circular-heating element was ordered for testing but arrived broken. Another element has been ordered to replace it. A castable ceramic insulation has been obtained in place of the preformed insulation planned for previously, which will significantly decrease the cost and increase the flexibility of the reactor while maintaining design performance.

Component 4 -- Fundamental Sulfur Capture Experiments

<u>Literature Review</u> -- The literature review of sulfur capture by sorbents was continued during the last quarter. Gullett and Bruce (1987) conducted a series of tests at 800° C. They showed that calcined CaCO₃ has a cylindrical pore structure, while Ca(OH)₂ has a slit-like pore structure, which is important when modeling the sulfur capture reaction. Increased conversion of Ca(OH)₂ from calcium oxide to calcium sulfate, evident only at times longer than 40 seconds in their experiments, is due to greater particle expansion of the hydrate. Sintering the sorbent at the test temperature decreases the surface area but has little effect on the porosity or the sorbent conversion.

Simons et al. (1987) used a pore-tree representation to model the sulfur capture reaction at various pressures. They showed that the rate constant has a first-order dependence on SO₂ partial pressure. Their study is only the second at elevated total pressure, using 2 and 9.5 atmospheres for the sulfur capture experiments. The sorbents used were 42-78 μ m dolomite particles and 1-15 μ m limestone particles. The sulfation reaction rate decays faster with calcium utilization at low pressure than at high pressure. However, higher pressure during calcination yields a lower initial surface area, which decreases the initial rate of reaction. Simons also quoted a study by Beittel et al. (1984) that showed that sintering was insignificant when sorbent was injected for 1.3 seconds in a temperature field that ranged from 1478 K to 1225 K.

<u>Other Activities</u> -- One of the senior investigators met with Dr. David M. Slaughter of General Electric Co., Corporate Research and Development, to discuss the interest of GE in the planned studies of sulfur capture with sorbents and char oxidation at high pressure.

<u>Plans</u>

During the next quarter, chars from Utah bituminous coal will be prepared in the BYU gasifier and the hot-tube reactor, and char properties will be measured and compared. Char from the gasifier will be fractionated into quantities with average particle diameters of 45 μ m and 70 μ m. These particle sizes will enable comparison with char oxidation measurements at atmospheric pressure planned for a separately-funded study in the BYU Combustion Laboratory. The fabrication of the high-pressure reactor will be essentially completed during the quarter. Plans for modification of the high-pressure reactor for sulfur capture by sorbent will be made, with emphasis on achieving rapid mixing of the SO_2 and sorbent in the hot zone. Existing, entrained-flow reactors for sulfur capture will be reviewed, and a method for calculating the residence time of the sorbent will be developed. Assembly of the optical instrumentation for particle temperature, size and velocity will be initiated.

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, sulfur capture, and ignition will be performed during Phase I to allow validation of submodels in Phase II.

Accomplishments

Studies of ignition and soot formation in flames were continued in the transparent wall reactor (TWR). Attention is being focused on what controls ignition (heterogeneous or homogeneous oxidation) and soot formation. Seven additional samples have been completed in addition to the four reported in the Annual Report. Flame properties were compared with characteristics of the samples to determine the factors which control flame behavior. A comparison of the ignition of several samples suggests that the rate of ignition correlates with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars is heterogeneous; ignition of high rank coals is homogeneous; but low rank coals exhibit both homogeneous and heterogeneous contributions to ignition. Soot formation in combustion correlates well with tar yield in pyrolysis suggesting that tar is the chief precursor of soot.

Coal Flame Experiments

Experimental Apparatus

The experimental apparatus and FT-IR diagnostics were described in the annual report. Figure II.C-1 shows photographs of three flames: a) a lignite which ignites close to the nozzle, b) a low volatile bituminous coal which ignites



Indian Head Zap

Pocahontas

Pittsburgh Seam

Distance Above Injector

Figure II.C-1. Photographs of a) Zap North Dakota Lignite Flame and b) a Pocahontas Bituminous Coal Flame. The Scale in the Center is Distance Above the Injector Nozzle. c) is a Close up of a Pittsburgh Seam Bituminous Coal Flame.

5th Quarterly 2/00 WP#/1

(apparently homogeneou. y in the gas phase) higher up, and c) a close up of a high volatile bituminous coal flame showing volatile flames surrounding the particles which are much larger than the particles which they surround.

<u>Samples</u> - The samples used in these experiments were sieved fractions of a lignite, a subbituminous coal, and several bituminous coals. Samples have been demineralized by the Bishop and Ward (1958) technique. Chars were prepared from some of the coals in nitrogen in the entrained flow reactor. The characteristics of the coals have been previously published by Serio et al. (1987), Vorres, (1987), and Best et al., (1987). Table II.C-1 summarizes the coals, preparation procedures, and references to the previously published data. The samples were also characterized in a TGA to determine their weight loss at constant heating rate in nitrogen (to determine the volatile content) and in air (to provide a relative measure of the samples' reactivity and the ash concentratior).

Results for Seven Flames

Results have been obtained for a series of samples including coal, demineralized coal and char. FT-IR measurements are made along the cent of the flame at several positions above the coal injector. It is recognized that the flame is not spatially homogeneous along the line-of-sight. In this case, a: lication of the analysis yields the average properties along a line-of-sight. Work is currently in progress to develop tomographic methods to obtain spatially resolved data. Data on the four Rosebud samples were presented in the Annual Report. Data for the new coals (except the Pocahontas for which insufficient data were obtained due to its unstable ignition very high up in the reactor) are presented in Tables II.C-2 to II.C-7 and Figs. II.C-2 to II.C-7. The figures present, as a function of distance above the nozzle, the particle and CO_2 temperatures and the black-body multiplier, M, in the upper pannel and the soot, CO2 and part the concentrations in the lower pannel. For a completely homogeneous sample of grey-body particles, M would be the particle's emissivity For the case considered here, some particles may be unignited, or ash particles may be present at a much lower temperature than the coal particles and have a very low emittance. Then fis approximately the fraction of particles ignited times their emissivity.

<u>A Correlation of Flame Properties with Sample Characteristics</u> - Several flame characteristic, which varied with sample properties were examined to determine what sample properties were the controlling factors and why. A comparison of the CO₂ concentration profiles, which is a by-product of the ignition behavior, is

- 47 -

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SAMPLE CHARACTERISTICS

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TGA Analysis

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Sample	Sample Abbrevlation in Floures	Classification or Prevaration Conditions*	Kominal Farticle size ("um)	Z Ash**	X DAF Volatile ^{4.44} Hatter	I _{cr} (*c)****	TION METGHE Lossee (°C)	Sample Rcf.
Zap	2	North Dakota Lignite, Dry	45-75	7.3	43.5	434	360	Serio et al. (1987)
Zap 900°C Char	2C 900	EFR Pyrolysis, 1 m/s 900°C, 66 cm, in Hz	45-75	12.7	22.0	418	388	Serio et al. (1987)
Zap 1500°C Char	20131	EFR Pyrolysis, 1 m/s 1500°C, 66 cm, in H2	45-75	14.3	8,8	494	458	Serio et al. (1987)
Argonne Zap	νz	North Dakota Llynlte, Dry	45-75	8.2	40.5	418	335	Vorres (1987)
Zap Demineralized	20	HC1, HF washings, Ory	45-75	0.5	44.7	650	E8E	Solomon et al. (1906)
Rosebud	ж	Subbituainous Coal, Dry	45-75	15.1.	42.8	485	400	Serio et al. (1987)
Rosebud 900°C Char	RC 900	EFR Pyrolysis, 1 m/s 900°C, 66 cm, in 112	45-75	5.55	1.91	443	440	Serio et al. (1987)
Rosebud 1500°C Char -	r RC 1500	EFR Pyrolysts, 1 m/s 1500℃C, 66 cm, 1∩ N2	45-75	23.4	2.6	545	515	Serio et al. (1987)
Rosebud Deminerali	zed DR	HCI, HE Washings, Ory	45-75	3.7	39.1	500	432	Solomon et al. (1986)
Argonne Pittsburgh	Pit	Bituminous coal (NVAD)	45-75	3.2	37.2	600	488	Varres (1987)
Argonne Pocahontas	æ	Bituminous coal (LVB)	45-75	5.1	20,0	62 8	512	Vorres (1987)
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EFR - Entrained Flow Reactor
TGA analysis in air at 30 K/min to 900°C
TGA analysis in lp at 30 K/min to 900°C
TGA analysis in lp at 30 K/min to 900°C
TGA analysis in lp at 30 K/min to 900°C
TGA analysis in lp at 30 K/min to 900°C
TGA analysis in lp at 30 K/min to 900°C
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TGA at 30 K/min to 900°C
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Height	Derticle	<u> </u>	% of Grav	Dartiala	Soot	CO-	H-O
Tabi Injec	le II.C-2. ction Nozzel	Flame P for Zap	roperties as North Dak	a Function ota Lignite.	of Distan	nce Above	the

Height (cm)	Particle R ^b n(K)	со ₂	% of Gray Body	Particle Conc.	Soot Conc.	CO ₂ Conc.	H ₂ O Conc.
1910) - MARCHARD (2010)	1470	1070		7.74	A	^ E B	0.10
12	1700	1880	65	4 84	6.56	26 17	2.24
15	1730	2065	75.2	4.52	5.63	33.23	2.82
18	1765	2064	58.1	3.95	3.42	36.14	3.00
23	1790	1951	43.5	2.94	1,51	36.04	2.89
33	1810	1827	32.2	1.39	0.15	32.73	2.52

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Height (cm)	Particle R ^b n(K)	co ₂	% of Gray Body	Particle Conc.	Soot Conc.	CO ₂ Conc.	H ₂ O Conc.
5	1100	1335	0	7.88	0	1.04	0.20
7	1250	1590	0	7.98	o	2.06	G.21
10	1750	1474	17	6.85	0	17.35	1.23
11	1980	2195	46	5.15	0	22.60	1.51
12	2035	2338	48	5.05	0	24.61	1.75
13	2070	2460	56	4,89	0	27.61	2.08
16	2030	2420	49	3.94	0.11	29.63	2.07
19	2100	2320	40	2.92	0.05	34.33	1.97
24	2130	1980	.20	0.86	0	25.43	1.35
32		1500		0.51		20.26	1.32

Table II.C-3. Flame Properties as a Function of Distance Above the Injection Nozzel for Zap North Dakota Lignite 900°C Char.

Height	rticle	CO ₂	% of Gray	Particle	Soot	CO2	H ₂ O
(cm)	∩ ^m (K)	-	Body	Conc.	Сопс.	Conč.	Conc.
5	210	974	0	9.88	0	0.40	0.06
9	910	1545	٥	8.15	0	0.40	0.09
14	1620	1780	27	6.22	0	3.02	0.47
15	1800	2650	32	7.46	σ	5.10	0.59
16	1940	2780	32	7.85	0	9.21	0.70
17	2000	2405	33	6.73	0.1	16.58	1,19
18	2015	2275	42	4.64	0.38	20.37	1.60
19	2020	2305	52	4.64	0.52	21.52	1.78
20	2025	2315	62	3.95	0.44	23.47	1.80
21	2030	2155	28	3.80	0.48	23.92	1.44
23	2100	2000	12	3.66	0.45	23.53	1.31
26	2070	1785	11	2.87	0.33	25.56	1.21
44		1660	0	0.51	0	10.30	0.56

Table II.C-4. Flame Properties as a Function of Distance Above the Injection Nozzel for Zap North Dakota Lignite 1500°C Char.

Height (cm)	Particle R ^b n(K)	co ₂	% of Gray Body	Particle Conc.	Soot Conc.	CO ₂ Conc.	H ₂ O Conc.
5	650	800	0	5.73	0	0.04	0.54
9	810	1375	0	4.12	0	3.30	0.65
10	1920	2275	9.5	3.50	0	4.98	0.64
11	1940	2390	11	5.56	0.10	4.84	0.72
12	2040	2490	15	4.28	0.14	11.1	1,11
13	2040	2450	32	3.70	0.45	28.1	2.25
14	2040	2425	37	3.65	1.15	32.5	2.59
15	2000	2420	63	3.46	1.60	36.9	2.81
16	1970	2415	53	3.43	1.70	42.1	2.85
17	2040	2410	39	2.49	0.95	34.0	2.42
21	1980	2240	35	1.43	0.72	37.8	2.62
26	1900	1815	16	0.98	0.33	38.0	2.33
38		1740		0.11	0	6.3	0.45

Table II.C-5. Flame Properties as a Function of Distance Above the Injection Nozzel for Argonne Zap North Dakota Lignite.

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Height (cm)	Particle R ^b n(K)	со ₂	% of Gray Body	Particle Conc.	Soot Conc.	CO ₂ Conc.	H ₂ O Conc.
5	670	1055	o	5.9	0	0.98	0.29
10	1705	2405	88	5.5	8.6	15,16	1.81
14	1595	2075	95	5.8	8.9	27.22	2.81
17	1575	1865	80	5.6	7.6	31.22	2.99

Table II.C-6. Flame Properties as a Function of Distance Above the Injection Nozzel for Demineralized Zap North Dakota Lignite.

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Height (cm)	Particle B ^b (K)	CO_2	% of Gray Body	Particle Conc.	Soot Conc.	CO ₂ Conc.	H ₂ O Conc.
	1 1 1 1 1 1 1 1 1 1					****	
4	665	2160	0	4.07	0	0.4	0.05
5	1565	2274	88.5	12.01	17.40	19.7	1.97
6	1500	2112	84.0	14.05	20.30	28,4	3,30
7	1400	2078	71.4	11.16	24,49	31.9	3.45
10	1325	1829	79.4	16.56	24.75	36,7	3.87
12	1325	1668	106.4	13.36	10.20	33,9	3.35
15	1200	1537	86.7	11.56	11.55	31.5	2,97
20	1160	1503	60.0	9.92	10.64	24.7	2.29
30	1040	1335	57.4	5.56	4.05	14.0	1.28

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Table II.C-7. Flame Properties as a Function of Distance Above the Injection Nozzel for Argonne Pittsburgh Seam Bituminous Coal.



Figure II.C-2. Flame Properties as a Function of Distance Above the Injection Nozzel for Zap North Dakota Lignite. a) Concentrations of CO₂, Particles and Soot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.



Figure II.C-3. Flame Properties as a Function of Distance Above the Injection Nozzel for Zap North Dakota Lignite 900°C Char. a) Concentrations of CO₂, Particles and Soot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.



Figure II.C-4. Flame Properties as a Function of Distance Above the Injection Nozzel for Zap North Dakota Lignite 1500°C Char. a) Concentrations of CO₂, Particles and Scot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.



Figure II.C-5. Flame Properties as a Function of Distance Above the Injection Nozzel for Argonne Zap North Dakota Lignite. a) Concentrations of CO₂, Particles and Soot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.



Figure II.C-6. Flame Properties as a Function of Distance Above the Injection Nozzel for Demineralized Zap North Dakota Lignite. a) Concentrations of CO₂, Particles and Soot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.



Figure II.C-7. Flame Properties as a Function of Astance Above the Injection Nozzel for Argonne Pittsburgh Seam Bituminous Coal. a) Concentrations of CO₂, Particles and Soot and b) Temperature of Particles and CO₂ and Percent of Particles Ignited Times Emissivity.

Sth Quarterly 2/66 WP#/1

presented in Fig. II.C-8a, for the raw and demineralized Rosebud coal, and Rosebud chars produced at 900°C and 1500°C. Ignition for the coals is accompanied by a more rapid increase in CO_2 than seen for the chars. This is believed to be due to the rapid release of energy from the combustion of volatiles. The position of the ignition also varies for the four samples.

To determine what controls the ignition, measurements have been made of the weight loss of coal in a TGA, both under inert and oxidizing conditions. The objective is to correlate what happens in the TGA at temperatures from 450°C to 600°C to what happens during ignition in the TWR at similar particle temperatures. As shown in Fig. II.C-8b, the ignition distance correlates well with the temperature for 10% weight loss in air measured at a constant heating rate of 30°C/min in a TGA. The lower the temperature to achieve 10% weight loss in the TGA, the shorter the ignition distance in the TWR.

In the case of the previously formed chars, the TGA weight loss is almost exclusively due to char oxidation and hence, the ignition in the TWR must be heterogeneous (i.e., within the porous solid matrix). For high rank coals, the first 10% weight loss in the TGA under oxidizing conditions is mostly due to pyrolysis, consistent with homogeneous ignition in the TWR. For low rank coals, however, there is a significant early weight loss in the TGA due to heterogeneous oxidation, and it appears that there is a significant heterogeneous contribution to the ignition in the TWR. This is consistent with the observation that the demineralized Rosebud coal (which is less reactive to oxidation than the raw coal) is more difficult to ignite (Fig. II.C-8a). The results are also consistent with the measurements of Midkiff et al. (1986) who conclude that there is a significant weight loss due to heterogeneous oxidation in combustion for low rank coals.

A comparison of the soot concentration for 3 samples is shown in Fig. II.C-8c. The demineralized Rosebud produces about twice the soot as the raw sample, and the char produces almost none. As shown in Fig. II.C-8d, the soot production correlates well with the yield of tar as determined in pyrolysis experiments. Pyroly: was performed in the entrained flow reactor. The higher the tar yield, the higher the soot yield. The relationship between tar and soot is consistent with the results of Wornat et al. (1981) and Nenniger et al. (1983).

Figure II.C-8e compares M for the raw coal, the demineralized coal and the 900°C char. M can be less than 1.0 due to unignited particles and/or a low value of emissivity. Prior to ignition, all three samples have low values of M due to

- 61 -



Figure II.C-8. Selected Flame Measurements and Correlation of Flame Measurements with Coal Properties. a) Comparison of CO₂ Concentration in Flames of Four Samples, b) Correlation of Ignition Point with TGA Weight Loss in Air, c) Comparison of Soot Yields for three Samples, d) Correlation of Scot Yield with Tar Yield in Pyrolysis, e) Comparison of Black Body Multiplier for three Samples, and f) Correlation of Black Body Multiplier with Ash Content of the Coal.

unignited particles. At ignition, M for the two coals goes up rapidly as the particles ignite and soot is formed. Above the ignition region, where all the particles are expected to be ignited, M drops rapidly for the raw coal but remains high for the demineralized coal. The source for this effect appears to be ash particles which are on the surface or are shed from the burning char particles. The ash particles that are shed will increase (100%-transmittance) without adding significantly to the radiance because of their low temperature and low emissivity. TGA analysis of the captured samples of char showed that a significant fraction of the minerals (30%) had already been shed. An alternative explanation is that the unshed ash particles act as diffuse scatterers which lowers the emissivity. However, a direct measurement of the emissivity of captured char particles using the E/T technique at a lower temperature (800°C), shows that the emissivity due to surface ash is not important.

Figure II.C-8f presents a correlation between M above ignition (where all particles should be ignited and the soot has been consumed) with the ash content of the coal. The higher the ash content, the lower M, in agreement with either hypotheses.

Cenclusions

The FT-IR E/T technique is a versatile technique for coal combustion diagnostics allowing measurements of particle concentrations and temperatures and gas compositions, concentrations, and temperatures.

A comparison of the ignition of several samples suggests that the rate of ignition correlates with the initial rate of weight loss in air in a TGA experiment at lower temperatures. Ignition of chars is heterogeneous; ignition of high rank coals is homogeneous; but low rank coals exhibit both homogeneous and heterogeneous contributions to ignition.

Soot formation in combustion correlates well with tar yield in pyrolysis suggesting that tar is the chief precursor of soot.

Plans

Continue the flame experiments for the remaining standard samples.

5th Quarterly 2/88 WP#71

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. Emphasis during Phase I will be on the acquisition of data which will be utilized for model development in Phase II. 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.

Mineral matter in coal is a source for slagging and deposits on reactor or down stream component walls, causing corrosion of equipment. Minerals can also catalyze reactions or can poison processing catalysts. The objective of this research is for the development of a model for the prediction of ash behavior and the correlation of the behavior with the original chemical composition, particle size, physical properties of the minerals and the process conditions. A model will also be developed to predict the catalytic effect of minerals on coal conversion.

Accomplishments

During the fifth quarter, two sample collection probes were constructed that can be inserted into the transparent wall reactor (TWR) to allow for the collection of char with its transforming mineral matter from the flame at various 5th Quarterly 2/88 WP#71

stages of burnoff, and of fly ash from above the flame. Both probes result in no visual disruption of the stability, size or ignition delay time of the flames. Initial sample collections were performed.

Ash Collection

The fly ash collector (in stack) consists of an inlet nozzle, large particle preseparator, cascade impactor and adjustable air pump. The char collector (in flame) consists of a water cooled nozzle that adds cold helium gas to the removed hot particle stream. After quenching, the particle stream passes through a large particle cyclone separator, and then through the preseparator and cascade impactor.

The char collector nozzle inlet temperature was maintained below 300°C by the He addition. The fly ash collector nozzle was placed in the flame exhaust stack having a typical radial temperature profile as presented in Fig. II.D-1.

Table II.D-1 and Fig. II.D-2 show collection and separation data for a Rosebud subbituminous coal and a Zap lignite under similar collection conditions. TGA weight loss measurements on the in flame collected samples indicate that both cyclone fractions have a large amount of burnable material remaining (\sim 60%). SEM photomicroyraphs (Figs. II.D-3 and II.D-4) show both materials to contain etched particles of the same size range of the starting materials, with some particles having discrete globules of ash stuck to the particle surface and others with a more uniform coating (possibly smaller globules) of ash as indicated by the bright (charging) areas. The Zap cyclone fraction appears to contain more particles with ash globules on particle surfaces and more ash that has apparently released from the char. This is also indicated in the size separation data presented in Fig. II.D-2. For the Zap sample there is more material collected downstream of the large particle separators than for the Rosebud. Figure II.D-5 compares two stages of in stack collection for the Zap, and clearly shows the individual spheres. These photomicrographs also indicate the particle sizing ability of the cascade impactor.

To verify a difference in the ability of the starting material to "shed" ash, samples of Zap and Rosebud, pyrolysis chars were quantitatively combusted in the entrained flow reactor to various levels of burnoff. The partially combusted material was collected in a cyclone separator that would clean the char of the

- 65 -

Table II.D-1. Sample Collection Data for Zap and Rosebud Flames.

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Percent Weight Loss in TGA*	Collection Time Wt. of Sample Cyclone Fraction Preseparator Fraction Minutes Collected (mg)	2 856.0 62.24	3 158.8 59.42	10 81.5 6.10	20 22.1 3.43	
	Collection Point	7 cm above Ignition Point (in flame)	7 cm above Ignition Point (in flame)	In Stack 75 cm above Injector	In Stack 75 cm above Injector	
	%Ash (12.7	7.3	12.7	7.3 I	
*()*41971107110404	Sample	200 x 325 Dry Rosebud	200 x 325 Dry Zap	200 x 325 Dry Rosebud	200 x 325 Dry Zap	
HEN PROCESSION	Run #	1	4	5	10	

* TGA analysis in air at 30K/min to 900°C

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- 66 -



Figure II.D-1. Air Temperature Profile Across TWR Exhaust Stack with Rosebud (200x325) Flame On. Distance Above Injector: ■, 70 cm; ◆, 75 cm.

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Figure II.D-2. Particle Separation Distributions for In Flame and In Stack Collections for Rosebud Subbituminous Coal and Zap Lignite.



Figure II.D-3. SEM Microphotograph of Cyclone Fraction of In Flame Collection for Rosebud Coal. Magnification: X400.



Figure II.D-4. SEM Microphotograph of Cyclone Fraction of In Flame Collection for Zap Lignite. Magnification: X400.



Figure II.D-5. SFM Photomicrographs of Fly Ash Collected Above a Zap Lignite Flame. a) ge #2 and b) Stage #4 of Cascade Impactor. Magnification: X910.

5th Quarterly 2/88 WP#71

smaller released ash and any fragmented particles. TGA weight loss analysis was then performed on the combustion char to indicate the fraction of ash present in the particles, and from this, the percent ash retained from the starting material can be calculated by

% ash retained = <u>% combustion sample x % ash in combustion sample</u> % ash in starting material

Table II.D-2 presents the percent ash retained values for several levels of combustion. The data appears to indicate two points: 1) the samples shed to a relatively constant ash level early in the combustion process, and 2) the Zap initially sheds more of its ash than the Rosebud. Further tests will be done to see if a gradual release of ash occurs earlier in the combustion process; and to see if the extent of pre-charring effects this process.

To study the mineral matter to fly ash transformation, a comparison was made by SEM/dispersive x-ray analysis of the solidified ash spheres on the Zap char's surface with particles collected in the preseparator above the flame. The ash spheres on the chars surface are rich in Ca, moderately rich in Al and Si and have varying amounts of Fe, K and Mg. Representative qualitative analyses for these particles are presented in Table II.D-3. It appears that the coal's organically bound calcium accumulates in the form of molten liquids, along with the fine clay and pyrite particles.

Figure II.d-6a shows a photomicrograph of particles collected above the flame. Some of these particles have melted to form spheres and some have not. Qualitative analyses of the numbered particles are presented in Table II.D-4. In the figure, samples 1 and 2, which appear to have melted and crystallized, are almost pure iron oxide. Figure II.d-6b shows a close-up of the highly crystallized surface structure for these kinds of particles. Sample 3, which has not melted is almost pure calcite. Sample 4 shows a region which has not melted which is almost pure quartz, like sample 5, and a part which has melted which is a mixture of elements. Particles 1-5 appear to have been derived from individual extraneous mineral grains (pyrite, calcite, and quartz) without significant contamination by other mineral components. Small spheres (6 and 7, and those captured on the stages of the cascade impactor) as well as larger spheres (8 and 9) are mixtures of Si, Al, Ca, Fe, K and Mg, like the particles attached to the chars surface captured in the flame. Qualitative analysis of other particles similar in appearance to particles 1-9 are presented in Table II.D-5.

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Sample	% Sample Recovered after Partial Combustion	% Ash Retained
Zap*	39.0	44.7
	27.0	37.2
	16.5	40.0
	7.6	35.0
Rosebud**	66.7	66.1
	28.0	71.0
	22.3	75.4
	21.1	67.1

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Table II.D-2. Percent Ash Retained in Partially Combusted Samples.

* 900°C Zap Char

** 1500°C Rosebud Char

TABLE II.D-3

REPRESENTATIVE QUALITATIVE* X-RAY ANALYSIS FOR ASH SPHERES ON CHAR PARTICLE SURFACES AS SHOWN IN FIG. II.D-4

Mineral Component	5c	6c	7c	8c	9с	12c
Al	4.89	0.93	0.69	1.21	1.37	1.86
Si	6.10	0.85	5.05	0.56	1.78	1.49
Fe	0.65	3.47	0.73	0	0	1.21
Mg	2.70	1.45	1.21	1.53	1.53	3.31
Ca	5.86	11.71	3.31	2.22	2.66	6.62
Ti	0.52	0.08	0.04	[.] 0 . 04	0	0.20
Na	-	0	0	0	0.65	0
к	0	0	0.04	0.04	0.04	0
Sulfur (0)	0.16	0.12	1.05	0.08	0.56	0.48
Sulfur (M)	0	0	0	214	1.53	0
x in FeS _x	0	0	0	2	2	0
Total Ash	35.86	25.73	19.06	11.87	16.44	22.45

Values are in weight percent

* Not matrix-corrected for coefficient of x-ray absorption for each component.

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2 67 k × 38 k ∪ 129

Figure ILD-6. SEM Microphotograph of Fly Ash Collected Above a Zap Lignite Flame, Preseparator Fraction. a) X 400 and b) Close-up of Sample 1, X 2,670.

TABLE 11.D-4

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QUALITATIVE* X-RAY ANALYSIS OF ASH PARTICLES PRESENTED IN FIG. 11.D-6

Values are in weight percent

Mineral -	1	2	3	4 (melted)	4 (not melted)	5	б	1	8	9
	0.23	0.19	0.36	12.18	2,52	2.20	9.78	0.84	9.13	9,55
Si	1.21	0.79	(1.66	38.28	33.96	65.44	29.82	1.50	29.81	32.07
Fe	86.05	90.16	0.30	1.38	0.54	0.15	0.84	0,72	0.41	0.38
Ma	0,56	0.47	1.08	1.80	1.14	0.78	1.86	2.1	1.02	0.80
тэ Га	2.75	0.37	78,54	0,66	-	0.10	1.68	3.66	0.38	0.41
ti	0	0	0.18	0.18	0.06	0	0.06	0.06	0.19	0.03
tia.	0	0	. 0	2.04	0	0	4.14	0	1.18	2.70
ĸ	0	0.09	0	7.14	0,90	0	0.84	0	6.81	5.15
 Sulfur (0)	0	0	0	0.06	0	0.05	0.06	0	0	0
Sulfur (M)	0	0	0.60	0	0	0	0	0	0	0
r in FeS.	0	0	2	0	0	0	0	0	0	0
Total Ash	129.69	131.41	113.46	125.22	79.98	145.46	101.10	12.36	95.55	102.60

Not matrix-corrected for coefficient of x-ray absorption for each component.

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TOBLE (1.2-5 QUALITATIVE" 1-DAY ADALTSIS OF ASH PARTICLES SIMILAR UN APPEARANCE TO Particles on Fig. 11.0-6 and table 11.0-4

Values are in weight percent

	(51	Partici Ilar in appe	e Number aranék Ep 1 + 2}	(*	Parcici imilar in a 4 (mut	e Number Ippearance (ueited) = 1	(a 5)
Mineral Component				<u> </u>	76	64	24
A1	0.24	0.29	3.20	2,16	2.46	2.33	2.15
51	1.08	0.70	0.29	€ . 72	56.34	65.20	\$Z.22
Fe	73.36	91.27	91.27	0.94	1 - 36	a.;9	3.19
×ç	J.56	0.53	0.54	0.34	0.76	0.39	0_7e
C4	12.24	0.53	0.24	0.05	0.14	0.24	0
71	٥	٥	0	0.06	c	0.35	э
R.a.	٥	٥	0	0.18	6.26	2.57	2
ĸ	٥	0.35	0.10	0.12	0.36	0.;C	υ
Sulfur (0)	0.35	۵	0.35	٥	0.36	D	0.35
Sul fur (R)	٩	a	c	0	٥	С	o
x (n Feúx	٥	٥	a	C	C	C	٥
Total Asn	131.70	124.50	132.10	146.46	153.66	149.25	128.25

Pa	1.5	icle Number		
{Similar	in	appearance	to 3)	
Ineral				

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Particle Number (Similar in appearance to 6 + 7)

Mineral Component	21			24	. 12
A1	0.30	0.23	4.14	3.82	9.42
51	7.82	0.49	11,10	27.72	29.44
Fe	Q.36	0.27	1.08	0.66	6.1
rs.	1.02	0.15	1.12	2.28	<u> </u>
сı	76,74	45.95	-	1.56	۲.0
TI	0-18	0.06	٥	0.36	٥
Ne	٥	0.06	¢	0.42	4.0
ĸ	٥	C. 83	0.18	9.18	0.1
Sulfur (0)	0.24	0.12	0.06	٥	0
Sulfur (M)	٥	D	٥	0	0
z in FeSz	C	٥	0	٥	٥
Total Ash	114_84	67.73	37.56	92.88	107.4

	(51	Par milar in app	ticle Rumber earance to 8	. 9 + 4 (me)	ted)]
Rineral Component	31	22	28	مل	15
AI	8.89	10.38	6.42	7.00	13.52
51	29.09	26.20	26.58	37.89	39.42
Fe	0.85	5.53	Z1.42	6.16	3.06
нg	1.22	7.43	5.16	6.07	3.12
G	0.46	0.58	5.16	2.10	0.16
T1	0.12	C. 34	0,48	c -2	C.48
Ne	0.58	1.00	2.04	0.47	0.84
ĸ	7.97	2.13	0.42	2.05	2.46
Sulfur (0)	0.03	٥	٥	0	0.06
Sulfur (H)	c	D	D	0.05	٥
z in Fe3 _z	D	٥	o	Z	0
Totc1 Ash	94.50	94.4 7	122,22	120.63	126,36

"Not matrix-corrected for coefficient of x-ray absorption for each component.

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JUA QUALLETTY 2/80 WP#/1

Also of interest is that many of the pure mineral particles are of the same size (some larger) than the starting coal particles. Differences in color, magnetic attraction, and density (hoilow vs. solid) have also been observed.

<u>Plans</u>

Continue collection and characterization of ash particles produced in the TWR. Size distribution analysis will be performed once flow conditions are arrived at that will minimize reentrainment (high air flow) and inetticient separation (low air flow) of particles in the cascade impactor. A device for measuring the ash sticking behavior will be designed and implemented in the TWR reactor for monitoring the fouling and slagging behavior of ashes of different ranks of coal.

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 (> 0.5 mm) 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 literature review of heat and mass transport effects in coal pyrolysis was completed. A critical evaluation was made of two models from the literature that have been used to describe coupled reaction and transport in large particles.

A major effort was made on design of the fixed-bed reactor. This reactor will have on-line analysis of evolved volatile products and on-line measurement of weight loss, functional group composition and particle temperature.

Evaluation of Pyrolysis Heat/Mass Transport Models

During the past quarter, a more detailed examination was made of the models of Devanathan and Saxena (1985,1987) and Bliek et al. (1985) in order to choose a starting point for a model of large particle pyrolysis.

The original model of Devanathan and Saxena (1985) was developed for the devolatilization of large non-plastic coal particles. Their objective was to develop a comprehensive pyrolysis model considering heat and mass transport resistances. Since the primary focus of their work was the effects of the transport parameters, the initial (Devanathan and Saxena, 1985) paper used a simple single-reaction model with a global activation energy for primary pyrolysis.

- 79 -

They also ignored the temperature variation of the physical properties (heat capacity, thermal conductivity). The latter simplification is a major weakness of their approach, but can be easily remedied. In addition, they assumed pyrolysis is thermally neutral, which is probably not a bad assumption, as discussed in the Second Quarterly Report.

This model was developed to describe non-plastic coals which largely retain their pore structure during pyrolysis. The volatile species were lumped into a single component. An effective diffusion coefficient was assumed to account for volatile transport by diffusion and convective flow under small pressure gradients.

The pyrolysis reaction in this model is represented by:

C (Coal) → A(Volatiles) + S(Char)

The nonlinear partial differential equations obtained for the material and energy balances were solved using the DPDES routine of IMSL. This routine uses the method of lines which reduces the system of partial differential equations into a system of ordinary differential equations, which are subsequently solved with a Gear Integration method. The equations were solved for various values of the Thiele modulus, corresponding to high, medium and low reaction rates.

Using an assumed set of kinetics, thermal properties and diffusion coefficients, they identified regimes of chemical reaction control (at low reaction rates), and heat and mass transfer control (at high reaction rates). By dring parametric studies they identified the Thiele modulus (chemical reaction rate/diffusion rate), the Lewis number (thermal diffusivity/mass diffusivity) and the heat transfer Biot number (ratio of external to internal heat transfer rate) as important dimensionless groups. The analogous mass transfer Biot number was found to be unimportant since the external film resistance was assumed to be negligible.

A second paper (Devanathan and Saxena, 1987) extended the mode! to include secondary reactions. The description of the volatiles was also extended to three components (tar, gas, hydrogen). The global primary and secondary pyrolysis reactions were:

> Coal Tar Gas + Hydrogen + Char Gas + Hydrogen + Char

In this paper, Devanathan and Saxena used the primary pyrolysis kinetic parameters of Suuberg et al. (1978) instead of the parameters of Kobayashi et al. (1977) used in the previous paper. This change was presumably to accommodate a multicomponent pyrolysis model. However, it is surprising that the authors do not comment on the significantly higher kinetic rates implied by the former set of parameters. Again, the physical properties were assumed to be constant, the heat of reaction assumed to be zero, and the mass transfer model utilized an effective diffusion coefficient to account for volatile transport both by molecular diffusion and convective flow under a small pressure gradient. It was also assumed that tar was only present in the vapor phase. The kinetics for the tar decomposition reaction were based on the values assumed by Suuberg et al. (1979). The numerical scheme used to solve the set of 7 partial differential equations for a 3component system was a similar technique as discussed above.

The authors used the expanded model to examine the effects of bulk temperature, pressure, and particle size on the extent of secondary reactions and volatile yields. Qualitative comparisons were made to the data of Suuberg et al. (1978) for Montana Lignite for the effect of pressure, temperature and particle size. Comparisons were made to the data of Stubington and Sumaryono (1984) for product evolution profiles from large particles. The simulations indicated two peaks in the H₂ evolution curve in agreement with Stubington and Sumaryono (1984). The first peak in the model was due to primary pyrolysis reactions while the second was due to tar decomposition.

One weakness of their approach is that the secondary reactions of tar outside the particle are ignored so that the predictions which show tar yield leveling off at relatively high temperatures do not make sense. They also predict a temperature of 750°C for the maximum tar yield, which is 150-200°C higher than most experimental observations. By assuming an inverse relation of the diffusion coefficient with pressure, they can predict the type of pressure dependence indicated by the Jata of Suuberg et al. (1978). One interesting prediction of their model is the fact that the pressure dependence is more prominent in the later stages of devolatilization since the volatiles e to travel a further distance to get to the surface.

The total volatile yield was found to depend weakly on particle size while the total devolatilization time was found to depend strongly on particle size. These particle size trends, as well as the trends with pressure and temperature discussed above are in qualitative agreement with literature results. However, when

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quantitative comparisons are made, such as the temperature for maximum tar yield, the predictions are often far off, as noted above. This is a result of the fact that the physical and chemical parameters which go into the model were selected somewhat arbitrarily. The authors did note that some of these parameters could not be estimated accurately and did a sensitivity analysis on the external heat transfer coefficient, thermal diffusivity, external mass-transfer coefficient, effective diffusion coefficient and porosity. Of this set, the choice of the effective internal diffusion coefficient was found to be crucial. This parameter is also one the most difficult to specify. Unfortunately, the authors did not examine the sensitivity to the kinetic parameters.

A comprehensive model for large particle pyrolysis was also developed by Bliek et al. (1985). They used essentially the same global pyrolysis scheme (including tar secondary reactions) as Devanathan and Saxena (1987). One difference in the kinetic models was to assume that each of the three volatile components evolves by a reaction which is second-order in the amount of volatiles yet to be released. This is a simpler alternative to the distributed activation energies model to describe the "tailing" of volatile evolution curves at higher temperatures. This model also treats coals which essentially retain their pore structure.

One of the major differences of this model when compared to that of Devanathan and Saxena (1987) is in the treatment of internal mass transfer. Bliek et al. chose to use the continuum limit of the Dusty Gas model (Mason et al., 1967; Mason and Malinauskas, 1983). This model can account for the combined transport of volatiles by viscous flow and diffusion. Viscous flow becomes more important as the particle size increases, so this approach should be applicable over a wider range of particle sizes. The model requires an estimate of the viscous permeability, the effective Knudsen diffusivity, and the effect binary diffusivity The latter quantity also appeared in the diffusive mass transport model of Devanathan and Saxena (1987). Bliek et al. (1985) used literature values of permeability parameters obtained from stationary mass flux experiments.

The transport of volatiles from the particle outer boundary to the ambient gas was assumed to be infinitely fast. This assumption is probably alright for light gases but not for heavy tars. The heat of devolatilization was assumed to be zero as did the Devanathan and Saxena (D-S) model. Unlike the D-S model, Bliek et al. did not concern themselves with the details of external heat transfer and specified the particle surface temperature. However, they did account for the temperature variation of the particle thermal conductivity and heat capacity, which the D-S

model does not include. Bliek et al. also did pyrolysis experiments in a TGA with particles 50-1000 microns in size in order to extract primary pyrolysis kinetic information and generate data for model validation. The equations were solved numerically using an implicit backward descretization scheme. This transformed the partial differential equations to non-linear algebraic equations, which were subsequently linearized. A combination of iteration and the algebra of diagonal matrices was used to produce the numerical results.

The qualitative results of the simulations largely agree with those of the D-S model since both were developed to agree with the experimental observations of Suuberg et al. (1978), among others. The more detailed description of mass transfer allowed Bliek et al. to establish regimes of particle size and heating rate where mass transfer was controlled by either diffusion or viscous flow. The most interesting prediction was that the tar yield went through a maximum with heating rate. This was explained by the fact that at high heating rates, the volatiles would have to diffuse through a hot outer layer of char. However, this trend has not been observed experimentally. The model also did not agree well with the effects of ambient pressure observed for bituminous coal by Anthony and Howard (1976). However, this could be due to the fact that it was developed for a non-plastic coal.

While both the Bliek model and the D-S model are important contributions to understanding large particle pyrolysis, the published versions are lacking in several respects. The major problem is the relative lack of care which has gone into the choice of the physical and kinetic parameters. A corresponding defect is the lack of a complete sensitivity analysis. If we compare the choices of physical and chemical parameters made for the two models, which are shown in Tables II.E-1 and II.E-2, respectively, the magnitude of the problem is apparent. For example, there are several orders of magnitude variation in the species diffusivities. As discussed above, this was identified as a crucial parameter in the partial sensitivity analysis done by Devanathan and Saxena (1987).

Additional problems with these two models include an oversimplified description of tar secondary reactions, and the inability to describe plastic coals. We plan to address these and other deficiencies in our large particle model development.

- 83 -

Table II.E-1. Comparison of Physical Parameters for Two PyrolysisReaction / Transport Models.

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Property .	Units	Devanathan and Saxena (1987) 25°C 500°C	Bliek et al. (1985) 25°C 500°C
Thermal Conductivity	cal/(cm s K)	5.497×10^4	4.45×10^4
Heat Capacity	cal/(g K)	0.916	0.27 0.51
Density	g/cm ³	1.5	0.9
Thermal Diffusivity	$\mathrm{cm}^{2}/\mathrm{s}$	4×10^4	1.8×10^{-3} 9.7 x 10^{-3}
Gas Molecular Weight	g/g-mol	30	20
Tar Molecular Weight	g/g-mol	216	325
H ₂ Diffusivity	$\mathrm{cm}^{2}/\mathrm{s}$	4×10^{-3}	
Gas Diffusivity	$\mathrm{cm}^{2}/\mathrm{s}$	4×10^{-4}	4.2×10^{-1} 3.2×10^{-1}
Tar Diffusivity	$\mathrm{cm}^{2}/\mathrm{s}$	$.4 \times 10^{-5}$	4.2×10^{-1} 3.2×10^{-1}
Coal Porosity		0.4	0.10
Char Porosity			0.25

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			Devanathan and Saxena (1987)	Bliek et al. (1985)
v ₁	(ultimate yield of H_2)	ឌ/ឌ	0.005	0.000
v_2	(ultimate yield of gas)	g/g	0.381	0.358
V_3	(ultimate yield of tar)	g/g	0.054	0.160
\mathbf{f}_4	fraction of tar which can react		1.0	1.0
^k 01	preexponential	s-1	1018	
^k 02	preexponential	s-1	10^{12}	8.0×10^4
k ₀₃	preexponential	s-1	10 ¹⁷	7.6×10^{11}
^k 04	preexponential	s-1	10 ¹³	2.7×10^4
E ₁	•	kçal/mole	80	
E_2		kcal/mole	50	22
E3		kcal/mole	75	37
${f E}_4$		kcal/mole	65	14

Table ILE-2. Comparison of Kinetic Parameters for Two PyrolysisReaction / Transport Models.

Design of Fixed-Bed Reactor

Several different design configurations were considered for the fixed-bed reactor (FBR). These were narrowed down until a single design approach was agreed upon and then a more detailed design was developed. A schematic of the proposed FBR is shown in Fig. II.E-1. The integration of the reactor with a PC is shown in Fig. II.E-2. Notes for both figures are given in Table II.E-3.

In this system, 0.2 - 10g of coal (0.5 - 3mm particle size) will be placed on the sample holder (14). The sample holder can be accessed by removing the window (4) and taking out the upper part of the joint (13). The sample holder is a 31 mm 1.D., 25 mm long quartz tube. It is heated by a hot stream of gas produced in an electric preheater (16) which can also produce steam by the introduction of water. The preheated gas is forced to pass through the sample by making the path through the sample the only way for gas to exit the reactor. To allow for continuous monitoring of the sample, the sample holder is attached to the reactor enclosure using a bellows (12).

The entire sample compartment/bellows system is suspended from a balance to measure the weight loss of the sample. To avoid a change of the weight due to a temperature change of the bellows, it is protected by a water cooled plate. There is also a pressure difference between the two sides of the bellows which might change during the experiment, causing a change in the load on the balance. This is compensated for by a differential pressure transducer (18), which measures the actual pressure difference and sends it to, the computer. The computer can deduct this load change from the output value of the balance using previously obtained calibration curves. The reactor head is made of fused quartz to withstand the high heat load.

The composition of the product gases and tar are measured in the cell (6) using FT-IR transmission. The temperature of the coal surface is measured by an emission FT-IR method through a window (4) using either a separate FT-IR spectrometer or the same one used for the transmission measurements. To be able to measure surface reactions of the coal particles, an additional IR source (17) is required. By switching on the IR source (17) (opening a shutter), the emission spectrum will contain the diffuse reflectance spectrum together with the emissivity spectrum of the same particle or particles. By closing the shutter we measure emissivity only. The diffuse reflectance spectrum will be the difference of the two spectra.

- 85 -



Figure ILE-1. Schematic of Fixed-bed Pyrolysis Reactor.



Figure II.E-2. System Diagram for Fixed-bed Pyrolysis Reactor.

Table II.E-3. Notes for Figures II.E-1 and II.E-2.

- 1-5 KBr Windows
- 6 Tube for FT-IR Transmittance Measurements of Product Gases and Tars
- 7-9 Concave Reflection Mirrors
- 10 Flat Mirror
- 11 Electrobalance for Weight Loss Measurements
- 12 Double Bellows
- 13 Quartz Taper Joints
- 14 Coal Sample Holder (quartz wool cloth on metal screen)
- 15 Quartz Reactor Head
- 16 Gas Heater
- 17 IR Source with Shutter and Beam Condensor
- 18 Differential Pressure Transducers and Solenoid Valves

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- 18 Mass Flow Controller
- 20 Regulated Power Supply
- 21 Flow Meter
- 22 Water Deionizer
- 23 Filter
- 24 Thermometer

<u>Plans</u>

Develop a detailed design for the fixed-bed reactor, including part specifications. Begin ordering parts. Begin model development for large particle submodel. Consider interface of this model with the BYU fixed-bed model.

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

Senior Investigator - Angus U. Blackham Combustion Laboratory Brigham Young University Provo, Utah 84602 (301) 378-2355

Objective

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

Accomplishments

No work planned.

Plans

No work planned.

II.G. SUBTASK 2.G. -- SO_X/NO_X SUBMODEL DEVELOPMENT

Senior Investigators: L. Douglas Smoot and B. Scott Brewster

Brigham Young University Provo, Utah 84602 (801) 378-4326 and (801) 378-6240

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 nonequilibrium 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.

The principal task for the past quarter was to include the capability of predicting thermal NO in the NO_X submodel. Complete restructuring of the existing NO_X submodel was an auxiliary task of this effort. A literature search of SO_X reactions in combusting flows was also scheduled to begin.

Accomplishments

The components of this subtask are 1) extension of an existing pollutant submodel to high pressure and fuel-rich conditions (including thermal NO formation), 2) modification of the current comprehensive code to include sorbent particle injection and reactions (including sulfur capture), and 3) extension of the pollutant submodel to include SO_x formation. A revised NO_x Revisions to the previous model include submodel has been completed. simplification of the overall flow of subroutine calls and calculation Non-standard Fortran statements and awkward logical gating were procedures. replaced in order to facilitate transfer of the code to Unix operating In addition, a generalized subroutine for convolving species and systems. rate equations over the joint probability of the progress variables was developed to provide a means for implementing alternative rate expressions and kinetic models. With thermal NO formation turned off, prediction of fuel NO

by the revised model matched that of the former code for a swirling-flow, coal combustion case. A literature survey of SO_x chemistry was initiated to identify the important aspects of predicting SO_x behavior. This effort will receive increased emphasis in the upcoming cuarter. Work relating to the second component is ongoing at the University of Utah and will be used as a basis for Component 2 of this subtask. Last-quarter progress is described below for each subtask component.

Component 1 -- NOx at High-Pressure/Fuel-Rich Conditions

The goal of this subtask is to extend the current pollutant submodel in the comprehensive code to be applicable to high-pressure, fuel-rich conditions such as are common in gasification processes. An important part of this extension is the inclusion of thermal NO formation which may be significant at the higher temperatures typical of gasification in oxygen.

The overall approach of the NO_X submodel is the prediction of NO formation with a global, 3-reaction, fuel-NO mechanism and a single reaction expression derived from the Zeldovich mechanism. The fuel-NO mechanism was developed for reacting coal flows where the contribution of thermal NO is relatively low. The set of reaction equations is listed here:

fuel-N		HCN	(II.G-1)
$HCN + O_2$		NO +	(II.G-2)
HCN + NO	>	N ₂ +	(II.G-2)
NO + (M)char		N ₂ +	(II.G-4)
$N_2 + O_2$		2N0	(II.G-5)

Equation II.G-1 represents fast conversion of fuel-N to gaseous HCN during devolatilization and char oxidation. Equations II.G-2 and 3 are the conversion of HCN to NO and N₂ respectively. Equation II.G-4 accounts for the decay of NO by heterogeneous reaction with char. Equation II.G-5 is the overall stoichiometric reaction of nitrogen and oxygen due to thermal fixation. Kinetic rate expressions for Equation II.G-5 were given in the first annual report.

- 92 -

The overall rate of NO formation is calculated by summing the time-mean rates of formation/depletion by the reactions in Equations II.G-2 through 5. It is, however, the calculation of mean reaction rates that introduces complexity to the theory. The calculation can be accomplished by integrating the individual instantaneous reaction rates over the joint probability of f (inlet gas mixture fraction) and n (coal gas mixture fraction) as described by Smoot and Smith (1985). Local, instantaneous species mass fractions are calculated by scaling their fully-converted values with a linear factor as follows:

$$Y_i = \pi Y_i^r$$
 (II.G-6)

The linear factor π is taken to be independent of the turbulent fluctuations and thus may be calculated by the ratio of Favre-mean mass fractions,

$$\pi = \tilde{Y}_{i} / \tilde{Y}_{i}^{f}$$
 (II.G-7)

In the case where only fuel-NO is considered, the fully-reacted values are constant since the total amount of HCN is fixed. This quantity also represents the maximum amount of NO possible in this case:

$$Y_{HCN}^{f} = Y_{NO}^{f}$$
(II.G-8)

For oxygen, the fully-reacted value is taken as the equilibrium value at steady state for the reacting system.

With the inclusion of the thermal NO rate expression, the definition of fully reacted NO is no longer valid, since NO is the combination of both fuel and thermal contributions. The fully reacted value has initially been estimated by:

$$Y^{f}_{NO} = Y^{f}_{HCN} + \{2Y^{ec}_{O2} \text{ or } Y^{eq}_{N2}\}_{limiting}$$
(II.G-9)

The limiting reactant (Y_{N2} or Y_{O2}) will vary from extremes such as coal gasification in oxygen-enriched reactors to combustion in air.

Similarly, Y_{N2} is defined as

$$Y_{N2} = Y^{eq}_{N2} + 0.5(Y^{f}_{HCN})$$
(II.G-10)

With the exception of these definitions, the calculation of the reaction rates in the revised model follows the same technique as the previous model.

In addition to the redefinition of fully-reacted species values, revisions were made to the code for conformation to standard Fortran and to render the code adaptable to alternative rate equations. The revised subroutines will facilitate the development of new kinetics-limited submodels, such as SO_x .

Integration of the revised NO_X submodel into PCGC-2 and debugging program errors have been completed. Predictions have been made to evaluate the new Initially, the thermal NO rate equations were set to zero to submodel. compare the results of the revised code for predicting fuel NO with the old version. The definition of the fully-reacted species values were also defined on a similar basis. The case predicted was for a swirling-flow, coal-fired reactor. The predictions for both NO_x submodels were identical, thus verifying the new method and modification of subroutines. A separate comparison was made by redefining the fully-reacted species as described above. In general, the new model predicted NO concentrations approximately 9% lower than the former method. An effluent value of 251 ppm was formerly predicted compared to 228 ppm predicted by the redefined fully reacted species values.

The next level of model validation is to activate the thermal NO rate expression and determine the predicted contribution of thermal effects to the formation of NO. A more rigorous investigation of the model will be made by attempting to predict thermal NO formation in well-characterized, laboratory-scale gas combustors. For this purpose, a literature survey was conducted to establish a data base of experimental measurements. Table II.G-1 lists the candidate systems and describes the details and limitations of the data. It is first necessary to choose a system that can be simulated using PCGC-2 in order to predict the correct flame structure. Second, profile data

Tab	le 1. Prospective Data Sources For T	hermal NO Model Evaluation.	
<u>Reference</u>	Reactor System and Fuels	<u>Available Data</u>	Limitations
Drake el al., (1987) Drake el al., (1984)	Horizontally fired 15 x 15 duct x 1000 cm ³ duct; 3.2 mm turbulent-flow fual injection tube; co-ellowhg taminar air stream; CO/112/N2 and CO/H2 /NH3 mixtures.	Axial and radial profiles for NO. temporature, reacting species, and products.	Non-axisymmetric combustion chamber.
Tang and Churchill (1981)	Vertically fired 9.7 mm diameter tube; 251 mm long; premixed flow, isothermal, non-turbutent combustion; hexane/air mixtures.	Exit values for temperature, CO, and NO _X as a function of equivatence ratio.	Difficulty in predicting the laminar flow and correct temperature in a narrow diameter tube.
Takagi and Ogasawara (1981)	Vertically fired 133 mm diameter; 1 m long reaction tube; turbulent diffusion fuel injoctor tube; co-eflowing air stream; hydrogen and propane in air mixtures.	Radial and axial profilos for H2O, H2, N2, Temperature, CO2, and NO; air preheat; effect of air preheat studied.	Prompt NO contributions to tho NO pool for propano/air mixturos uncertain.
Thompson et al., (1981)	Variable-length, vertically`fired 24.5 mm diameter, 24.5-245 mm long reactor tube; premixed flamé combustor; 7.3%-9.2% methane/air flàmes.	Axial data for centerline and wall NO, CH_4 , H_2 , and temporature.	Prompt NO contribulions uncortain, small roaclor size, temperature measured by baro wiro thormo- couples.
Semerjian and Vranos (1984)	Vertically fired 7.6 x 3.8 x 25 cm ³ . rectangular duct; premixod combustor; pre-vaporized Jet A fuel.	Axial profiles of CO.CO2 , NO _X , and temperature.	Non-axisymmetric rectangular duct; prompt NO formation uncertain.
Sadakat et al., (1981) -	Single and staged, vertically fired combustor; 80 mm diameter tube, 805 mm long; staging tocation at 585 mm; 3 mm nozzle burner, co-eflowing air stream; city-gas fuel (CO, H ₂ , CH ₄ <0.01, 'C ₂ H ₄ <0.01); NH ₃ seeded.	Data measured at 710 and 805 mm ($\theta x it$) for NO, HCN, NH $_3$; correlated to variation of air preheat and air to fuel ratio.	Separation of fuol and thormal NO, and prompt NO uncortain.
Karlsruhe University	Data in process of procurement.		
Pershing and Wondt (1977)	Vertically fired premixed coal reactor; 15 cm diameter, 1.5 m long; four coals combusted in air and $Ar/CO_2/O_2$ oxidizer.	Exit data for fuel and thermal NO.	Axial profilo data unavaliablo.

- 95 -

of NO concentrations as well as major species and temperature are desired. The largest concern with the majority of the experimental data available is separating the contribution of prompt NO from thermal NO for hydrocarbon flames. Efforts are also being made to procure data from Karlsruhe University in West Germany which consists of NO profiles for both thermal NO and fuel NO from NH₃-seeded flames of methane and air.

Two issues are necessary to validate the thermal NO rate predictions. The first is to determine which form of the rate equations presented in the annual report is preferred. Recent work has been accomplished by Drake et al., (1987) who investigated the effects of super-equilibrium radical species concentrations. In summary, they concluded that super-equilibrium increases average OH concentrations by a factor of 4-6 and increases thermal NO_X by factors of 2.5 at 1 atm and 1.4 at 10 atm. Comparison of theoretical calculations with their experimental data were made in arriving at this conclusion. They predicted thermal NO using rate equations identical in form to those developed on this project and a two-scalar pdf model similar to the approach of the NO_X submodel. A separate investigation will be made in this study to verify their results and establish recommended rate expressions for different reacting environments and conditions.

The second issue is to verify the combined fuel NO and thermal NO submodel for systems where both are significant. The experimental data for this case will be the investigation made by Pershing and Wendt (1977), who separated the relative contributions of each mechanism in a coal-fired laboratory reactor with air- and N₂-substituted oxidizing mixtures.

Component 2 -- Sorbent Particle Chemistry

This ibtask component is aimed at modifying the comprehensive code to include downstream injection of sorbent particles and their subsequent reactions with the gas phase. The work will be based on current work at the University of Utah, where a sorbent chemistry submodel is being developed for fuel-lean conditions. This subtask component has not yet been initiated.

Component 3 -- SO_x Formation

This subtask component will model the gas-phase reactions that generate the sulfur species for input to the sorbent capture model developed under Component 2 of this subtask. A literature search of work related to measurement and prediction of SO_X chemistry in combustion flames has been initiated.

<u>Plans</u>

Validation of the revised submodel will be continued by predicting gaseous combustion systems. The ability to predict the correct magnitude of combined fuel and thermal NO will also be investigated. Concurrent with the model validation effort, an exhaustive literature survey on SO_X chemistry will be made to begin formulation of the key reaction mechanisms.

II.H. SUBTASK 2.H. -- SC_x/NO_x SUBMODEL EVALUATION

Senior Investigator -- Paul O. Hedman

Brigham Young University Provo, UT 84602 (801) 378-6238

Objectives

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

Accomplishments

This subtask is being carried out under three subtask components: 1) A cold-flow investigation of sorbent mixing fluid mechanics, 2) modifications of the laboratory-scale reactor to accommodate sorbent particle injection, and 3) space-resolved sulfur and nitrogen pollutant measurements in the laboratory-scale reactor.

Component 1 -- Sorbent Mixing Fluid Mechanics

The BYU cold-flow facility is being used to simulate the flows that exist in the entrained-flow gasifier when sorbent is injected in a flow that is perpendicular to the main gasifier flow. Previous investigators (see Webb and Hedman 1982; Jones, et al., 1984; and Lindsay, et al., 1986) have used the BYU cold-flow facility to simulate the flows that exist in one of the BYU coal combustors and the BYU entrained-flow gasifier. The existing cold-flow facility is being modified to include crossflow jets for sorbent injection. Also, the flow chamber design is being changed from previous studies. The new

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flow chamber is being made of transparent plastic to simplify LDA measurements and to enable qualitative flow visualization with smoke. Smoke visualization will provide a qualitative means of examining the rate of mixing of the crossflow injection of the sorbent jets.

The modifications to the cold-flow facility to be used in this study were designed and fabrication was completed during the period. The design simulates the geometry of an entrained-flow coal gasifier/combustor; it incorporates an inlet block and flow chamber with the same dimensions as the BYU gasifier. The flow chamber is made out of clear plastic pipe, with flanges in the pipe at regular intervals to allow for sorbent injection and tracer gas extractions. The design also allows for laser-doppler anemometer (LDA) readings to be taken over the entire cross section of the flow, at regular downstream intervals. A schematic drawing of the flow chamber showing the location of the gas sampling points was included in the first annual report.

A commercial, smoke-generating liquid, sprayed onto a heated plate, has been found to generate adequate amounts of tracer smoke at a fairly steady rate. A smoke generator based on injection of this fluid onto a heated plate has been designed and is being fabricated. The smoke from this apparatus will be entrained into a flow of gas that will be directed through the cross-flow jets into the flow chamber. The smoke particles may also be adequate seed for the LDA velocity measurements. If, the smoke proves to be inadequate, additional 1-2 micron seed particles (sorbent) will also be injected into the mixing chamber through the cross-flow jets.

To obtain quantitative mixing rate measurements of the sorbent injection streams, a tracer gas (CO_2) will be introduced through the cross-flow jets, and the local concentration will be determined by extracting gas samples from the mixing duct with sample probes, and analyzing the samples for the local concentration of CO_2 in an on-line CO_2 analyzer. The concentration of CO_2 is directly related to gas mixture fraction, which is a direct indication of the extent of mixing between the two gas streams.

A method of extracting tracer gas samples from the flow was also designed and fabricated during the period. The design allows for extractions to be made along with the LDA measurements, over the entire flow cross section, at regular downstream intervals. The position of the probes will be fixed mechanically, to allow for replication of the experiments and to insure precise positioning at the desired extraction point. The system uses seven separate probes that can be selectively inserted into the duct to collect gas samples from a rectangular grid. A schematic drawing of this sampling system is shown in Figure II.H-1. Only one probe is to be inserted into the flow at Unused probes will be recessed into the flow chamber wall to keep a time. flow disturbances to a minimum. The probe will be attached to the on-line gas analyzer by a flexible plastic tube that can switched from probe to probe during the course of the experiment. The gas samples will be analyzed on-line with an infra-red CO₂ detector. Thus, all the data needed at one axial location can be obtained from a single flow test, without having to shut down the test facility. The gas sampling system has been designed, and fabrication has been nearly completed.

Previous research has shown (see Categen, 1987; and Kamotani, 1974) that the two most important criteria in the mixing of subsonic, crossflow jets are the jet-to-main-flow-diameter ratio, and the jet-to-main-flow-momentum-flux ratio. Both of these effects will be investigated in this part of the study. The lower sorbent injection limit is established by the minimum amount of sorbent which can be entrained in a given amount of gas, and the upper sorbent injection limit is established by the amount of gas and sorbent flow which would adversely effect the stoichiometry of the gasifier. Researchers have varied the sorbent-to-sulfur ratio between one and four (Lindgren and Pershing, 1987). The upper limit will model the worst case condition of a high sulfur coal, with a high sorbent-to-sulfur ratio.

A literature review in the areas of cold flow modeling and sorbent injection continued during the period. Cetegen et. al., (1987) have conducted similar cold-flow testing for sorbent mixing in a simulated, wall-fired, coalburning utility boiler. They found empirical jet relationships to provide preliminary estimates of sorbent injection parameters, and developed a method of coupling this jet mixing data with sorbent sulfation data to predict the



Figure II.H.1. Sample probe collar for tracer gas tests.

impact of sorbent injection on SO_2 capture. Kamotani and Gerber (1974), and Keffer and Baines (1963) have developed similar empirical relationships for jets injected into a cross flow. These relationships are being considered for use in this study to assist in predicting the behavior of the screent jets.

Component 2 -- Laboratory-Scale Reactor Modifications

This subtask component is aimed at modifying the laboratory-scale reactor to accommodate sorbent particle injection. The lower limit of the sorbent/sulfur ratio will be determined by the amount of sorbent which can be entrained in a given amount of gas while maintaining an adequate sorbent/sulfur ratio, and the upper limit will be determined by the amount of gas and sorbent flow which would overly dilute the gasifier effluent. One of the modular reactor sections will be modified to allow the sorbent to be injected perpendicularly into the main gasifier flow through either three or four injection ports uniformly positioned around the circumference of the reactor section. In addition, it will be necessary to design and construct a new pressurized feeder for sorbent injection, and connect the feed to an inert gas flow system that will be used to transport the sorbent to the crossflow injectors.

During the reporting period, a new research team (one M.S. candidate, and two undergraduate research assistants) was assembled, and training in operation of the reactor was begun. The gasifier research team carefully inspected the reactor and the gasification facility, and attempted two experimental tests using natural gas and air. The purpose of these tests was to gain familiarity with the equipment, and to determine if any repairs or improvements were necessary. The inspection and tests were very informative, and defective parts and equipment problems were identified. As experience is gained, operation with coal will be undertaken.

It was anticipated that there would be some problems with the facility, and that some maintenance would be needed even before modifications for sorbent testing could begin, since no maintenance had been done on the facility since the conclusion of the last gasification test program several months ago. Several problems with the facility were found; however, none of the problems was serious. Overhauling and maintenance for the entrained-flow gasitier was also initiated. Valves, tittings, and piping were cleaned or replaced along with the installation of new gaskets and O-rings. The primary feed tube was replaced. The exhaust gas flare was repaired. The exhaust system was disassembled and cleaned. Several thermocouples were replaced. Calibration of the instrumentation was also initiated during this quarter. Repairs are continuing to correct all of these problems.

Modifications to the facility are also proceeding. A rotary plate sorbent feeder that will be enclosed inside a pressure vessel was designed and is under construction. Figure II.H-2 presents a schematic drawing of the feeder. This feeder will permit the pulverized sorbent to be injected into the gasifier in an even and steady flow for a zero-to-twenty-atmosphere range of operating pressures. An eight-inch-inner-diameter, schedule-80 pipe will serve as the hopper and pressure vessel for the sorbent feeder. The feed rate will be varied by changing the rpm and/or the volume (depth and/or width) of the groove machined into the rotary plate.

Design work is proceeding on a flash tank for the gasifier exhaust system to allow noxious exhaust gases that are dissolved in the exhaust gas quench water at elevated pressure to be separated from the quench water. The gases will be discharged to the exhaust gas flare that is mounted on the roof of the laboratory building. This system will prevent the gases from entering the sewer system of the laboratory building where they could be vented into occupied work areas. Also, the current sampling system is being modified to eliminate the problem with the gas species dissolving in the quench water. This should also improve the accuracy of the test results for the gas species. Design of the modified reactor section that will incorporate the cross-flow sorbent injection jets was also initiated.

Component 3 -- Space-Resolved Sulfur and Nitrogen Pollutant Measurements

This subtask component is aimed at making detailed measurements of sulfur and nitrogen pollutants and char in the laboratory-scale reactor. Work on this subtask will follow the completion of Component 2.



Figure II.H-2. Pressurized rotary plate sorbent feeder and hopper.

<u>Plans</u>

Component 1 -- Sorbent Mixing Fluid Mechanics

During the next quarterly reporting period, the facility modifications will be completed, and testing will be initiated. Checkout testing will be initiated to gain familiarity with the system, and to expose any potential problems which need correction. The measurement devices used to quantify the mixing rate of the sorbent and gasification flows will be calibrated, along with the IR analyzer to insure accurate measurements. Testing with smoke injection will then be initiated. The smoke injection studies will provide information on jet momentum, size and location which result in good mixing of the cross-flow jets and the main flow. Jet flow rates will simulate calciumto-sulfur ratios ranging from one to four. Next, tracer gas measurements will be made to quantify the information obtained in the smoke tests and to provide more precise information on the level on mixing. Finally, LDA measurements will be made. The LDA will allow for direct measurement of the local mean and rms velocity of the gas streams in the cross-flow jets.

Component 2 -- Laboratory-Scale Reactor Modifications

Plans for this subtask component include: 1) additional experiments at elevated pressures with natural gas and air, and with coal and oxygen, to continue to develop familiarity and understanding of the gasifier operation, and to identify potential problems, 2) continued repairs to the facility to bring the gasifier into working condition, 3) installation of a sorbent feeder system, and 4) further checkout and training tests to develop the necessary familiarity with the facility, and to insure that all repairs and modifications have been properly accomplished. The installation of the facility modifications will be an ongoing activity as will the repair and inspection of the facility in preparation for the beginning of actual experimentation with sorbent injection.

Component 3 -- Space-Resolved Sulfur and Nitrogen Pollutant Measurements

The next quarterly reporting period will be spent in making repairs, performing maintenance on the facility, and in incorporating modifications to the facility to allow sorbent injection. Space-resolved sulfur and nitrogen pollutant measurements with or without sorbent injection are planned for a subsequent quarter.