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TECHNICAL PROGRESS REPORT

KINETICS OF COAL PYROLYSIS AND DEVOLATILIZATION

By

D. J. Seery, J. D. Freihaut and W. M. Proscia

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P.O. Box 10940
Pittsburgh, PA 15236

By

United Technologies Research Center
East Hartford, CT 06108

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INTRODUCTION

The objective of these coordinated experimental and modeling studies is to develop an improved understanding of the kinetics of coal devolatilization which are relevant to suspension firing of powdered coal. These fundamental kinetic studies address several topics related to an improved understanding of pulverized coal combustion and includes both homogeneous and heterogeneous reactions. The principal topics include: (a) the pyrolysis and devolatilization of coal; and (b) the formation of char. Research activities include small-scale experimentation, interpretation of experimental results in terms of mechanistic understanding and the development and validation of kinetic models of fundamental processes.

SCOPE OF PROJECT

The experimental research is carried out in small, idealized reactor systems in which the effects of heat and mass transport are minimized or precisely known. Such experiments coupled with appropriate theoretical treatment allow reactor-independent kinetic rates to be extracted from observed behavior. It is generally accepted that to obtain useful kinetic data, the following experimental parameters must be known, estimated or be systemically varied:

- coal type including rank, geological province, and proximate and ultimate analyses
- amount and nature of mineral matter
- particle size and size distribution
- extent of particle dispersion
- reaction temperature
- heating rate
- ambient pressure
- ambient gas composition
- reaction time
- prior history of reactants

Because of the complexity of the phenomena involved in coal combustion, no single experimental technique can be expected to provide all of the required information. Therefore a broad range of experimental methods will be applied, each of which has its own strengths and weaknesses, but which taken together can provide the basis for comprehensive understanding of the overall processes. The qualitative and quantitative information derived from such careful experimentation can be used to develop hypotheses of behavior which can in turn be either validated or disproven. Inherent in this process

is a methodology which closely couples experimentation with theoretical development and analytical modeling.

Because of the complexity of the fundamental chemical and physical processes involved in the pyrolysis and combustion of coal, identification of the dominant factors is difficult. However, quantification of these various factors is a principal objective of this research. Therefore careful and deliberate method of planning and executing the specific experiments and analyses employed is required and considered an integral part of the research effort.

The major tasks of this proposal can be summarized accordingly:

1. Improved engineering kinetics models will be developed at Ohio State for use in coal combustion calculations. The models will not be based solely on weight loss measurements but will include volatile product distribution and char properties and how these two are altered by temperature history.
2. An improved understanding of devolatilization and char formation will be obtained from a multi-reactor approach at three laboratories (i.e., United Technologies Research Center (UTRC), Penn State and Massachusetts Institute of Technology (MIT)). The data will be obtained by experienced workers in well-controlled experiments and special attention will be paid to the accuracy of temperature measurements, particle size determination and the interaction between these parameters.
3. Special efforts will be made to characterize the devolatilization products for a range of experimental conditions. The analysis will include not just the light gases but also the chemical composition of the tars and the reactivity of the chars. The chemical analysis of the tars will not attempt to measure every

molecule but rather to determine molecular weight distribution, aromaticity, PAH size distribution, C/H, etc. The chars will be analyzed for elemental composition, particle size, BET surface area and pore size distribution, and intrinsic reactivity to air.

4. The results of the experimental work will be integrated into a fundamental model of devolatilization kinetics that will include heat and mass transport as well as chemical reactions. The model will also include consideration of secondary reactions of tars, and plastic behavior of coals.

TECHNICAL APPROACH

Task 2.1: Engineering Kinetics of Coal Devolatilization

Objective

The objective of this task is to develop global (engineering) rate equations which describe coal pyrolysis kinetics. The equations are to be "computer tractable" in the sense: (a) that they do not greatly increase computational time of general flame codes for coal combustion; and (b) the degree of detail concerning product distributions and characteristics is software selectable.

The first level of detail is to describe particle weight loss as a function of coal characteristics, particle size and heating conditions. The second level of detail is to include major product distribution, that is, the mass fraction of coal evolved as char, tar and light gas species. The third level of detail is to include mean combustion characteristics of the major product types: average molecular weights of tar products and enthalpy contents of product types relative to the parent coal. The fourth level of detail is to include molecular weight distributions of tars, some estimation of initial char reactivity, and estimations of average elemental composition of tars and char particles. Figure 1 shows the logic diagram that forms the basis of the Task 2.1 objective. Detail Levels 1 and 2 are to be explicitly achieved by use of the Approach outlined below. Detail Levels 3 and 4 are to be implemented in relationships to Tasks 2.2 and 2.3 discussed below.

Approach

The approach consists of the performance of the following subtasks:

- 1) formulation of the problem;
- 2) evaluation of existing data bases and models;

TASK 2.1: ENGINEERING KINETICS OF COAL DEVOLATILIZATION - LOGIC DIAGRAM

*(i) = level of detail selected by user

Fig. 1

- 3) comparison of models and data bases; and
- 4) formulation and testing of a composite model or set or submodels for use in general combustion codes.

1. Background and Formulation of the Problem (Ohio State Univeristy - Essenhigh)

The practical or engineering interest in coal pyrolysis, in relation to combustion, stems from the influence pyrolysis can have in a flame such as: rapid weight loss or conversion to gases in a very short time; or soot production from volatiles in air deficient regions, for example, which drastically affects local radiant intensities. Such factors emphasize the major practical significance of pyrolysis; and, by the same token, pyrolysis is thus identified as a major component to be included in mathematical models of flames. Hence, the starting point is examination of pyrolysis behavior per se.

Flame models that also include heat transfer and combustion aerodynamics in addition to pyrolysis and combustion kinetics, are already complex, to the point that the detailed knowledge of pyrolysis that already exists can lead to subroutines that are not necessarily tractable in association with the other flame-model components. Thus we identify the problem of Engineering Kinetics of Coal Devolatilization as one of reducing knowledge of pyrolysis to a "necessary and sufficient" basis: to be able to generate necessary predictive results, of accuracy that is sufficient for the purpose.

It is also clear that the judgment used to determine what is necessary and sufficient must primarily be in the context of the total coal flame. On that account the starting point we have chosen is a brief examination of a "single" coal particle in a flame for context. Such a single particle is effectively in a finite volume (unit volume) that will

condition the particle response, including the pyrolysis, in different ways.

- (1) If the cloud is (locally) fuel lean, the volume will be quite large: the particle is most likely then to burn in the "oil drop" mode of a thin circumambient flame during pyrolysis. This would generally be clean burning with respect to soot production, with no escape of unburnt volatile matter (VM) products to the interparticle space (other than possibly CO on account of disassociation at the local temperatures). Under these conditions the molecular nature of the hydrocarbons is of secondary importance to the overall pyrolysis/devolatilization rate, and heating value of the volatiles is not directly addressed. Burning nitrogen or sulfur containing volatiles in a locally fuel rich or fuel lean atmosphere is expected to result in significant variations in fuel-related NO_x .
- (2) At the other extreme, however, if the pyrolysis rate overwhelms the local oxygen concentration and/or the cloud is (locally) fuel rich, the oil-drop model may not apply at all; VM products should be dispersed somewhat uniformly throughout the interparticle space to react homogeneously and, if oxygen is deficient, carbon can be formed. Under these

conditions, the nature of the VM products as well as the production rates will be of major importance.

Problem Structure. The above line of argument splits the problem into two parts (essentially inside and outside the particle) with two limiting case extremes for each. We identify:

I. The fundamental problem of volatiles formation and pyrolysis inside the particle.

(1) for small particles; that is to say, under such "rapid escape" conditions that the delay between VM production and escape from the particle is negligible. This implies or assumes volumetric pyrolysis of a particle of uniform temperature with zero residence time of the VM products in the particle.

(2) for "large" particles; that is to say, for conditions where the rate of escape is long compared to volatiles formation times, thus allowing capture, cracking, or other reactions inside the particle and/or allowing for variable temperature through the particle.

II. The Fate of the VM Products Outside the Particle in Flames:

(1) for conditions of such oxygen surplus that "oil drop" combustion conditions prevail and the VM pyrolysis/combustion behavior can be adequately described by the circumambient thin flame model

with coupling to the pyrolysis rate (polymer model).

- (2) for conditions of such low or deficient oxygen levels that the reaction zone broadens and/or extinguished to allow escape of VM products to the space between the particles, attended by product cracking, carbon deposition on other particles, and/or carbon formation.

2. Evaluation of Existing Data Base and Models

Data Base Differences. The wide differences in reported rates is now well recognized. As much as four orders of magnitude difference in range of rates, and substantial differences in slope (i.e. activation energy) are reported. Of all the factors that can be responsible for these differences the one that would seem to have been given least attention is the effect of non-uniform temperatures through the particles. This has usually been examined in the past on the basis of showing that the center of a particle of given size is generally within a few percent of the surface temperature. At the higher heating rates, however, it is possible that the temperature profiles that must exist are sufficient to result in "anomalous" data.

Model Differences. Numerous models have now been developed. The very simplest (first-order, one-step) is well known to be less than adequate but is still used on account of simplicity, nonetheless, in many cases. In establishing the "best" model there are two courses to pursue. First, quantitative comparisons of model predictions must be made. In this respect the level of detail (see Fig. 1) is chosen and the comparisons made on that

basis. To a large extent, differences in rate coefficients included as a component part of a model may only reflect differences in the data bases used to obtain the coefficient values in the first place. Second, the validity of the models can be tested, in principle, by demonstrating agreement or otherwise with the functional trends in the experimental data base. However, the difficulty in doing this is self-evident, at present, on account of the problem of the Data Base differences.

Model's Basis. The biggest problem of the models is the lack of a mechanistic basis. This requires some form of mechanistic model of coal constitution. Without such a mechanistic base, the models are essentially phenomenological, that is, no absolute source terms for the rate equations can be established. In this respect a set of source terms must be estimated from available data bases and the improved data base expected to be generated by the other Tasks of this program.

Summary of Task 2.1 Accomplishments

The objective of Task 2.1: Engineering Kinetics of Coal Devolatilization has been clearly defined in terms of a flow diagram (see Fig. 1) and "Levels of Detail" to be included in the model by a cyclic approach to the problem. Levels 1 and 2 will be established by a critical review of the literature, existing Data Bases and Models. Levels 3 and 4 are to be established by modification of the initial model (Levels 1 and 2) as the new Data Base is established in the current program activities (Tasks 2.2 and 2.3).

The problem has been formulated in the context of intra and inter-particle pyrolysis in both fuel-rich and fuel-lean interparticle conditions.

The approach to the problem has been clearly set forth and the criteria to be used in examining existing Data Base and Models set forth.

Future Activities

- (1) Development of a "raw" data base, of pyrolysis rates at the given temperatures, diameters, coal type and other conditions, for reference in due course.
- (2) Construction of a set of mathematical models; as the working basis; these models will then be compared with each other to establish significant agreement/ differences.
- (3) Development of a data base of reported kinetic constants for use in the models and for inter-comparison.
- (4) Review of the details of the different experimental methods to account for the difference in the reported values of rate parameters, and introduction of correction factor(s) for the data.
- (5) Re-evaluation of model(s) using the corrected data base, and combination/reduction/reconstruction of models accordingly.

Task 2.2 and 2.3: Fundamental Mechanisms and Kinetics of Volatile
Formation and Evolution

and

Fundamental Mechanisms and Kinetics of Char Formation

Objective

The objective of Tasks 2.2 and 2.3 are to establish a fundamental understanding and quantitative model of primary volatiles formation, release and volatiles reactions which occur during coal devolatilization and in heating conditions comparable to those found in pulverized coal combustion systems. Fundamental mechanisms of volatiles formation and release are to be established. An understanding of the influence of parent coal chemical structure and heating conditions on the volatiles formation, release and secondary reactions are to be established. Regimes of chemical, transport and coupled chemical and transport control are to be established.

Background and Approach

It is generally accepted that the combustion of pulverized coal particles occurs in two temporally distinct, but physically coupled phases: 1) volatile release and combustion; and 2) char combustion and burnout. Figure 2 illustrates the combustion sequence generally attributed to bituminous coal particles greater than 30 microns. This ignition and combustion sequence for fine coal particles ($d_o < 30 \mu m$) is not as universally accepted. Hydrocarbon volatile concentrations around such particles may never be sufficient to initiate homogeneous ignition. The ignition criteria obviously depends on the rate of hydrocarbon devolatilization and these kinetics are not well-established.

Development of a fundamental understanding and model of coal combustion, then, depends in the first place on progress being made in the

COAL COMBUSTION SEQUENCE

Fig. 2

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following areas: 1) the kinetics of intra-particle formation of volatiles in a heating coal particle; 2) the kinetics of volatiles release during the transient heating of a particle; 3) the relationship between the freshly formed char structure and the volatiles release process; 4) the change in intrinsic reactivity of a char with time and temperature in fuel rich or fuel lean conditions; 5) the kinetics of volatiles combustion; and 6) the kinetics of char oxidation.

It is generally accepted that the thermal devolatilization of a high volatile bituminous coal occurs in three sequential stages for conditions in which transport factors are minimized: a) tar formation and release; b) light gas release dominated by hydrocarbons, carbon oxides and water; and c) a slow char degassing phase dominated by H_2 , CO and HCN release. Tar formation is not necessarily coincident with the onset of tar release. The kinetics of tar release to the vapor phase are dependent on the heat and mass transport related parameters of the experimental or combustion system. A number of recent experiments have indicated that a wide range of coals tend to devolatilize according to the sequence noted above (Freihaut, 1982a; Calkins, 1983); although the yield structure and degree of overlapping of the various stages varies significantly with the conditions of heating, the chemical characteristics of the parent coal, the presence of a reactive gas (Anthony and Howard, 1975; Suuberg, 1980; Tyler, 1980).

From a more practical perspective, the tar formation and release characteristics of a coal are significant in that tar species are known to represent a major fraction of the mass for a range of coals; tar species are linked to soot formation in coal combustion conditions (Seeker, 1980; McLean, 1980; Nenninger, 1983); light gas yields and characteristics are directly coupled to the fate of primary tars formed early in the

devolatilization process; early fuel nitrogen release as HCN species is directly coupled to the fate of tar species (Freihaut, 1981, 1982a).

The softening and swelling of bituminous coals and, consequently, the physical parameters of char reactivity are coupled to the mode of tar release - capillary wicking, convective flow through pore structures, bubble formation and bursting in the plastic stage. High speed films of tar release from a softening coal indicate all three modes contribute to the tar release process but at different stages of the transient heating process. Figure 2 indicates the initial char reactivity properties are developed in the initial phase of the devolatilization process. This process is shown schematically in Fig. 3 wherein the "activated" bituminous coal particle "devolatilizes" by a tar release/char formation process accompanied by an initial light gas formation (light gases 1). Char oxidation, burnout, and char coking reactions dominate the combustion sequence after the main phase of volatiles combustion. The char burnout time (char oxidation) depends on the char reactivity properties developed in the devolatilization/volatiles combustion phase of the combustion sequence. Figure 4 indicates the relationship of the single particle char burnout rate $R_{\text{char}}^{O_2}$ to the char reactivity properties. k_{chem} is the chemical kinetic rate constant for the carbon-oxygen reaction. As indicated by the form of the equation, the instantaneous rate of particle burnout, per cm^2 of superficial surface area, depends not only on the chemical reactivity, k_{chem} , but also on the accessibility of the active carbon sites to oxygen attack as indicated by the R_s term. The interphase mass transfer coefficient, in turn, also depends on devolatilization since the final particle diameter is determined during this process. (See Table I and II for definitions of symbols and complete set of equations.)

COAL DEVOLATILIZATION/PYROLYSIS

Fig. 3

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SINGLE PARTICLE CHAR BURNOUT

$$R_{\text{char}}^{\text{O}_2} = \frac{0.75 \text{ Pe}^{\text{O}_2}}{\left\{ \left(\frac{\alpha_s}{k_{\text{chem}}} \right) + \left(\frac{1}{h_m^{\text{O}_2}} \right) \right\}} \quad \alpha_s = 4.5 / (SA \cdot \xi \cdot \sigma \cdot d_{\text{char}})$$

Fig. 4

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TABLE I

CHAR BURNOUT EQUATIONS

$$(1) \quad \frac{du}{dt} = \frac{6}{\sigma_o d_o} \cdot y^{1-\alpha-\beta} \cdot R_{\text{coupled}}$$

$$(2) \quad R_{\text{coupled}} = \frac{0.75 P_e^{02}}{\left(\frac{\alpha_s}{k_{\text{chem}}} \right) + \left(\frac{1}{h_{\text{mt}}^{02}} \right)}, \quad m = 1$$

$$(3) \quad \frac{dT_P}{dt} = \left(\frac{1}{C_P} \right) \left\{ \frac{\Delta H}{y} \cdot \frac{du}{dt} - \left(\frac{12 k_f}{d_o^2 \sigma_o^2} \right) \left(\frac{T_P - T_g}{y^{2\alpha + \beta}} \right) - \left(\frac{6 \sigma_{SB} E_F}{d_o \sigma_o} \right) \left(\frac{1}{y^{\alpha + \beta}} T_P^4 - T_R^4 \right) \right\}$$

$$(4) \quad \sigma = \sigma_o (1 - u)^\beta$$

$$(5) \quad d = d_o (1 - u)^\alpha$$

$$(6) \quad k_{\text{chem}} = k_o e^{-E_{\text{chem}}/R \cdot T_P}$$

$$(7) \quad h_m^{02} = \left\{ D_o^{02} \left(\frac{T_f}{T_o} \right)^{1.75} \left(\frac{P_o}{P_e} \right) \right\} / d$$

$$(8) \quad \alpha_s = 4.5 / (S_A \cdot \xi \cdot \sigma_{\text{char}} \cdot d_{\text{char}})$$

$$(9) \quad \xi = f(\theta, n)$$

TABLE II
NOMENCLATURE

<u>Symbols</u>	<u>Interpretation</u>
$h_m^{O_2}$	oxygen mass transfer coefficient, cm/sec
$C_g^{O_2}$	ambient concentration of oxygen, g/cm ³
$C_s^{O_2}$	surface concentration of oxygen, g/cm ³
$D_o^{O_2}$	diffusion coefficient of oxygen, cm ² /sec
P_o	reference pressure, atm
$p_e^{O_2}$	oxygen partial pressure ambient phase, atm
P_e	total ambient pressure, atm
$p_s^{O_2}$	oxygen partial pressure at particle surface, atm
T_f	film temperature $(T_p + T_g)/2$, K
T_p	particle temperature, K
T_g	gas (ambient) temperature, K
T_r	radiant sink temperature, wall temperature, K
d_{coal}	initial coal particle diameter
d_o	initial char particle diameter, cm
d	char particle diameter in time
k_o	pre-exponential, g/cm ² -sec-(atm) ^m
k_f	film thermal, conductivity, cal/cm-sec-K
k_{chem}	carbon-oxygen rate constant $(k_o \cdot e^{-E_{chem}/RT_p})$, g/cm ² -sec (atm) ^m

TABLE II (Cont'd)

NOMENCLATURE

<u>Symbols</u>	<u>Interpretation</u>
E_{chem}	carbon-oxygen reaction activation energy, kcal/mole
E_A	apparent activation energy, kcal/mole
R	gas constant, kcal/mole-K
m	order of carbon-oxygen reaction with respect to oxygen concentration at surface
n	order of carbon-oxygen reaction with respect to ambient oxygen
S_A	total pore surface area, cm^2/g
S_f	swelling factor, d_o/d_{coal} , dimensionless
R	rate process, $\text{g}/\text{cm}^2\text{-sec}$
Y	mass fraction of char remaining
u	mass fraction char burnout
t	time, sec
α	empirical constant for mode of burnout, dimensionless
β	empirical constant for mode of burnout, dimensionless
α_s	available surface area factor = $4.5/(S_A \cdot \xi \cdot d)$, dimensionless
ΔH	heat release/g carbon oxidized, cal/g
σ	char particle density
ξ	active surface area factor, dimensionless
η	geometric utilization factor, dimensionless
θ	fraction of surface chemically active, dimensionless

TABLE II (Cont'd)

NOMENCLATURE

<u>Symbols</u>	<u>Interpretation</u>
ϵ_F	emissivity of char
σ_{SB}	Stefan-Boltzmann constant
σ_0	initial char density
σ	char particle density in time

Of primary concern in kinetic modeling efforts and understanding is the low temperature sensitivity observed for the tar formation and evolution process. Part of the explanation undoubtedly resides in the manner in which some experiments were performed, assumptions made in data interpretation and analysis, and in assumptions regarding the bonding structure of coal. For example, recent wire grid experiments performed by Freihaut, et. al., (1982a); Hamilton, et. al., (1979); and Niksa (1981), have all conclusively demonstrated that accurate and reproducible temperature measurements in such a device are nontrivial. Maloney and Jenkins (1984) have demonstrated that what appear to be slight changes in the transport properties of an entrained flow reactor can cause significant changes in devolatilization behavior.

Ignoring thermal and mass transport considerations in rapid devolatilization experiments and devolatilization models, particularly in the tar release phase, has led some investigators to reactor dependent rate constants (see Task 2.1 Background). However, even when great care is taken to either eliminate interphase thermal transport control or properly account for reactor characteristics, low temperature sensitivity observations of initial tar formation and release are preserved (Maloney, 1983; Niksa, 1981; Doolan, 1982). Thus, assumptions regarding the bonding structures in coal, that is, the molecular structure of coal and the nature of the chemical kinetic reaction pathways in devolatilization need to be re-examined.

In view of the central importance of the tar formation and release process in the coal combustion process, a concerted effort must be directed: 1) to understand the underlying chemical and transport mechanism controlling observable behavior; and 2) to develop predictive, quantitative kinetic models of the tar evolution process. The understanding

of light gas formation and development of char structure are intimately coupled to advances in our understanding of the tar component of coal devolatilization. The evolution of comprehensive kinetic models of coal combustion hinges upon significant increases in our knowledge of the tar formation and evolution in the first phase of coal combustion.

A program adequately investigating these phenomena to establish regimes of transport and rate control and fundamental, mechanistic understandings must necessarily have the following attributes: a) multi-reactor and multi-laboratory based; b) experimental and analytical interplay; c) planned and explicit interaction with laboratories doing important related work but not officially involved in the contract (e.g., Sandia Laboratories; CSIRO, Australia, University of North Dakota Energy Research Center (UNDERC); research conducted at Department of Energy Research Centers - Morgantown and Pittsburgh); and d) coordinated efforts using the same set of coals to avoid duplication of efforts and to generate meaningful results from a variety of environments that have overlapping temperature regimes, but different transport characteristics.

The complex interaction of phenomena at work in tar formation and release necessitates the use of a variety of reactors to sort out transport-related and chemical kinetic effects. The same reasons justify the use of a multi-investigator approach since each investigator tends to emphasize a particular aspect of a phenomena in which many coupled aspects can make important contributions to observable behavior. Modeling and analytical aspects should be two-pronged: engineering and mechanistic so that immediately useful relationships can be put forth while a fundamental understanding is developed. Interaction between the two approaches tends to keep participants in both lines of thought focused on important aspects of the phenomena. In addition, experimental and modeling efforts must

also be coordinated. In such a complex phenomena, no set of experimental observations can immediately give fundamental information and no a priori modeling can provide insight into the relative significance of a particular chemical or physical process. Results from modeling and experimental efforts must be made concurrently and in a coordinated manner.

Coal Selection, Storage, Preparation and Procurement

Table III lists coal samples and amounts to be selected from the Coal Sample Bank being established by the Coal Research Section of the Pennsylvania State University. The selected samples are subsets of a much larger set of coal samples (50) being collected and stored under carefully controlled conditions for use in a variety of coal characterization, liquefaction, gasification and combustion related programs. The establishment of this Coal Sample Bank and Data Base at Pennsylvania State University is being sponsored in large part by DOE-PETC funding in a separate program. Sample selection was also coordinated (meetings at DOE-PETC on February 14, 1985 and May 1, 1985) as much as possible with sample selections required by closely related DOE programs at Sandia National Laboratories, University of North Dakota Energy Research Center (UNDERC), TRW - California, California Institute of Technology, and research laboratories at DOE-PETC and DOE-METC. Such sample coordination in these present studies, with long term storage of reserve supplies of the same samples at PSU, is a unique and invaluable approach to establishing a useful, transferable Data Base and comprehensive understanding of coal combustion properties.

Discussions were held with DOE personnel (May 1, 1985) and UNDERC regarding the proper handling, storage, and characterization of low rank coals (lignite and subbituminous for use in the program. There is concern

TABLE III

Suggested Samples		Required from Penn State			Required for Experiments				
		UTRC	PSU	MIT	Total	UTRC	PSU	MIT	Total
1.	Pittsburgh								

that various laboratories may not be able to grind low rank samples to specific size cuts under humidified argon conditions. A high humidity inert gas environment is desirable to prevent H_2O absorbed on the "virgin" coal surface from degassing, in low humidity environments, with subsequent chemisorption and physisorption of O_2 molecules. Measures to control and maintain sample quality of the PSU collected low rank coals for use in the program are being considered by DOE-PETC personnel.

PSU has notified UTRC that it has procured coal #1 of Table III. Samples are being prepared for shipment to UTRC and the subcontractors. A sample of a hvA Bituminous coal (PSOC 997) has been obtained from PSU to begin reactor calibration. The elemental characteristics of this coal are described below. This specific HvA Bituminous Coal was selected since it has been employed in recent MIT testing and the quality control of the stored sample was recommended by PSU personnel.

Sample Characterization

Table IV lists the results of the elemental analyses of nine samples of PSOC 997 ground to +325-270 mesh under nitrogen. Also indicated are the mean values, standard deviations and dry-ash-free averages. The close agreement among results indicate the grinding, quartering and sieving techniques to produce uniform samples.

TABLE IV: ELEMENTAL ANALYSIS: PSOC 997*

	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%Ash</u>	<u>%(S+O)</u>
1.	76.74	5.03	1.52	5.39	11.32
2.	76.43	5.10	1.51	5.68	11.27
3.	76.53	5.12	1.56	5.71	11.13
4.	76.52	5.02	1.48	5.80	11.18
5.	76.99	5.18	1.54	6.11	10.19
6.	76.89	5.16	1.54	5.93	10.48
7.	76.69	5.25	1.52	5.16	11.38
8.	76.97	5.18	1.53	5.96	10.36
9.	76.87	5.13	1.53	5.77	10.84
Ave.	76.74	5.13	1.53	5.77	10.85
S.D.	0.20	0.07	0.02	0.32	0.49
DAF	81.43	5.44	1.62	----	11.50

* +325 - 270 MESH

DAF - dry ash free average

S.D. - standard deviation

Heated Grid Apparatus

Calibration

Figure 5 displays the relationship between steady state, center thermocouple temperatures versus the input power to two different heated grids, noted A and B. Plots AB and AL display the blank and carbon fiber loaded (3.5 mg) temperatures for screen A whereas BB and BL display the same data for screen B. Screen B was loaded with 21.3 mg of carbon fiber. The carbon fiber provides a non-volatile, black body "dummy load" on the screen. It has a mean heat capacity (0.17 cal/g C) which approximates non-volatile coal chars. Table V lists the mean edge and center temperatures, as well as mean current and grid voltages which provided the input for Fig. 5. Figure 6 displays the center and edge thermocouple plots for screen B under loaded conditions. Several aspects worth noting are:

- a.) the load does slightly affect the steady state temperature achievable by a given screen at a given power input;

AB=Blank Screen A; AL = Screen A loaded with 3.5 mg carbon fiber
over center 2 cm

BB=Blank Screen A; BL = Screen B loaded with 21.3 mg carbon fiber
over center 2cm

Fig. 6

- b.) the specific screen cut has a greater effect on achievable steady state temperature than the load for these loading conditions;
- c.) the edge thermocouple 0.5 cm from electrode clamp and 3.0 cm from the center thermocouple is 30-40 C lower, on average, than the center thermocouple temperature.

Several conclusions emerge from these observations:

- 1.) at steady state conditions, the temperature profile of the 7cm grid is fairly uniform except at points very close to the electrode. This follows from the poor thermal conductivity of the stainless steel material of the grid and electrodes. Consequently, loading the sample 2-4 cm from the center point of the grid should insure uniform heat transfer conditions to the sample.
- 2.) The clamping technique is reproducible for each screen. This follows from the observation that each specific screen required approximately the same power input to achieve the same steady state temperatures after repeated unclamping and reclamping of the screen to insert the dummy loads.
- 3.) The power requirements to maintain a given steady state temperature vary significantly with each cut of screen. Thus each screen must be tared and prefired individually for a given set of heating conditions. After determining the power

requirement for each screen the sample can be loaded in the screen.

TABLE V: STEADY STATE TEMPERATURE, POWER DATA

	<u>CTR. TC(C)</u>	<u>EDGE TC(C)</u>	<u>CURRENT(AMPS)</u>	<u>VOLTAGE(V)</u>
AB	426 (23)	368 (15)	2.76 (0.43)	7.28 (0.61)
AB	532 (14)	505 (19)	3.59 (0.41)	9.49 (0.57)
AB	637 (15)	605 (22)	4.65 (0.41)	12.07 (0.60)
AB	754 (41)	736 (13)	6.58 (0.14)	15.95 (0.17)
AB	856 (29)	852 (21)	7.97 (0.13)	19.32 (0.18)
AB	962 (28)	935 (12)	9.92 (0.15)	24.30 (0.16)
AL	429 (14)	396 (10)	2.88 (0.43)	7.33 (0.57)
AL	526 (23)	506 (27)	3.82 (0.43)	10.00 (0.60)
AL	642 (28)	617 (22)	4.93 (0.43)	12.91 (0.57)
AL	731 (25)	731 (19)	6.34 (0.33)	15.68 (0.47)
AL	862 (24)	836 (28)	7.72 (0.14)	19.36 (0.19)
AL	957 (58)	932 (13)	9.28 (0.14)	23.22 (0.17)
BB	434 (18)	375 (12)	2.54 (0.14)	6.05 (0.20)
BB	539 (12)	490 (15)	3.29 (0.15)	8.17 (0.19)
BB	645 (25)	604 (22)	4.30 (0.15)	10.56 (0.19)
BB	747 (26)	718 (14)	5.28 (0.14)	13.17 (0.22)
BB	865 (20)	832 (18)	6.63 (0.13)	16.53 (0.19)
BB	958 (24)	938 (14)	8.16 (0.14)	20.75 (0.19)
BL	430 (18)	383 (24)	2.57 (0.13)	6.43 (0.20)
BL	535 (23)	507 (13)	3.49 (0.14)	8.53 (0.19)
BL	637 (17)	625 (13)	4.49 (0.13)	10.90 (0.17)
BL	752 (23)	740 (21)	5.52 (0.13)	13.80 (0.20)
BL	862 (25)	847 (15)	6.80 (0.14)	17.00 (0.18)
BL	954 (73)	939 (13)	8.48 (0.14)	21.74 (0.17)

AB = Blank Screen A; AL = Loaded Screen A, 3.5 mg carbon fiber over 2 cm center of screen

BB = Blank Screen B; BL = Loaded Screen B, 21.3 mg carbon fiber over 2 cm center of screen

(Numbers) represent one standard deviation.

Flash Lamp Apparatus

Calibration

Figure 7 shows typical pyroelectric detector response signals for given capacitor bank voltages. These signals were obtained by an external detector mounted perpendicularly and 2.5" from the helical flash coil.

Fig. 7

External Pyroelectric Detector Response Curves

```

CN = 02  A- .400  B- 4.00  HALTED
TRACE A    TRIGGER +00028  + SLOPE A
TIME 000.002 000  DISPLAY 00000 + 0
DATA ACQUIRED - COMMAND?  SWEEP# 009
  
```

Capacitor Bank Voltage

- a = 1.4 kv
- b = 1.6 kv
- c = 1.8 kv
- d = 2.0 kv
- e = 2.2 kv

These signals are to be converted into transient radiant flux profiles by matching signal levels with the calibration curve generated for the detector.

Preliminary Reactor Testing with PSOC 997

Figure 8 shows volatiles yields obtained from PSOC 997 in a series of flash lamp lens with +325-270 mesh particles in the reactor at the relative conditions noted. Of interest is the substantial tar yields obtained before measureable light gas yield.

Product Characterization

Molecular Weight Estimations

Gel permeation chromatography separates molecules according to their degree of penetration into the pores of a gel column packing, when eluted with a suitable solvent. Currently, two Styragel columns (500Å and 100Å poresize) in series are being used with tetrahydrofuran as the mobile phase. The columns contain divinylbenzene/polystyrene gel which has been used successfully for g.p.c. separation of coal tars and other coal-derived liquids. Polar solvents, such as THF, are used to minimize absorption effects on retention volume.

Tetrahydrofuran is known to interact with species capable of hydrogen bonding, e.g., compounds containing a phenolic hydroxyl group. A series of aromatic compounds have been injected into the g.p.c. system to characterize retention behavior. As expected, phenol and the cresols elute at a lower retention volume than toluene and the xylenes, indicating a larger molecular size in solution due to interaction with the THF. Coal-tar samples will be acetylated and their g.p.c. chromatograms compared with underivatized coal-tar samples.

Benzene and naphthalene were found to elute at the same retention volume. Several investigations have observed that polycyclic aromatics

Fig. 8

Particle Size: +325-270 mesh
Ambient Pressure: 0.001 torr
PSOC 997

exhibit absorption effects on divinylbenzene/polystyrene gels. Solvents of higher polarity than THF such as: p-dioxane, pyridine, and dimethyl formamide may be effective in minimizing absorption. Pyridine at 60 C has been reported to improve the g.p.c. separation of a technical coal extract when used as the mobile phase for sephadex LH 60 gel. Alternative solvents will be investigated, however solvent selection is a trade-off between minimizing absorption, UV cut-off and safety.

The picolines were observed to elute approximately 0.2-0.3 ml after toluene. This could be attributed to the influence of heteroatoms on absorption behavior. However, the retention volume shift is small and could also be caused by mobile phase flow rate variation between runs. A column heater will be purchased to control column temperature 1 C which will present flow rate variations due to mobile phase viscosity changes.

Further progress in this reporting period was limited by equipment down time. The varian HPLC pump seals have been replaced and the chromatix UV-vis scanning detector flow cell is currently being refurbished.

Elemental Analysis

A new Perkin-Elmer Model 240C CHN Analyzer has been obtained and is being calibrated. A Columbia Scientific XMET 840 analyzer has been obtained and is being calibrated to determine total sulfur contents of tars and chars obtained from the experiments.

Heating Value

A Parr Instruments Semi-micro Adiabatic Bomb Calorimeter has been obtained and is being installed. This instrument will be used to measure the heating value of the products obtained from various phases of coal devolatilization.

Radiative Flow Reactor

Feed_System

The porous cone, jet stirred feed system has been assembled and tested. Steady state operation of +2 hours have been achieved. The expansion cone entrance to the reactor is being tested.

Optical Monitoring System

The housing for the optical monitoring of the feed system has been constructed. Discussions with D. Holve (Sandia Laboratories) have been initiated to determine the correct optical system for real time particle counting.

Reactor: Housing, Lamps, Flow Controller

All reactor housing, lamp components and control systems have been received and are being assembled.

Phase Separator System

The Anderson Inspector train has been delivered and is being assembled.

Summary of Tasks 2.2 and 2.3

1. Sample identification and selection has been accomplished in coordination with the Pennsylvania State University Coal Research Section program to establish a Coal Sample Bank.
2. Sample coordination with related programs has been established, that is, with Sandia Laboratories, UNDERC, TRW, and research programs at PETC and METC.
3. Reactor calibration has been started for the Heated Grid and Flash Lamp reactors.
4. Preliminary runs with PSOC 997 have been performed to establish heating conditions in each which generate the

initial tar release during devolatilization of a hvA Bituminous Appalachian Province coal.

5. Product characterization systems to perform the following analyses have been obtained and are being calibrated:
 - (1) CHN - PE Model 240C;
 - (2) S_{total} - Columbia Scientific Model XMET 480; and
 - (3) Heating Value - Paar Instruments Adiabatic Calorimeter Model 1243.
6. Radiative Field Flow Reactor is being assembled. The critical component - the feed system - has been constructed and is being tested.

Task 2.4 Fundamental Model Studies

Introduction

UTRC is to develop a general, fundamental model of single particle coal devolatilization which notes regimes of heat, mass, and chemical kinetic control as a function of coal type. UTRC is also to relate the fundamental model studies to the Engineering Kinetic expressions developed in Task 2.1. Most of this effort is to occur as the Data Base to be generated in Tasks 2.2 and 2.3 emerge. MIT (J. Howard) is also developing a fundamental model of devolatilization of softening coals. This work Modeling of Single Particle Coal Devolatilization is to commence in August, 1985.

Modeling of Single Particle Coal Devolatilization

Background

A great deal of data exists which describes the devolatilization/pyrolysis behavior of a range of coals. A general understanding of the coal pyrolysis process has been established. This understanding is more phenomenological than mechanistic and, with respect to regimes of transport or chemical control, more qualitative than quantitative. Progress in achieving a fundamental understanding of coal devolatilization now appears contingent upon the development of more fundamental models of single particle coal devolatilization. The models must include transport as well as chemical kinetic expressions. The DOE-PETC Coal Pyrolysis Program currently underway provides an excellent environment in which to develop an initial model. This program involves several research laboratories and many devolatilization studies of a common set of coals. Consequently, an excellent context exists in which continual interplay can be maintained between empirical results and theoretical analysis.

Salient Points Emerging From Discussion

A comprehensive modeling effort should select a reference coal and a reference set of conditions. Due to the complexity of the pyrolysis process and the intimate coupling among transport and chemical phenomena, the efforts should initially concentrate on modeling the devolatilization process in conditions in which transport contributions are thought to be minimal. Of the four UTRC reactors to be employed in the two programs, the Flash Lamp Reactor and Radiative Field Flow Reactor were determined to be most amenable to fundamental modeling efforts. Radiant flux profiles to the coal particles are well-defined in these reactors, allowing more certain estimation of coal particle temperature profiles. In time, transient particle temperature profiles (surface temperatures) may be measurable in these reactors.

Results obtained from experimental work at UTRC indicate that the tar evolution phase of the devolatilization process is the most critical to the course of the pyrolysis process. It is also the most complex, and consequently, analytical efforts directed at this specific phenomenon would be of aid in developing an understanding of the entire devolatilization process. Results also indicate that tar evolution is most adequately traced by relating amounts, molecular weights and heteroatom contents of tars evolved at different heating conditions to that of the parent coal particles. Variation in sulfur, oxygen and nitrogen content of tars with conditions of heating provides a marker of secondary reactions of tars.

Approach

The modeling effort should have the following characteristics:

- 1.) selection of a specific set of parametric dependencies of the tar formation and release process to be examined;

- 2.) selection of a devolatilization experiment which most closely approximates an ideal set of transport conditions;
- 3.) iterate between experimental and analytical results until predetermined agreement criteria are satisfied; and
- 4.) use the model to predict parametric variations in another set of experimentally achievable conditions.

Specific Approach

The specific tar evolution phenomena to be investigated initially are:

- 1.) the initial tar formation and release phase - the initial 10 - 20% of the particle mass loss - is to be investigated in the following conditions (see Tasks 2.2 and 2.3 Report):
 - a.) short contact time, high heating rate to moderate particle temperatures (700 - 1000K);
 - b.) low ambient pressure conditions;
 - c.) a hvA Bituminous, Appalachian coal; and
 - d.) closely sized, small particles (approximately 40 microns);
- 2.) variations with respect to the following parameters are to be examined:
 - a.) ambient pressure;
 - b.) thermal conductivity of the ambient gas;
 - c.) coal characteristics; and
 - d.) particle size characteristics;

- 3.) the Flash Lamp Reactor is to be employed for the initial model studies;
- 4.) the following characteristics of the tars are to be used as the "chemical references" in the model studies:
 - a.) elemental composition, particularly with respect to sulfur, oxygen and nitrogen concentrations relative to the parent coals;
 - b.) infrared absorption characteristics relative to the parent coal; and
 - c.) composition of light gases evolved;
- 5.) the Radiative Field Flow Reactor should be the reactor employed to test the initial model.

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