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TECHNICAL PROGRESS REPORT

KINETICS OF COAL PYROLYSIS AND DEVOLATILIZATION

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TABLE OF CONTENTS

	<u>Page</u>
Executive Summary.....	1
Introduction	3
Scope of Project.....	4
Fundamental Mechanisms of Volatiles Formation and Evolution	
and Fundamental Mechanisms of Char Formation.....	6
Sample Characterization.....	6
Hot Wall-Hot (HWHG) Gas Reactor Characterization.....	27
HWHG Reactor Devolatilization Results.....	43
Dry, Ash Free Mass Fractin Loss	43
Relative Gas Yield Structure.....	46
Tar Characteristics.....	46
Char Characteristics.....	46
Coal Devolatilization Modeling.....	74
Approach.....	74
Basic Assumptions.....	75
Reactor-to-Particle Heat Transfer Modeling.....	76
Particle Devolatilization Kinetic Models.....	81
Coupling Heat Transfer and Kinetic Models.....	84

EXECUTIVE SUMMARY

Size-separated samples of five coals have been received from DOE-PETC via Pennsylvania State University. These samples range in rank from lignite to a high volatile A bituminous coal and include samples from five major geologic provinces. High temperature ash analyses of each of the nine size cuts indicate substantial variance in the mineral content with size range of a particular coal. The Eastern Appalachian and Central Interior Province samples display greater variation in ash content with particle size cut than the lignite and Rocky Mt. bituminous coals. It is postulated that such variations with coal type reflect the "included" form of mineral matter in Appalachian and Interior Province coals compared to the "inherent" nature of the mineral matter found in low rank and Rocky Mt. bituminous coals.

Infrared absorbance studies of the five coal types indicate the expected variation in relative concentrations of aliphatic H, aromatic H, oxygen functionalities and condensed ring aromatic structures with coal type. Elemental compositions for 63 - 75 micron size cuts of each coal type are presented.

Devolatilization results are presented for rapid devolatilization experiments performed with the 20 - 30 micron size cut of the reference coal - PSOC 1451D - a high volatile bituminous, Appalachian Province coal. In agreement with behavior observed in rapid, radiant transient heating experiments - flash lamp - and moderate heating rate - heated grid - experiments for the same coal, the devolatilization process is observed to occur in four distinct phases: intraparticle heavy hydrocarbon detachment and transport; heavy hydrocarbon desorption; low temperature reformation reactions producing light gases; high temperature secondary reactions of tars and char degassing. Mass fraction yields, light gas yields and tar and char characteristics are presented for a range of reactor temperatures which support the phenomenological picture.

A phenomenological model is presented which indicates the distinct phases of devolatilization and the importance of heat transfer conditions on both the overall rate of particle mass loss and the observable volatiles product distribution. The approach taken to model heat transfer conditions in each of the devolatilization reactors employed in the overall investigation is outlined. Predicted weight loss results are shown for three different sets of overall devolatilization kinetic parameters given heat transfer conditions in the UTRC Hot Wall - Hot Gas Reactor.

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 rates to be extracted from 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.

FUNDAMENTAL MECHANISMS OF VOLATILES FORMATION AND EVOLUTION AND FUNDAMENTAL MECHANISMS OF CHAR FORMATION

Sample Characterization

Coal Types and Rank Designation:

Table I contains a list of coals received from Penn State, the coal identification number, and the rank designations.

Infrared Absorbance Characteristics and Coal Type:

Figures 1 through 5 display the infrared absorbance characteristics of the five coal types received to date. These spectra were obtained from finely ground samples extracted from -20 mesh sample cans obtained directly from Penn State, and, consequently are not identified as the PSOC XXXX "D" samples. Figure 6 provides a spectra of a high volatile bituminous coal with identified functional groups responsible for the absorption bands in the spectra. Table II provides an interpretive key. Examination of the spectra indicate substantial variation in functional group distribution with rank.

Lower rank coals are characterized by more intense absorbance of oxygen functional group bands and ill-resolved aromatic hydrogen bands. As observed in previous studies, the Rocky Mountain subbituminous coal has more intense aliphatic hydrogen bands than the coals of other rank. Also as observed previously, the higher the rank characteristics of the coal the more intense the so-called amorphous "background" absorption band in the 6700 - 4000 cm^{-1} region of the spectra. Figure 7 displays the "background" absorption in the 6700-3900 cm^{-1} (1.5-2.5 micron) region for each of the coals. Figure 8 shows the spectra of all five

TABLE I
COAL SAMPLES - I.D. AND RANK DESIGNATIONS

<u>COAL PSOC NUMBER</u>	<u>PROVINCE</u>	<u>SEAM</u>	<u>REPORTED RANK</u>
1507	Northern Great Plains	Beulah Zap	Lignite
1443	Lower Gulf	Wilcox	Lignite
1445	Rocky Mountain	Blue #1	Subbituminous
1493	Interior	Illinois #6	HVB Bituminous
1451	Eastern Appalachian	Pittsburgh #8	HVA Bituminous

Figure 1
IR ABSORBANCE

PSOC 1507

-20 MESH WIG-L-BUG GRIND

Figure 2
IR ABSORBANCE

PSOC 1443
-20 MESH WIG-L-BUG GRIND

Figure 3

IR ABSORBANCE

PSOC 1445

-20 MESH WIG-L-BUG GRIND

Figure 4
IR ABSORBANCE

PSOC 1493
-20 MESH WIG-L-BUG GRIND

Figure 5
IR ABSORBANCE

PSOC 1451
-20 MESH WIG-L-BUG GRIND

Figure 6
IR ABSORPTION BAND IDENTIFICATION

TABLE II
STRUCTURE ASSIGNMENTS IN ABSORPTION SPECTRA
HYDROCARBON STRUCTURES

<u>BAND (CM-1)</u>	<u>ASSIGNMENT OF STRUCUTRE</u>
700 - 900	AROMATIC RING H OUT OF PLANE BENDING
3000 - 3100	AROMATIC RING H STRETCHING
2000 - 4000*.....	CONDENSED AROMATIC RING STRUCTURES
2600 - 3000	ALIPHATIC H STRETCH
2000 - 3620	HYDROXYL AND AMIDE H IN VARYING STATES OF HYDROGEN BONDING
<u>PEAK/SHOULDER (CM-1)</u>	
3560.....	HYDROXYL H IN PHENOL GROUPS
3420.....	AMIDE BONDED H; PYROLE RING H
3240.....	HYDROXYL H IN PHENOL GROUPS WHICH ARE HYDROGEN BONDED TO HALIDE MATRIX AND INTRA-MOLECULAR HYDROGEN BONDED
2965, 1385.....	H CONTAINED IN -CH3 GROUPS
2860, 2930, 1465.....	H CONTAINED IN -CH2 GROUPS
1140.....	ETHER OXYGEN
1220, 1270.....	HYDROXYL H

* BROADBAND BACKGROUND ABSORPTION DUE TO PHOTO PROMOTION OF VALENCE BAND ELECTRONS TO CONDUCTION BANDS OF MOLECULAR ORBITALS ESTABLISHED IN CONDENSED AROMATIC RING STRUCTURES. HYDROXYL H AND AMIDE H ABSORPTION BAND (2000 - 3620 CM-1) "RIDES" ON TOP OF THIS BAND. BACKGROUND ABSORPTION INCREASES WITH EXTENT (NUMBER DENSITY AND SIZE DISTRIBUTION) OF AROMTIC RING CONDENSATION WITHIN A SAMPLE.

Figure 7

BACKGROUND ABSORBANCE VS. COAL TYPE

Figure 8

BACKGROUND ABSORBANCE VS. COAL TYPE

coals in the 6700 cm^{-1} (1.5 micron) to 400 cm^{-1} (25 micron) region. Finally, the shape of the hydroxyl (-OH) and amide (-NH) band ($3900 - 3100\text{ cm}^{-1}$) varies significantly with coal sample. This band is due to the stretching vibrations of -OH and -NH groups found in the organic matrix of a particular coal. These bands are sharp in the spectra of model compounds contained in KBr pellet but are always broadband in coal-KBr spectra. The band always displays local maxima or inflection points around 3560 cm^{-1} , 3420 cm^{-1} and 3240 cm^{-1} but the relative intensities vary appreciably with coal type. These bands reflect hydroxyl, amide and hydrogen-bonded hydroxyl groups within the coal. The distribution of these functional groups, as others, varies substantially with coal rank and geologic province.

Infrared absorbance characterization of the size separated PSOC XXXX D samples is being pursued. A previous examination of the UTRC size-separated samples revealed only slight variation in IR absorbance characteristics due to organic structure composition changes with size separation. However, substantial variation in mineral matter composition with particles size was observed.

Elemental Composition of PSOC XXXX D Samples

The elemental composition of the size-separated PSOC XXXX D samples is being determined. Table III displays the results obtained for the 63 - 75 micron cut of the five coals obtained to date. Table IV contains replicate analyses. Figure 9 displays the ash free location of each of the samples on the a coalification band plot. The elemental composition confirm the general observations made with respect to the changes in infrared absorbance characteristics with changes in coal rank. For example, the lower rank coals show much greater levels of oxygen than the HVA bituminous reference coal (PSOC 1451). The Illinois No. 6 coal shows high levels of sulfur + oxygen for a high volatile bituminous coal, primarily due to its high levels of organic sulfur. The Rocky Mountain subbituminous coal shows large levels of hydrogen for a low rank coal, relative to the Texas or North Dakota lignite. As the IR absorbance spectra indicates, the hydrogen is contained in aliphatic carbon functional groups. PSOC 1451 contains a comparable level of hydrogen as

TABLE III

ELEMENTAL COMPOSITION (DAF) OF 63 - 75 MICRON PSOC XXXX D SAMPLES

<u>COAL</u>	<u>C%</u>	<u>H%</u>	<u>N%</u>	<u>S+O %</u>	<u>H/C</u>	<u>O/C</u>
PSOC 1507	65.00	4.55	0.89	29.55	0.84	0.34
PSOC 1443	64.83	5.02	1.18	28.95	0.93	0.33
PSOC 1445	74.77	5.41	1.28	18.52	0.87	0.19
PSOC 1493	74.35	5.12	1.39	19.12	0.83	0.19
PSOC 1451	82.55	5.53	1.59	10.32	0.80	0.09

TABLE IV
Replicate Analyses of 63-75 Micron PSDC XXXX D Coals

(a)

FILE: COALPSOC1507D6375-1
SAMPLE I.D.: COAL PSOC1507D
LOWER SIZE (MICRONS): 63
UPPER SIZE (MICRONS): 75
SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	54.85	%C(DAF):	64.9200001
% H:	3.82	%H(DAF):	4.52
% N:	.73	%N(DAF):	.87
%(S+O):	25.08	%(S+O)DAF:	29.69
% ASH:	15.5		
H/C :	.835		
O/C :	.342		

FILE: COALPSOC1507D6375-2
SAMPLE I.D.: COAL PSOC1507D
LOWER SIZE (MICRONS): 63
UPPER SIZE (MICRONS): 75
SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	54.7	%C(DAF):	64.73
% H:	3.87	%H(DAF):	4.57
% N:	.76	%N(DAF):	.89
%(S+O):	25.16	%(S+O)DAF:	29.81
% ASH:	15.5		
H/C :	.847		
O/C :	.345		

FILE: COALPSOC1507D6375-3
SAMPLE I.D.: COAL PSOC1507D
LOWER SIZE (MICRONS): 63
UPPER SIZE (MICRONS): 75
SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	54.92	%C(DAF):	65.14
% H:	3.87	%H(DAF):	4.59
% N:	.76	%N(DAF):	.9
%(S+O):	24.74	%(S+O)DAF:	29.37
% ASH:	15.69		
H/C :	.845		
O/C :	.338		

FILE: COALPSOC1507D6375-4
SAMPLE I.D.: COAL PSOC1507D
LOWER SIZE (MICRONS): 63
UPPER SIZE (MICRONS): 75
SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	54.9	%C(DAF):	65.21
% H:	3.82	%H(DAF):	4.53
% N:	.77	%N(DAF):	.91
%(S+O):	24.7	%(S+O)DAF:	29.34
% ASH:	15.8		
H/C :	.833		
O/C :	.337		

TABLE IV (Cont.)

(b)

FILE: COALPSOC1451D6375-1
 SAMPLE I.D.: COAL PSOC1451D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	79.06	%C(DAF):	82.50
% H:	5.3	%H(DAF):	5.54
% N:	1.54	%N(DAF):	1.6
%(S+O):	9.89	%(S+O)DAF:	10.33
% ASH:	4.19		
H/C :	.805		
O/C :	.093		

FILE: COALPSOC1451D6375-2
 SAMPLE I.D.: COAL PSOC1451D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	79.28	%C(DAF):	82.66
% H:	5.3	%H(DAF):	5.52
% N:	1.53	%N(DAF):	1.59
%(S+O):	9.73	%(S+O)DAF:	10.23
% ASH:	4.09		
H/C :	.801		
O/C :	.092		

FILE: COALPSOC1451D6375-3
 SAMPLE I.D.: COAL PSOC1451D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	79.31	%C(DAF):	82.79
% H:	5.3	%H(DAF):	5.54
% N:	1.47	%N(DAF):	1.54
%(S+O):	9.69	%(S+O)DAF:	10.13
% ASH:	4.19		
H/C :	.802		
O/C :	.091		

FILE: COALPSOC1451D6375-4
 SAMPLE I.D.: COAL PSOC1451D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	79.03	%C(DAF):	82.23
% H:	5.3	%H(DAF):	5.52
% N:	1.56	%N(DAF):	1.63
%(S+O):	10.19	%(S+O)DAF:	10.62
% ASH:	3.9		
H/C :	.805		
O/C :	.096		

(c)

FILE: COALPSOC1493D6375-1
 SAMPLE I.D.: COAL PSOC1493D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	65.06	%C(DAF):	74.36
% H:	4.5	%H(DAF):	5.15
% N:	1.2	%N(DAF):	1.38
%(S+O):	16.71	%(S+O)DAF:	19.1
% ASH:	12.5		
H/C :	.831		
O/C :	.192		

FILE: COALPSOC1493D6375-2
 SAMPLE I.D.: COAL PSOC1493D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	64.95	%C(DAF):	74.32
% H:	4.49	%H(DAF):	5.13
% N:	1.2	%N(DAF):	1.38
%(S+O):	16.74	%(S+O)DAF:	19.17
% ASH:	12.6		
H/C :	.828		
O/C :	.193		

FILE: COALPSOC1493D6375-3
 SAMPLE I.D.: COAL PSOC1493D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	65.03	%C(DAF):	74.31
% H:	4.45	%H(DAF):	5.09
% N:	1.23	%N(DAF):	1.41
%(S+O):	16.76	%(S+O)DAF:	19.19
% ASH:	12.5		
H/C :	.821		
O/C :	.193		

FILE: COALPSOC1493D6375-4
 SAMPLE I.D.: COAL PSOC1493D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	64.96	%C(DAF):	74.42
% H:	4.48	%H(DAF):	5.13
% N:	1.22	%N(DAF):	1.4
%(S+O):	16.62	%(S+O)DAF:	19.05
% ASH:	12.69		
H/C :	.827		
O/C :	.191		

TABLE IV (Cont.)

(d)

FILE: COALPSOC1445D6375-1
 SAMPLE I.D.: COAL PSOC1445D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	72.37	%C(DAF):	74.85
% H:	5.23	%H(DAF):	5.4
% N:	1.27	%N(DAF):	1.31
%(S+O):	17.82	%(S+O)DAF:	18.44
% ASH:	3.29		
H/C :	.865		
O/C :	.184		

FILE: COALPSOC1445D6375-2
 SAMPLE I.D.: COAL PSOC1445D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	72.37	%C(DAF):	74.68
% H:	5.25	%H(DAF):	5.41
% N:	1.25	%N(DAF):	1.28
%(S+O):	18.02	%(S+O)DAF:	18.62
% ASH:	3.09		
H/C :	.869		
O/C :	.186		

FILE: COALPSOC1445D6375-3
 SAMPLE I.D.: COAL PSOC1445D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	72.34	%C(DAF):	74.8
% H:	5.24	%H(DAF):	5.41
% N:	1.25	%N(DAF):	1.29
%(S+O):	17.86	%(S+O)DAF:	18.5
% ASH:	3.29		
H/C :	.867		
O/C :	.185		

FILE: COALPSOC1445D6375-4
 SAMPLE I.D.: COAL PSOC1445D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	72.31	%C(DAF):	74.78
% H:	5.25	%H(DAF):	5.42
% N:	1.22	%N(DAF):	1.27
%(S+O):	17.9	%(S+O)DAF:	18.52
% ASH:	3.29		
H/C :	.869		
O/C :	.185		

(e)

FILE: COALPSOC1443D6375-1
 SAMPLE I.D.: COAL
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:	
% C:	53.52
% H:	4.16
% N:	.96
%(S+O):	24.43
% ASH:	16.89
H/C :	.933
O/C :	.342

FILE: COALPSOC1443D6375-2
 SAMPLE I.D.: COAL PSOC
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	53.79	%C(DAF):	65.13
% H:	4.02	%H(DAF):	5.12
% N:	1.01	%N(DAF):	1.2
%(S+O):	23.95	%(S+O)DAF:	28.
% ASH:	17.2		
H/C :	.897		
O/C :	.334		

FILE: COALPSOC1443D6375-3
 SAMPLE I.D.: COAL PSOC1443D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	53.87	%C(DAF):	65.13
% H:	4.24	%H(DAF):	5.12
% N:	.96	%N(DAF):	1.16
%(S+O):	23.63	%(S+O)DAF:	28.59
% ASH:	17.29		
H/C :	.943		
O/C :	.329		

FILE: COALPSOC1443D6375-4
 SAMPLE I.D.: COAL PSOC1443D
 LOWER SIZE (MICRONS): 63
 UPPER SIZE (MICRONS): 75
 SAMPLE NOTES: AS RECEIVED SAMPLE

RAW DATA:		ASH FREE DATA:	
% C:	53.67	%C(DAF):	64.83
% H:	4.23	%H(DAF):	5.1
% N:	.98	%N(DAF):	1.19
%(S+O):	23.9	%(S+O)DAF:	28.87
% ASH:	17.2		
H/C :	.944		
O/C :	.333		

Figure 9

H/C VS. $(S+O)/C$: P50C XXXX D COALS
63 - 75 MICRON SIZE RANGE

the subbituminous coal (5.53% versus 5.41%) but the distribution of hydrogen group types is shifted to larger concentrations of hydrogen attached to aromatic carbons as opposed to hydrogen contained in aliphatic carbon structures.

Devolatilization Implications

The substantial variation in elemental composition and infrared absorbance characteristics with coal type (rank and geologic origin) lead one to expect substantial variations in observable devolatilization and pyrolysis behavior. The changes in elemental compositions and infrared absorbance characteristics strongly imply not only a change in the mix of molecular structures with coal type but also a change in the distribution of bonding types and strengths which interconnect the molecular structures. Such changes in the nature of the "reactant" material further imply: not only a change in the product distribution observed from various coals in a given heat transfer field but a change in the rate of evolution of a given product type; a wide variation in the thermal stability of heavy hydrocarbons evolved from the parent coal material once evolved from the particle into a given ambient environment; a substantial change in the rate of mass evolution and product distribution with particle heating rate for a given coal.

High Temperature Ash

The recommended ASTM technique for determining high temperature ash was followed to determine the high temperature ash characteristics of each of the size-separated, "D" coals. Table V lists the values obtained for each replicate analysis and the arithmetic average of the replicate results. As noted in sieve and cyclone separated samples of PSOC 1451 produced at UTRC, a large variation in the ash content with particle size cut is also displayed by the Vortec separated samples of this coal. Variations are also observed in the other coal samples but the "irregularity" observed in the Appalachian Province coal is more pronounced. The relatively uniform distribution of ash in the low rank coals probably reflects the "inherent" nature of the mineral matter in these coals. That is, these coals tend to have large percentages of

TABLE V
ASTM HIGH TEMPERATURE ASH - PSOC XXXX D COALS

<u>COAL</u>	<u>SIZE RANGE (MICRONS)</u>	<u>-----REPLICATE-----</u>			<u>AVERAGE</u>
		<u>1</u>	<u>2</u>	<u>3</u>	
PSOC 1451D	20 - 30	9.2	9.2	9.2	9.2
	30 - 45	6.8	6.9	6.7	6.8
	45 - 63	11.8	11.8	11.7	11.8
	63 - 75	4.2	4.2	4.3	4.2
	75 - 106	13.7	13.8	13.7	13.7
	106 - 125	15.2	15.4	15.1	15.2
	210 - 250	20.0	19.7	19.2	19.6
PSOC 1493D	20 - 30	11.7	11.9	11.9	11.8
	30 - 45	9.4	9.4	9.4	9.4
	45 - 63	14.9	14.8	14.8	14.8
	63 - 75	12.4	12.5	12.4	12.5
	75 - 106	12.3	12.2	12.4	12.2
	106 - 125	11.5	11.5	11.7	11.6
	210 - 250	15.6	15.4	15.9	15.6
PSOC 1445D	20 - 30	4.8	4.8	4.9	4.8
	30 - 45	3.7	3.7	3.7	3.7
	45 - 63	4.3	4.4	4.4	4.4
	63 - 75	3.3	3.3	3.2	3.3
	75 - 106	2.8	2.8	2.8	2.8
	106 - 125	3.3	3.3	3.3	3.3
	210 - 250	4.0	4.0	4.0	4.0
PSOC 1443D	20 - 30	19.9	19.9	19.9	19.9
	30 - 45	18.4	18.4	18.4	18.4
	45 - 63	17.2	17.3	17.2	17.2
	63 - 75	16.8	16.8	16.8	16.8
	75 - 106	15.0	15.0	15.0	15.0
	106 - 125	17.2	17.2	17.1	17.2
	210 - 250	11.0	11.0	11.0	11.0
PSOC 1507D	20 - 30	15.3	15.3	15.3	15.3
	30 - 45	14.7	14.7	14.9	14.7
	45 - 63	20.9	20.7	20.6	20.8
	63 - 75	14.2	14.2	14.3	14.2
	75 - 106	16.5	16.4	16.6	16.5
	106 - 125	13.1	13.3	13.5	13.3
	210 - 250	6.5	6.5	6.6	6.5

mineral matter present in colloidal form or as chelated complexes. Appalachian and Interior Province coals tend to have large percentages of associated mineral matter in the form of included, but distinct inorganic particles. As a result, the grinding and size separation technique employed to create size-separated samples of these coals would have a significant influence on the distribution of inorganic material in each coal particle size cut. Since the inorganic matter in low rank coals is more intimately distributed and attached to the organic matrix one would expect less variation in ash content with particle size cut or separation technique.

Hot Wall - Hot Gas Reactor Characterization

Phase Separation:

Figures 10, 11, and 12 display the overall reactor design, aerosol-char separation device and the aerosol and char separation trains. Generally, approximately 75% of the total reactor flow is diverted to the aerosol train. Both the cyclone (char) train and impactor (aerosol) train are followed by final filters. These filters consist of porous metal disks to ease in removal of tar species. Approximately 90% of the tar mass appears to collect on the final filters, with some deposition on stages 7 and 8 of the impactor train.

SEM analysis of the impactor and cyclone stages as well as the final filters reveal the phase separator extracts particulates and aerosols less than 2 microns from the particulate flow at 75% gas flow removal. Tar material deposited on the final filter substrates consists almost entirely of condensed heavy hydrocarbons having no particulate boundary structure. Particulate material is efficiently removed by the impactor and cyclone stages.

Gas Analysis - Multipass IR Cell System and Calibration

As noted in Figure 12 the total reactor flow is recombined after the separated flows pass through the final filters. This total flow is then passed through a multipass, selectable path length gas cell attached to

FIGURE 10

ENTRAINED FLOW REACTOR FOR COAL DEVOLATILIZATION

RA1132TX.011

FIGURE 11

AEROSOL - CHAR SEPARATION APPARATUS

FIGURE 12

SAMPLE COLLECTION SYSTEM

FIGURE 13
CH₄ CALIBRATION CURVE

FIGURE 14

HWHG REACTOR TOTAL AND RADIATIVE FLUX PROFILES
840 C WALL TEMPERATURE
ARGON

FIGURE 15

HWHG REACTOR TOTAL AND RADIATIVE FLUX PROFILES
927 °C WALL TEMPERATURE
ARGON

FIGURE 16

HWHG REACTOR TOTAL AND RADIATIVE FLUX PROFILES
1017 C WALL TEMPERATURE
ARGON

FIGURE 17

HWHG REACTOR TOTAL AND RADIATIVE FLUX PROFILES
1097 °C WALL TEMPERATURE
ARGON

FIGURE 18

HWHG REACTOR TOTAL AND RADIATIVE FLUX PROFILES
1187 C WALL TEMPERATURE
ARGON

TABLE VI

HWHG REACTOR GAS TEMPERATURE VS. WALL TEMPERATURE

$T_{\text{wall}}[C]$	$T_{\text{gas}}[C]$
840	444
927	599
1017	650
1097	591
1187	666

NOTE: Centerline gas temp. at axial location of max. convective flux.
Gas temp. calculated from measured convective flux (total flux - radiative flux) and by approximating the flux probe as a flat plate with characteristic length of .41 cm.

TABLE VII
ASPIRATED, SHIELDED THERMOCOUPLE TEMPERATURES

<u>REACTOR WALL TEMPERATURE (C)</u>	<u>ASPIRATED THERMOCOUPLE (C)</u>
840	165
930	231
1020	313
1100	374
1190	430
1270	496

FIGURE 19

ASPIRATED THERMOCOUPLE TEMP.
VS. REACTOR WALL TEMP.

an Fourier Transform Infrared Spectrometer (FT-IR). The nature and composition of the devolatilization/pyrolysis gas yields by comparison to calibration spectra and matching peak heights to calibration curves. Non-interfering wavelengths, that is, wavelength peaks specific to each gas must be used in determining the calibration concentration curves.

The multipass IR cell is calibrated statically and with flow for purposes of cross checking calibration curves developed for each gas. Calibration curves have been developed for CH₄, CO, C₂H₂, C₂H₄ and HCN. Figure 13 is a sample calibration curve developed for the 3086 cm⁻¹ peak characteristic of CH₄.

Heat Transfer Characterization

Figures, 14 - 18 displays the radiation and total flux measurements obtained for various reactor wall temperatures. Wall temperatures were determined by optical pyrometer readings. The argon carrier gas was not preheated in order to minimize gas phase secondary reactions of tars. As Figure 14 - 18 indicates, the main mode of heat transfer to the probe is via radiation at each of the reactor wall temperature settings, the convective flux being determined by the difference between the total and radiative flux readings at a particular position.

In order to estimate particle temperature trajectories, the carrier gas temperature must be determined as a function of reactor position. Three methods were employed to determine gas phase temperatures. One involved calculating the gas temperatures needed to produce the measured convective fluxes to the probe surface. The determined values are listed in Table VI. The second method involved making a series of aspirated thermocouple temperature measurements. This method involves pulling the reactor gas rapidly past a shielded thermocouple assembly. Table VII lists the center position temperature measurements made in this manner. Figure 19 shows these aspirated thermocouple measurements as function of reactor wall temperature. A third method involves making a series of temperature measurements made with thermocouple beads of varying size characteristics. Extrapolation to zero bead size eliminates, in

principal, the radiation component of heat transfer, leaving the estimated entrained gas temperature. Figure 20 displays the center thermcouple temperature measurements obtained as a function of bead size for two wall temperatures. An analysis of the data is being performed to determine the gas temperature obtained by mathematical extrapolation of the bead size curves.

The aspirated thermcouple and zero-bead size estimates appear to converge to similar gas temperature values. However, these are substantially lower than those estimated from the flux probe measurements. The flux probe measurements will be retaken with greater precision and the calculated gas temperatures re-estimated. In addition, the zero bead size technique will be performed at other wall temperatures and compared to the aspirated thermcouple temperature measurements.

Hot Wall - Hot Gas (HWHG) Reactor Devolatilization Results

Coal Feed Characteristics:

The first set of HWHG reactor runs were performed with the 20 - 30 micron cut of PSOC 1451D samples provided by DOE-PETC. Because the PSOC XXXX D coals were size separated by aerodynamic means it was originally thought that the size specific ASTM ash could be used as the basis for calculating mass fraction loss via the ash tracer technique. However, using this value gave negative weight loss results for the low wall temperature runs. Inspection of the gas analysis system data and the filter stages of the cyclone and impactor trains indicated substantial devolatilization was occurring. It became apparent that the feed system was not delivering coal particles having the same average ash content as measured for the gross sample for this particular size cut. Consequently, the reactor system was operated in the a cold wall, cold flow mode with the delivered coal particles collected in stage 0 of the cyclone separator considered as representative of the actually delivered samples. It was noted that immeasurably small samples of fines were deposited in the impactor train or subsequent stages of the collection system.

FIGURE 20

Table VIII lists the elemental compositions observed for the 20 - 30 micron cut of the parent coal PSOC 1451 D sample, the delivered particles captured in stage 0 of the cyclone collector, and the residual particles remaining in the feeder bed after several runs. Obviously, the feed system delivers 20 - 30 micron particles having lower average mineral densities than that observed for the gross parent sample. The residual particles, that is, the particles left in the feeder bed have higher average mineral densities than the gross parent sample. Despite the fact that the size separation system employed by Vortec and the UTRC feeder system both employ aerodynamic principles, segregation does occur in the reactor feed process. As a result it was deemed necessary to perform cold flow runs with each sample to generate baseline ash data for determining mass fraction yields by ash tracer calculations.

HWHG Reactor Devolatilization Results: PSOC 1451D 20-30 Micron

Dry, Ash Free Mass Fraction Loss:

The dry, ash-free mass fraction loss was determined using the following relationship:

$$u = 1 - (f_{\text{coal}}^{\text{ash}} / f_{\text{char}}^{\text{ash}}) * (1 - f_{\text{char}}^{\text{ash}}) / (1 - f_{\text{coal}}^{\text{ash}})$$

where $f_{\text{coal}}^{\text{ash}}$ represents the mass fraction of high temperature ash present in the parent coal.

As noted above, the parent coal feed ash must be determined by cold flow runs using the size specific parent coal and capturing the delivered coal in the collection system. In this case the mass fraction of delivered coal for the 20-30 micron cut of PSOC 1451D was determined to be 0.047. Figure 21 shows the estimated mass fraction loss as a function of the each of the reactor wall temperatures. The argon carrier gas was not preheated and, as a consequence, the main mode of particle heating was radiant flux from the reactor walls.

TABLE VIII

ELEMENTAL COMPOSITION OF PARENT, DELIVERED AND RESIDUAL PARTICLES:
PSOC 1451D, 20 - 30 MICRON PARTICLES

<u>SAMPLE</u>	<u>%C</u>	<u>%H</u>	<u>%N</u>	<u>%S+O</u>	<u>%ASH*</u>
PARENT-1	75.19	4.94	1.48	9.66	8.69
PARENT-2	75.25	4.95	1.45	9.52	8.80
PARENT-3	75.00	4.91	1.45	9.82	8.80
PARENT-4	75.06	4.90	1.45	9.78	8.80
DELIVERED-1	78.49	5.08	1.53	10.08	4.80
DELIVERED-2	78.54	5.08	1.50	10.36	4.50
DELIVERED-3	78.56	5.12	1.51	10.09	4.69
DELIVERED-4	78.59	5.08	1.48	10.01	4.80
RESIDUAL-1	74.46	4.91	1.41	9.49	9.69
RESIDUAL-2	74.42	4.89	1.43	9.84	9.39
RESIDUAL-3	74.45	4.90	1.45	9.99	9.19
RESIDUAL-4	74.44	4.91	1.45	9.78	9.39

* NOTE: ASTM ASH ANALYSIS OF THE GROSS PARENT SAMPLE FOR THIS SIZE
WAS DETERMINED TO BE 9.2% (SEE TABLE V).

FIGURE 21

Gas Yield Structure:

Figures 22 through 26 display the relative composition of the light gases evolved as a function of reactor wall temperature. The yields are normalized with respect to the highest concentration observed, that is, yields obtained at the highest wall temperatures. Absolute values will be assigned to these values as the calibration of the multipass cell is completed.

Tar Characteristics - Infrared Absorption and Elemental Composition:

Figures 27 through 33 display the infrared absorption characteristics of the tar collected on the impactor train final filter stage. Results are presented in order of increasing reactor wall temperature. When measurements were made, the elemental composition associated with each tar sample is indicated on the figures. Figure 34 indicates the changing H/C ratio of the tar samples as a function of reactor wall temperature. The parent coal ratio is shown for reference.

Char Characteristics - Infrared Absorption and Elemental Composition:

Figures 35 - 41 through display the infrared absorption characteristics of the char collected in stage 0 of the cyclone separator. Results are presented in order of increasing reactor wall temperature. When measurements were made the elemental composition of the chars are presented as well. Figure 42 indicates the H/C ratio of the char samples. The parent coal ratio is shown for reference.

Devolatilization Model

Coal Structure Assumptions:

The devolatilization model for micronized coal is based on the following assumptions regarding coal structure:

FIGURE 22

CH4 VS. REACTOR WALL TEMPERATURE (C)
VORTEC P50C 1451 20-30 MCIRONS 600 MSEC

FIGURE 23

FIGURE 24

C₂H₄ VS. REACTOR WALL TEMPERATURE (C)
VORTEC P50C 1451 20-30 MICRONS 600 MSEC

FIGURE 25

C₂H₂ VS. WALL TEMPERATURE (C)
VORTEC P50C 1451 20-30 MICRONS 600MSEC

FIGURE 26

FIGURE 27

IR ABSORBANCE - IMPACTOR TAR

PSOC 1451D, 20-30 MICRON 600 MSEC

REACTOR WALL = 790 C

%C = 84.02
%H = 6.36
%N = 1.64
%(S+O) = 8.28
%ASH = 0
H/C RATIO = 0.866

FIGURE 28

$T_W = 840$
 $\%C = 84.03$
 $\%H = 5.94$
 $\%N = 1.67$
 $\%(S+O) = 8.36$
 $\%ASH = 0$
 $H/C = 0.848$

FIGURE 29
IR ABSORBANCE - IMPACTOR TAR
PSOC 1451D, 20-30 MICRON
600 MSEC

T_w = 885

%C = 84.61
%H = 5.55
%N = 1.68
%(S+O) = 8.16
%ASH = 0
H/C = 0.7871

FIGURE 30
IR ABSORBANCE - IMPACTOR TAR
PSOC 1451D, 20-30 MICRON
600 MSEC

$I_w = 1020 \text{ C}$

%C = 84.62
%H = 5.55
%N = 1.68
%(S+O) = 8.15
%Ash = 0
H/C = 0.787

FIGURE 31

IR ABSORBANCE - IMPACTOR TAR
PSOC 1451D, 20-30 MICRON
600 MSEC

$T_w = 1100$

%C = 85.22
%H = 5.41
%N = 1.73
%(S+O) = 7.66
%Ash = 0
H/C = 0.761

FIGURE 32

IR ABSORBANCE - IMPACTOR TAR
PSOC 1451D, 20-30 MICRON
600 MSEC

$T_w = 1190$

%C = 85.54

%H = 5.27

%N = 1.74

%(S+O) = 7.45

%ASH = 0

H/C = 0.739

FIGURE 33

IR ABSORBANCE - IMPACTOR TAR
PSOC 1451D, 20-30 MICRON
600 MSEC

$T_w = 1270\text{ C}$

%C = 86.00
%H = 5.08
%N = 1.73
%(S+O) = 7.19
%ASH = 0
H/C = 0.709

FIGURE 34

H/C RATIO (DAF) OF IMPACTOR TAR VS. WALL TEMPERATURE (C)
VORTEC PSOC 1451 20-30 MICRONS 600 MSEC

FIGURE 35
CYCLOWE CHAR - IR ABSORBANCE
PSOC 1451D, 20-30 MICRON
600 MSEC

REACTOR WALL = 790 C

%C = 82.82
%H = 5.15
%N = 1.56
%(S+O) = 10.45
%ASH = 5.43
H/C RATIO = 0.746

FIGURE 37

CYCLONE CHAR - IR ABSORBANCE
PSOC 1451D, 20-30 MICRON
600 MSEC

REACTOR WALL = 885 C

%C = 82.81
%H = 4.97
%N = 1.59
%(S+O) = 10.63
%ASH = 5.60
H/C RATIO = 0.719

FIGURE 38

CYCLONE CHAR - IR ABSORBANCE
PSOC 1451D, 20-30 MICRON
600 MSEC

REACTOR WALL = 1020 C

%C = 82.72
%H = 4.76
%N = 1.62
%(S+O) = 10.90
H/C RATIO = 0.690

FIGURE 39

CYCLONE CHAR - IR ABSORBANCE
PSOC 1451D, 20-30 MICRON
600 MSEC

REACTOR WALL = 1100 C

%C = 83.07
%H = 4.58
%N = 1.66
%(S+O) = 10.69
%ASH = 6.5
H/C RATIO = 0.662

FIGURE 40

CYCLONE CHAR - IR ABSORBANCE
PSOC 1451D, 20-30 MICRON
600 MSEC

REACTOR WALL = 1190 C

%C = 83.72
%H = 4.42
%N = 1.66
%(S+O) = 10.22
%ASH = 7.8
H/C RATIO = 0.634

FIGURE 41

CYCLONE CHAR - IR ABSORBANCE

PSOC 1451D, 20-30 MICRON

600 MSEC

REACTOR WALL = 1270 C

%C = 84.13

%H = 4.02

%N = 1.69

%(S+O) = 10.61

%ASH = 8.1

H/C RATIO = 0.57

FIGURE 42

- 1.) an Appalachian Province high volatile A bituminous coal consists of a distribution of alicyclic, aromatic and aromatic structures of varying size parameters - chain length, number of rings, arrangement of rings relative to each other (linear, condensed)- and chemical composition - heteroatom content, functional group distribution;
- 2.) the alicyclic, aliphatic and aromatic structures are bonded to each other by a distribution of bond types ranging from physical forces - hydrogen bonding, van der Waals interactions - to covalent bonding;
- 3.) the distributions of structure types and bonding types varies significantly with coal rank and geologic province - consisting primarily of covalently bonded alicyclic and aliphatic structures for lignites, physically and covalently bonded aromatic structures for Appalachian Province high volatile coals, and physically and chemically bonded condensed ring aromatic ring structures for medium volatile bituminous coals and greater rank;
- 4.) the fuel nitrogen is distributed uniformly throughout the mix of structure types contained in a particular coal type and thereby varies significantly with coal rank;
- 5.) the distribution of coal associated sulfur - total and organic to inorganic ratio - varies primarily with geologic province rather than rank;
- 6.) the distribution of inorganic matter between physical and chemical attachment varies appreciably with coal rank - low rank coals containing a large fraction of chemically attached and chelated forms - with the major mass fraction of mineral matter in bituminous coals occurring as physically distinct mineral particles.

Devolatilization Sequence - High Volatile A Bituminous Coal

Figure 43 - 45 display the sequence of the volatiles formation and release, particulate physical changes, product types and temperature regimes of an Appalachian Province, high volatile A bituminous coal. As indicated the transformation from parent coal particle to char particles involves the following phenomena:

I. Detachment of Attached Tar Precursors (ATP)

In light of the view of coal structure postulated above, a significant fraction of the parent coal mass consists of heavy hydrocarbon species physically attached to the mix of covalently bonded structures of similar size and structure parameters. The detachment of tar precursors involves both physi-desorption (k_{DET}) from and thermally stimulated cleavage (k_{CLEV}) of the of the three dimensional covalent network in the parent coal structure.

II. Intraparticle Transport and Reformation Reactions of Detached Tar Precursors (DTP):

The detached tar precursors must then be transported to the particle surface (k_{im}) before they can be transferred to the boundary layer surrounding the particle and thereby to the ambient field. Reformation (k_{REF}) reactions may occur in these species depending on the mode of transport to the particle surface and the temperature of the surrounding intraparticle substrate. It is expected that measureable light gas production will be associated with any significant pyrolytic reactions of the detached tar precursors.

FIGURE 43

COAL DEVOLATILIZATION / PYROLYSIS

FIGURE 44

COAL DEVOLATILIZATION / PYROLYSIS

LG1 = (CH₄, CO₂, CO, C₂H₆, C₃H₈, H₂O)

LG2 = (H₂, CO, C₂H₂, C₂H₄, HCN)

T'_v = Soot precursor, soot

FIGURE 45

COAL DEVOLATILIZATION / PYROLYSIS

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III. Desorption of Heavy Hydrocarbons

The desorption (k_{DES}) of heavy hydrocarbons from the particle surface to the surrounding gas phase may occur by a variety of transfer modes: heavy hydrocarbon vaporization (k_{VAP}), non-equilibrium desorption (k_{NED}), convective entrainment in escaping gases (k_{CONV}). The dominant mode of transport in any one set of devolatilization conditions appears to depend heavily on the mode and rate of heat flux to the particles. Conditions which enhance vaporization and/or convective transfer involve reformation reactions (k_{REF}) of tar precursors which produce molecular species having vapor pressures great enough to escape the particle substrate and light gas byproducts. These same light gases are produced by pyrolytic reactions of the intact coal substrate and consists mainly of CH_4 , C_2H_6 , C_2H_4 , CO , CO_2 , H_2O .

IV. High Temperature Substrate Pyrolysis Reactions Producing Light Gases

The completion of the tar evolution process is followed by the pyrolytic, degassing reactions of the residual "virgin" char (k_{CHAR}). These reactions occur as the initial char seeks to achieve its thermodynamically preferred graphitic-like structure. The main gases produced in these relatively slow reactions are CH_4 , CO , H_2 , and HCN .

V. High Temperature Secondary Reactions of Tars

Low temperature ($< 900\text{ C}$) reformation reactions of tar precursors and tars produce the light gas structures noted above. High temperature ($> 900\text{ C}$) pyrolytic reactions of tars (k_{TAR}) produce soot precursors, soot, H_2 , CO , C_2H_2 and HCN . These reactions can be fast and occur within the particle, in the particle-gas boundary layer or in the ambient gas field surrounding the particle.

It should be obvious that the phenomenological model outlined above leads to the conclusion that the observable product distributions and

measureable kinetic rates - particularly weight loss - are highly dependent on the experimental conditions that determine particle heating rate, plateau temperature, and residence times of particles and evolved tars in heating conditions. Because of the complex nature of coal constitution - both from a molecular composition and a bond distribution point of view - the observable behavior is intimately coupled to the conditions of heating. Stated in another manner, the experimentally determined kinetic parameters that describe the overall devolatilization/pyrolysis process should vary with experimental conditions because the stage of the process emphasized by a particular process would vary with the conditions of heating. A comprehensive semi-empirical model of the process can only be developed by the use of a number of reactor systems in a coordinated manner to develop estimates of the rate processes for each phase.

Coal Devolatilization Kinetic Modeling

Approach:

A mathematical model has been formulated which describes the transient devolatilization kinetics of a single coal particle exposed to transient heat transfer conditions. The heat transfer characteristics of the various reactors have been measured and are used as inputs to the model. The particle energy balance includes terms for rate of internal energy gain, net radiative gain, net conductive gain, and energy dissipation due to heat of devolatilization. Single-step, two-step, distributed activation energy (DAEM), distributed-energy chain (DISCHAIN), or our phenomenological devolatilization model (see above) may be used to describe the devolatilization kinetics.

The influence of intraparticle heat transfer is neglected. The effect of intraparticle mass transport is accounted for only in our kinetics model by including a global rate term for the transport of detached tar precursors to the particle surface.

Basic Assumptions:

The following definitions and assumptions are used in deriving the model:

- 1) The particles are spherical.
- 2) The extent of reaction is defined as

$$u = \frac{m_o - m}{m_o}$$

- 3) The remaining mass fraction is given by

$$y = 1 - u$$

- 4) Particle swelling can be described by

$$d_p = d_o (1 - u)^\alpha$$

- 5) Particle density can be described by

$$\rho_p = \rho_o (1 - u)^\beta$$

The parameters α and β are defined to be functions of extent of reaction.

- 6) The rate of mass loss per unit superficial surface area is defined as

$$R_{dev} = \dot{m} / (\pi d_p^2)$$

- 7) The particle temperature is initially at ambient temperature.

Additional Assumptions Applicable to the HWHG Reactor

- 8) The gas temperature at the entrance to the reactor is at ambient temperature.
- 9) The particle velocity at the injection point is equal to the primary flow in which it is entrained and the secondary flow is also matched to this velocity.
- 10) The gas velocity profile at the reactor entrance is flat.

Reactor-to-Particle Heat Transfer Modeling

The energy conservation equation for a devolatilizing coal particle exposed to radiative and conductive gains/losses is:

$$\rho_p \text{VOL}_p C_p \frac{dT_p}{dt} = \alpha_p S_p I(t) - \epsilon_p S_p \sigma T_p^4 + \bar{h}_{Nu} S_p (T_g - T_p) - \Delta H_{Dev} S_p R_{Dev}$$

Substituting the definitions given above and rearranging yields:

$$T = \frac{6}{C_p \rho_o d_o} \frac{1}{y^{\alpha+\beta}} \left[\alpha I(t) - \epsilon_p \sigma T_p^4 + \bar{h}_{Nu} (T_g - T_p) \right] - \left(\frac{\Delta H}{C_p} \right) \left(\frac{1}{y} \right) \dot{u}$$

The initial and boundary conditions used are a function of the particular reactor environment being modeled. The coal and gas properties used in the calculations are given in Table IX.

Heated Grid

The radiative input to a coal particle between the folds of a stainless steel heated grid is given by

TABLE IX
PROPERTIES OF COAL AND GASES

THERMAL CONDUCTIVITY

MONATOMIC GASES

$$\lambda_i = (4.184)(1.9891E-4)\sqrt{T/MW_i} / (\Omega_{v,i} \sigma^2) \quad [W/cm-K]$$

POLYATOMIC GASES (EUCKEN APPROX.)

$$\lambda_i = \left[C_{p,i} + (5/4)(8.314/MW_i) \right] \mu_i$$

VISCOSITY

$$\mu_i = 2.6693E-5 \sqrt{MW_i T} / (\Omega_{v,i} \sigma^2) \quad [g/cm-s]$$

$$\Omega_{v,i} = 1.16145(kT/\epsilon_i)^{-.14874} + .52487 \exp(-.77320 kT/\epsilon_i) + 2.16178 \exp(-2.43787 kT/\epsilon_i)$$

COAL HEAT CAPACITY (MERRICK MODEL)

$$C_p = y_{daf} C_{daf} + y_{ash} C_{ash} + y_{water} C_{water} \quad [J/g-K]$$

$$C_{daf} = (8.314/MW_c) \left[g(380/T) + 2g(1800/T) \right]$$

$$g(z) = \frac{e^z}{\left(\frac{e^z - 1}{z}\right)^2}$$

$$C_{ash} = .754 + (5.86E-4) T \quad (\text{with } T \text{ in } [C])$$

$$C_{water} = 4.187$$

$$I(t) = \epsilon_{\text{grid}} \sigma T_{\text{grid}}^4$$

The temperature of the grid is measured in all experiments. The emissivity of the grid is a function of temperature and has been found experimentally to be:

$$\epsilon_{\text{grid}} = 0.43 + 1.13 \times 10^{-4} T_{\text{grid}}$$

with T_{grid} in $^{\circ}\text{C}$

The conduction heat transfer is calculated using a Nusselt number of two and assuming that the gas temperature in the vicinity of the grid is at the grid temperature. A correction for blowing is applied to the convective heat transfer coefficient.

$$h_{\text{Nu}} = \frac{\bar{N}_{\text{u}} \lambda_g}{d_p} \left(\frac{B}{e^B - 1} \right)$$

where

$$B = \frac{C_{pg} \dot{m}_o}{2 \pi \lambda_g d_p}$$

Conductive losses in vacuum runs are possible due to the formation of a tar cloud in the reactor. The conduction loss through the tar cloud is estimated using a thermal conductivity value of 1.40×10^{-4} [W/cm-k]. This value has been estimated by assuming that the thermal conductivity of gaseous tar is 1/10 that of liquid tar. The importance of including this effect under high heating rate conditions, such as occur in the flash lamp, will be discussed below.

Flash Lamp

Irradiance measurements at the flux levels used in the flash lamp have been made previously and provide the necessary $I(t)$ values.

The inert gas temperature in the reactor is assumed to remain at the initial ambient temperature throughout the approximately 15 msec. flash pulse. Conduction heat transfer is calculated in the same manner as for the heated grid experiment. The conductive losses through the tar cloud in a vacuum experiment are significant. Table X lists the peak particle temperatures predicted in flash lamp vacuum runs with no conduction and with conduction through the tar cloud. If the conduction losses are not included unrealistically high particle temperatures are predicted.

Hot Wall-Hot Gas (HWHG) Reactor

The irradiance as a function of axial position in the HWHG reactor is obtained from previous measurements using a radiative flux probe. Determination of the gas temperature in the reactor has been discussed above in the section on HWHG Reactor Characterization.

The conduction heat transfer is calculated using a Nusselt number given by:

$$Nu = 2 + 0.6 Re^{1/2} Pr^{1/3}$$

where the Reynolds number is based on the relative velocity between the particle and the gas flow.

The particle velocity is determined from the following force balance:

$$m_p \frac{dv_p}{dt} = m_p g - \rho_g g VOL_p + \frac{1}{2} C_D A_{PR} \rho_g (v_g - v_p) |v_g - v_p|$$

$$A_{PR} = \frac{\pi d_p^2}{4}$$

which can be rearranged to give:

$$\frac{dv_p}{dt} = \frac{(\rho_p - \rho_g)g}{\rho_p} + \frac{3 C_D \rho_g (v_g - v_p) |v_g - v_p|}{4 \rho_p d_p}$$

TABLE X
PREDICTED PEAK PARTICLE TEMPERATURES [C]

<u>KV/NDF</u>	<u>RFL</u>	NO CONDUCTION		GAS PHASE TAR CONDUCTION	
		<u>10μm</u>	<u>50μm</u>	<u>10μm</u>	<u>50μm</u>
1.8/30	0.7	2480	1300	1175	1150
1.5/60	1.0	2750	1550	1450	1375
1.5/90	1.5	3100	2000	1950	1825
2.2/60	2.2	3750	2900	2850	2750

where

$$C_D = \frac{24}{Re} \left[1 + 0.15 Re^{.687} \right]$$

An additional equation is used to determine the axial position of the particle in the reactor, since the irradiance and gas temperatures are known as functions of position:

$$dz_p/dt = v_p$$

Particle Devolatilization Kinetic Models

One-Step Model

The one-step model proposed by Badzioch and Hawksley utilizes a single Arrhenius rate expression to represent the conversion of unreacted coal to volatiles and residue:

where V^* is the ASTM proximate analysis volatile matter yield.

Given sufficient time at temperature the one-step model will always predict the same yield regardless of temperature or heating rate.

Two-Step Model

The two-step model consists of two competitive reaction steps, one predominating at low temperatures and the other at high temperatures:

$$dV/dt = (\alpha_1 k_1 + \alpha_2 k_2) C$$

where V_i = volatiles, R_i = char residue, and C = unreacted coal.

Distributed Activation Energy Model (DAEM)

Anthony and Howard proposed that coal devolatilization is the result of numerous independent chemical reactions with each type of bond breakage given by a simple first-order irreversible rate equation:

$$dV_i/dt = k_i(V_i^* - V_i)$$

The rate of total volatiles production is obtained by summing the contribution from each reaction or integrating over all values of activation energy where it is assumed that the k_i 's all have the same pre-exponential k_0 . The result for a Gaussian distribution of activation energies with mean E_0 and standard deviation σ is:

$$\frac{dV}{dt} = \frac{V^*}{\sigma \sqrt{2\pi}} \int_{E_0-2\sigma}^{E_0+2\sigma} A \exp(-E/RT) \exp\left[-\int_0^t A \exp(-E/RT) dt'\right] \exp\left(-\frac{(E-E_0)^2}{2\sigma^2}\right) dE$$

Distributed-Energy Chain Model (DISCHAIN)

Niksa and Kerstein have devised a model which is based on the macromolecular configuration of coal as a linear straight chain of aromatic units linked by labile bridges with peripheral groups branching from the aromatic units. The rate equations used in the model are summarized in Table XI.

TABLE XI
DISTRIBUTED ENERGY CHAIN MODEL (DISCHAIN)

B	labile bridges/initial bridges (Bo)	B(0) = 1
C	stable char links/Bo	C(0) = 0
T	tar/Bo	T(0) = 0
P	peripheral groups/init. periph./bridges (Po/Bo)	P(0) = 2
G	light gases/Po/Bo	G(0) = 0
M	free aromatic units/Bo	M(0) = 0
D	char caps/Bo	D(0) = 0
H	pure char chains/Bo	H(0) = 0

REACTION	A Factor -1 s	Activation Energy cal/mole
bridge dissociation	2×10^{10}	40,000 ($\sigma = 7,000$)
tar formation	8×10^6	30,000
char formation	1×10^6	25,000
gas formation	1×10^3	10,000

$$f(E) = \frac{1}{\sqrt{2\pi}} \exp \left[-\frac{(E-E_0)^2}{2\sigma^2} \right]$$

$$\begin{aligned} dB/dt &= - \int_{E_0-2\sigma}^{E_0+2\sigma} k_B \exp \left[- \int_0^t k_B dt' \right] f(E) dE \\ dC/dt &= - k_C M (2H + 2B(1-B) + M) \\ dT/dt &= - 2 k_T M \\ dP/dt &= - k_G P + a_B / P_0 (-dB/dt) \\ dG/dt &= - k_G P \\ dM/dt &= - 2(1-B)(1-D/(2B(1-B))) dB/dt \\ &\quad - (2M+2B(1-B)+2H)/(M+2B(1-B)+2H) dC/dt \\ &\quad - 1/2 dT/dt \\ dD/dt &= - k_C M (2B(1-B)-D) + (D/B) dB/dt \\ dH/dt &= - (D/B) dB/dt + k_C M^2 \end{aligned}$$

Coupling Heat Transfer and Kinetic Models

The rate equations in the kinetic models are dependent on the particle temperature. The energy equation is dependent on the rate of devolatilization (or rate of change of extent of reaction) and on the particle diameter and density which are defined as functions of the extent of reaction. Additionally, in the HWHG reactor, the particle velocity (and therefore residence time) is coupled to the energy equation by temperature and to the kinetics model by particle diameter and density.

Most of the various kinetic models allow calculation of the volatiles yield directly, with the exception of the DISCHAIN model and our phenomenological model. In these models, mass loss is due to the escape of tar and light gas species, which are summed to give the extent of reaction.

The resulting set of coupled ordinary differential equations are solved using LSODE. Some preliminary results for the HWHG reactor at a wall temperature of 1187 C are shown in Figures 46 and 47. Predicted particle temperatures and extents of reaction for the two-step, DAEM, and DISCHAIN models are given. The temperature for a non-reacting particle is also plotted. The effect of an assumed heat of devolatilization of 100 cal/g is seen to have a negligible effect on particle temperature for all kinetic models. However, the different kinetic models predict widely varying extents of reaction.

FIGURE 46
PREDICTED PARTICLE TEMPERATURES IN THE HWHG REACTOR
1187 C WALL TEMP AR 50 micron

FIGURE 47

PREDICTED EXTENT OF REACTION IN THE HWHG REACTOR
 1187 C WALL TEMP AR 50 micron

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