

SECTION II. TASK 2. SUBMODEL DEVELOPMENT AND EVALUATION

OBJECTIVES

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

TASK OUTLINE

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

The literature search on transport properties during pyrolysis was completed. The review, performed by Eric Suuberg, is presented in Appendix A. Work was initiated on computing the optical properties of particles during the coal to char transformations. A paper was prepared for Combustion and Flame, it is included as Appendix B.

COAL CHARACTERIZATION

Characterization of the coal samples for this program was performed by quantitative FT-IR analysis, pyrolysis, and char reactivity. Six jars of coal were received from the Argonne National Laboratory for coals 1,2,4-7 listed in Table II.A-1. Due to the broad particle distribution, each jar was well mixed and a small representative sample was removed, handground and sieved to obtain the 200 x 325 mesh fractions.

Quantitative FT-IR Analysis

The six Argonne coal samples were subjected to FT-IR analysis using approximately 1 mg of dry ground sample in approximately 300 mg of KBr. A spectral synthesis routine was applied to the dry mineral matter and baseline corrected spectra (Figs.

II.A-1c -II.A-6c) to generate the organic functional group data which is shown in Table II.A-2. Table II.A-3 lists the mineral matter data.

To obtain optical properties for the coals CsI, pellets were prepared in addition to the KBr pellets. Figures II.A-1a and 1b - II.A-6a and 6b show the dry uncorrected KBr and CsI pellet spectra for the Argonne coals.

Pyrolysis in Thermogravimetric Analyzer (TGA)

Chars of the hand ground 200 x 325 mesh sieved Argonne coals as well as Montana Rosebud and Zap were prepared by pyrolysis using the TGA. With a N₂ flow of 400 cc/min and a N₂ purge flow of 40 cc/min, the coal particle temperatures reached 700°C and 900°C with heating rates of 30°C/min. Plots of the TGA pyrolysis runs are shown in Figs. II.A-7 - II.A-10.

Char Reactivity in TGA

The chars used in this study were prepared by pyrolysis as described above. The char reactivity measurements were made by employing a non-isothermal technique using the TGA. With an air flow of 40 cc/min and a N₂ purge flow of 40 cc/min, the samples were heated at a rate of 30°C/min until 900°C was reached. The resulting critical temperatures are listed in Table II.A-4 and are also plotted in Figs. II.A-11 and II.A-12 as functions of oxygen in the parent coal.

Pyrolysis in Entrained Flow Reactor (EFR)

The 200 x 325 mesh sieved fractions of 5 of the Argonne coals were vacuum dried at 5°C for 1 hour prior to EFR runs. The pyrolysis results reported in Table II.A-5 were accumulated using 2 analytical techniques: 1) FT-IR Calibration Program and 2) Gas Chromatograph.

The coal was fed at rates of 1 1/2 - 2 g/min with a N₂ carrier. Particle residence time was approximately 0.66 seconds with the injector height position adjusted to 24" and the furnace operated at 1400°C.

Pyrolysis data for the Pittsburgh #8 is not yet available. Due to its swelling properties, difficulty was encountered when running it through the reactor.

2nd quarter METC/BYU 5/87 WP#25

PLANS

Continue coal characterization, develop viscosity model, and add mass transport effects to FG/DVC model.

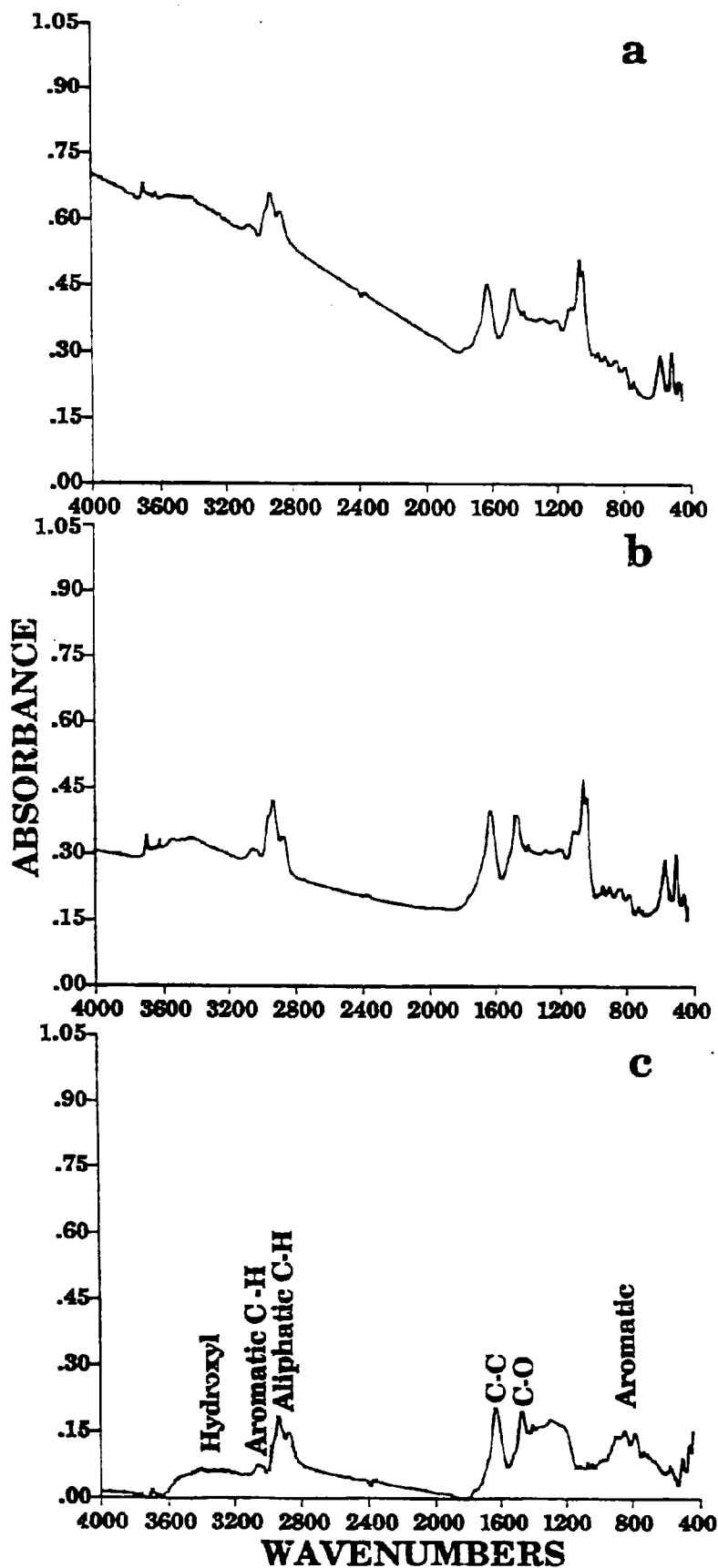


Figure II.A-1. FT-IR Spectra of Upper Freeport Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

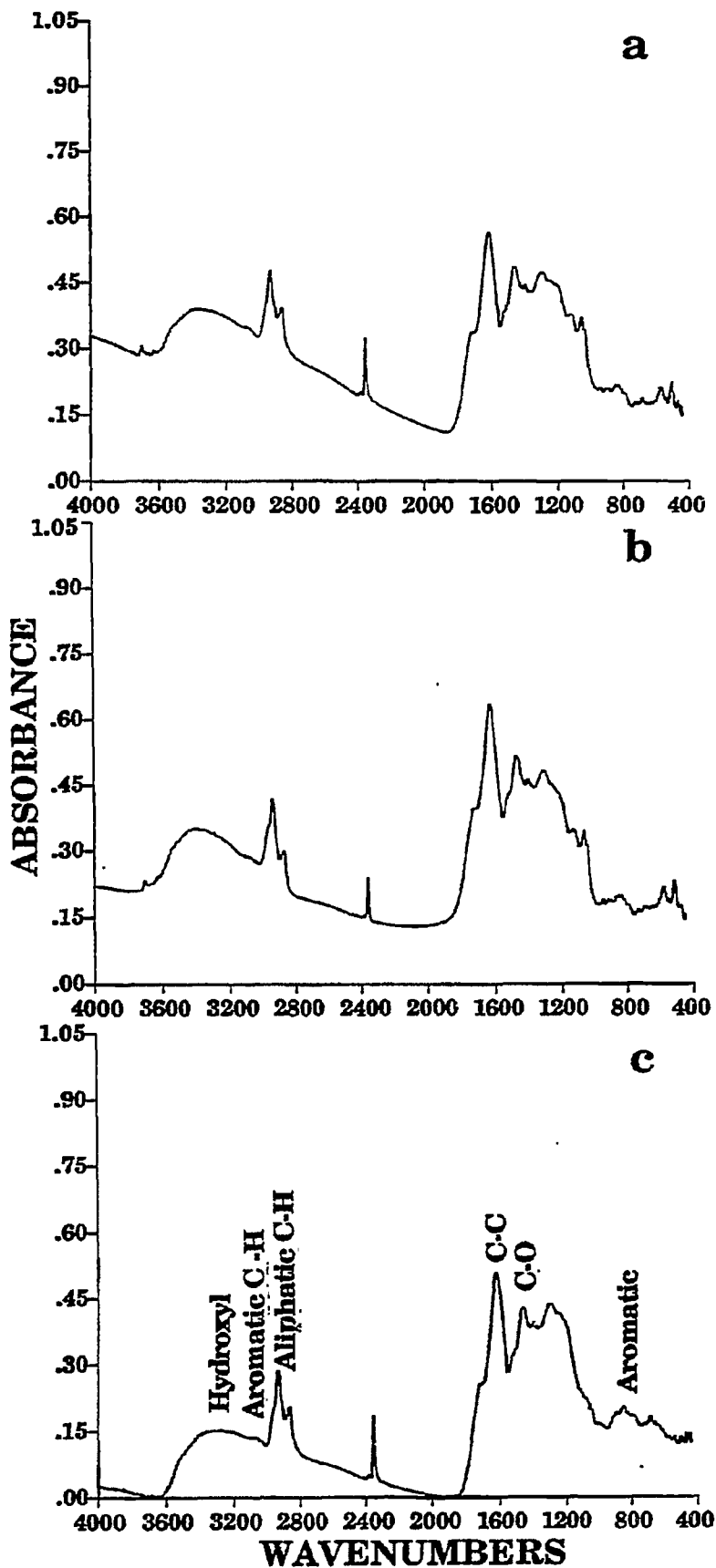


Figure II.A-2. FT-IR Spectra of Wyodak Subbituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

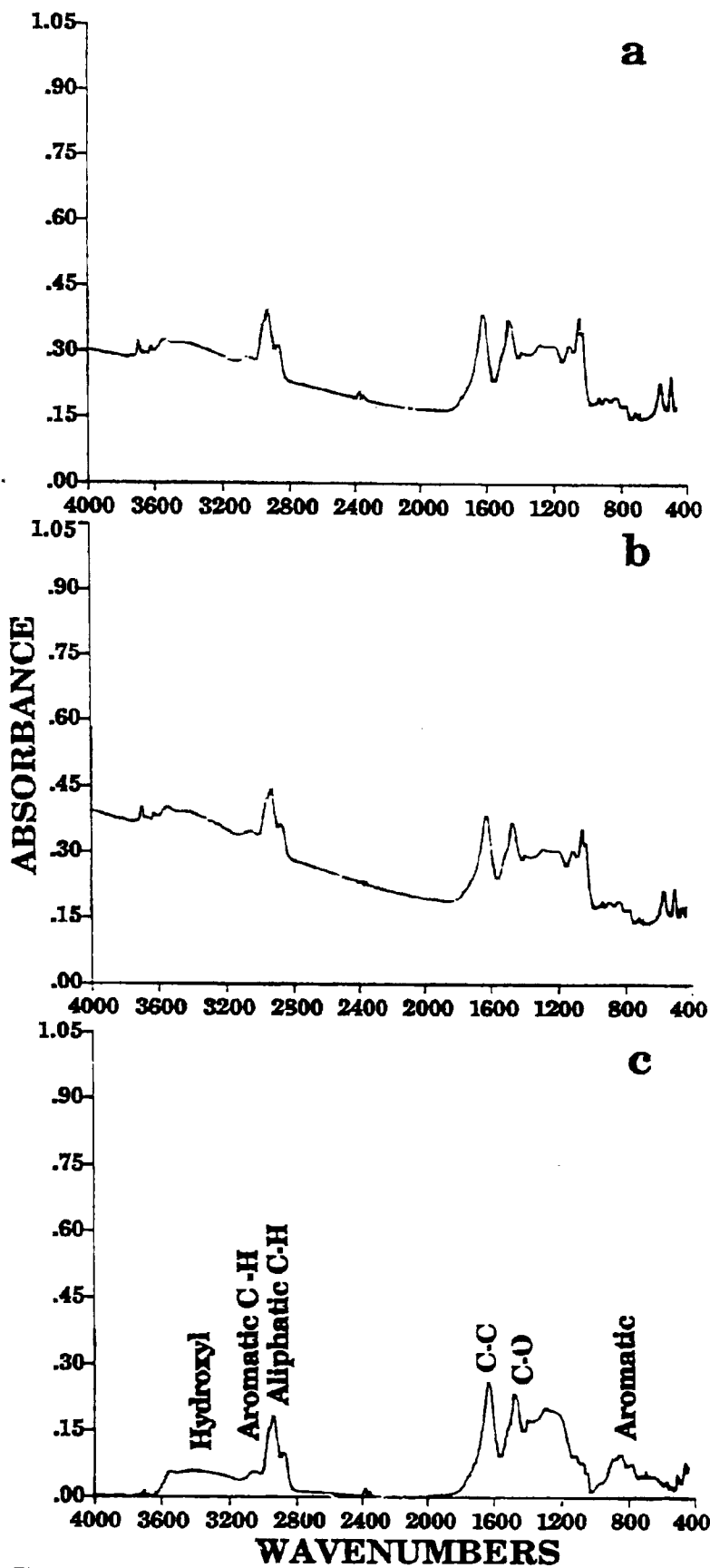


Figure II.A-3. FT-IR Spectra of Pittsburgh Seam Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

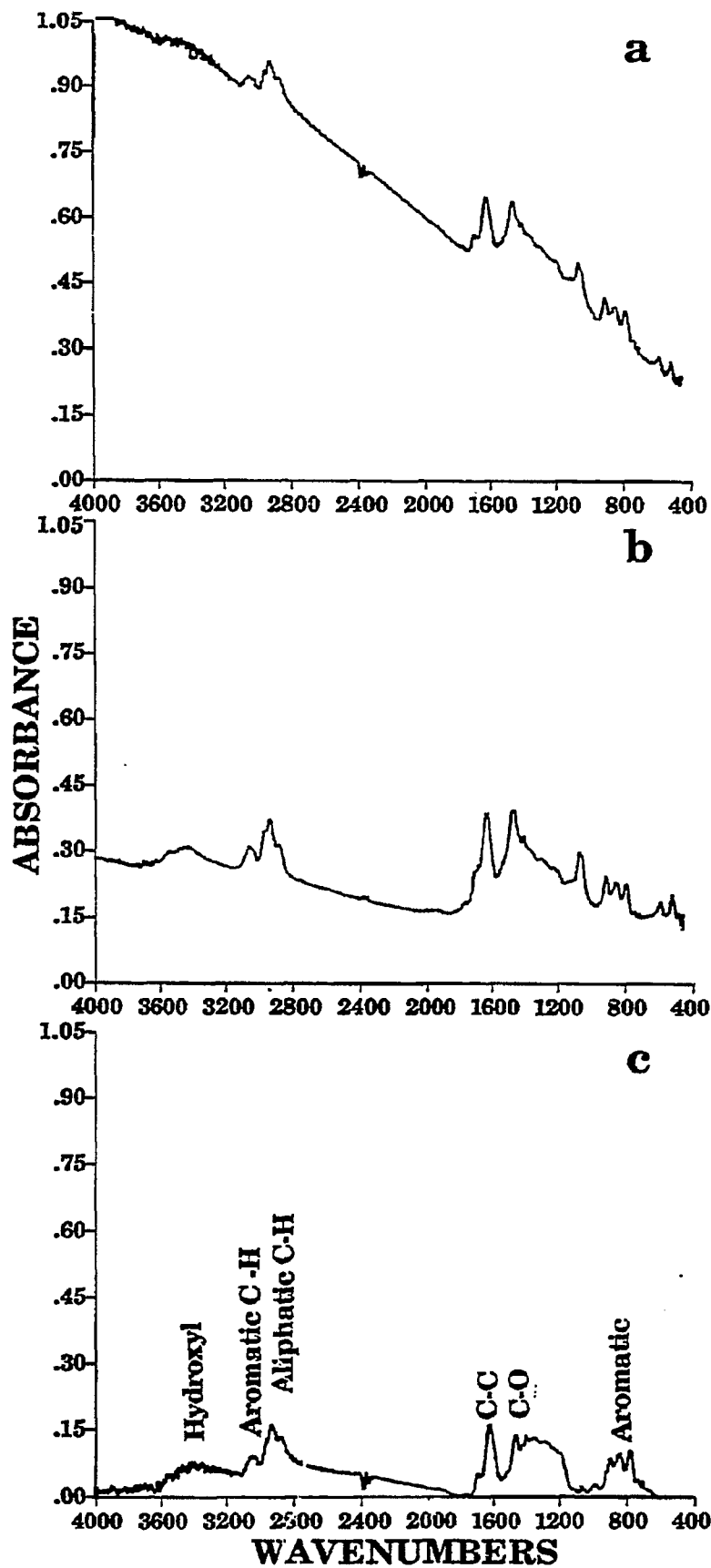


Figure II.A-4. FT-IR Spectra of Pocahontas Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

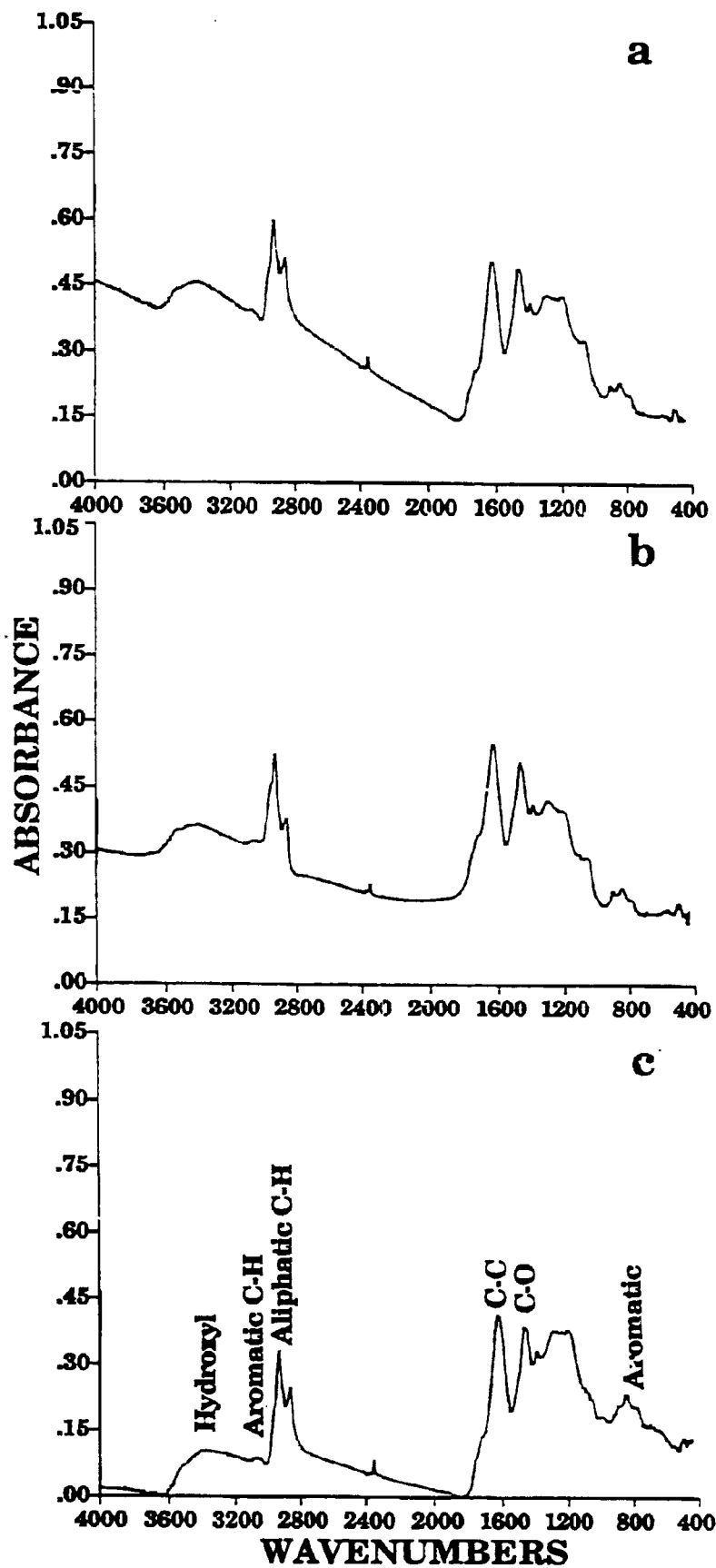


Figure II.A-5. FT-IR Spectra of Utah Blind Canyon Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

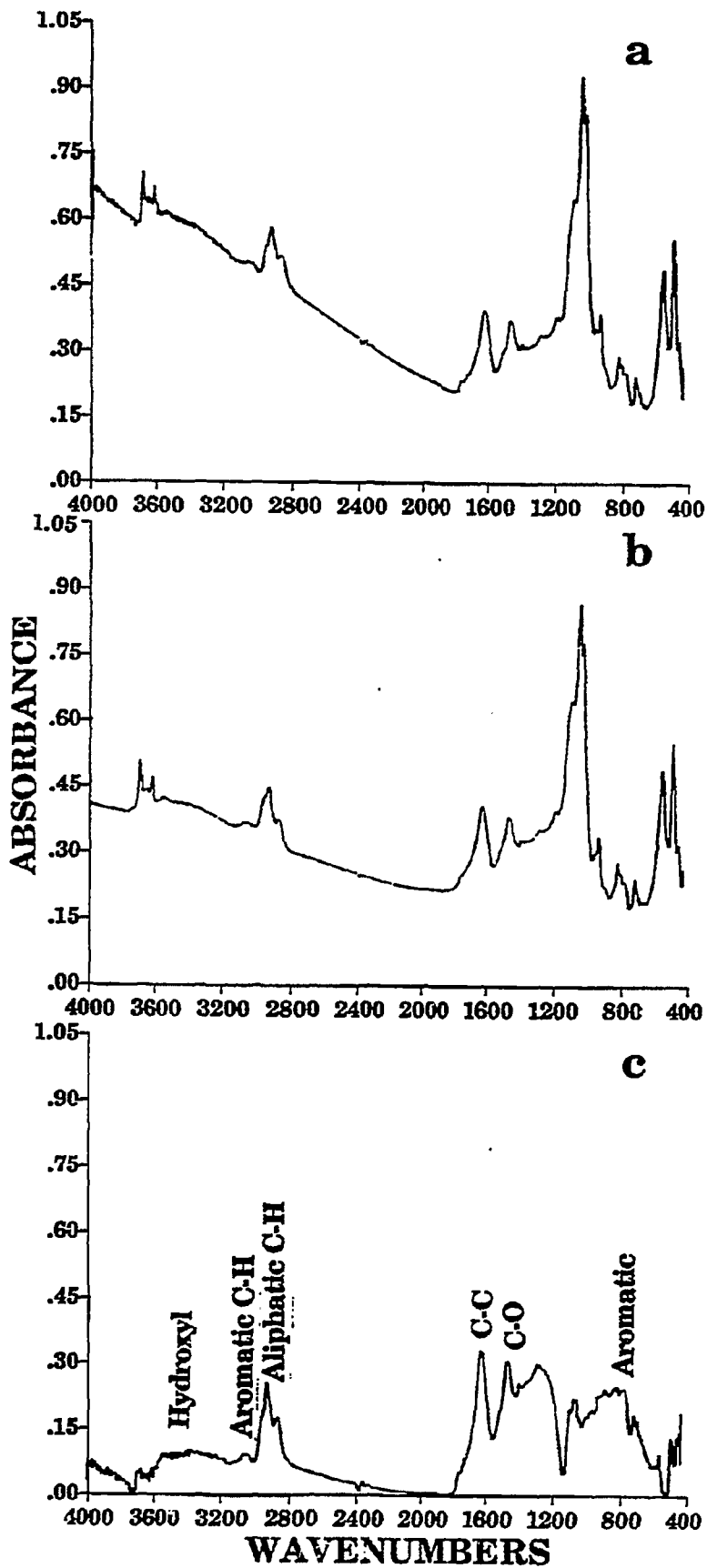


Figure II.A-6. FT-IR Spectra of Upper Knawha Bituminous Coal. a) KBr, b) CSI, and c) KBr Pellet, Mineral Matter Corrected.

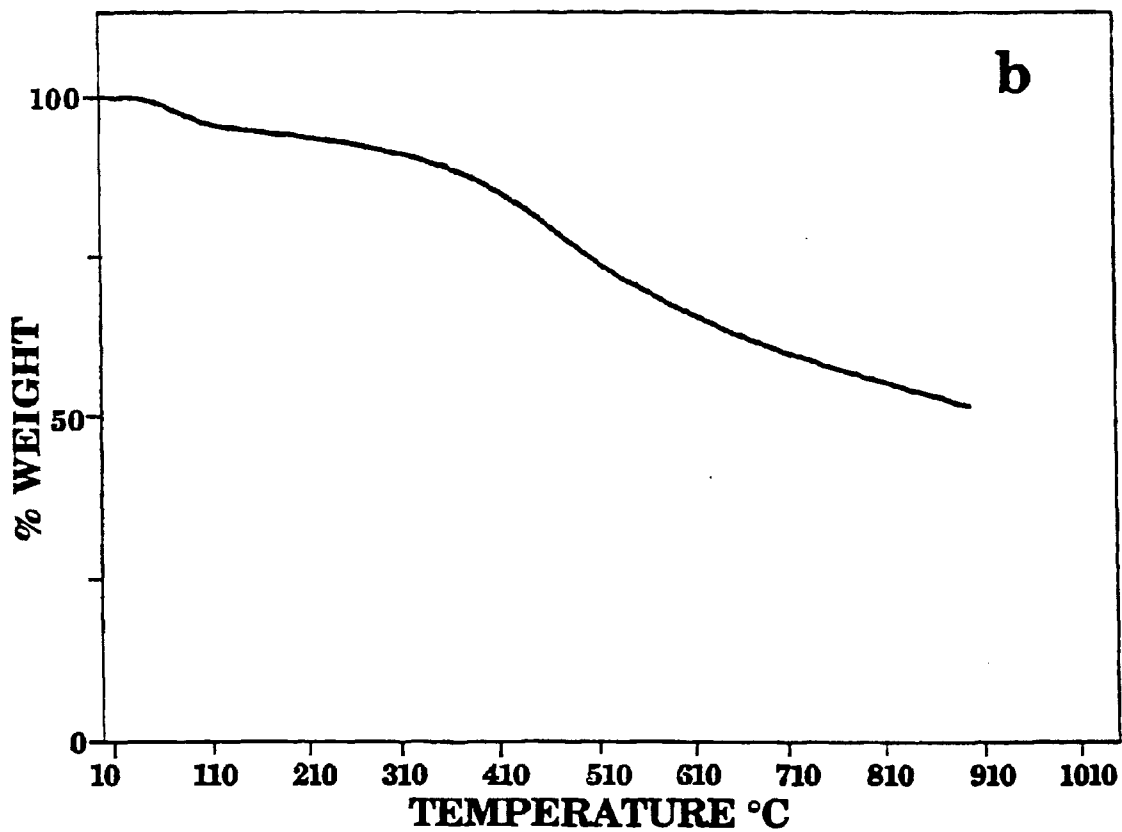
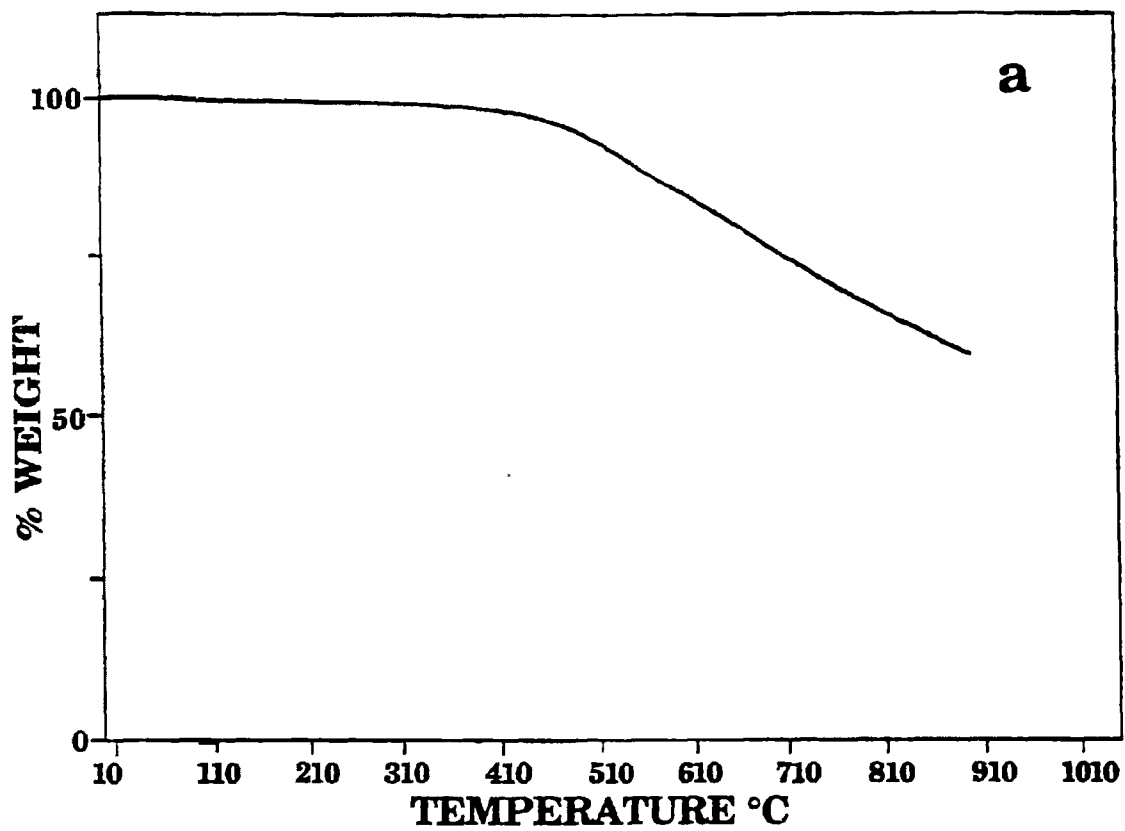


Figure II.A-7. Pyrolysis of a) Upper Freeport Bituminous Coal and b) Wyodak Subbituminous Coal in TGA at 30°C/min to 900°C in N₂.

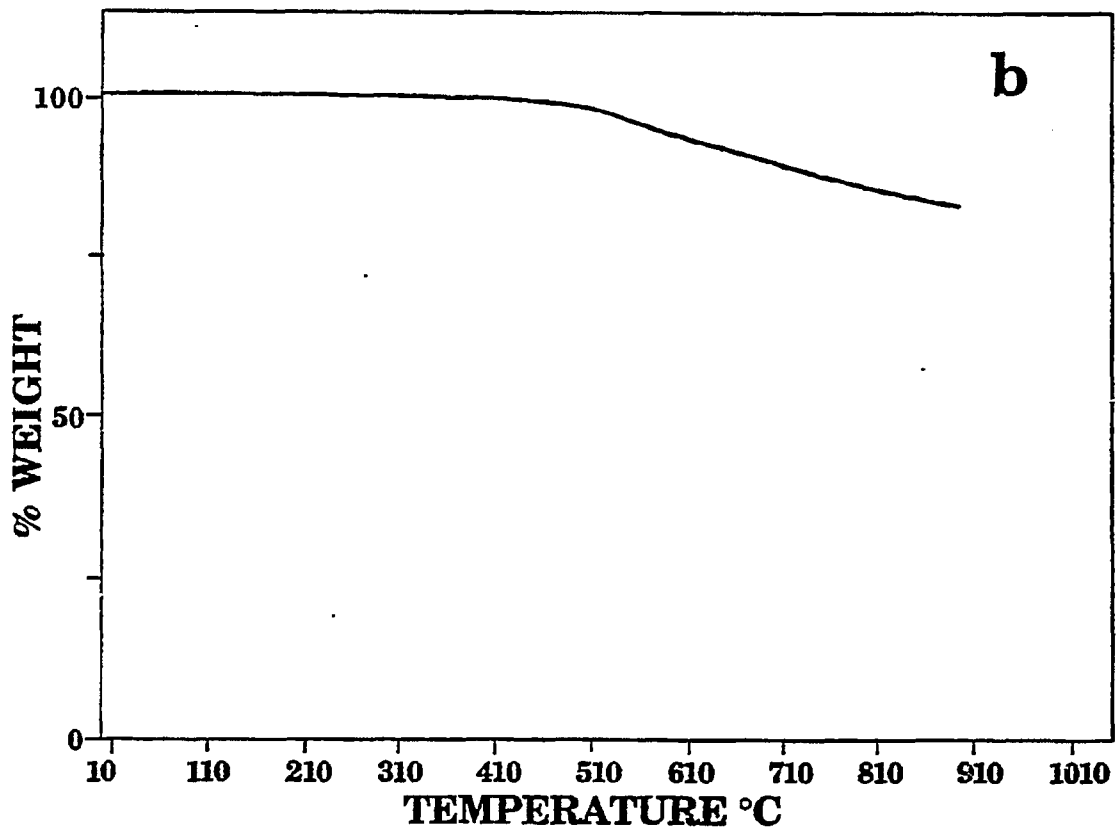
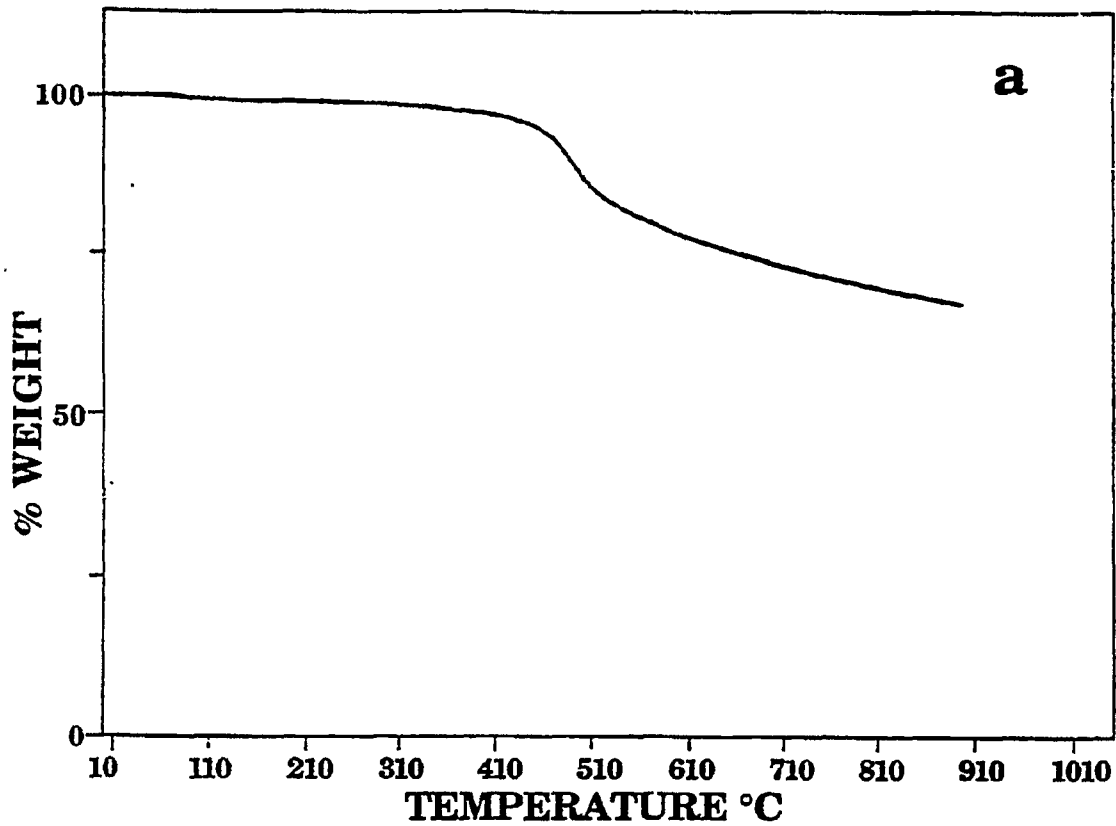


Figure II.A-8. Pyrolysis of a) Pittsburgh Seam Bituminous Coal and b) Pocahontas Bituminous Coal in TGA at 30°C/min to 900°C in N₂.

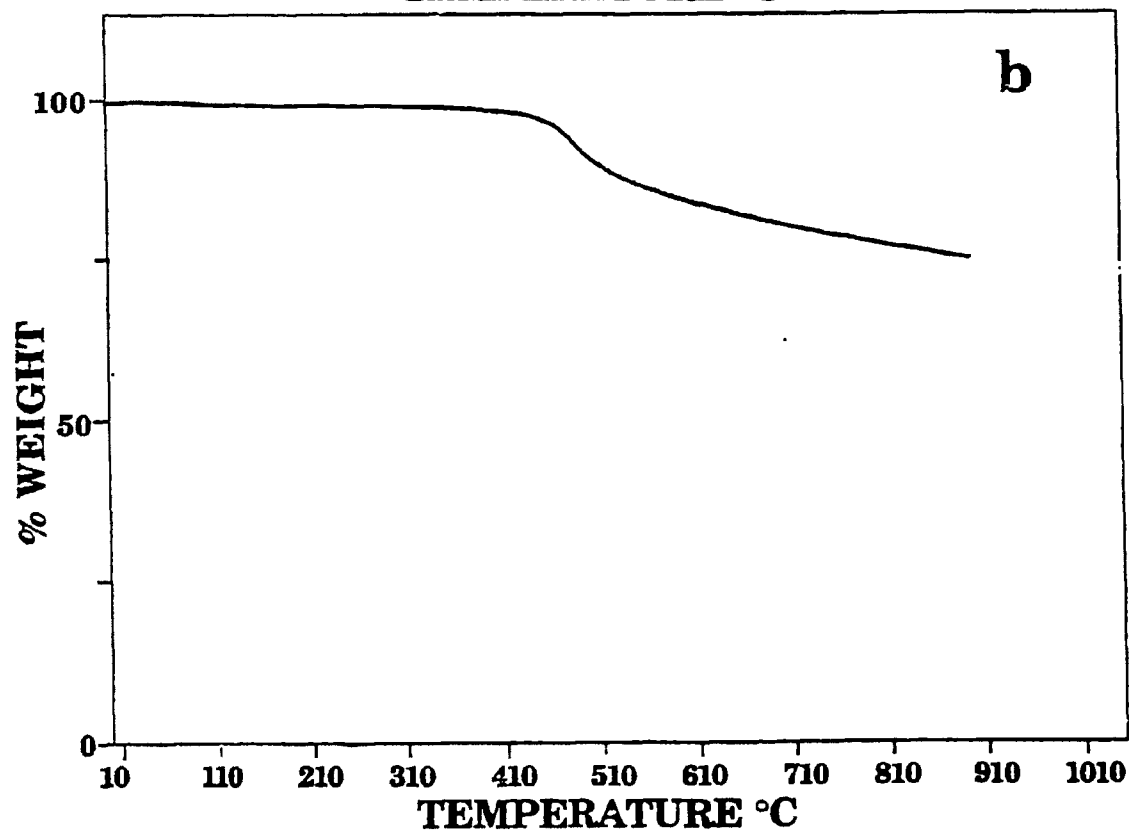
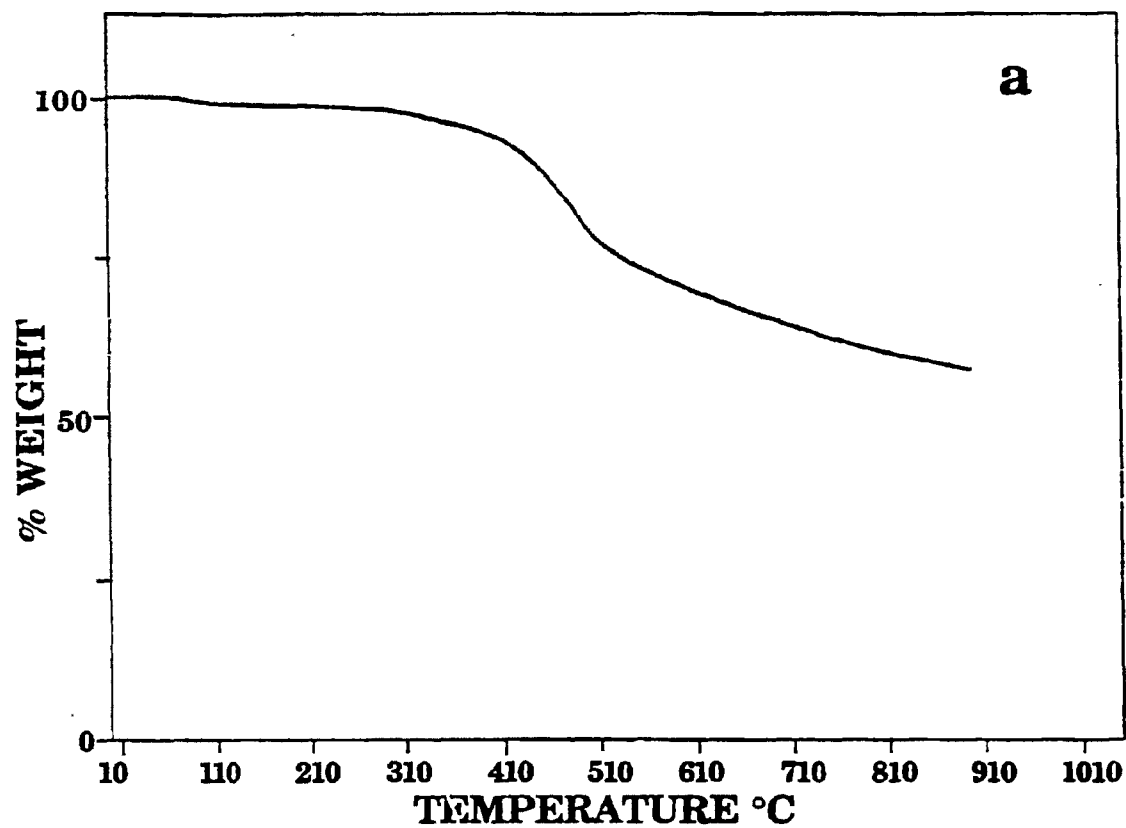


Figure II.A-9. Pyrolysis of a) Utah Blind Canyon Bituminous Coal and b) Upper Knawha Bituminous Coal in TGA at 30°C/min to 900°C in N₂.

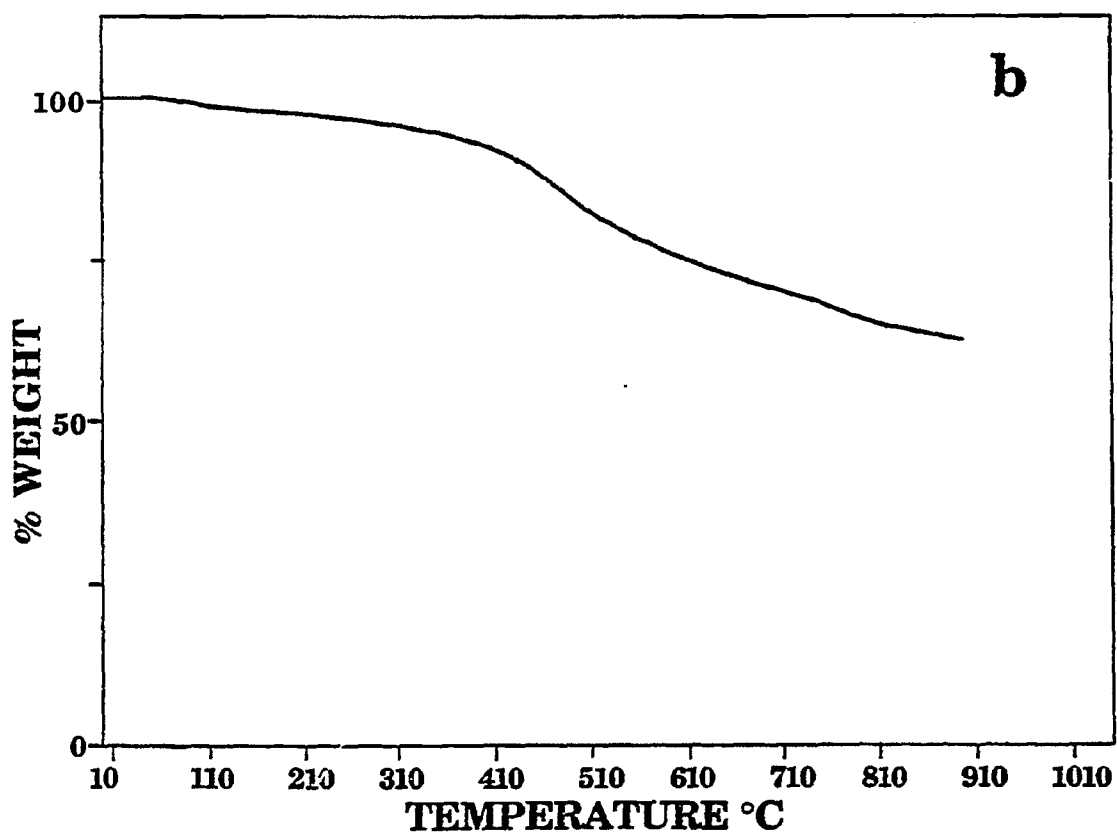
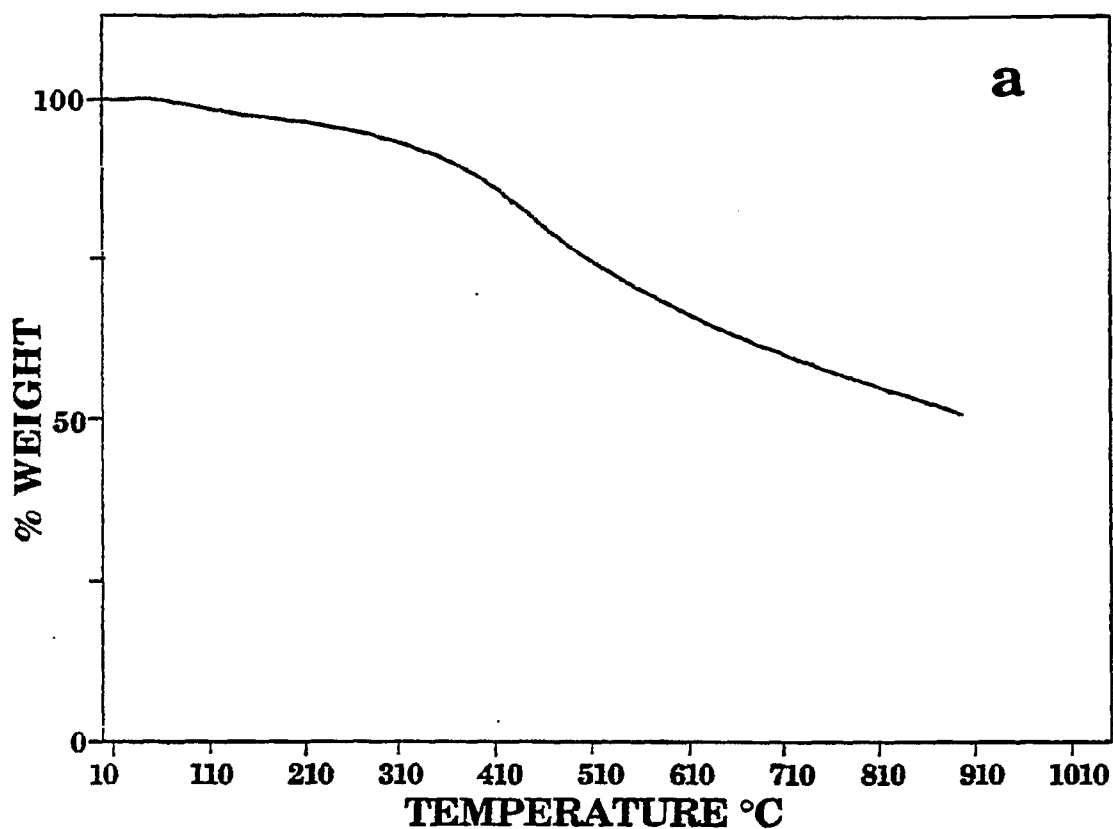


Figure II.A-10. Pyrolysis of a) Zap North Dakota Lignite and b) Montana Rosebud Subbituminous Coal in TGA at 30°C/min to 900°C in N₂.

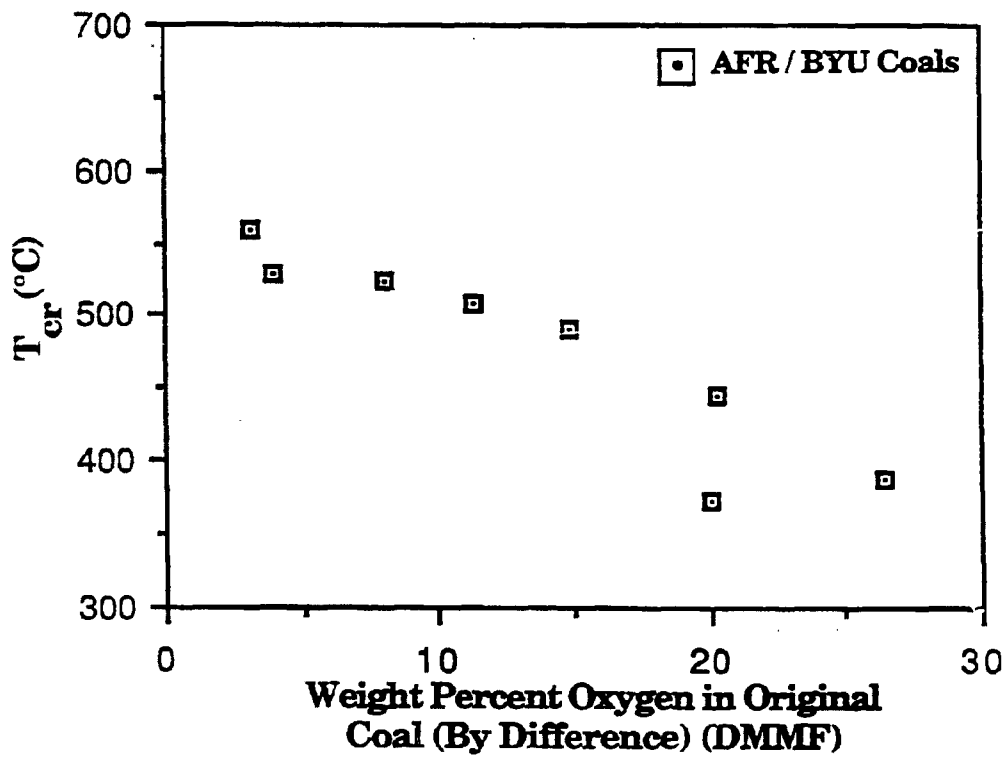


Figure II.A-11. Variation of Reactivity with Coal Rank for Chars Prepared by Heating Nitrogen at 30°C/min to 700°C.

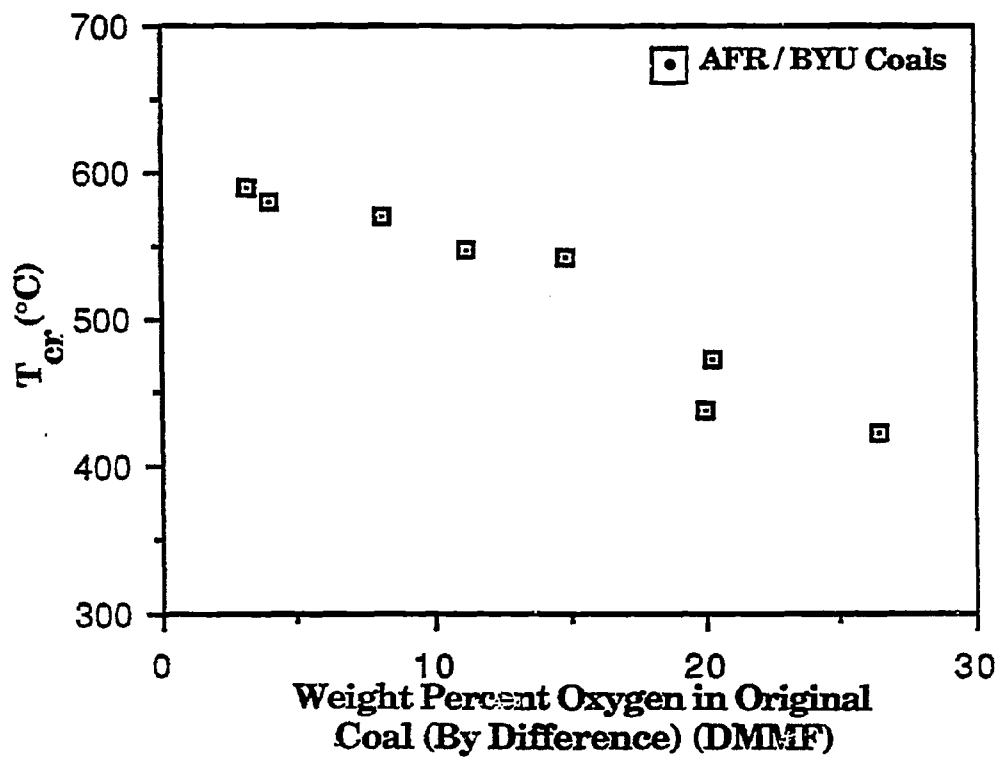


Figure II.A-12. Variation of Reactivity with Coal Rank for Chars Prepared by Heating Nitrogen at 30°C/min to 900°C.

TABLE II.A-1
 AFR/BYU Program Coal Samples

Coal Name	Rank	Mine/Location	Source
1. Upper Freeport	Medium Volatile Bituminous	Texas	ANL
2. Wyodak	Subbituminous	Wyoming/S. Dakota	ANL
3. Illinois #6	High Volatile Bituminous	Macoupin, Illinois	ANL
4. Pittsburgh #8	High Volatile Bituminous	Washington, PA	ANL
5. Pocahontas #3	Low Volatile Bituminous	West Virginia	ANL
6. Utah Blind Canyon	High Volatile Bituminous	Utah	ANL
7. Upper Knawha	Medium Volatile Bituminous	Eastern, WV	ANL
8. Texas Lignite	Lignite	Texas	ANL
9. North Dakota	Lignite	Mercer, N. Dakota	UND
10. Montana	Subbituminous	Rosebud, Montana	METC

TABLE II.A-2
DATA ON COALS (WT PERCENT DMF)*

	<u>Hydrogen</u>				<u>Aromatic Hydrogen</u>			<u>Carbon</u>	<u>Carbonyl</u>	<u>Oxygen</u>		
	H _{al}	H _{oh}	H _{ar}	H _{total}	H _{ar} /H _{total}	1 Adj	2 Adj	3 or More	C _{al}	Units (Abs. x cm ⁻¹)	O _{oh}	O _{ether}
UF	2.64	0.14	1.59	4.57	0.35	0.50	0.59	0.50	18.93	0.12	2.23	1.11
Y	3.10	0.34	1.74	5.18	0.34	0.54	0.78	0.42	20.67	0.73	5.50	4.53
PITT	3.02	0.11	1.57	4.70	0.33	0.54	0.63	0.40	20.13	0.39	1.75	1.44
POC	1.96	0.13	2.19	4.28	0.51	0.68	0.75	0.76	13.06	0	2.06	0.40
UT	4.65	0.20	1.96	6.81	0.29	0.52	0.89	0.55	31.00	0.77	3.25	4.00
W	3.77	0.19	1.59	5.55	0.29	----	----	----	25.13	0.33	3.09	2.48

* Except Carbonyl: Relative Peak Area

TABLE II.A-3
DATA ON COALS (DRY WT PERCENT)

<u>Minerals</u>					
<u>Sample</u>	<u>Mixed Clay</u>	<u>Quartz</u>	<u>Calcite</u>	<u>Kaolin</u>	<u>Total</u>
1. UF	9.06	0.86	1.98	2.63	14.53
2. WY	3.52	1.34	0.59	2.00	7.45
4. PITT	5.65	0.64	1.49	2.90	10.68
5. POC	4.91	0.53	3.88	0.45	9.76
6. UT	3.31	0.48	2.23	0.24	6.26
7. WV	21.40	4.79	1.08	8.44	35.71

TABLE 11.A-4
DATA ON CHAR REACTIVITY

Coal Name	Abbreviation	Rank	WT % Oxygen in Original Coal Sample by Difference (DMMF)	0-900°C		0 700°C	
				T _{cr} °C	N ₂ Char Ash %	T _{cr}	N ₂ Char Ash %
1. Upper Freeport	UF	Medium Volatile Bituminous	4.0	579	19.72	529	14.74
2. Wyodak	WY	Subbituminous	20.0	437	16.27	372	11.62
4. Pittsburgh #8	PITT	Low Volatile Bituminous	8.1	569	12.41	524	8.46
5. Pocahontas #3	POC	Low Volatile Bituminous	3.2	590	5.81	560	5.57
6. Utah Blind Canyon	UT	High Volatile Bituminous	14.9	542	7.09	491	2.81
7. Upper Knawha	WV	Medium Volatile Bituminous	11.3	547	38.25	509	36.20
9. North Dakota	Zap	Lignite	26.5	422	11.80	387	9.08
10. Rosebud		Subbituminous	20.3	472	19.12	447	22.14

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) Measure and correlate fundamental reaction rate coefficients for pulverized-coal char particles as a function of char burnout in oxygen at high temperature. The effect of high pressure will be investigated. 2) Provide fundamental kinetic rate measurements of sulfur species with sorbents for a range of stoichiometries under laminar, high-pressure conditions.

The specific objectives for the quarterly reporting period include:

1. Organize the interdisciplinary research team.
2. Meet regularly to address technical aspects of the subtask and to coordinate activities.
3. Review appropriate literature in pertinent areas.
4. Develop the experimental test plan for both elements of the subtask.
5. Survey existing high pressure reactors in preparation for design of a high pressure reactor for this study.
6. Develop a preliminary design for the high pressure reactor.

ACCOMPLISHMENTS

The research team was organized and consists of two senior investigators, a doctoral student and an undergraduate research assistant. A second graduate student is being sought. Development of the detailed experimental program was initiated, and design of a small-scale high pressure reactor was also begun.

Research Team Organization

This subtask study was initiated during the last two months of this quarter. The research team was organized with two senior investigators (faculty from the Chemistry and Mechanical Engineering Departments), a mechanical engineering doctoral candidate, and a mechanical engineering undergraduate research assistant. A Chemistry graduate student is being sought to join the group. The research team has met weekly during the reporting period.

Experimental Plan and Reactor Design

The team met twice with the project director to discuss the general modeling approach for char oxidation and sulfur capture with sorbents, as a foundation for developing the detailed experimental plan.

Literature pertaining to char oxidation measurement and modeling, as well as modeling sorbent capture sulfur, was identified and reviewed. Additional publications which describe high pressure reactor design and operation have also been sought. This work will assist in finalizing the experimental plan and the design of a dual purpose reactor for both experimental programs.

One senior investigator visited AFR, at no expense to this contract, to become acquainted with the high pressure reactor facility and instrumentation which was developed by AFR for other projects.

High pressure reactor facilities at Penn State, Morgantown Energy Technology Center, Stanford and MIT have been identified to be investigated to assist in reactor design. Some publications which describe the facilities at Stanford and MIT have been obtained.

PRELIMINARY REACTOR DESIGN - The potential problems of operating a small scale combustion facility at high temperature (1700 K) are exacerbated by the high pressure (up to 20 atm) requirements of this study. Preliminary design contemplates a vertical, small bore cylindrical downfired reactor in which electric or backfired heating is used to achieve isothermal conditions. Two senior design mechanical engineering students have assisted in the design of reactor heating and particle feeding.

Other Activities

Members of the research team participated in the annual ACERC technical review meeting, the NSF review of ACERC first year activities as well as an annual technical review of this study for AFR, all of which were held at BYU.

PLANS

The specific main objectives for the next quarter include the following:

1. Finalize preliminary high pressure reactor design.
2. Identify a location for the reactor with access to advanced optical, non-intrusive instrumentation.
3. Finalize preliminary high pressure experimental program for char reactivity and sorbent capture of sulfur.

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) 528-9806

OBJECTIVE

The objective of this subtask is to develop and evaluate by comparison with laboratory experiments, an integrated and compatible submodel to describe the 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 were begun in the transparent wall reactor (TWR). Attention was focused on what controls ignition - heterogeneous or homogeneous oxidation. The initial evidence points on the latter. A paper was prepared on the initial observations for the International Coal Combustion Symposium. The manuscript is presented as Appendix C.

PLANS

Continue investigation of ignition and soot formation.

II.D. Subtask 2.d. - Ash Physics and Chemistry Submodel

Senior Investigator - D. Billy Yang
Advanced Fuel Research, Inc.
87 Church Street, East Hartford, CT 06108
(203)528-9806

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 second quarter, a literature search was initiated to identify the important effects of coal minerals in gasification. Work was also performed on designing the methods for ash collection and analysis.

LITERATURE REVIEW TITLE

Critical Issues on the Physical Transformation of Minerals

Volatilization and chemical interaction of mineral matter are particularly important during coal conversion. The formation of slag and deposits of minerals depends on the particle size, its chemistry, and its physical-chemical behavior during coal conversion processes. Most of the work done in the area of predicting slagging and fouling behavior of ash of a pulverized coal has been based on the mean ash composition of the whole coal.

The literature (Markowski, G.R. et al., 1980; McElroy, M.W. et al., 1980; Quann, R.J. et al. 1982; Neville, M., et al, 1981; Haynes, B.S. et al. 1982) indicates that the fly-ash derived from the transformation of the mineral matter in coal during combustion is bimodally distributed with respect to particle size. The large particle size (0.5 to 50 microns) correspond to the mineral residue of completely burned pulverized coal particles. Particles within the submicron size range, formed from the vaporization and subsequent condensation of a small fraction of the mineral matter (Quann, R.J., et al., 1982; Neville, M. et al., 1981; Flagan, R.C. et al., 1978; Quann, R.J. and Sarofim, A.F., 1982). A methodology is required to determine the mineral composition distribution in coal from which the behavior of the ash formation in coal conversion may be predicted.

Most of the work done in this area has been carried out under a combustion environment. Very little work has been done under gasification conditions. The objective of this work is also to determine ash transport in the reactor, ash radiative properties and the potential for slagging and for fouling in the gasification reactor.

Critical Issues on Catalytic Effects of Minerals

The presence of the inorganic minerals can either facilitate or impede coal gasification: The alkali, alkaline earth and some transition metals may have a catalytic effect on the gasification process (Hippo, E.J., 1977). Some inorganic compounds such as sulfur can prevent gasification by poisoning the catalyst, whereas silicon oxide can convert the alkali and other metals to silicates and become inert for its catalytic effect. A methodology is required which determines the mineral size and composition distribution so that the behavior of individual particles may be predicted for its catalytic effect during

gasification or combustion.

Background on Ash Fouling, Slagging and Corrosion Studies

Most of the work on ash slagging and fouling has been done under combustion conditions. This work is being considered as background for the corresponding processes in gasification.

In pulverized-coal fixed boilers the mineral matter in the coal is released into the furnace gases as fly ash and vapors. This material may form insulating and corrosive deposits on the heat transfer surface. The process of deposit initiation and growth usually involves either liquids formed on the tube, such as condensed alkalis ('sticky tube mechanism'), or low viscosity supercooled impinging fly ash particles ('sticky particle mechanism'). It is proposed (Boow, J., 1972) that this low viscosity material may be provided by an alkali-enriched surface layer, formed by an alkali-ash reaction in either the char or the furnace gases. The ash particles whose outer layer is enriched in sodium may readily wet the heat transfer surface, allowing rapid bond formation due to the dissolution of the surface iron oxide at the particle surface. Most research done in this area has focused on the study of the correlation of the physical behavior of ash with fouling and slagging formation.

Some empirical correlations have been established between the slagging behavior of a coal with such properties as viscosity of the coal ash (Reid, 1971; Watt, 1969b; Watt, 1969a; Urbain, et al., 1981; Schobert, et al., 1985), temperature of critical viscosity (Sage, W.L. et al., 1960; Hoy, et al., 1964) and fusion temperature (Corey, 1974), and surface tension (Falcone, 1986). Empirical factors such as slagging factor (Attig et al., 1969), fouling factor (Attig et al., 1969), dolomite percentage (Babcock & Wilcox, 1971), ferric percentage (ASME, 1974) and base-to-acid ratio (Reid, W.T., 1971) have been devised. Most of these indices of slag behavior are based on tests of the mean coal ash.

Background on Catalytic Effect of Minerals on coal Gasification Studies

The catalytic effect of minerals on both gasification and combustion have been reported. For example, a correlation between char reactivity and amount of CaO present in the char has been established and these results strongly suggest that gasification was being catalyzed by the presence of calcium (Hippo, et al., 1975). The addition of calcium to char by ion exchange has shown an increase of

the reactivity linearly with an amount of calcium added. For example, Wilks (1974) and Johnson (1974, 1975) reported that ion exchange Ca and Na are able to increase the reactivity of lignite chars in both steam and hydrogen coal gasification. Some studies also showed that the removal of the mineral components of the coal by acid treatment lead to a decrease in char activity (Jenkins et al., 1973; Linares, et al., 1979; Otto et al., 1979). However, with coals of high rank the reverse effect was observed, probably as a result of an increase in the surface area and porosity on the demineralization (Jenkins, 1973). Hank and Hutterer have reported that addition of iron, by impregnation, also increases the activity of the coke in steam gasification. It is generally concluded that in the presence of mineral matter, the catalytic effect is dependent upon the concentration and dispersion of inorganic species which act as specific carbon gasification catalysts.

However, the minerals in coal have also some undesirable effects. In catalytic coal gasification, the original mineral content in coal has been shown to influence the catalyst performance. The interaction of the added catalyst with minerals of the coal during gasification have been studied by Kuhn et al. They concluded that during the gasification, the added catalyst reacts with the minerals to form a new crystalline phase. Similar evidence has also been shown by Sulimma et al. (Sulimma, et al., 1981) that in K_2CO_3 catalyzed gasification, a considerable part of this catalyst is deactivated by reaction with the mineral matter of the coal.

Work needs to be undertaken to predict the catalyst behavior of minerals of coal and its interaction with added catalysts, based on its composition, particle size and distribution.

Background on Catalytic Effect of Minerals on Combustion Studies

Pohl has reported that the effect of mineral matter Na, Ca, on the rate of combustion can be as high as a factor of 100 at low temperature. A review has shown that one of the major uncertainties in the rate of char combustion is the catalytic influence of mineral matter (Pohl, et al., 1983). Other experiments have also shown that small amounts of mineral matter can accelerate the rate of char combustion (Smith, et al., 1972; Essenhigh, 1981; Patai, et al., 1952). At present, insufficient information is available to assess the influence of catalysis by mineral matter at coal combustion temperature, therefore, work needs to be undertaken to determine the acceleration of char combustion by minerals under combustion environments.

EXPERIMENTAL STUDY OF MINERAL MATTER TRANSFORMATION

The objective is to determine mineral transformation in the reactor, its radiative properties, its potential for slagging and fouling of the reactor, and its catalytic effect on gasification or combustion.

Experimental Methods

1. The sample of coal will be reacted in the EFR, laboratory scale burner, TWR and TGA furnace.

2. Experimental methods, similar to the procedures described in the literature (Neville and Sarofim, 1985) for ash particle collection will be designed and implemented

The ash sample collection system consists of an Andersen Model Mark III, eight stages stack sampler and a cyclonic preseparator. During the sample collection, all particulate products from the burner will be continuously collected and quenched by a water-cooled collection probe. From the probe, the ash particles enter a cyclonic preseparator for separating larger particles, the remainder enter the cascade impactor for aerodynamic size classification of ash particles. Depending on the gas flow velocity and temperature, eight discrete particle size cuts can be obtained. For example, in a given set of conditions of temperatures at 300°F and flow rate at 0.6 ACFM, eight discrete size cuts with mean diameters of 13.6, 8.6, 5.6, 4.0, 2.5, 1.3, 0.8, and 0.54 μm will be obtained. The submicron particle (<0.54 μm) generated by the vaporization and subsequently condensation of ash, pass through the impactor for collection and isolation on a back-up glass fiber filter.

3. Techniques will be developed for measuring solid and vapor species concentration for both organic and inorganic constituents. For example, quartz, kaolin and mixed clay in coal will be analyzed by transmission FT-IR. The inorganic minerals will be analyzed by a coal microanalyzer which uses an electron beam to excite characteristic x-rays from mineral components. The correlated spatial distributions for elements, Na, Mg, Al, Si, K, Ca, Ti, Fe and S, can be obtained. These data will allow a better determination of ash fusion temperature than can be obtained from average ash elements. The vapor phase of

organic species can be obtained by TGA/EGA. The method for studying vapor phase of inorganic species by using FT-IR will be explored. The known inorganic vapors by feeding inorganic compounds into H_2/O_2 flame, will be used for calibration.

4. Temperature-time history measurements in a practical gasifier (or burner) will be made using emission FT-IR measurements. This method has been demonstrated successfully by AFR.

5. Analysis of the bulk and discrete size ash particle's chemical and physical properties will be performed. Chemical compositions will be obtained by x-ray, SEM, AA. Physical - density, size porosity, surface area, viscosity, etc.

6. The interaction of minerals with known additives during ash particle formation will be determined. The fate of added minerals, such as Na, K, Ca, will be examined by tracing their distribution in different particle size ranges.

7. The catalytic effect of minerals as compared with the demineralized coal will be determined, and their gasification rates for different coal ranks measured.

8. The effect of operation conditions, e.g. temperature, flow rate, pressure, oxygen concentration, on ash behavior and gasification performance will be measured.

9. The correlation between mineral content and fouling and slagging, combustibility and gasification rate will be developed.

PLANS

Install ash collection probe and initiate experiments in the TWR.

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.

ACCOMPLISHMENTS

A review of heat and mass transport effects in coal pyrolysis was undertaken as part of the literature review for this subtask. Given the large particles used in fixed-bed gasifiers, it is likely that transport effects nearly always play a role. However, it is also true that at the very high heat fluxes encountered in some gasification and combustion processes, gradients may be important for particles in the pulverized fuel range. Since mass transfer effects are well covered in the review by Eric Suuberg (see Appendix A), this review has focused primarily on heat transport processes.

Heat and Mass Transport Effects in Coal Pyrolysis

INTRODUCTION - The first objective was to examine previous experimental and modeling studies of heat transport. A close examination of this work indicated widely different assumptions about the values of coal physical properties and how these change with temperature and the extent of pyrolysis. Consequently, it was decided that a review of literature on coal physical properties would also be necessary.

EXPERIMENTAL STUDIES - In many studies it is not always clear whether the effects of particle size, for example, are due to heat transfer, mass transfer or both. Some of the recent work in this area has been that of van Heek and coworkers at Bergbau-Forschung, using a Curie-Point pyrolysis reactor (Wagner et al., 1985; Eklund and Wanzl, 1981). This work was a continuation of earlier work, reviewed by Juntgen and van Heek (1979), where parametric studies were done to define a "critical particle diameter (d_c)" as a function of heating rate where the reaction changed from chemical reaction control to transport control. In the recent studies using the Curie-point reactor, the d_c was determined as a function of pressure also. In this reactor, the coal sample (5-6 mg) was placed in a ferromagnetic sample tube and heated with an induction heater at rates from 500 to 10000 Ks⁻¹. The final pyrolysis temperature was determined by the Curie-point of the sample tube (the temperature at which the tube material becomes paramagnetic, thus avoiding further absorption of energy, which was usually around 800° C.

The determination of d_c was done by varying diameter at a given pressure or heating rate until a diameter was reached where pyrolysis is sensitive to particle size. An example of this is shown in fig. II.E-1 from Wagner et al. (1985). The results from such experiments are plotted as in Fig. II.E-2, where d_c is shown to be an inverse function of pressure and heating rate. These results were interpreted by Wagner et al. as a mass transfer effect. They reasoned that at high heating rates the instantaneous rate of product formation inside the particle increases until it exceeds the escape rate of volatiles from the particle. Similarly, as the ambient gas pressure increases, it retards the escape of volatiles. Although the studies done by Wagner et al. were done at relatively low heating rates of 500 - 10,000 Ks⁻¹, the values of d_c were high enough to suggest that heat transfer played as important a role as mass transfer. However, the inverse correlation with pressure, which would not be expected for a pure heat transfer effect, suggests that mass transfer effects were contributing to the observed results.

Some early work on heat transfer control was done in Germany by Peters and Berltng (1965). They developed the following empirical equation to explain an apparent zero-order reaction observed for particles of 250 - 1000 μ m diameter pyrolyzed at high heating rates (10⁴ K/s) in a fluidized bed reactor:

$$\frac{dy}{dt} = 0.03 \frac{(T_a - 330)}{d^{0.25}} \quad (1)$$

This result was attributed to the propagation of an evaporation front through the particles with the rate being controlled by the overall temperature gradient. The relatively weak dependence on particle diameter, however, suggests that this was not the only mechanism operating.

Later studies were done by Koch et al. (1969) and Schwandtner (1971) where a shrinking core model was used to describe the pyrolysis rate:

$$\frac{dv}{dt} = (V_g(t) - V(t)) \cdot k_0 \exp(-E/RT) \quad (2)$$

where

$$V_g(t) = V_g \left(1 - \frac{(1 - k_t t)^{3/2}}{d}\right) \quad (3)$$

and

- t = time
- V_g = volume to be released in one shell
- V = total volume released at time t
- d = diameter of coal particle
- k_t = thermal conductivity

Some calculations using this expression are shown in Fig. II.E-3. The gas evolution is shifted toward higher temperatures with increasing particle size and for particles larger than 0.4 mm (400 μm) in diameter, tailing is observed. For particles of 1 mm in size (not shown) the rate of gas evolution becomes almost invariant with time (reaction order of zero) which implies that heat transport control is dominant.

Versions of this equation were used by Koch et al. (1969) and Schwandtner (1971) to calculate for a given heating rate the particle size at which the mechanism changes from chemical reaction to heat transport control. These calculations are shown in Fig. II.E-4 along with some experimental measurements.

Entrained Flow Reactor Studies - Recently, several investigators have presented evidence which indicates that pyrolysis rarely occurs isothermally in entrained flow reactors at temperatures much above 600°C. Maloney and Jenkins (1984) showed that the extent of pyrolysis in furnace tests from 1073 to 1273 K was strongly dependent on the carrier gas composition (N₂ or He). Similar conclusions were

reached by Tsai and Scaroni (1984) and Sundaram et al. (1983). Recent entrained flow reactor studies at AFR (Solomon et al., 1986; Serio et al, 1987) which have included actual particle temperature measurements, has provided further proof of the non-isothermal nature of the pyrolysis process in such reactors. These studies have also shown the difficulty in obtaining accurate kinetic data for pyrolysis kinetics in the absence of temperature measurements.

Heated Grid Reactor Studies - The heated grid reactor has been used by numerous investigators. The assumption is made that the coal particles follow the temperature of a thermocouple bead which is next to or attached to the electrically heated screen. This is done despite the knowledge that the thermal properties and the thermal response of the coal particles is significantly different from the thermocouple bead. To our knowledge, no heat transfer analysis has been published in the open literature to validate this technique. A qualitative study was published by Freihaut et al. (1982) indicating that the heat effects associated with tar release perturbed the coal time-temperature history. A modeling study was reported as part of an MIT Ph.D. thesis (Oh et al., 1985) which indicated that the assumption was not valid under vacuum conditions but appeared to be alright at atmospheric and higher pressures at heating rates of 1000°C/s and lower. However, these conclusions rested on several assumptions which need further testing and scrutiny.

Laser Pyrolysis Studies - In relatively few cases have kinetic studies been done with laser heating. Given the high heat fluxes and the difficulty in omnidirectional heating, the particle temperature profile is nearly always nonuniform. Hertzberg et al. (1987) have demonstrated the progression of a pyrolysis wave through the particle by examining particle sections. This phenomenon is the likely explanation for the low apparent pyrolysis kinetics obtained by Witte and Gat (1983). In these experiments the surface temperature was measured by three color pyrometry. It is likely that the temperatures at which pyrolysis was occurring (inside the particle) was much lower.

While lasers are useful for demonstrating the effect of non-isothermal pyrolysis at high heat fluxes, they are of relatively little use in purely kinetic studies.

MODELING STUDIES - Since much of the work on devolatilization in the last several years has included rapid pyrolysis of fine (pulverized) particles or slow pyrolysis of large particles, most pyrolysis studies and models have not been concerned with internal transport effects. However, with the relatively recent interest in

pyrolysis under fluidized-bed or moving-bed conditions, where large ($> 1\text{mm}$) particles are pyrolyzed at relatively high heating rates (10 to 1000 K/s) the interest in internal transport has increased.

Models for simultaneous heat and mass transport for devolatilization have been developed by Mills et al. (1975) and James and Mills (1976) for plastic coals and by Devanathan and Saxena (1985, 1987) and Bliek et al. (1985) for non-plastic coals. Freihaut et al. (1977) and Agarwal et al. (1984a, b) have developed coupled reaction and heat transport models for nonplastic coals.

Heat Transfer/Reaction Models - A model by Freihaut et al. (1977) considered the combined influence of heat transfer, heats of reaction and chemical kinetics on intraparticle temperature gradients during pyrolysis. Not many details of the model have been published in the open literature. Mass transfer effects were neglected.

Agarwal et al. (1984) have developed a general devolatilization model for large non-plastic particles under fluidized bed conditions which includes coupled reaction and heat transfer. Good agreement was obtained for devolatilization times measured for Mississippi lignite. A simpler version was developed for the pure heat transfer control regime (Agarwal et al., 1984b). Neither version includes a treatment of mass transfer or secondary cracking effects.

Heat Transfer/Mass Transfer Reaction Models - Workers at UCLA (Mills et al., 1976) developed a model for particles undergoing rapid pyrolysis which included a fundamental description of heat transport starting with the conservation equations. A consecutive reaction scheme, similar to that of Chermin and van Krevelen (1957) was used. The porosity of the particle was assumed to be governed by a foaming law and the particle was allowed to swell and shrink, accordingly. The thermal conductivity was assumed to decrease linearly with the decrease in particle density. The model was primarily concerned with the variation in thermal response of a particle with the variation in parameters such as particle diameter, ambient temperature, heating rate, heats of reaction and activation energies. The equations were solved numerically by a finite-difference method. The model was successful qualitatively in describing many important features of coal pyrolysis, as shown in Figs. II.E-5 and II.E-6 for the effect of particle size on the instantaneous and cumulative gas evolution with time. Figure 7 shows the effect of particle size on the average gas evolution rate. The kinetic control limit (no diameter dependence) is evident for the lowest ambient temperature ($T_e = 972\text{ K}$).

For higher temperatures, the kinetic limit would only occur for particles smaller than 30 μm . The curves in Fig. II.E-7 approach the 45° slope for heat transfer control for the large particle sizes.

Mills et al. (1976) also evaluated the work of Peters and Berling (1965), discussed above, who injected 1000 - 1500 μm particles into a fluidized bed at temperatures ranging from 600 to 1100°C. They noted that the relatively weak diameter dependence observed by Peters and Berling ($d_0^{-0.26}$) is evidence that the experiments were primarily controlled by chemical reactions and not dominated by heat transfer, as was suggested by Peters and Berling.

The model of Mills et al. was improved in a later paper by James et al. (1976). In order to account for pressure and particle size effects, models were included to describe (1) the porous structure of a coal particle; (2) the flow of gases through voids and pores, and the resultant pressure distribution, (3) evaporation of tar species and (4) cracking of gaseous species as they percolate through the pores. Again, the qualitative predictions of the model were in good agreement with expectations, but this version of the model was never rigorously validated against experimental data.

Devanathan and Saxena (1985,1987) have developed a model which considers both heat and mass transfer effects for large nonplastic coal particles. The later version of this model was improved to include secondary cracking reactions of tar so that particle size effects could be predicted. The authors also included a sensitivity analysis which indicated that results were very sensitive to the assumed internal diffusivities for the volatiles species. The Thiele modulus (ratio of reaction rate/diffusion rate), the Lewis number (ratio of thermal diffusivity/mass diffusivity) and the heat transfer Biot number (ratio of internal to external heat transfer resistance) were identified as crucial parameters in determining devolatilization times. One problem with analyses such as the one done by Devanathan and Saxena is that not much attention was paid to the choice of devolatilization parameters or the temperature dependence of physical properties like the heat capacity and thermal conductivity. They chose the kinetic parameters of Kobayashi et al. (1977) which have recently been shown by Jamaladdin et al. (1987) to severely underestimate devolatilization times.

A model which is as comprehensive as the one by Devanathan and Saxena has recently been developed by Blik et al. (1985), also for non-plastic coals. This model includes transient devolatilization kinetics, intraparticle heat and mass

transport, and secondary deposition of volatiles. Model predictions were made for variations in particle size, ambient pressure, and heating rate on the tar, gas and total volatile yield during devolatilization. The authors made comparisons to their own data and data from the literature and usually obtained at least qualitative agreement. However, the model has so many adjustable parameters that this agreement does not necessarily validate their assumptions about the controlling mechanisms. The authors did do a good job in attempting to account for the variations in physical parameters with temperature.

PHYSICAL PROPERTIES - It was expected that there would be variations in the pyrolysis kinetic parameters chosen in different modeling studies. However, significant variations in assumed physical properties were also observed and variations in these properties with temperature and extent of pyrolysis are often neglected. What follows is a preliminary evaluation of literature on the key physical parameters important in a heat transfer analysis.

Specific Heat - The values of the specific heat used in heat transfer calculations are typically in the neighborhood of 0.25 to 0.30 cal/g°C. While these values are appropriate for room temperature, they are significantly low at elevated temperature. The literature in this area has recently been reviewed by Merrick (1983, 1987) and will not be repeated here.

Merrick developed a new model for the specific heat of coal and coke which is based on the Einstein form of the quantum theory specific heat description of solids. The theory led to an equation which reasonably describes the temperature and composition dependence of the specific heat of coal. This model predicts a maximum specific heat for coal which is nearly twice the room temperature value. Some predictions of this model are shown in Fig. II.E-8. The neglect of the significant rise in the specific heat with temperature is primarily responsible for the large endothermic heats of carbonization reported by Kasperczyk and Simonis (1971) and Agroskin (1972) of 272 and 250 cal/g, respectively. It is obvious that accurate models and measurements of the specific heat are a prerequisite to accurate measurement of the pyrolysis heat of reaction.

Heats of Reaction - The heats of reaction of coal have been studied by differential thermal analysis (DTA), which generally indicates a succession of endo and exothermic reactions which correspond to evolution of different products. The value of DTA has been called into question because of lack of agreement among different studies.

One of the earliest calorimetric studies was that of Davis and Place (1924) who used an adiabatic twin calorimeter to study heats of reaction of various American coals and arrived at values ranging from +37 to -14 cal/g. In general, exothermic reactions were found to be more pronounced in high-oxygen coals and at temperatures below 500°C.

The determination of the heat of pyrolysis requires assumptions about the specific heat of the vacuum dried coal and the resultant char along with an allowance for the loss of moisture and the presence of ash. Most of the variations in the literature can be accounted for by differences in assumptions about the relative specific heats. Usually, the specific heat of coal and char are assumed to be the same. However, recent work by Merrick (1983) has clearly demonstrated that this is not the case.

Merrick's model for the specific heat shows a maximum value at about 500°C which is supported by recent experimental data. His observations suggest that the apparently high endothermic reaction heats reported in some papers between 400 and 600°C (Kasperczyk and Simonis, 1971; Agronskin et al., 1972) can probably be explained solely in terms of sensible heat requirements.

Merrick (1983, 1987) calculated net reaction heats of 111, 147, and 156 cal/g (exothermic) for 15, 25, and 35 wt% volatile matter coals, respectively. His values depend upon certain assumptions about the heat of combustion (or equivalently, heats of formation) of the coal, char, and tar).

Calorimetric studies using DTA methods have been reported by Mahajan et al. (1976, 1977) and recently by Hefta et al. (1986). Hefta et al. estimated the heat of pyrolysis of Zap, Indian Head Lignite to be between 17 and 26 cal/g (exothermic) through temperatures up to 580°C. This compares with a value of 28 cal/g reported by Mahajan et al. (1976, 1977) for the same coal. Both of these studies assumed the specific heats of coal and char were equal (coal is higher) so it is not surprising that the values are lower than those calculated by Merrick (1983, 1987).

Thermal Conductivity - Literature studies on the thermal conductivity of coal are rather sparse. The literature in this area has also been reviewed by Merrick (1983, 1987). All of the experimental measurements show a rise in thermal conductivity with increasing temperature which has been attributed to: a) radiant heat transfer across pores and cracks and b) changes in the conductivity of the

coal due to pyrolysis, c) changes in the intrinsic conductivity with temperature. It is likely that at temperatures below 600°C, where most of the measurements have been made, the first effect is relatively unimportant. Evidence for the second effect comes from the fact that the room temperature conductivity of coke is about twice as high as the value for the raw coal (depending on carbonization temperature). The variation of the thermal conductivity of a solid with temperature depends on the type of material being considered. The conductivities of most pure metals decrease with temperature, whereas the conductivities of nonmetals increase (Bird et al., 1960). The trends in thermal conductivity usually parallel those of electrical conductivity. Since coals fall in the nonmetal category, much of the large rise in conductivity observed at temperatures below 600°C is likely to be due to this effect.

Merrick proposed the following equation:

$$1/k = \left(\frac{C}{1.47} + \frac{H}{0.0118} \right) \frac{(273)}{T}^{0.5} \text{ mK/W} \quad (4)$$

where T is the absolute temperature (K) and C, H are the mass fractions of carbon and hydrogen. This equation assumes the contributions for each element are additive, as was the case for the specific heat. Note the strong effect of the hydrogen concentration. The temperature dependence is consistent with values reported for pure amorphous carbon, as shown in Fig. II.E-9. The constants in the equation were adjusted to fit room temperature measurements for pure carbons and coals.

Emissivity - The spectral emittance or the emissivity (the average emittance over wavelength) must be known to calculate the rate of particle heatup and energy radiated by the particle during pyrolysis. For small particles, the spectral emittance is usually not measured. Rather, it is calculated using the complex index of refraction, $N_{\gamma} = n_{\gamma} + ik_{\gamma}$, from the standard equations of electromagnetic theory. For spherical particles these calculations can be performed using Mie theory (Bohren and Huffman, 1983).

Unfortunately, some controversy surrounds the value of k_{γ} for coal (Brewster and Kunitomo, 1984). Large discrepancies in the value of k_{γ} have been reported in the literature ranging from less than 0.05 (Brewster and Kunitomo, 1984; Huntjens and van Krevelen, 1954) to more than 0.3 (Foster and Howarth, 1968; Blokh, 1974). Brewster and Kunitomo (1984) have suggested that a possible reason for these

discrepancies is that measurements of k_v for coal using reflection techniques are inaccurate due to an inherent limitation in the ability to get sufficiently smooth, and homogeneous coal surfaces. Using a transmission technique for small particles in KBr, they obtained values of k_v 0.05 over most regions of the infrared spectrum between 400 and 4000 cm^{-1} . If the previously measured values of k_v are too high, then values of emissivity based on them are also too high.

Absorptivities (equal to emissivity) for coal particles were recently measured by Grosshandler and Monteiro (1982). But the authors point out that their analysis is valid only for the higher values of k_v reported by Foster and Harworth (1968). The analysis is not valid for the values of k_v reported by Brewster and Kunitomo (1984).

AFR has recently developed a new method for on-line, in-situ monitoring of particle streams to determine their spectral emittance, chemical composition, size, and temperature (Best et al., 1985; Solomon et al., 1986,1987). The technique uses a FT-IR spectrometer to perform both emission and transmission (E/T) spectroscopy for a stream of gas suspended particles. The technique has been applied to measure spectral emittance of coal. Measurements on a variety of samples show that coal of pulverized particle size is not grey, having values of emittance near 0.9 for some regions of the spectrum but has values substantially less than one in many regions. The spectral emittance is dependent on rank, particle size, and the extent of pyrolysis, approaching a highly absorbing grey-body for char, anthracite, or large particles. The measured emittances were, in general, much lower than expected, confirming the results of Brewster and Kunitomo (1984).

Transpiration Cooling - A fact that is often not recognized or neglected in discussions of heat transfer in rapid pyrolysis processes is the particle "blowing" correction. The mass transport of volatiles away from the surface of a pyrolyzing particle will impede the transfer of heat to the particle. This principle is used in cooling rocket nose cones upon reentry. This phenomenon has been discussed by Reed et al. (1980) for the case of biomass pyrolysis but there are few mentions of it in the coal pyrolysis literature.

Reed et al. (1980) cite calculations which indicate that the heat transfer coefficient can be reduced to less than 10% of its original value under conditions of strong transpirational cooling. Of course it is also true that radiation heat transfer will not be affected by mass transfer unless the gases being formed are opaque at the active wavelengths.

A good example by Reed and Diebold (1984) is the fact that a water drop boils ten times faster in a skillet at 100°C than in a skillet at 600°C. This is known as the Leidenfrost phenomenon. The excess source temperature forms a gaseous film of water which insulates the drop from the hot surface. This illustrates the point that the important fact is the amount of heat transferred to the surface and not necessarily the source temperature.

The magnitude of the blowing correction can be determined for a hypothetical spherical particle in a stagnant gas from film theory:

$$\text{Nu}/\text{Nu}_0 = B/[\exp(B)-1] \quad (5)$$

where Nu_0 is the Nusselt number for heat transfer in the absence of blowing and B is related to the total gas production from the particle by the following expression:

$$B = r C_{p_g}/(2\pi d k_g) \quad (6)$$

where r is the total gas production rate, C_{p_g} is the gas heat capacity, d is the particle diameter and k_g is the gas thermal conductivity.

Smoot and Smith (1979) have considered the blowing correction and note that the correction derived from film theory can lead to large errors in many cases since the assumption of a stagnant film on the surface of the particle usually does not hold. They cite a model developed by Hoffman and Ross (1972) which is reported to be valid for Schmidt numbers between 0.7 and 10 and for Reynolds numbers up to 400.

$$\text{Nu}/\text{Nu}_0 = \exp(-0.6 B) \quad (7)$$

Solomon et al. (1986) have recently used the above correction scheme in modeling heat transfer in rapid pyrolysis experiments up to 935°C. They noted that the maximum correction to the calculated particle temperature was 7°C.

Kalson (1983) has considered the effect of vapor efflux from a spherical or flat particle on heat transfer from a hot gas. He concluded (erroneously) that the magnitude of the correction factor depended on geometry. He also suggested that the correction factor used by James and Mills (1976) in modeling heat transfer during pyrolysis was incorrect. These errors resulted from an incorrect definition

2ndqtrly metc/byu may, 1987 wp 25

of the heat transfer coefficient for the two cases and were pointed out in subsequent communications by Stewart (1984), Mills (1984), and Krishna (1984).

PLANS

Continue literature review and analysis for heat and mass transfer effects.
Prepare a paper for publication.

NOMENCLATURE

d = particle diameter, mm

E = activation energy, Kcal/mole

k_0 = preexponential factor, min⁻¹

m = heating rate, K/min

Nu = Nusselt Number for heat transfer

ϕ = foaming constant (m²s/kg)

t = time, s

T_a = ambient temperature, °C

T_e = ambient temperature, K

T_0 = initial particle temperature, K

v = volatiles mass, g

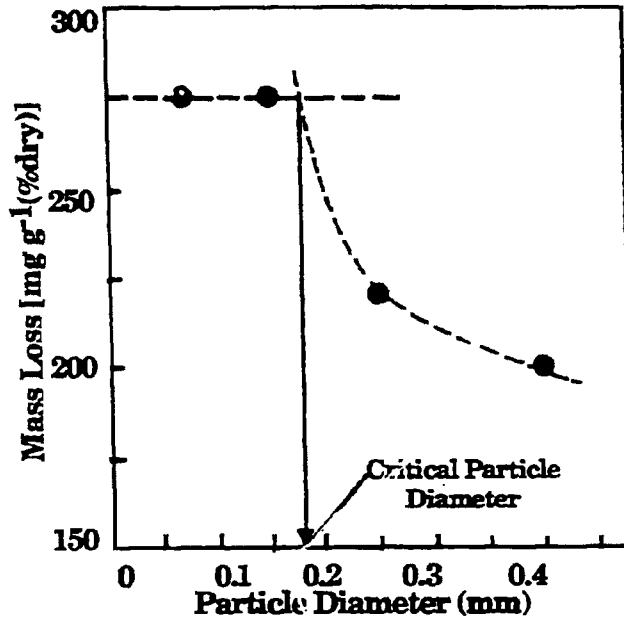


Figure II.E-1. Determination of the Critical Particle Diameter from Mass Loss Measurements at Incomplete Pyrolysis. Coal Westerholt; Heating Rate, 6000 K s^{-1} ; Pressure 10 Bar; Ambient Gas, N_2 ; Maximum Temperature, 1073 K from Wagner et al. (1985).

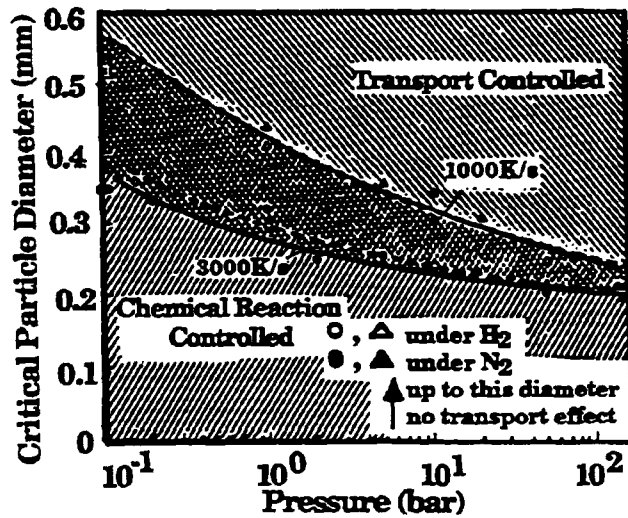


Figure II.E-2. Transition from Chemical Reaction Rate Controlled to Transport Rate Controlled Pyrolysis Using Westerholt Coal. Maximum Temperature, 1073 K from Wagner et al. (1985).

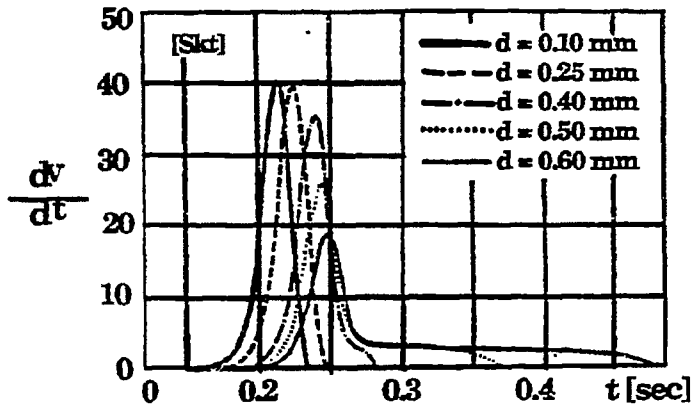


Figure II.E-3. Calculated Devolatilization Curves Assuming $E = 60$ kcal/mol; $k_0 = 10^{17} \text{ min}^{-1}$ and $m = 2 \cdot 10^5 \text{ grd/min}$ (Skt = arb. units) from Juntgen and van Heek (1979).

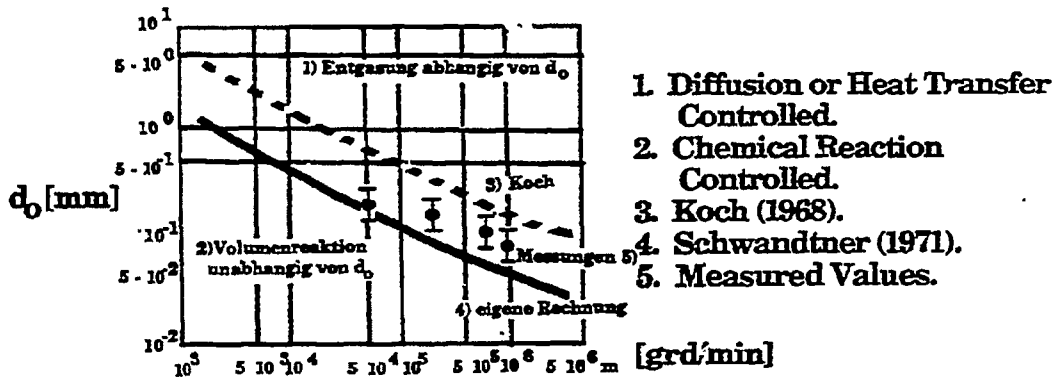


Figure II.E-4. Transition from Chemical Reaction Controlled to Diffusion or Heat Transfer Controlled Pyrolysis as a Function of Rate of Heating (m) and Grain Size (d_0), from Juntgen and van Heek (1979).

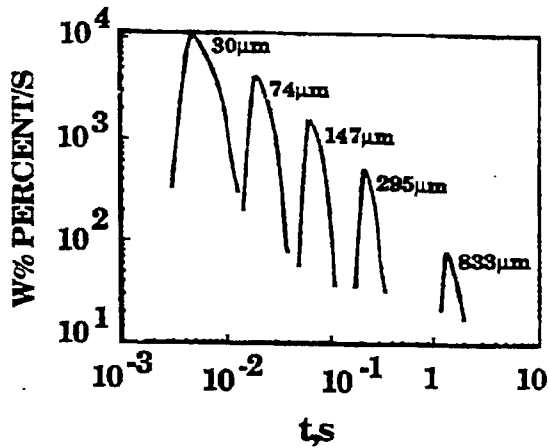


Figure II.E-5. Effect of Particle Size on Instantaneous Gas Evolution Rate. $T_0 = 303\text{K}$, $T_e = 1250\text{K}$, $Nu = 2.0$, % V.M. = 40, $\phi = 45$ from Mills et al. (1976).

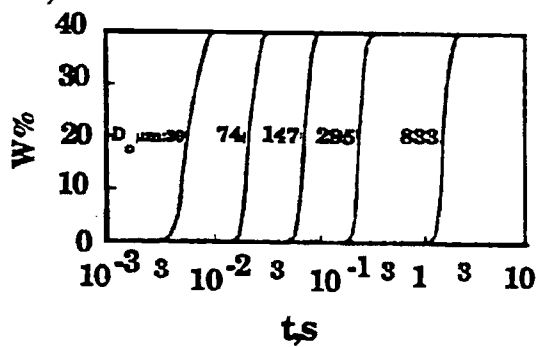


Figure II.E-6. Effect of Particle Size on Cumulative Gas Evolution. $T_e = 1250\text{K}$, $Nu = 2.0$, % V.M. = 40, $\phi = 45$ from Mills et al. (1976).

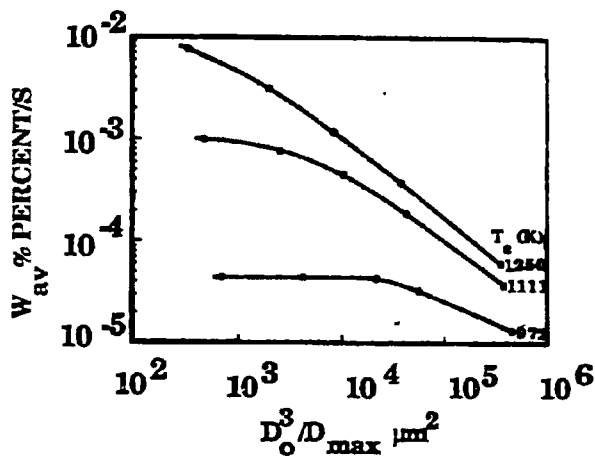


Figure II.E-7. Effect of Particle Size on Average Gas Evolution Rate. $T_0 = 303\text{K}$, $Nu = 2.0$, % V.M. = 40, $\phi = 45$ from Mills et al. (1976).

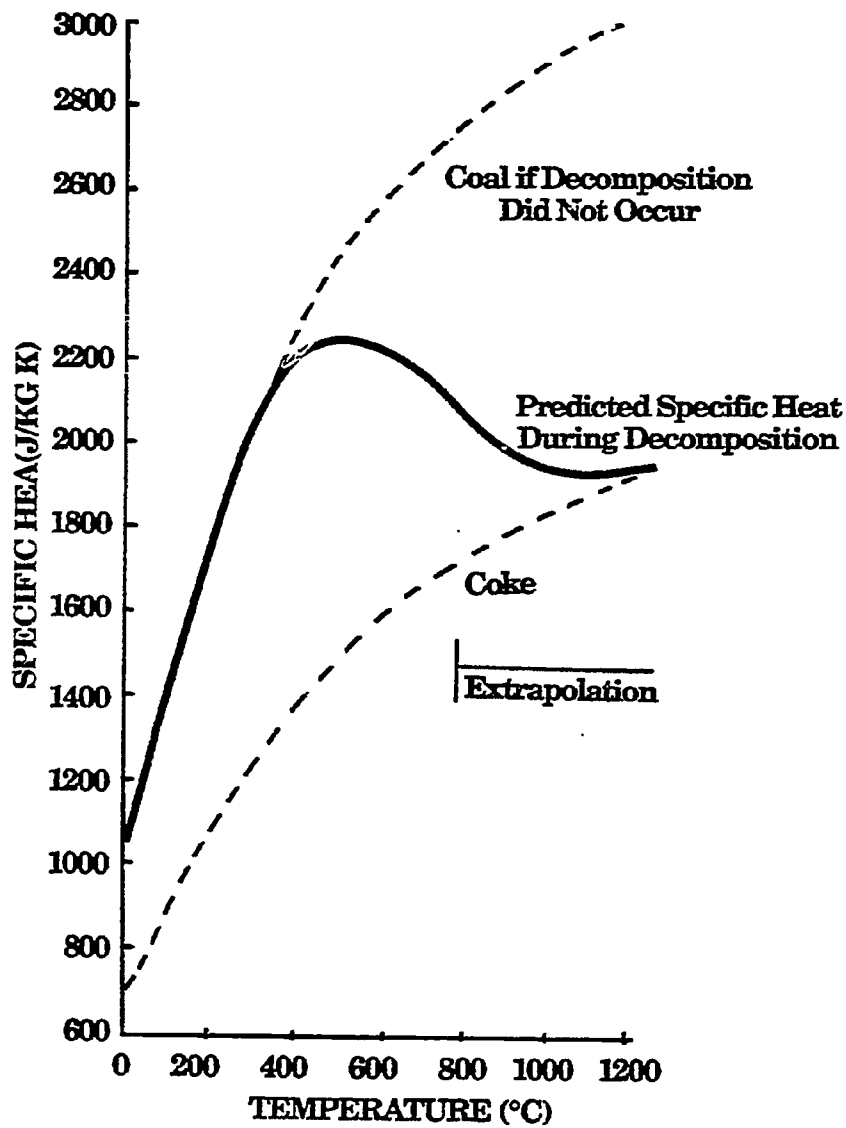


Figure II.E-8. Prediction of Variation in Specific Heat with Temperature for Coal and Coke According to Merrick (1983) Model. Heating Rate, $3^{\circ}\text{K}/\text{min}^{-1}$, DAF Coal; 25 wt% vm.

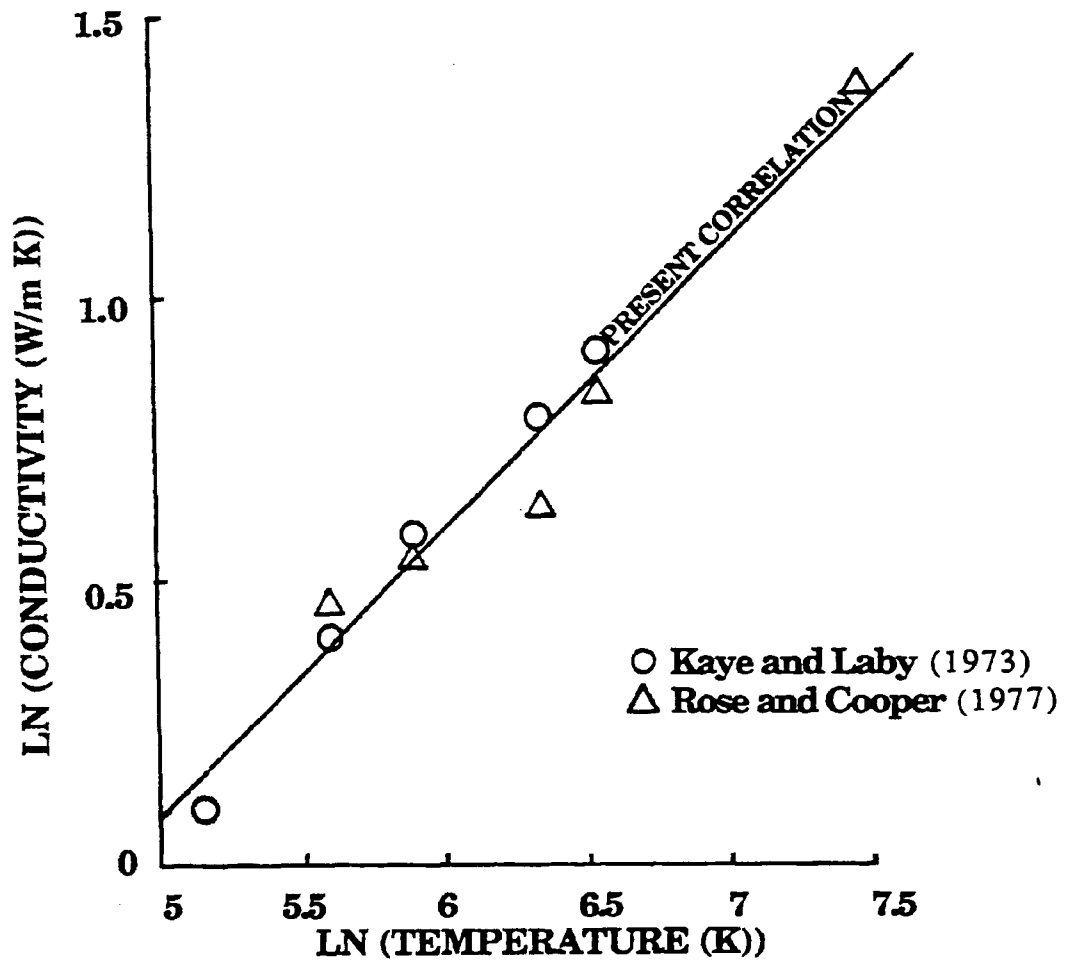


Figure II.E-9. Variation of the Thermal Conductivity of Amorphous Carbon with Temperature from Merrick (1987).

II.F. Subtask 2.f. - Large Char Particle Oxidation at High Pressures

Senior Investigator - Angus U. Blackham
Combustion Laboratory
Brigham Young University
Provo, Utah 84602
(801) 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.6. 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 to extend an existing pollutant submodel in PCGC-2 for predicting NO_x formation and destruction to include thermal NO. The submodel will also be extended to include SO_x reactions and SO_x-sorbent reactions. The effects of fuel-rich conditions and high-pressure on sulfur and nitrogen chemistry in pulverized systems will be considered along with the effects of SO₃ nonequilibrium in the gas phase.

ACCOMPLISHMENTS

This subtask was authorized to be initiated on January 30, 1987. During the first two months of the study, emphasis was placed on refinement of objectives and plans and on recruiting of a doctoral research assistant. Mr. Richard Boardman, a graduate research assistant in Chemical Engineering, has accepted this position. Mr. Boardman is just completing his research work toward a master of science degree on the closely related topic of evaluation of a NO_x submodel, under separate funding. Mr. Boardman will initiate his work on this subtask on about June 1, 1987.

Mr. Boardman attended the 1987 Joint Symposium on Stationary Combustion NO_x Control, sponsored by EPA/EPRI. This conference, held March 23-26, 1987, in New Orleans, La., provided an opportunity to review on-going NO_x control work, in preparation for establishing a detailed approach on this subtask. A more detailed report of the insights from this conference will be given in the next quarterly report.

Work on the development of a SO_x capture submodel is being conducted under separate funding from the joint Advanced Combustion Engineering Research Center by Prof. David Pershing at the University of Utah. Two coordination meetings were held with Prof. Pershing regarding this work. It is planned that this SO_x capture submodel will be integrated into the comprehensive code, PCGC-2, for use

in this investigation.

PLANS

During the next quarter, Mr. Boardman will initiate specific research work on this research subtask. A more specific work plan will be outlined. Key results from the independently funded NO_x model evaluation will be noted. Key developments in the independently funded SO_x capture (sorbent) model will also be reviewed.

II.H. Subtask 2.h. - SO_x/NO_x Submodel Evaluation

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

OBJECTIVES

The objectives of this subtask are 1) to obtain detailed turbulence measurements for radial crossjet injection of sorbent particles in a cold-flow facility designed to replicate the geometry of a 2-D combustor/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 study was initiated at a modest level in the second month of the quarter. A graduate student interested in the cold-flow portion of the study was identified and hired. He has begun to familiarize himself with the LDV instrument. David Pershing (University of Utah) has been contacted, and has agreed to help locate information on the design characteristics of a commercial electric power plant that will be using sorbent injection downstream of the burner injection point. Literature on sorbent injection in combustors is also being collected. This data base will provide the basis for the design of the cold flow facility, and the necessary modifications to the entrained flow gasifier.

PLANS

During the third quarter, the design of the sorbent injection system for the entrained flow gasifier will be completed. Cold-flow hardware that simulates this sorbent design will be fabricated, and cold-flow simulation tests will be initiated. Plans for actual sorbent testing in the entrained flow gasifier will be initiated.