

## COLD ATMOSPHERE PYROLYSIS OF PULVERIZED COAL USING 10.6 $\mu$ M LASER HEATING

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### ABSTRACT

The pyrolysis behavior of three different coals was explored in a unique experimental arrangement that inhibited secondary reactions of the primary volatiles. They were transported as particulate suspensions in room temperature nitrogen, and heated to particle temperatures in the range 1300-1800K at about  $10^5$ K/s by a 10.6 $\mu$ m laser beam. This approach allows well-controlled heating with good time/space resolution, and very rapid thermal quenching of primary volatiles by diffusion into the cold nitrogen. A key result is that gas phase C species account for less than one percent of the coal C although H<sub>2</sub>O comparable to the coal moisture content is evolved. Residual solids have proximate and ultimate analyses very close the raw coals but significantly enhanced solubility. It appears that tarry volatiles are produced with minimal change in chemical bonding and recondense in the cold gas flow. This suggests that primary coal volatiles are of high molecular weight, with subsequent gas phase decomposition giving low molecular weight products in hot atmospheres.

### INTRODUCTION

The extensive measurements of coal devolatilization performed over the past two decades have almost exclusively employed conductive heat transfer from a hot environment to the coal sample under test<sup>(1-5)</sup>. This results in a significant volatile residence time in a hot environment, relative to the time scale required for particle devolatilization. Consequently, it is difficult to give assurance that the observed product species are in fact primary volatiles. It is also unclear to what extent the composition of the gas environment used in various experiments affects primary volatile yield, and to what extent it reacts at elevated temperatures to stabilize volatiles as lower molecular weight or hydrogenated species.

It has also proven to be difficult to explore heating rate and temperature regimes corresponding to pulverized fuel combustion or entrained flow gasification, typically in the range  $10^4$ - $10^6$  K/s, and with peak temperature approaching 2000K. Heated grid experiments have been limited in absolute heating rate and peak temperature, and leave some uncertainty regarding coal particle tracking of the grid temperature.<sup>(1)</sup> Also, the physical scale of the heater and typical experiment time scales suggest that the primary volatiles may be cooled relatively slowly by diffusive mixing. Flow tube reactors of course allow relatively rapid diffusion of primary volatiles away from the parent particle, but into a hot gas environment.<sup>(3,4,6)</sup> Further, the usual use of hot walls for the reactor renders particle temperature measurement by pyrometry questionable, and predictive approaches based on particle dispersion and heat transfer modeling are quantitatively uncertain.

A third experimental approach uses radiative heating to establish particle temperatures sufficient for devolatilization measurements under high heating rate, high temperature conditions. Initial experiments used pulsed laser heating of relatively large particles, followed by averaged product analysis.<sup>(7,8)</sup>

Transient thermal diffusion into the bulk sample resulted in a wide range of thermal history contributing to the total yield. The product appeared to range more or less continuously from H<sub>2</sub> to "tars". More recently, the availability of high power, constant output infrared lasers has allowed the development of steady, entrained flow particle heating experiments. This is analogous to a flow tube reactor concept, except that heating is radiative, with the carrier gas and local structures remaining cold.

Radiative heating of an entrained flow of particles allows several gains in experimental environment control and diagnostics.<sup>(9)</sup> The primary advantage results from particle dispersion in a carrier gas, with gas heating occurring only indirectly, by diffusion from the radiation absorbing particles. This results in complete decoupling of bulk gas temperature from the particle heating rate and temperature. Consequently, primary volatiles diffuse into a cold environment on a minimal time scale. It corresponds to 5ms or less for spherically symmetric diffusion from a 50µm nominal particle diameter in a room temperature N<sub>2</sub> atmosphere. The observed phenomenon of volatile jetting would result in much more rapid cooling. While not instantaneous, the cooling time scale appears to approach a practical minimum. This results in minimum decomposition or reaction of primary volatile species after leaving the parent particle. Use of laser heating of a dilute entrained particle flow also allows the imposition of arbitrary temperature-time profiles by tailoring of the spatial laser beam power distribution. This allows, for example, exploration of the relative effects of heating rate and final temperature on devolatilization behavior, and correspondingly a possible gain in basic understanding of devolatilization mechanisms.

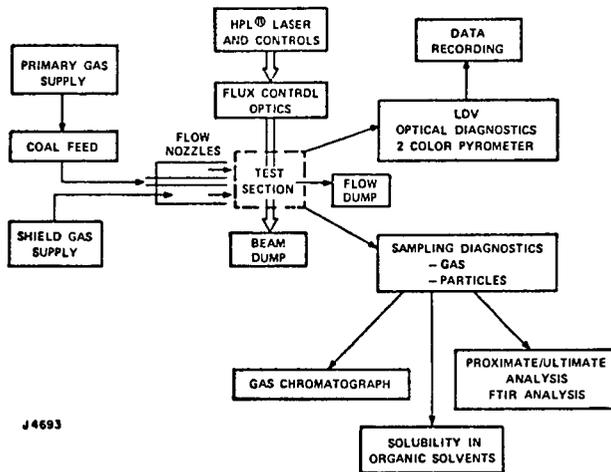
Structurally, the need for a hot walled flow confinement structure is eliminated. For one atmosphere experiments, no wall structure is required, with all flow control based on aerodynamic techniques. This allows very extensive diagnostic and radiative heating access, and eliminates secondary wall radiation as a factor in direct particle temperature measurement.

## EXPERIMENT DESIGN

The overall experiment approach was based on the time shared availability of a 15 KW CW CO<sub>2</sub> laser, (Avco HPLS<sup>(8)</sup>). It provides a continuous output at 10.6µm wavelength, with power level adjustable by the user. It was used to irradiate a dilute coal particle suspension transported in a room temperature gas. Figure 1 shows the key experiment components in block diagram format. They break down into three major groupings: Fluid supply and flow control; radiative heating system; and diagnostics. These are discussed in sequence below.

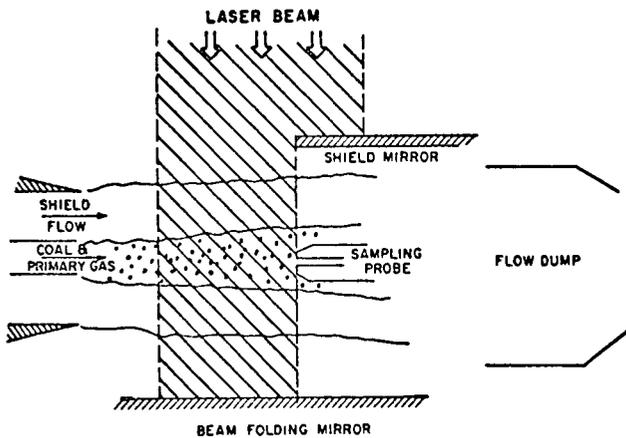
### Fluid Supply and Flow Control

This has as its purpose the establishment of a well defined, steady flow of pulverized coal entrained in a carrier gas. A fluidized bed feeder is used as the primary coal supply, with the feeder supported on a precision electronic balance to give time averaged flow rate information. The coal/carrier stream is delivered to a nozzle designed to homogenize the particle dispersion and give a uniform velocity distribution. Dispersion was checked for space and time uniformity using HeNe beam transmittance, and velocity monitored using an LDV. As shown in Figure 2, a shield flow was also used. Nitrogen was chosen to avoid air entrainment and consequent oxidation reactions with the coal, and velocity matched to the core flow. This coaxial flow passed through the heating and diagnostic volume, and was then collected using an extractor fan and particles filtered out before venting to the atmosphere.



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Figure 1 - Component Schematic of Experimental System for Steady Flow Radiative Coal Devolatilization



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Figure 2 - Conceptual Schematic of Flow Structure in Radiative Heating Zone

Coal particle loading was chosen as a compromise between uniform radiative heating across the flow, and sufficient concentration to permit quantitative analysis of the expected gas phase volatiles. Dimensions were chosen to ensure existence of an undisturbed potential flow core for measurements over a residence time up to 30ms, with high spatial, and hence time resolution. This is related to particle heating rate and laser beam power as shown in Figure 3. The "Experimental Resolution Parameter" plotted is equivalent to the number of discrete data points obtainable at a given particle heating rate. For fixed input power, higher rate implies a smaller heated volume, which for fixed spatial resolution in the flow gives fewer data points. As shown, heating rates of direct interest to pulverized fuel applications require about 10KW delivered laser power for useful time resolution of data points.

### Radiative Heating System

The laser source used delivers an output at 10.6 $\mu$ m wavelength, with power adjustable up to 15KW. The output is spatially nonuniform and requires optical homogenization for this experiment, although not for normal metalworking applications. Optics are fabricated from copper, highly polished, and actively water cooled. A beam integrator was used to spatially overlay multiple segments of the source beam to give a spatially uniform structure. To provide relatively uniform particle heating, this is split into two beams using a roof prism mirror. They are again reflected to cross at circa 160 degrees in the coal flow, defining the heating zone. This gives uniform heating of both sides of the particles, and appears to be an adequate approach to  $4\pi$  steradian illumination. Uniform particle heating across the flow implies limited beam absorption, resulting in significant (>90 percent) power wastage. This is absorbed on zirconia faced water cooled copper beam dumps, maintained at low temperature to avoid secondary thermal radiation.

### Diagnostics

Diagnostic systems include monitoring of input flows and laser power, real time optical measurement of particle conditions, and post-test analysis of gaseous and solid samples. As discussed above, particle flow is monitored using a precision balance with the fluidized bed feeder. Gas flows are set, and monitored using rotameters. Laser power is set at the source, using the HPL<sup>R</sup> control system.

Particle conditions are monitored using a single component LDV and a two-color pyrometer. These are mounted with a sampling probe and ancillary shield mirrors on a traverse system, set up to move the sampling point along the flow axis. The physical relationship of some of these components is shown in Figure 4. The velocity measurement is used to relate position to particle heating time scale. It was found, as anticipated, that particle velocity and gas velocity are defined by the nozzle source condition, with downstream heating effects negligible. Particle cloud temperature is monitored using a unique two color pyrometer. It was built around two cooled PMTs with extended red sensitivity ( $\lambda < 8500\text{\AA}$ ), and was calibrated in the range 670 to 2000K. Use of a 10.6 $\mu$ m laser heating source, and cooling of the beam dumps to minimize re-radiation, precludes direct optical interference effects.

Interpretation of the pyrometer output signal in this experiment requires a priori knowledge of the particle size distribution, and some modeling of their thermal behavior. Very good spatial resolution, together with extremely low particle loading, could preclude this difficulty by presenting individual particle radiators to the system. This was not feasible for the product sampling approach

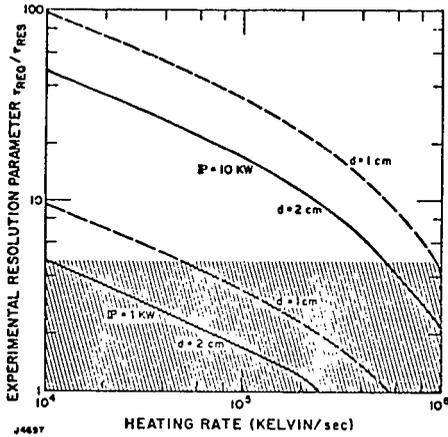


Figure 3 - Dependence of Discrete Sample Resolution on Heating Rate and Laser Source Power

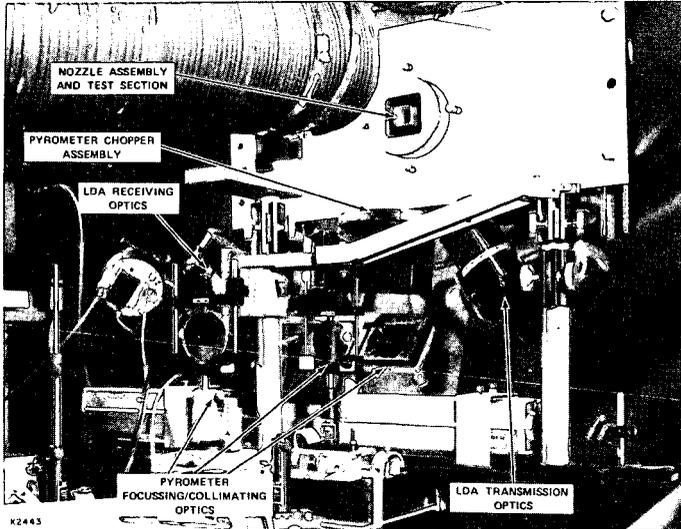


Figure 4 - Experimental Hardware Layout, Showing Flow Source and Optical Diagnostics

TABLE I  
COAL SOLIDS ANALYSIS

Sample No.	Coal Mass Loading	Gas Comp.	Residence Time (ms)	Local Coal Temp., K	Proximate Anal.*			Ultimate Analysis				Solubility % WGT DAF		
					H <sub>2</sub> O	Vol.	F. C.	Ash	C	H	N		S	Ash
Coal: Wyoming Subbituminous														
1	0.026	0.91 N <sub>2</sub>	0	300	2.8	37.9	48.8	10.6	64.9±0.3	4.34±0.03	1.14±0.09	-	-	3.7
2	0.026	0.09 CO <sub>2</sub>	2.5	1680±60	3.3	37.3	48.1	11.3	64.2±0.2	4.02±0.05	1.22±0.06	-	-	8-12
3	0.026	"	10	1780±50	2.0	38.8	48.9	10.3	66.0±0.8	4.05±0.09	1.20±0.03	-	-	45-51
4	0.026	"	12	1440±35	2.7	37.0	48.1	11.5	64.5±0.1	4.18±0.08	1.43±0.27	-	-	19-36
5	0.026	"	16	1264±40	1.6	38.9	48.9	10.6	66.5±0.3	3.93±0.02	1.19±0.04	-	-	10-22
6	0.037	N <sub>2</sub>	3.5	1665±100	2.3	38.3	48.1	11.4	-	-	-	-	-	8-14
7	0.037	N <sub>2</sub>	6	1450±36	3.1	36.4	47.8	12.7	-	-	-	-	-	10
8	0.037	N <sub>2</sub>	8.5	--	2.2	37.3	48.8	12.2	-	-	-	-	-	14-16
9	0.037	N <sub>2</sub>	11	1340±40	2.0	38.2	47.7	12.2	-	-	-	-	-	27
Coal: Montana Rosebud														
10	-	N <sub>2</sub>	0	300	9.7	34.6	42.0	13.7	59.3±0.1	2.94±0.01	0.82±0.14	0.29±0.12	16.4±0.3	3
11	0.071	N <sub>2</sub>	13.8	1660±130	4.8	31.9	46.2	17.1	57.0±0.7	3.34±0.10	0.61±0.12	0.17±0.06	14.8±1.6	11-12
12	0.059	N <sub>2</sub>	13.8	1390±40	5.5	35.0	43.0	16.9	57.6±0.3	3.62±0.10	0.85±0.01	0.12±0.03	12.5±0.3	8-10
Coal: Pittsburgh No. 8														
13	-	N <sub>2</sub>	0	300	1.4	39.0	53.4	6.2	75.2±0.1	5.03±0.01	1.56±0.04	0.25±0.1	6.14±0.02	4-9
14	0.042	N <sub>2</sub>	4.6	1930±300	1.4	39.0	53.0	6.6	74.9±0.1	5.23±0.8	1.79±0.5	0.28±0.1	6.72±0.15	7
15	0.033	N <sub>2</sub>	21.8	1570±75	1.6	39.0	53.5	6.0	75.3±0.3	4.72±0.05	1.64±0.05	0.06±0.01	6.06±0.20	14-18
16	0.051	N <sub>2</sub>	14.8	1330±40	1.4	38.6	54.0	6.1	76.0±0.1	4.76±0.04	1.86±0.4	0.18±0.05	6.74±0.01	15-17
17	0.059	N <sub>2</sub>	6.9	1585±20	0.8	39.2	53.5	6.5	74.9±0.2	4.71±0.03	1.74±0.02	0.20±0.02	6.62±0.14	11-17
18	0.056	N <sub>2</sub>	27.6	2090±120	0.6	36.8	55.8	6.7	70.4±0.2	4.38±0.3	1.62±0.3	0.15±0.05	5.85±0.05	24-27

\* Repeatability ±0.5%

chosen, so an attempt was made to provide a relatively monodisperse coal particle size distribution. Figure 5 shows results of a prediction of radiative heating of such a distribution, together with the inferred pyrometric temperature. It is based on an area weighted sum of the predicted particle size group contributions at the two measurement wavelengths. For this calculation, the heating source beam is a triangular waveform, of duration 16ms (controlled by particle/carrier gas flow through the heating volume) and spatial mean flux  $500 \text{ w/cm}^2$ .

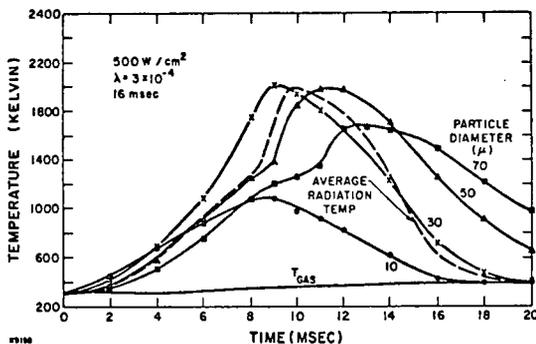


Figure 5 - Predicted Thermal History of Coal Particle Flow in Nitrogen, and Corresponding Radiation Temperature at Pyrometer Wavelengths

Particle thermal behavior is somewhat different in this environment than in a hot flow experiment. The low thermal inertia of small particles, relative to their surface area, results in a rapid initial temperature rise. However, the achievable steady state temperature decreases with decreasing particle size, due to increased thermal diffusive loss to the cold carrier gas. As a result, very fine particles roughly track the spatial flux distribution of the laser beams. Consequently, at longer times the larger particles can overshoot the fines in temperature. Local slope discontinuities in the curves for 50 and 70 $\mu\text{m}$  particle sizes result from use of an assumed endothermic devolatilization process.<sup>(4,10,11)</sup> Curves for 20, 40, 60 and 80 $\mu\text{m}$  particles were also obtained for the size distribution, but not included on the plot. Heat transfer from particles to gas results in limited gas temperature change, in this case from 300K to 400K. The predicted radiation temperature curve is shown as a dashed line. It is close to the temperature of the mass mean particle size, and hence may be a useful indicator of mean temperature. However, the wide distribution of temperatures of the various size particles during the transient heating period renders direct inference of kinetic rates difficult, except for the case of a nearly monodisperse supply. Use of the fluidized bed feeder, while appropriate from a feed rate and control viewpoint, may have exaggerated the size distribution via preferential elutriation.

Flow sampling was based on a simple tubular stainless steel probe, aligned coaxially with the flow. It was protected from the incident laser beam using shield mirrors, as shown schematically in Figure 2. No probe cooling or quenchant was used, as the sampled particles were in a cold gas environment, and additional cooling would be ineffective. The sample stream was drawn through a filter system to capture condensed phase material, and samples taken of the cleaned gas stream using one liter pyrex bottles. As indicated on Figure 1, subsequent sample analysis included gas chromatography, and extensive measurement of the condensed phase material properties. This analysis is continuing, and further data will be reported separately.

## EXPERIMENTAL RESULTS

Data was taken over a limited range of heating conditions using three coals; Pittsburgh No. 8, Wyoming sub-bituminous, and Montana Rosebud. Heating rates in the range 1-3  $10^3$ K/s to temperatures in the range 1000-2000K were obtained, with heating times up to 30 ms. Test conditions are given in Table 1 for the three coals used. While calibrated screen sample sizing was used in an effort to minimize the range of particle size distribution, sample analysis shows considerable variability.<sup>(9)</sup> Overall, negligible gaseous products were observed, and no liquids found. Color and physical appearance of the collected solids differed from the raw coal, and solubility of the solids was considerably increased, while ASTM ultimate and proximate analysis of the bulk samples showed little change from the raw coals.

### Gas Analysis

Gas samples from all test conditions were analyzed using a chromatograph, calibrated using a dilute mixture of expected light volatiles in nitrogen carrier.\* This gave detection limits corresponding to expected sample conditions, typically  $10^{-4}$  by volume. At this level of sensitivity, in no case were any gaseous products observed other than  $H_2O$ , which was found at concentrations consistent with the raw coal moisture content. These results imply that not more than two to four percent of the feed coal carbon content is converted to light volatiles in this environment, and that negligible free hydrogen was produced. Table 2 shows results for two gas samples analyzed using a flame ionization detector. Samples were chosen for maximum heating and residence time conditions. As shown, the Wyoming sub-bituminous coal gave less than 0.2 percent carbon conversion to light volatiles, and the Pittsburgh No. 8 less than 0.01 percent. Since heating time and measured area mean temperature were comparable to those for extensive devolatilization to light species in hot gas environments, these results suggest that the primary volatiles are of relatively high molecular weight.

TABLE 2  
ANALYSIS OF GAS SAMPLES FOR VOLATILES

	Gas Concentration (ppm)							Coal Mass Loading in $N_2$	Volatile Carbon Yield
	$CH_4$	$C_2H_2$	$C_2H_4$	$C_2H_6$	$C_3H_6$	$C_3H_8$	$C_4$		
Sample # 1 Wyoming (1700K, 30ms)	49.7	2	16.4	7.6	5.0	2.0	ND*	0.025	<0.2%
Sample # 11 Pitt # 8 (1560K, 30ms)	8.9	ND	2	ND	ND	ND	ND	0.075	<0.01%

\* ND = < 1 ppm, resolution limit of G.C.

### Solids Analysis

Captured solids were examined in several ways, at various levels of detail. These include visual observation; particle size analysis; ASTM ultimate and proximate analysis; FTIR spectroscopy\*\*; and solvent extraction. Further study using SEM of the collected solids, GPC of the solvent extract, and particle size analysis has been initiated, and will be reported separately.

\* Species calibrated were:  $H_2O$ ,  $H_2$ ,  $CO_2$ ,  $CO$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_3H_4$ ,  $C_3H_6$ ,  $C_3H_8$ ,  $C_4H_x$ ,  $H_2S$ ,  $CO_2S$ .

\*\* Performed by Advanced Fuel Research, East Hartford, CT.

Both raw coal and heated samples were gathered on the sample filters using the complete feed, flow, and sampling system. These raw coal samples were used for subsequent baseline analysis. Visually, samples subjected to heating showed a progressive tendency to clump or cake on the filter elements and a distinct color shift from black toward dark brown. Results of proximate and ultimate analysis of various coal samples are given in Table 1. These are readily summarized, as indicating very little or no change in properties between raw coal and radiatively heated samples, except some moisture loss from the Montana Rosebud samples. Since samples were stored in the laboratory environment, with no control of atmospheric moisture absorption, the measured H<sub>2</sub>O content is perhaps not surprising. FTIR analysis\* of Wyoming samples 1, 5, and 9 of Table 1 gave no discernable indication of structural bond changes between the raw coal and extensively heated samples.

Solvent extraction tests were carried out, using a reflux of stabilized THF\* in air at one atmosphere pressure. Temperature in the extraction volume was about 310 to 320K, and reflux period was typically two hours. Results are given in Table 1. Dried extract was typically a brown to black tarry material. Overall, the radiatively heated samples had significantly increased solubility, relative to the parent coals. Some limited extractions with MEK and with hot dilute NaOH/H<sub>2</sub>O showed similar behavior. While the range of heating rates and temperatures attained preclude direct comparison, there may also be some decrease in yield with increasing coal rank. Also, for each coal, there may be a trend toward increased soluble fraction with increased heating rate or peak temperature, which is related to size distribution as well as heating environment.

## DISCUSSION

The observations given above are consistent with a phenomenological picture of evolution of primary volatiles from the heated particles as high molecular weight compounds. Rapid diffusion of them into the cold gas atmosphere minimizes secondary decomposition, and results in some homogeneous nucleation and condensation.<sup>(1)</sup> Sample withdrawal through a fine filter results in capture of a mixture including decomposed coal particles, volatile condensate particles, and trapped volatile vapors. The volatiles, possibly together with a direct contribution from the heated coal particles, appears to be the component extracted by solvent treatment. This is supported by preliminary SEM images of fresh and solvent extracted solid material samples. The soluble product yield is observed to be generally lower than the ASTM proximate analysis, and much lower than volatile yield observed at high heating rate and temperature conditions. This may be due to the effect of particle size distribution on achievable particle temperature, shown in Figure 5. In particular, preferential elutriation of fines from the coal feeder could result in most of the input solids feed being temperature limited by diffusive heat transfer to the gas while a minor fraction of coarse particles provides the pyrometer signal, as well as pyrolysate.

Based on these observations, it would appear that primary volatile species are of high molecular weight, with the gaseous products in other experiments resulting from secondary decomposition or reactions in hot environments. Also, the proximate and FTIR results can be interpreted as suggesting that the devolatilization process may involve very limited chemical bond breaking or rearrangement.

(1) Resulting particles are small, and equilibrate at low to moderate temperature in the heating volume.

\* Tetrahydrofuran; suggested by Dr. Peter Solomon of Advanced Fuel Research.

## CONCLUSIONS

Use of an high powered laser as a means of providing a controlled heating environment for particles in a gas flow has been shown to be practical. This approach allows decoupling of the particle heating from fluid stream mixing and gas composition and temperature. It also allows choice of background gas composition, for example for study of high temperature heterogeneous reactions. Choice of background gas temperature also allows rapid cooling of vapor phase products, and the potential for selective gas phase reaction conditions.

Measurement of devolatilization behavior of three coals resulted in no observable gaseous products, and enhanced solubility of the solid product. Also, the solid product showed minimal change in proximate and ultimate analyses relative to the raw coal, and minimal change in its FTIR spectrum. These results suggest that primary devolatilization may occur with minor change of chemical structure of the organic material.

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