University of Maryland Eastern Shore
Department of Natural Sciences
Princess Anne, MD 21853

F O S S I L

STRUCTURE AND THERMOCHEMICAL KINETIC STUDIES OF COAL PYROLYSIS

FINAL TECHNICAL REPORT

Contract No. DE-FG22-90PC90296

prepared for
USDOE
PITTSBURGH ENERGY TECHNOLOGY CENTER

by
Joseph N.D. Dodoo, Ph.D

Consultant
Dr. Martin Hetzberg

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Final Report**

**By
Joseph N. D. Dodoo**

Work Performed Under Contract No. FG22-90PC90296

**For
U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, Pennsylvania**

**By
University of Maryland Eastern Shore
Princess Anne, Maryland**

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**PETC Project Officer
Dr. Phuoc X. Tran**

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ABSTRACT

The structure and kinetics of low rank coals, namely, Montana Rosebud subbituminous and Beulah lignite coals have been studied. CO₂ laser heating of separated arrays of particles at high flux levels has made possible the investigation of the pyrolysis and char oxidation processes of lignite and subbituminous coal particles as a function of exposure time at laser fluxes of 200-300 w/cm². The Beulah lignite and Rosebud subbituminous coals studied were supplied by the Penn State Coal Sample Bank. They had been collected, ground, and packaged in an inert atmosphere. The coal samples were subsequently stored, sieved, carefully dried, and maintained in a glove box under dry nitrogen. The moisture loss of the as-received samples was within experimental error of the supplied ASTM analysis. The mass loss vs. time reported here are for particles that were dried at 120°C under nitrogen. The morphological changes in the particles with laser exposure was monitored by scanning electron microscopy. Correlation of weight loss data with microscopic observation has been made for the devolatilization in air atmosphere. Care was taken to insure that mass loss did not reflect loss of particles. Pyrolysis rates were determined for particles in air and in a nitrogen flow, and compared with the results of corresponding laser pyrolysis studies of high and low-volatile bituminous coal particle arrays. Elemental analysis of the char particles were also carried out. The studies were extended to a typical run-of-the mill coal samples collected from a power generating company.

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1 BACKGROUND

The University of Maryland Eastern Shores's, (UMES) Advanced Coal Research program had its beginnings with the Summer faculty research participation at both the Pittsburgh Energy Technology Center, (PETC) and the Morgantown Energy Technology Center, (METC) through the Oak Ridge Associated Universities, (ORAU). The moderately equipped Advanced Coal Research laboratory at the department of Natural Sciences at UMES provided facility for the successful completion of two research contracts for the U.S. Department of Energy in October, 1991 (for METC) and September, 1992 (for PETC). The present work has been made possible through a cooperative agreement between the U. S. Department of the Interior, Bureau of Mines, Pittsburgh Research Center, (PRC) and the University of Maryland Eastern Shore. The cooperative agreement made available the laser pyrolysis and the scanning electron microscope laboratory at the Fires and Explosions Division at the PRC to this author. The major portion of the work reported here was carried out at the Pittsburgh facility.

A little over a year after the project began a major fault developed in the CO₂ laser. Considerable time was expended in a desperate effort to restore the laser to its full operating capacity. The Joel JSM U3 scanning electron microscope was soon to be dismantled and placed on the excess property list. A new JOEL 6400 scanning electron microscope with a LINK Analytical energy dispersive X-ray system was subsequently installed. This made it possible to carry out microscopic and elemental analysis of the coal particles. The primary objective of the research described in this report were to:

1. carry out pyrolysis and devolatilization studies of finer particle sizes in the 50 μm range and below, and to lower rank sub-bituminous coals and lignites.

2. adapt the laser pyrolysis/SEM microstructure method to study the mechanisms and structure of the ash transformation processes occurring during coal particle devolatilization and subsequent char combustion.

2 INTRODUCTION

Coal is a heterogeneous substance, the end product of a sequence of biological and geological processes, containing both organic and inorganic substances. The complex nature of coal is readily appreciated whenever coal is appraised for specific use. Movable coal seams derive from expansive peat deposits spanning several millennia. Because of the differences in the starting material and age, (degree of coalification) coal can range from soft lignites with their organic origins very much in evidence to meta- anthracites that contains over 98% pure carbon. The chemical and physical properties of coal change considerably during the process of metamorphism, so much so that the differences in properties produced by coalification are as great or greater than the differences between different types of coal. These differences are referred to as differences of coal rank. In the United States a coal classification scheme has been devised which separates coals according to their volatile matter contents and calorific value. The scheme devised under the ASTM heading D388V is shown in Table 1. Thus it is important to specify the type of coal that are the subject of study in order that differences in the various coals may be delineated and also so as to facilitate comparison of data for the same type coal from different studies.

Table 1 ASTM Classification of Coal by Rank

Class	Group	Heating Value		Agglomerate	% VM (d,mmf)	OR Max Volatile (mmf)	% Moisture (mmf)	% C (<.....dry, mmf.....>)	% O	% H	FSI
		Btu/lb (Moist,mmf)	MJ/kg								
Anthracite	Meta-anthracite	> 14000	> 32.5	No	<2	>4.5	1.3	>94	1-2	1-2	
	Antracite	> 14000	> 32.5	No	2-8	2.2-5.0	0.5-2.0	90-97	2-4	2-4	
	Semi-anthracite	> 14000	> 32.5	No	8-14	1.8-2.6	<1.5	89-93	3-5	3-5	
Bituminous	Low volatile	> 14000	> 32.5	Yes	14-22	1.5-2.0	< 1.5	87-92	3-5		1-9
	Med. Volatile	> 14000	> 32.5	Yes	22-31	1.0-1.7	<1.5	84-91	4-9		7-9
	High volatile A	> 14000	> 32.5	Yes	31-45	0.6-1.2	1-7	78-88	6-10		4-9
	High volatile B	13k - 14k	30.2-32.5	Yes	35-50	0.5-0.8	5-12	80-84	7-12		2-7
	High volatile C	10.5k - 13k	26.7-30.2	Yes	35-55	0.4-0.7	10-25	76-83	8-18		1-5
Subbituminous	Subbituminous A	10.5k - 11k	24.4-26.7	No	35-55	0.3-0.7	18-25	60-80	15-28		
	Subbituminous B	9.5k - 10.5k	22.1-24.4	No	35-55	0.3-0.7	20-30	60-80	15-28	4.5-6.0	
	Subbituminous C	8300-9500	19.3-22.1	No	35-55	0.3-0.7	25-38	55-73	23-35		
Lignite	Lignite A	6300-8300	14.6-19.3	No	40-65	0.2-0.4	31-50	55-73	23-35	5-7	
	Lignite B	<6300	<14.6	No	40-65	0.2-0.4	45-60	55-73	23-35	5-7	

2.1 COMBUSTION PROCESS

Coal combustion can be broken into six sequential steps: heatup, ignition, devolatilization, char burnoff, particle breakup and extinction. Each step is characterized by different dominant processes which may overlap with the processes of one or more other steps. The extent of overlap of the individual processes can influence the processes of other steps. This is particularly true of devolatilization and char burnoff. To a large extent devolatilization determines the physical structure of the resulting char. Also of importance is the type and rank of coal involved.

2.2 DEVOLATILIZATION

Devolatilization plays a significant role in coal combustion because volatile evolution rates have an influence on ignition, flame location and flame structure,[1-3]. The importance of these characteristics to the understanding and prediction of overall combustion performance has been recognized and, consequently coal devolatilization has been the subject of extensive study. During the rapid heatup of a coal particle, tars, hydrocarbons and water vapor are released. This is the devolatilization process. The extent of mass loss due to this mechanism is strongly dependent upon particle temperature and type of coal. In a typical coal combustion application about 30 to 70 pct of the original mass may be lost during this process. In the presence of oxygen the emitted hydrocarbons react to release large quantities of energy during a relatively short period of time. A review of some considerable extent has been presented by Howard, [4] in a chapter of a much larger work. The survey shows that many uncertainties persist for coal devolatilization rates. Thus, a generally accepted understanding or description of global devolatilization is lacking. The work of Kimber and Gray, [5] provided much insights into the effects of high temperature

devolatilization. Under high temperature devolatilization the fraction of matter lost as volatiles is in general significantly more than the fraction lost as volatiles using the ASTM method of coal classification. This finding was subsequently confirmed by Kobayashi and coworkers, [6] who found that the rate of particle devolatilization was strongly temperature dependent. Also of importance is coal particle swelling which has been observed to occur during devolatilization. Pohl et al, [7] have investigated the swelling behavior of two different coals under various heating rates and temperatures and found them to swell under certain conditions. Other studies, [8-12] have yielded swelling ratios of up to 1.8 for bituminous coals. Recent studies on Pittsburgh hvA bituminous coal particles using well characterized laser pulses have shown that the swelling characteristics for these coals have a bimodal behavior, [13] with the swelling ratio reaching a value of 1.3 for one mode and between 1.7 and 1.8 for the second mode.

3 EXPERIMENTAL FACILITY

Most of the coal produced in the world is eventually pulverized and consumed by direct combustion in boilers, kilns and large scale utility furnaces for generation of electrical power. The stability of the burner flames that power all of the above systems depends on the rate of particle devolatilization and yield of combustible volatiles [14-18]. The rate of char burnout in boilers depends mainly on the microscopic porosity of the char [19], and on the molecular orientation dimensions of the microtexture of the pore walls in the char structure [20,21]. The char structure is generated by the same pyrolysis and devolatilization process that occurs in the burner flame. Industrial operation in coal-fired boilers, furnaces and kilns involve such large-scale systems and such varied dynamic interactions that it is usually impractical to isolate or

accurately control any single, fundamental variable in order to study its intrinsic effect on system performance. Such variables are, however, more easily controlled in laboratory scale systems, and the data have shown that the basic parameters controlling devolatilization of coal during pyrolysis are: conductive-convective and/or radiant heat flux, exposure temperature, particle size, rank of coal, oxidizing or reducing atmosphere, flow-structure, pressure, exposure time, and exposure path. The laboratory techniques that have yielded the most data are the laminar flow furnace [6], the flat flame reactor [1], and wire mesh heating [22]. Several researchers have summarized the results of earlier investigators; however, the results of most recent investigations have clearly shown that early interpretations of those results were generally oversimplified, mainly because they ignored heat transport limitations and secondary decomposition reactions [23-26].

The laboratory scale system that most dramatically and directly illustrated the dominance of the heat transport rate limitative is the laser pyrolysis system [27,28]. The laser pyrolysis method has evolved as a means of studying heterogeneous combustion processes and has been applied to the study of the pyrolysis of coal particles, [29-31]. The laser pyrolysis method is thus employed in this study to further extend our knowledge of the structure and kinetics of typical run-of-the mill coal particles, and to low rank coals and lignites. The laser pyrolysis system employed in the present investigation was the high power CO₂ laser at the Bureau of Mines, Pittsburgh Research Center, PRC. It was a model C-41 laser manufactured by Coherent General. The maximum power output was 250 Watts, (c.w.). The laser action was obtained with a premixed gas mixture with mixture ratio of 6% CO₂, 18% N₂, and 76% He. The rated operating pressure was 15 - 25 Torr. However, throughout the studies the best conditions for operating was

when the pressure was 11 - 13 Torr. Flame fluxes and exposure times for coal particle pyrolysis and devolatilization were simulated by using a beam whose magnitude was comparable to the flame heating flux. The laser system was operated in a pulse mode which controlled the exposure time to match the residence time within the flame front.

3.1 EQUIPMENT SETUP

3.1.1 CO₂ LASER

In order to obtain heating fluxes comparable to those inside conventional boilers and furnaces, the CO₂ laser was tuned to produce a multi-mode beam pattern at a wavelength of 10.6 μm . This roughly uniform beam pattern was further smoothed by focussing the downward directed beam to a point near the bottom of a protective pipe through which an inert gas (N₂) was passed. The arrangement is shown in figure 1a. The schematic of the focusing system for providing a reasonably uniform beam of high flux ($> 200 \text{ W/cm}^2$) is shown in figure 1b. The somewhat diverging beam exited the pipe and passed through a water cooled orifice plate to a thermopile power sensor. The setup included replacement of the complete set of optics in the laser cavity as well as the output lens. Beam alignment was carried out with the aid of a He-Ne laser. The beam power was maximum at a beam current of 100 mA with an operating pressure of 13.5 mm Hg. The alignment ensured a Gaussian profile which was checked at regular intervals by observing the burn pattern on a thin wooden probe. The flux was determined by

Fig. 1a Arrangement for the laser irradiation of separated particles on a reflective (Al) substrate at high flux levels ($> 200 \text{ W/cm}^2$)

Fig. 1b Schematic of the beam focusing system for unidirectional irradiation of particles.

dividing the total beam power by the area of the circular burn pattern formed on the wooden probe on the orifice plate, using a short laser pulse. The power at the surface of the orifice plate (where the sample pan was positioned for sample irradiation), varied with the position of the output lens relative to the plate. The height of the lens above the orifice plate was varied by adjusting a micrometer screw attached to the lens housing. To avoid damage to the thermopile sensor, the output lens was lowered only to the point just below the focal point of the lens. Hence all the heating was carried out with a flux obtained from the diverging beam. The protective pipe around the lens ensured that this was always the case. The lowest position of the lens from the orifice plate was obtained when the protective pipe was lowered until it rested on the orifice plate. At this position the beam was still divergent, and the lens was approximately 7 cm from the orifice plate. The photograph in figure 2a shows the experimental arrangement of the CO₂ laser. The beam optics were enclosed in a protective shield of perspex which also served to provide a controlled environment for the studies. The lower picture figure 2b, shows the glove box in which all the sample preparation was carried out.

3.1.2 SCANNING ELECTRON MICROSCOPE

Computer controlled scanning electron microscopy (CCSEM) technique permits the study of the transformations of inorganic constituents from initial stages of coal combustion to the transformation that occur during ash deposition. Its specific application include: (1) determination of the size, composition, and association of minerals in coals; (2) determination of the size and composition of intermediate ash components and fly ash; (3) determination of the degree of the interaction in ash deposits and (4) identification and quantification of the

Fig. 2 Experimental setup of the CO_2 laser for unidirectional heating of coal particles. The beam optics were enclosed in a protective plastic shield which also served to provide a somewhat controlled environment. The lower picture shows the glove box used for preparing the samples before heating.

components in ash deposits that are responsible for the formation of ash deposits. In order to achieve the second objective the CCSEM was used to monitor the morphological changes, the structure of ash transformation associated with the laser irradiation of the low-rank coals. The CCSEM employed consisted of a JEOL JSM 6400 scanning electron microscope, a LINK Analytical backscatter electron detector, an ultrathin window energy dispersive (EDS), X-ray detector, a digital beam control, a LINK Analytical X-ray microanalyzer control system, and stage automation. The microanalyzer was interfaced with a personal computer for advanced data manipulation. The major components of the SEM system that make it possible to image, size and analyze inorganic particles include the backscatter electron detector, digital beam control and the ultrathin window EDS X-ray detector. The cathode filament is the source of electrons, which are accelerated by a high voltage. Condenser and objective lenses focus the electrons to a fine spot on the sample. Secondary electrons are produced by the interaction between the primary electrons (from the filament), and beam and the sample. The strength of the interaction varies from point to point according to the topography of and chemical composition of the sample. The production of secondary electrons also varies according to the sample material and the angle between the beam and the sample surface. Sample preparation for scanning electron microscopy is very simple. If the sample is conductive, such as a metal or semiconductor, and if it is small enough to be introduced into the sample chamber, no preparation is necessary. Care must be taken however, to ensure that the sample is clean and is sufficiently degassed so as not to disturb the relatively high vacuum inside the specimen chamber. For insulating (non-conducting) materials observation is still possible without preparation as in the conductive case. However, the image quality will suffer from charging effects due to accumulation of beam electrons absorbed by the insulator

having no conducting path for the absorbed electrons to dissipate to the electrical ground. The electron accumulation leads to space charge regions on the sample resulting in poor image quality. Space charge effects are eliminated by either operating the SEM at a low accelerating voltage or coating the sample with a conductive layer. A low accelerating voltage operation usually results in lowering the resolution. The better method is to apply a thin layer of conductive material on the insulator's surface. The conductive coating greatly reduces the electrostatic charging of the specimen by the electron beam, and allows the use of secondary electron emission for a moderate beam energy for better imaging. In addition to lowering the charging effects in SEM images, the application of the conductive coating also reduces damage to sample due to heating produced by the electron beam. Coal can sometimes be classified as an electrical semiconductor, but in a scanning electron microscopy it behaves somewhat like an insulator. Uncoated coal samples unless operated at relatively low accelerating voltages exhibit strong charging effects. Imaging was done on both uncoated and metal (Au/Pd) coated particles.

3.1.3 ENERGY DISPERSIVE X-RAY ANALYSIS

The scanning electron microscope has an electron beam-specimen interaction region, (generally produced from a much larger volume of the sample), which produces X-rays in addition to the secondary electrons, (produced from a focussed beam at depths of a few nanometers), which are employed to produce images. If the SEM has an energy dispersive X-ray analyzer attached to it then all the X-rays emitted from the sample can be collected and analyzed by energy to obtain spectra corresponding to the elements in the sample. Comparison of the spectra from

different particles would give semiquantitative information as to the relative concentration of elements in each by comparing relative intensities of the X-ray lines. A map of the distribution of a particular element throughout the sample can be obtained by collecting only the X-rays that originate from that element. Elemental X-ray maps provide information of the spatial distribution of the element of interest in relation to the rest of the sample.

3.2 SYSTEM CALIBRATION

3.2.1 LASER

Some modifications to the laser beam delivery system was carried before embarking on the system calibration. The original copper pipe through which quench gas passed was replaced with an aluminum pipe of a larger diameter (1-inc), which permitted a direct impact of the beam without any reflection from the inside the pipe. The pipe also served as the channel for the nitrogen gas for the non-oxidizing studies. A new set of beam optics was procured to replaced the old. New "O" rings were also employed to ensure a good vacuum seal. Beam alignment was then carried out with the aid of a low power He-Ne laser. Beam alignment of the laser cavity was relatively easy. The He-Ne beam is directed inside the CO₂ laser cavity to the rear total reflecting mirror. The reflected beam from the mirror was then adjusted until it was coincident with the incident beam. Further adjustment of the mirrors ensured that the beam exited from the center of the output lens. Once the beam was correctly aligned no reflection occurred inside the cavity and the full energy was delivered to the output lens. A spirit level was used to ensure that the laser was level.

The output power reaching the sample depended upon the relative position at the output focusing lens with respect to the specimen. To ensure that the beam intensity applied to the sample was optimized measurements were made of the laser power relative to the output lens position. The results which are shown in figure 3 provide the data for optimizing the beam intensity reaching the specimen. The value of the beam intensity in Watts/cm² was obtained by producing a burn pattern (circular with a properly tuned system), and calculating the area of the circle. The power was then divided by the area to obtain the necessary intensity.

3.2.2 SEM AND X-RAY UNITS

Both the JOEL JSM 6400 scanning electron microscope and the LINK Analytical energy dispersive system x-ray units were installed by the vendor and the initial calibration was also carried out by the vendor. Figure 4a the JOEL JSM 6400 scanning electron microscope with LINK X-ray detector. The LINK microanalysis system is shown in figure 4b.

4. EXPERIMENTAL PROCEDURE

4.1 MOISTURE ABSORPTION STUDIES

In order to determine the behavior of the low-rank coal in the laboratory setting a number of studies was carried out to determine the rate at which moisture was reabsorbed by the coal particles after being completely dried. All the samples studied were kept in a glove box under nitrogen. Inside the glove box a small hot plate and a microbalance were also kept to enable the sample to be dried and weighed. The atmosphere inside the glove box was regulated by first

Fig. 3 Beam intensity at the specimen position as the output lens is raised and lowered. The intensity was calculated for a mean beam pattern diameter of 0.456 cm

A

B

Fig. 4 The JOEL JSM 6400 scanning electron microscope (a) with a LINK X-ray detector. The LINK microanalysis system is shown below (b)

evacuating it and then allowing air back in until the required relative humidity was attained. About 4 to 5 g of powder from a given pack was placed on an aluminum foil and dried by heating to 300° F on the hot plate. The sample was completely dried when the difference in the dry mass and the initial mass equaled the as-received ASTM value. Once this was achieved the hot plate was turned off, the foil was removed and placed elsewhere inside the glove box. The just dried sample was left uncovered so that it would absorb the moisture inside the glove box. The amount of moisture absorbed by the specimen was recorded as a function of time. The resulting data are shown in figure 5 for the Beulah lignite at relative humidity of 65, 52, 44 and 30 % respectively. The corresponding data for the Montana Rosebud coals at 44% relative humidity are also shown. The rate of absorption of moisture was slower for the Rosebud subbituminous coals than for the lignite as can be seen from the graphs. Also the mass increase for the Rosebud coals did not deviate very much from the values shown in figure 5 when the relative humidity was increased hence the reason for showing only the data for 44% R.H. The most significant information derived from the graphs is that in the first one hour of drying the amount of moisture absorbed by the particles is significantly small such that under the right environment the sample if subjected to the laser heating flux within one hour of drying then may be considered initially dry specimen. All the particles used in the studies were exposed within 20 minutes of being taken out the glove box. A desiccator was kept close at hand so that unused specimens could be stored. The relative humidity inside the laboratory was maintained constant at between 40 and 45% as far as possible .

Fig. 5 The amount of moisture absorbed as a function of time for Beulah lignite and Montana Rosebud coals at different relative humidity.

4.2 DEVOLATILIZATION WEIGHT LOSS

Two types of coals Montana Rosebud subbituminous B (DECS 10) and North Dakota Beulah lignite (A) (DECS 11) were studied. They were obtained as sealed, inerted samples from the U.S. Department of Energy Coal Sample repository at the Pennsylvania State University. The as-received proximate and ultimate analyses of the coals are shown in Tables 2. They were placed in a dry, inerted glove box together with a balance, hot plate, and 200/230 mesh sieves. All preparation of the samples for heating such as, sieving and drying (see section 4.1), was carried out inside the glove box. The particles selected for study were -200/+230 mesh approximately 63 - 74 μm . Small quantities of coal were dried at 120°C for 30 minutes and stored in the glove box. The measured moisture content of the two coals was in good agreement with the supplied values listed in Table 2. To heat the particles the following procedure was employed. Particles were carefully separated and centered on a small (6 mm) aluminum foil sample pan whose mass had been predetermined. The particle laden pan was reweighed on a sensitive microbalance to 0.1 μg , and carefully placed over the 5 mm. orifice for irradiation by the pulsed laser beam. The particles were heated in both cold air and nitrogen environment. After irradiation, the particles were reexamined under an optical microscope for evidence of particle loss or movement outside the beam area, and reweighed on the microbalance. In prior work [32-33] the charred particles were picked off the substrate, which was then reweighed to determine the tar mass that condensed on the foil. The latter was then added to the volatile mass to determine the total devolatilization mass loss. This procedure was impractical for the lower rank coal particles due to the presence of many char fragments and little collected tar. The Al

Table 2. The as-received Proximate and Ultimate analyses of the low-rank coals

Rosebud Subbit. coal

Proximate Analysis	As Rec'd	Dry	Daf	Dmmf(Parr)
% Moisture	21.58			
% Ash	9.85	12.56		
% Volatile	32.68	41.67	47.66	46.86
% Fixed Carbon	35.89	45.77	52.34	53.14

Ultimate Analysis	As Rec'd	Dry	Daf	Dmmf(Parr) (14.20%MM)
% Ash	9.85	12.56		
% Carbon	53.62	68.37	78.19	79.69
% Hydrogen	2.89	3.69	4.22	4.30
% Nitrogen	0.72	0.92	1.05	1.07
% Sulfur(Total)	0.91	1.16	1.33	
% Oxygen(Diff.)	10.43	13.30	15.21	14.94

Beulah Lignite

Proximate Analysis	As Rec'd	Dry	Daf	Dmmf(Parr)
% Moisture	33.38			
% Ash	6.37	9.56		
% Volatile	37.36	56.08	62.01	61.63
% Fixed Carbon	22.89	34.36	37.99	38.37

Ultimate Analysis	As Rec'd	Dry	Daf	Dmmf(Parr) (10.73%MM)
% Ash	6.37	9.56		
% Carbon	44.07	66.15	73.14	74.10
% Hydrogen	2.68	4.03	4.48	4.51
% Nitrogen	0.60	0.90	1.00	1.01
% Sulfur(Total)	0.49	0.74	0.82	
% Oxygen(Diff.)	12.40	18.62	20.59	20.37

foil substrate served to support the particles during weighing and irradiation, and acted as a thermal quenching medium when the laser pulse was complete. The heating period was thereby better defined [32].

4.3 MASS LOSS CHARACTERISTICS

The irradiation time dependent mass loss for the Beulah lignite and Rosebud subbituminous coal particles is shown in figure 6., where they are compared with prior results from high volatile A (Pittsburgh, PA) and low volatile (Pocahontas, VA) bituminous coal particles (100 μm) obtained with the same laser configuration. The particle size fraction used in most of the runs was 63 - 74 μm , mean diameter 65 μm . The laser flux levels employed was 200-300 W/cm². The weight loss plots of the Pittsburgh and Pocahontas coals show a steady rise with time after a 6-9 ms induction period, followed by a final plateau. The curves for these bituminous coals have characteristics "S" - shapes and are reasonably described by the equation

$$V(t) = V(\infty)[1 - e^{-t/\tau}] \quad (1)$$

where $V(t)$ is the volatile yield for any exposure time t , $V(\infty)$ is the maximum volatile yield at $t \rightarrow \infty$ and τ is the time constant for volatile evolution. The lignite and subbituminous particles, however, feature a plateau at a 20 pct loss at exposure in the in the 20-100 ms range, after an induction period of 7-10 ms and a mass loss rate comparable to the high-volatile bituminous for 10-20 ms. On either side of the plateau the curve is reasonably represented by equation (1). It would appear that a strongly endothermic early (< 100 ms) devolatilization process such as

Fig. 6 Grouping of the devolatilization kinetics of 65 μm lignite and subbituminous coal particles at $> 200 \text{ W/cm}^2$ vs the kinetics of 100 μm high and low volatile bituminous coal particles.

removal of chemically bound water limits the temperature of the low-rank coal particles in this time range ("wet-bulb" temperature), and $V(t)$ is constant during this period. At the end of this process, the particle temperature rises strongly and further pyrolysis processes and mass losses ensue. It would be of interest, therefore, to determine whether or not the same hiatus in mass loss rate is observed for other low-rank coals under these conditions.

In figure 6, the mass loss ordinate is identical to the volatile yield $V(t)$ and is given by

$$V(t) = \frac{m_o - m(t)}{m_o} \times 100 \quad (2)$$

where m_o is the mass of the sample prior to exposure ($t=0$), and $m(t)$ is the sample mass after an exposure time t . It is easily shown that equation (1) leads directly to

$$\frac{dV(t)}{dt} = k[V(\infty) - V(t)] \quad (3)$$

which is seen as the standard first order rate equation, [34,35]. k is the rate constant and is equal to $1/\tau$. Hertzberg and Ng, [24] have stated that the devolatilization time is inversely proportional to some net flux level which is the difference between the input laser flux and some loss flux. Also the devolatilization time is directly proportional to the particle diameter.

There was no observed dependence of mass loss of the lignite particles on laser flux in the 200-300 W/cm² range studied. As indicated the particles were heated in a cold air environment. As such heat losses were relatively more significant as the particle size was reduced. Hence the net heat flux for smaller particles was less than the net heat flux for larger particles. Also although

heat flux for smaller particles was less than the net heat flux for larger particles. Also although the net heat flux was higher for larger particles, the surface heating rate for smaller particles was greater since the surface area per unit mass was larger. Also since the lower end of the flux used is 67% of the upper end of the range, it is safe to say that the overall average net heating rate was the same for the range of particles studied. There was no apparent difference in mass loss under a nitrogen flow or in air. It is quite possible that the nitrogen flow was inadequate for the lignite and subbituminous particles and may account for the similar losses upon irradiation in air or N_2 for the lignite, and the very high losses ($>90\%$) observed for longer term ($>2s$) irradiation of the subbituminous particles. The average losses for a given irradiation exposure are therefore plotted for the lignite. The data for the subbituminous coal in air, at a laser flux of 200 W/cm^2 , fall naturally into time interval sets. The average values of the sets, including a 22% loss from 30 to 90 ms are shown in figure 6. The data for the bituminous coals represent individual measurements at a flux level of 200 W/cm^2 in N_2 . The losses for the subbituminous coal are comparable to the lignite for exposures of less than 2 seconds. They become very high (80% or more), however, for exposures of 2 seconds or more in air. It would appear that char burnout occurs more readily for the Rosebud subbituminous than for the Beulah lignite particles. Further work is needed, however, using more definitive atmosphere control to establish the latter conjecture.

Some modification was made to the nitrogen delivery system in an attempt to improve the inert environment. The new improved delivery system appeared to make a difference in the weight loss data. However, only a few runs later the CO_2 laser broke down and the measurements were discontinued. The data obtained before the breakdown are discussed in section 4.4.

4.4 MICROSCOPOIC STRUCTURE

Scanning electron micrographs of several Rosebud coal particles exposed at 200 W/cm^2 in air environment for exposure times ranging from 10 ms to 6 secs. are presented in figures 7 A through L. Micrograph A shows the result of exposing the particles for 10 ms. The particles show very little change from the unheated state although protruding sharp edges managed to dislodge from their attachment. Some of the sharp edges are still visible on the unburned coal. The mass loss was quite small. In B the particles were exposed for 30 ms. The particles begin to crack in several places. Some edges are clearly charred and the mass loss begin to be substantial. The particle in the foreground has the appearance of melting at the surface. At 50 ms, C, chars begin to form. The particles are almost all completely devolatilized. When the heating time was increased to 60 ms ,picture D, the result was completely devolatilized particles leaving char residue. Further increase in the length of the exposure time resulted in increased mass loss with generally completely devolatilized char particles. Micrographs E through H are testimony to this. As exposure time increases the mass loss increases too peaking at around 80%. Photomicrographs I through L show completely devolatilized particles leaving char residue in each case.

At 4s exposure time ash cenospheres were formed with this particular sample pack (micrograph J). It is not quite clear why the cenospheres formed at this exposure time and not before or after for this sample pack. Much greater mass loss was associated with this pack and so have other specimens which have yielded cenospheres . This rather larger than usual loss of weight may be attributed to the fact that much of the bubbling particles release a good deal of their mass in gaseous state and what remains "hardens" after cooling to form the outer of the

Figure 7 A-L

Scanning electron micrographs of 63 - 74 μm diameter Montana Rosebud subbituminous coal particles heated in air with a laser flux of 200 - 300 W/cm^2 . The corresponding weight loss for the particles are shown in Figure 8.

A

B

C

D

E

F

G

H

I

J

K

L

resulting sphere. Jost and co-workers, [17] have shown that increased volatile yields are obtained in oxidizing environments. Energy is fed back from the burning volatiles to the coal particles permitting higher particles temperatures and hence faster devolatilization rates and greater volatile yields. The measured weight loss versus exposure times for this run is shown in figure 8. The data points for the photomicrographs A through K are represented by the + (plus) sign in figure 8. The data points marked with asterisk are for another run using a much higher beam intensity of 315 W/cm^2 . The photomicrographs for this run are not shown. The effect of the improved nitrogen delivery is much in evidence in the weight loss data. The largest weight loss was about 50%. Figure 9 A through D show selected SEM micrographs of Beulah lignite particles irradiated with a beam of intensity 200 W/cm^2 in air environment. The corresponding exposure times were 20 , 40 50 and 100 ms respectively. At 20 ms cenospheres have already formed. The char particles show more fragments than observed from the Rosebud coal particles. The weight loss, however, was somewhat smaller at this exposure time. More fragmentation are observed at 40 ms exposure time and the mass loss increases just as rapidly reaching above 80% in some cases just like in the case with the Rosebud subbituminous coal particles. Selected micrographs from the run with Beulah lignite coal particles in nitrogen environment are shown in figure 10 A through C. The corresponding mass loss versus exposure time characteristics are shown in figure 11. The graph also shows that the mass loss is reduced substantially in nitrogen environment. Evident in these pictures are several smaller particles due to fragmentation of the Beulah lignite particles during heatup.

Fig. 8 Devolatilization weight loss for Montana Rosebud subbituminous coal particles (63 - 74 μm dia.) heated in air with a laser flux of 200 - 300 W/cm². The corresponding weight loss obtained in nitrogen environment are indicated by the dots (.)

Fig. 9 Scanning electron micrographs of Beulah lignite particles
(63 - 74 μm dia.) heated in air with a laser flux of 200 - 300 W/cm².

Fig. 10 Scanning electron micrographs of Beulah lignite particles
(63 - 74 μm dia.) heated in nitrogen environment with a laser flux of
200 - 300 W/cm^2 .

Fig. 11 Devolatilization weight loss for Beulah lignite particles (63 - 74 μm dia.) heated in air with a laser flux of 200 - 300 W/cm^2 . The corresponding weight loss obtained in nitrogen environment are indicated by the Plus (+)

4.5 CORRELATION WITH WEIGHT LOSS DATA

The correlation of weight loss data with microscopic observation for devolatilization in air is shown in figure 12, where the volatility yields are reproduced with the letters A through K shown to indicate exposure times for which micrographs were obtained with the scanning electron microscope (SEM). The micrograph, from another set of runs, are shown in figure 13. The coal type, exposure times and magnification are listed in Table 3. Fig. 13A shows a coated Beulah lignite particle prior to laser irradiation. The particle is thickest in the middle and tapers to a thin edge at the right. This tapered edge was apparently normal to the laser beam during the 50 ms irradiation in air at 200 W/cm² flux. Figure 13B shows the very extensive devolatilization of this edge which left only a lacy residue, and the cracking of the rest of the particle along bedding planes. The particle lost about 20 pct of its initial mass in the process. The potential interference of the coating on both the irradiation and the fine detail of the resulting image argues for the use of uncoated specimens, whenever possible. Figure 13C shows such an uncoated lignite particle which had been irradiated in air at 200 W/cm² for 3 seconds and imaged using higher energy backscattered electrons that are less sensitive to charging. The appearance of "foam" cells is due to the penetration of the uncoated particle by the 4 kV beam, resulting in a tomographic view of the strongly heated particle. The lighter areas are rich in ash elements, which have a higher backscatter efficiency than carbon. Note also the filamentary appendages on the particle. None of the above features would be apparent in a metal coated specimen. Figure 13D shows some additional uncoated particles treated and imaged as in figure 13C. The formation of melted 10 μ m fragments, the ash cenosphere, and porous char is evident. Both of the particles shown in micrograph C and D incurred mass losses of up to 65 pct after

Fig. 12 The devolatilization and char oxidation weight loss for a function of time for Beulah lignite and Montana Rosebud coal particles heated in air at > 200 W/cm^2 . The weight loss data are correlated with the morphological changes in figure 13 according to exposure time indicated by the large squares.

Figure 13 A-K Scanning electron micrographs of 63 - 74 μm diameter Beulah lignite and Montana Rosebud subbituminous coal particles heated in air with a laser flux of 200 - 300 W/cm_2 for different times as indicated in Table 3 below. The corresponding weight loss for the particles can be obtained from the letters A through K near the squares in Figure 12.

Micrograph	Coal Type	Exposure	Magnification
A	Beulah	Unexposed	600
B	Beulah	50 ms	550
C	Beulah	3 s	1000
D	Beulah	3 s	750
E	Rosebud	Unexposed	425
F	Rosebud	10 s	1000
G	Rosebud	10 ms	600
H	Rosebud	100 ms	600
I	Rosebud	1 s	500
J	Beulah	3 s	2300
K	Rosebud	2 s	650

Table 3 Coal type, exposure time and magnification for the micrographs shown in Fig 13

A

B

C

D

E

F

G

H

I

J

K

3 s exposure in air at 200 W/cm^2 . Micrograph E shows a coated, unexposed Rosebud coal particle at 400X magnification. The plant origins of this particle are obvious, as are its capillary macropores. Similar Beulah lignite particles have been noted, but no such bituminous particles. The implied remnant cellulosic content of such low-rank coals may help account for the mass loss rate hiatus of these particles that was mentioned earlier. Figure 13F shows a coated Rosebud particle after a 10 s laser irradiation in air at 200 W/cm^2 . This particle has only a lace-like porous structure and ash cenospheres after its devolatilization and char burnout.

Micrographs G and H are both Rosebud coal particles exposed under identical conditions for 10 ms and 100 ms respectively. Cracking along bedding planes are clearly visible also in these particles such as those observed in the Beulah lignite in micrograph B. The mass loss for the particle in G was 10%. The corresponding mass loss for the 100 ms exposed particles was 22 pct. Micrographs I, and J show very similar appearance and leads one to conclude that the particles in both these specimens were completely devolatilized. This is not entirely surprising since in general the carbon skeletal structure of many chars of different ranks are somewhat similar than the diversity exhibited by their parent coals, [36]. The particles in micrograph I, (500X) is a Rosebud coal that had been exposed in air for 1s with a flux of 200 W/cm^2 . Its appearance after losing about 53 pct of its initial mass is quite similar to that in micrograph J, (2,300X), deep cracks in the chars. Micrograph J is a Beulah lignite exposed for 3 s under the same conditions. The mass loss for the lignite particle was 73 pct. The Rosebud particle shown in micrograph K appears only partially devolatilized in spite of losing nearly 65 pct of its initial mass after 2 s irradiation in air. The very small particles seen around the larger particles are the result of fragmentation that appears to proceed long after the particle has been exposed.

5 TRACE ELEMENTS

Advantage was taken of the analytical capabilities of the energy dispersive X-ray analyzer, the LINK microanalysis system, attached to the JSM 6400 scanning electron microscope. X-ray spectra were obtained for the coals to ascertain the trace elements in these coals. The X-ray spectra for the Rosebud subbituminous coals and the Beulah lignite are shown in figures 14 and 15. In figure 16 the X-ray spectra from a typical run-of-the mill coal fly ash are shown. The $K\alpha$ X-ray map for Beulah is also shown in figure 17. The map identifies three elements with heavy concentration in the coal, namely, sulfur, iron and calcium. Dots in the figure represent the concentration of the particular element. The Au and Pd lines observed in all the spectra are due to the metal coating applied to the samples prior to SEM analysis. In cases where uncoated samples were analyzed the lines of course, do not appear. Of particular importance is the substantial number of trace elements to be found in the fly ash. Inorganic elements observed in both Rosebud and Lignite coals are Si, K, Ti, Fe, Al, Ca, Na and Mg. More trace elements were observed in the run-of-the mill coals and fly ash than were observed in the Rosebud and Lignite coals. This abundance of trace elements in run-of-the mill coal can be attributed to the cleaning and grinding methods employed both at the vendor end and also by the utility industry prior to injection into the boiler. The spectra in figure 18 was obtained from the cenosphere of the Rosebud coal irradiated at 4s in air (see SEM micrograph 7J). The spectra indicates that the cenosphere formation is dominated by the elements silicon, phosphorous, chlorine and calcium. The presence of aluminum cannot be ruled out. However, the Al seen in the spectra is due to the specimen holder which is aluminum pan. Knowledge of the elemental composition of coal is useful as it makes it possible to develop effective means for cleaning the

Fig. 14 X-ray spectra for Rosebud subbituminous coal exposed at 200 W/cm² for 600 ms in air

Fig. 15 X-ray spectra for Beulah lignite particles exposed at 200 W/cm^2 for 700 ms in air

Fig. 16 X-ray spectra for a typical run-of-the mill coal flyash. The sample was obtained from Delmarva Power, Indian River Plant, DE

Fig. 17 $K\alpha$ X-ray map Beulah lignite showing large concentration of sulfur, iron and calcium.

Fig. 17 $K\alpha$ X-ray spectra of cenosphere from Rosebud subbituminous coal irradiated at $> 200 \text{ W/cm}^2$ in air for 4s.

coal as well as designing efficient boilers for their combustion. Elemental composition has also been used as tracers for the determination of mass loss due to pyrolysis,[1].

6 DISCUSSION

Microscopic observations such as those in this report should certainly contribute to improved theories of combustion. Investigators such as Smooth, Horton and their colleagues [37-38], published scanning electron micrographs of Pittsburgh seam coal particles before and after heating. During the short time (about 50 msec) that the particles traversed the flame front, they were observed to have lost their original sharp edges a angular appearance and become more spherical. Many particles showed blow holes due to escaping volatiles. From the SEM micrographs, the particles did not appear to change much in size during the passage through the flame front, but Coulter Counter size analysis of collected particles showed a slight increase in average size. Similar results were found by Milne and Beachey, [39], who used a flat flame burner to study coal dust flame propagation. Lightman and Street [9], extensively studied coal particles heated in furnaces, shock tubes and large combustors. At furnace temperatures of 400° to 500° C, they observed internal gas bubbles in the particles due to evolving volatiles an some blow holes as the volatiles escaped the surfaces of the particles. At higher temperatures (up to 1,200° C), various types of "balloons" or cenospheres were observed. These particles were as much as twice their original size. In a later study Street, Weight and Lightman [10], studied the structural changes in pulverized coal during rapid heating in drop-tube furnace in atmospheres of air and nitrogen. The structures of the chars formed in the oxidative and inert gases were found

to be different. The particles heated in nitrogen tended to be more open and form more cenospheres, they also had smaller pores than the particles heated in air. A further important finding of their work was that with the exception of fusain (which formed solid particle chars), it was impossible to relate exactly the char types to particular lithotypes of the original particles. Very few such studies, however, have been carried out in respect of subbituminous coals and lignites. Of particular importance is the work by Jost and coworkers, [17], who studied the reactivity and devolatilization of Montana Rosebud subbituminous coals among Utah and Illinois bituminous coals.

7 CONCLUSION

The similarities and differences in devolatilization behavior of supported low-rank and bituminous coal particles under high flux laser irradiation have been demonstrated. All coal particles show an induction time of 6-10 ms under these conditions, followed by increasing mass losses with exposure time, until a plateau is reached. For the low-rank particles, the climb to total devolatilization is interrupted by a plateau at 20-100 ms. The presence of chemically bound water, possibly in the form of remnant cellulosic species, is suggested as a mechanism for a limiting ceiling temperature and mass loss as long as any H₂O remains in the coal. The laser pyrolysis/scanning electron microscopy investigative method employed here has made possible the observation of the time resolved microstructure data and structural features of the Rosebud subbituminous and Beulah lignite coal particles. Similar studies have been conducted on bituminous and higher rank coals by other investigators employing more conventional methods

such as electrical screen heater reactor, [8,35] drop tube furnace, and shock tube furnace,[9,10].

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