

STRUCTURE/REACTIVITY STUDIES OF SINGLE COAL PARTICLES AT VERY HIGH HEATING RATES BY LASER PYROLYSIS GC/MS

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INTRODUCTION

Recently, Maswadeh et al. [1] reported on the design, construction and testing of a single particle levitation/laser devolatilization apparatus featuring an on-line gas chromatograph/mass spectrometer (GC/MS) system, enabling coal devolatilization experiments at heating rates in the 10^5 - 10^6 K s⁻¹ range. Analysis of bituminous coal particles revealed a high degree of qualitative correspondence with pyrolysis patterns obtained at much slower (10^2 - 10^0 K s⁻¹ range) TG/MS heating rates [1], thus providing mechanistic justification for extrapolating kinetic parameters obtained by slow pyrolysis techniques (e.g., TG/MS or TG/IR) to the high heating rates characteristic of full scale, suspension fired coal combustors.

A second observation made with the aid of laser pyrolysis GC/MS was that the distribution of devolatilization products observed at very high heating rates was not measurably influenced by the presence or absence of air [1]. A subsequent redesign of the system permitted the use of electron microscopy (EM) grids to support individual coal particles, thereby simplifying the experimental set up, improving collection efficiency of volatile products and facilitating optical alignment of the particles (microscopy, optical micropiprometry) as well as retrieval of residual char particles [2].

EXPERIMENTAL

Materials

Bculah Zap and Illinois #6 coal samples were obtained from the Argonne Premium Coal Sample Program. Minus 100 mesh samples were carefully sieved and the subfraction passing through a #170 mesh screen but retained by a #230 mesh screen was used for further analysis. Several coal particles were picked up by means of a glass rod and transferred over to the EM grid (see Figure 1). A single particle was then selected visually under the microscope and centered manually with the help of the two HeNe laser guide beams shown in Figure 1.

Two Color Micropiprometer

Since the temperature-time history of the particle is necessary for describing tar evolution kinetics, the two color micropiprometer depicted in Figure 1 was constructed. Light emitted from the hot particle is collimated in a Cassegrainian objective (Ealing x 15/.28) and subsequently chopped at 2 kHz (Stanford Research Systems chopper, model SR540, Palo Alto, CA). A 5.066-5.364 micron IR band pass filter transmits the 5 micron band to a 15x Cassegrainian objective focussed on the first IR detector and reflects the remainder of the beam through a 1.84-2.11 micron band pass filter (both filters from Optical Filter Corp. Natick, Mass.) to a 15 X Cassegrainian objective focussed on the second IR detector. The two detectors are dewar mounted, liquid nitrogen cooled InSb photodiodes (Barnes Engineering, Stamford Conn.). The flip mirror shown in Figure 1 is a manually controlled mirror inserted into the optical path when the video camera is employed.

Signal chopping is employed to eliminate and to take into account the d.c. drift in the measurements, to operate in the frequency region of maximum D^* for the detectors and facilitate an increase in the signal to noise ratio for the measurement system [3]. The detector current outputs are converted to voltages, fed to two filtered preamplifiers (Tektronix, model AM 502) and recorded by means of a Hewlett Packard Model 5183 dual channel, 4 Mhz storage oscilloscope. The filters eliminate spurious signals arising from pulsing the CO_2 laser.

Laser Py-GC/MS

Single, 60-120 μm dia. particles of Beulah Zap lignite were analyzed by means of CO_2 laser Py-GC/MS using single laser pulses ranging in duration from 2-20 msec. The particles were mounted on copper EM grids, as shown in Figure 1. Volatile products were sampled into a 6 ft long, 180 μm i.d. fused silica capillary GC column coated with DB5 (0.40 μm) using a valveless, automated vapor sampling (AVS) device (U.S. patent 4,970,905). In these experiments, the AVS was set to "inject" a 2 sec long vapor pulse into the capillary "transfer line" column 0.1 sec after the laser pulse. Subsequently, the capillary GC column was heated ballistically from ambient to 200 C over a 2 minute period while volatile pyrolysis products were being eluted directly into the high vacuum of the Finnigan MAT ion trap mass spectrometer (ITMS). Approximately 1,200 mass spectra were recorded at a rate of 4 spectra per second after each laser pyrolysis of a single coal particle.

RESULTS AND DISCUSSION

Two Color Micropyrometer Measurements

Following Spjut et al. [4] the single channel and two channel transient responses were calculated. These showed that the intrinsic 2-color pyrometer response time was on the order of 0.1 microsecond and that the 5 micron channel was nearly a factor of two faster than the 2 micron channel. However, parasitic impedances and impedance mismatches between the detectors and the preamplifiers slowed the response time considerably, so that chopping at frequencies of 1 Khz and above caused a degradation in response, especially in the 5 micron channel. This effect led to a small but systematic underestimation of the temperature in these data but has recently been eliminated using techniques to increase system electronic bandwidths. In order to minimize systematic errors, careful temperature calibration was performed over the 300-1100 K range using a specially constructed 0.88 mm dia. black body cavity radiator. This calibration is extrapolated to higher temperatures using standard radiation pyrometry theory. The results are shown in Figure 2.

As shown in Figure 3, two Beulah Zap lignite particles (63-90 μm) produced maximum temperature readings in the 1700-1850 K range, which is directly comparable to the characteristic operating temperatures of full scale pulverized coal combustors [5]. The temperature history profiles suggest a two step heating behavior with initial heating rates of approx. $2.10^5 Ks^{-1}$ giving way to lower heating rates (approx. $4.10^4 Ks^{-1}$) after 6-7 milliseconds. Laser beam intensities are known to remain essentially constant ($\pm 5\%$) throughout the duration of the pulse (after an initial 1 millisecond stabilization period). Partial obscuration of the particle surface by the rapidly expanding and cooling cloud of volatiles, combined with evaporative surface cooling effects could be the source of the observed temperature variations in the 6-15 millisecond range. Similar temperature profiles were obtained for a series of Illinois #6 particles (not shown here).

Laser Py-GC/MS Analysis

A typical GC/MS profile of the volatile laser pyrolysis products of a single Beulah Zap coal particle is shown in Figure 4, illustrating the good signal to noise ratio obtained in spite of the small particle size and the relatively low tar yields (<10% daf coal) of lignites. The largest GC peaks seen in the

total ion chromatogram (TIC) profile after the initial "air peak" in Figure 4a consist of toluene ($M^+ = m/z$ 91), phenol (m/z 94), cresols (m/z 108), C2 phenols (m/z 122), naphthalene (m/z 128), and methyl guaiacol (m/z 138), as further detailed by the selected ion chromatogram (SIC) profiles in Figure 4b-d illustrating the useful degree of chromatographic pre-separation achieved by the short capillary "transfer line" GC column. All major isomers are readily identifiable, thus providing a sensitive way of comparing pyrolysis mechanisms at high heating rates with those observable at much lower heating rate, e.g., in TG/MS experiments, as reported previously [1,2]. It should be noted here that the observed pyrolysis profiles of most Beulah Zap lignite particles are quite similar to the profiles obtained from the much slower (10^2 - 10^3 K s⁻¹) Curie-point Py-GC/MS experiments (not shown here), e.g., with regard to the dominant (alkyl) phenol series. As discussed before [1], however, the highly polar and reactive dihydroxy benzenes tend to be absent or underrepresented in laser Py-GC/MS profiles of low rank coals, presumably as a result of mass transfer limitations resulting in condensation reactions of the dihydroxybenzenes inside the char particle. The less reactive methoxyphenols characteristic for lignites and thought to represent typical building blocks of fossilized lignin [7] are readily detected as shown by the prominent methyl guaiacol peaks in Figure 4a.

By performing laser Py-GC/MS analysis of Beulah Zap coal particles at 8 different laser pulse durations and summing the quantitative response of the dominant tar components at m/z 108 (C1 phenols) and m/z 122 (C2 phenols) for each laser experiment, it proved possible to construct the tar evolution profile shown in Figure 5. Note that each point represents the average of 3-4 laser Py-GC/MS analyses. From previous experience it was expected that 20 milliseconds would suffice to obtain complete devolatilization. As demonstrated in Figure 5, however, the tar yield still seems to be increasing at 20 milliseconds, probably due to a somewhat reduced laser power output. Unfortunately, we omitted to determine remaining volatile matter content at 20 milliseconds by subjecting each remaining char particle to a second laser pulse of ample long duration. From the shape of the profile and the intensities of the mass spectra obtained, the tar yield at 20 milliseconds is assumed to be 60-80% of the maximum tar yield obtainable.

Kinetic Considerations

The tar evolution profile in Figure 5 invites the question whether kinetic parameters can be extracted from these data. In view of the relatively small number of data points and the large number of potential sources of error in this type of experiment the authors decided not to attempt a direct extraction of kinetic parameters (which involves differentiation of the curve in Figure 5) but rather to compare the measured profile with predicted yield profiles derived from low heating rate data, using appropriate kinetic models. Beulah Zap tar evolution profiles obtained by three different laboratories (Advanced Fuels Research, using TG/FTIR at 30 K min⁻¹ [8] and 10 K min⁻¹; and Lawrence Livermore National Laboratory, using Py-MS/MS at 4 K min⁻¹ [9]) are represented in Arrhenius plot format (Figure 6). All profiles show excellent agreement (max. 25 K difference in temperatures, corresponding to less than a factor 2 in rate constant difference, when correcting for variations in heating rate) in spite of the very different experimental set-up. The two TG/MS curves (Nie et al., unpublished data) were recorded in our laboratory with a new system operating at ambient pressure and featuring a molecular leak type quartz probe positioned within 5 mm of the TG crucible. When ignoring the minor temperature offsets between the curves, the average slopes and curvatures are quite similar with the possible exception of the TG/FTIR curve. In other words, three of the four curves appear to represent the same set of activation energies.

This brings up the important question how to interpret the observed curvature of all four profiles in the Arrhenius plot. Three possible options are: (1) multiple parallel reactions characterized by a particular distribution of activation energies [10]; (2) a continuously variable (conversion dependent) activation energy (see appendix); and (3) a single, constant activation energy with a heat or mass transfer controlled reaction rate. Most likely, we are dealing with a combination of all three scenarios. There is little doubt that multiple parallel reactions are involved in coal pyrolysis, as can be readily observed by time-resolved pyrolysis MS experiments [11, 12]. Similarly, it is well understood that continuous chemical alteration of the coal matrix takes place throughout the pyrolysis process, gradually transforming the original coal particle into a fully developed char particle. In other words, the chemical structure and composition of the coal particle halfway through the pyrolysis reaction are fundamentally different from that of the unreacted particle as can be readily determined by interrupting the pyrolysis process [13]. Obviously, the activation energy (and its distribution) are unlikely to remain constant throughout the entire process. Finally, evidence of mass transfer limitations (e.g., caking!) is readily observable in TG experiments, especially at heating rates above 5-10 K min⁻¹, depending on coal type and rank. Although all three phenomena: distributed activation energy, continuously variable activation energy and mass transfer limitations can readily explain the observed curvatures in the Arrhenius plot, each assumption leads to different rate and yield predictions at very high heating rates, as illustrated for the DAE (distributed activation energy) and VAE (variable activation energy) models in Figure 7. The numerical procedures used to obtain Figures 6-8 will be explained in detail elsewhere [6]. No attempt was made to predict the effects of transfer limitations due to the particle size dependence and the lack of information on the exact particle size distribution in the various experiments.

Interestingly, the DAE and VAE assumptions each lead to quite different predicted rate constants at high heating rates, thus opening up the possibility of direct experimental verification! Figure 8 compares the DAE and VAE predictions to the observed tar evolution profile. Although our VAE prediction appears to produce a better fit with the observed data, the current lack of quantitative information on the effect of transport limitations on the results of the devolatilization experiments at slow as well as at fast heating rates precludes the possibility of reaching a firm conclusion. Figures 5-8 merely illustrate that the experimental and numerical tools are in hand to start answering some of these questions and that experimental results obtained with different techniques and in different laboratories are starting to converge in a highly promising manner. Foremost among the problems that remain to be addressed however, appears to be the need to conduct systematic studies on the effects of heat and mass transfer limitations under slow as well as rapid coal devolatilization conditions.

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Appendix - VAE Calculation

1. From experimental rate $\left(\frac{dX}{dT}\right)$ versus temperature (T), integration is performed from $T_0 \rightarrow T$ to obtain conversion $X(T)$.
2. An Arrhenius plot is made which is a plot of $\text{Ln} \left(\frac{dX/dT}{1-X}\right)$ versus $\left(\frac{1}{T}\right)$.
3. The first derivative of this Arrhenius plot at different temperatures yields $(-Ea/R)$ and the intercept is equal to $\text{Ln}(A_0)$. These are plotted versus T.
4. From the plots of $-Ea/R$ versus T and X versus T a plot of (Ea) versus X is made.
5. A polynomial fit is made for the apparent activation energy (Ea) versus conversion X in Step 4.

$$Ea(X) = a_0 + a_1x^1 + a_2x^2 + a_3x^3 + \dots$$
 and the resulting frequency factor determined $(Ea = a \ln A_0 + b)$.
6. The relationship from step 5 is matched with the experimental rate using the standard equation below:

$$\frac{dX}{dT} = \left(\frac{Ea(X)-b}{a m}\right) e^{-\frac{Ea(X)}{RT}} (1-X)$$
7. The above equation is plotted for high heating rates using the $Ea(X)$ function obtained at low heating rates and compared to the high heating rate experimental data.

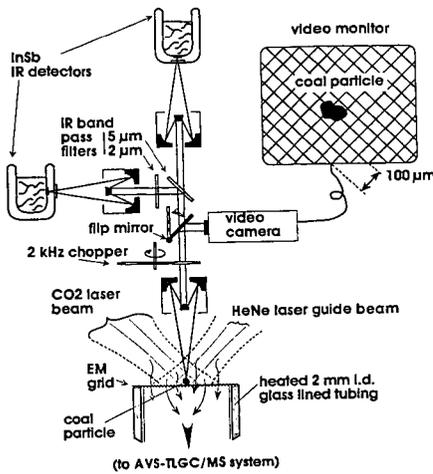


Figure 1. Schematic overview of two-color micropyrometer module with grid supported coal particle, incident dual CO₂ and HeNe laser beams, and inlet to AVS-TLGC/MS system.

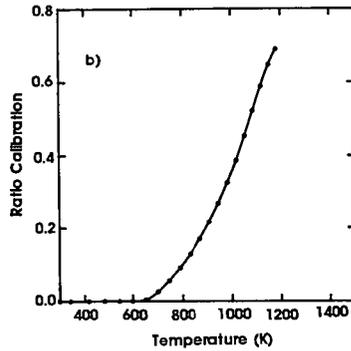
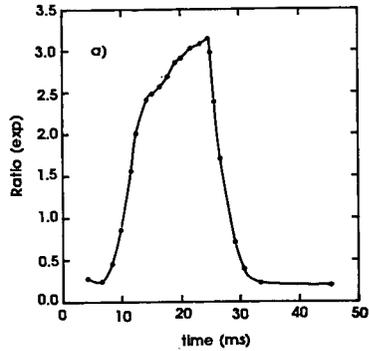


Figure 2. Pyrometer Calibration. The ratio of the outputs from the signal channels at 2.0 microns and 5.2 microns, as shown in (a), is converted to temperature using black body calibration, as depicted in (b). Above 1100 K, temperature is extrapolated using calibration using calibration and two channel pyrometry theory.

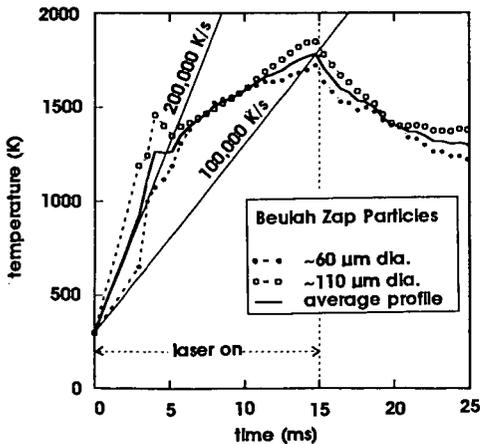


Figure 3. Temperature/time profiles of 2 Beulah Zap lignite particles during 15 millisecond CO₂ laser heating pulse and subsequent 10 millisecond passive cooling period.

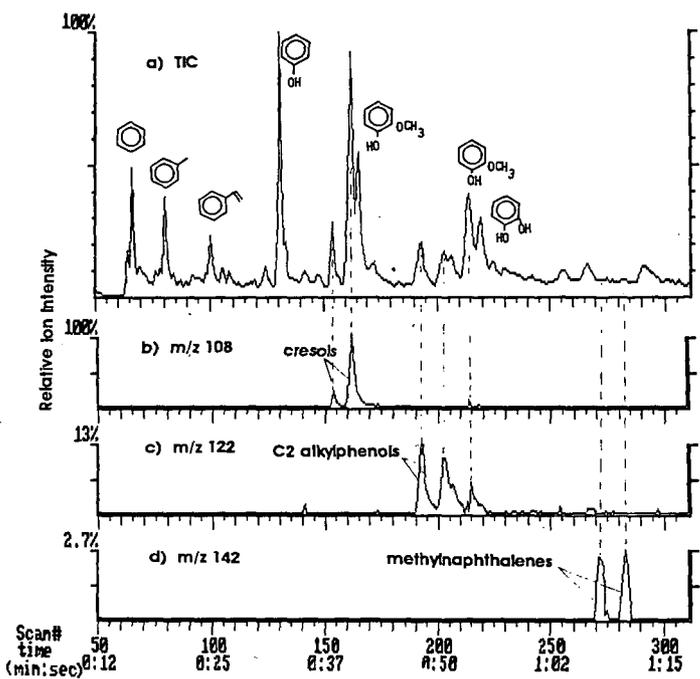


Figure 4. Typical laser Py-GC/MS profile of a 100 μm dia. Beulah Zap particle at 20 msec pulse duration. Note highly useful GC separation within approx. 70 seconds as well as dominant hydroxyaromatic signals (in agreement with low coal rank). Integrated area signals at m/z 108 and 122 were used to calculate "tar yields" shown in Figures 5 and 8.

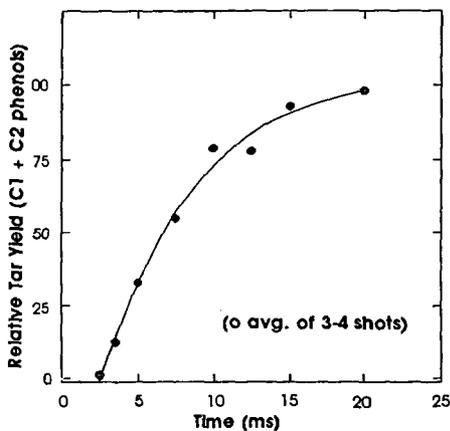


Figure 5. Relative tar yields (normalized to 20 ms yields) of 60-100 μm dia. Beulah Zap lignite particles at 8 different laser pulse times. Note that devolatilization still appears incomplete at 20 ms. Compare with Figures 3 and 4.

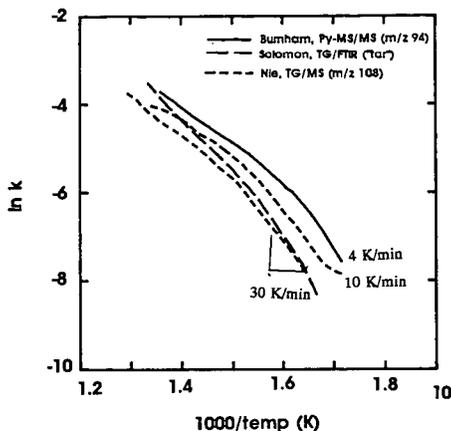


Figure 7. Comparison of VAE and DAE predictions of tar evolution kinetics at typical laser heating rates based on the 30 K min⁻¹ TG/MS profile shown in Figure 6. Note DAE model fit (42 ± 4 kcal/mol). For details of VAE prediction calculation, see Appendix.

Figure 6. Arrhenius plots showing very good agreement of literature data (Burnham, Solomon) on Beulah Zap tar evolution kinetics with our TG/MS data in spite of marked differences in experimental technique (and some variation in "tar" definition), especially when correcting for variations in heating rate. Note that entire tar evolution profiles were plotted (see Appendix).

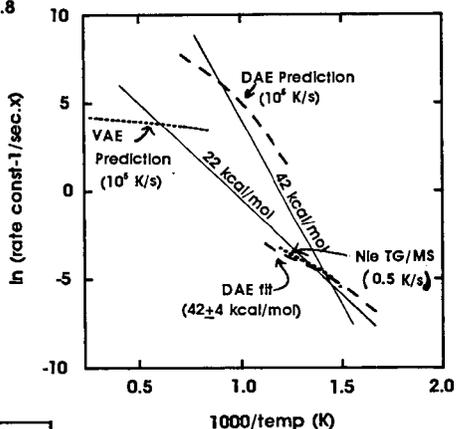


Figure 8. Measured and predicted relative tar yields of Beulah Zap coal particles. Note that VAE prediction indicates only 60% relative tar yield within 25 milliseconds. Measured points (o, o) represent averages of 3 or 4 laser shots. Single Ea (SAE) and Variable Ea (VAE) predictions use measured temp profiles (see Figure 3), DAA prediction uses linear heating rate (10^5 K s⁻¹).

