RICE

MECHANISMS AND OPTIMIZATION OF COAL COMBUSTION

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1. SUMMARY

During the past quarter, protocols for pyrolysis and combustion experiments were developed. The performance of the new control algorithms was evaluated, particularly for the rapid pyrolysis experiments where heating rates ranging from 100 to 1,000 ˚C/s were achieved. Finally, a new digital image analysis procedure was developed to detect and quantify thermal ignitions of burning coal or char particles.

2. SEQUENTIAL PYROLYSIS AND COMBUSTION EXPERIMENTS

The protocol for sequential pyrolysis and combustion experiments in the TGA/VMI is as follows:

1) The sample area is purged with 240 sccm N_2. A constant flow of nitrogen is used at all times, particularly when the reactor is unsealed, to ensure that atmospheric oxygen does not enter the reactor at any time.
2) Coal samples are loaded into the TGA/VMI reactor and spaced evenly to avoid contact during pyrolysis.
3) After loading the coal, nitrogen is allowed to flow for an additional 10 minutes.
4) The sample is heated to 200 ˚C and held there for 2.5 minutes to remove any moisture present.
5) The sample is then heated at the specified pyrolysis heating rate (0.1-20.0 ˚C/sec), until the temperature reaches the heat treatment temperature (HTT), generally 700 ˚C in this study, or some value just below the HTT to avoid overshoot. When the temperature reaches the HTT it is kept there for a soak time of either 0 or 3 minutes. A 3 minute soak time was most commonly used for this study.
6) After cooling the devolatilized char as quickly as possible to 200 ˚C using the reactor fan, a reactive mixture of oxygen and nitrogen is introduced and the system is allowed 10 minutes to equilibrate.
7) The char is heated at a rate of 20 ˚C/sec to the final combustion temperature and held there until the weight change is negligible.

8) The temperature is then raised to 800 ˚C, to burn off any remaining carbon. When the weight no longer changes, the reactor temperature is brought back to the original combustion temperature and the weight is recorded to determine the ash content of the sample.

Initiation of the video timer and VCR recording is performed automatically by the control program. For each experiment, the VCR was cued at the appropriate time to begin taping depending on the portion of the experiment which was of interest. For combustion experiments aimed at studying particle ignitions, the illumination system of the microscope was generally turned off to improve observation of faint light emissions. During both pyrolysis and combustion, the sample weight, reactor temperature, time, and temperature error are continuously written to a data file at a chosen rate for later analysis. For most experiments, data was written 10 times per second.

Experiments with heating rates between 0.1 and 20 ˚C/s will be carried out in the TGA/VMI reactor, while the hot stage reactor will be used for runs with heating rates ranging from 100 to 1,000 ˚C/s.

3. RAPID PYROLYSIS EXPERIMENTS

When experiments are conducted in the hot stage reactor, indentations are made in the mesh of the hot stage where the coal particles are placed. This is done to keep the particles from moving towards each other and agglomerating during pyrolysis. The mesh is also folded over, so that both the samples and the thermocouple are surrounded by the mesh heating element. This is necessary to avoid the large thermal gradients which exist in the hot stage reactor. Following pyrolysis in the hot stage, the devolatilized char is cooled to about 40 ˚C and transferred to a tared TGA/VMI reactor for combustion.

For a heating element having a width of 0.6 cm, only three 28-32 mesh sized particles fit in the reactor and thus multiple pyrolysis runs are conducted to obtain five char particles for combustion in the TGA/VMI. For heating rates below 100 ˚C/sec, the mesh is large enough to accommodate five 28-32 mesh coal particles. It should also be noted that the controller parameters used for temperature control (and particularly the gain) depend very strongly on the width (and hence the resistance) of the mesh used for each run.

As heating rates approach and exceed 100 °C/sec, consideration must be given to the lag in temperature between the thermocouple and reactor. For this reason, the heating rate is reduced progressively as we approach the final temperature, instead of switching abruptly from a linear ramp to a constant temperature. The hot stage reactor was tuned to achieve reproducible heating rates of up to 500 °C/sec. Figure 1 shows several repeated runs conducted in the hot stage at 500 ˚C/sec. The control is quite reproducible considering that in the ramp portion of the temperature program, the algorithm can only be performed about 50 times.

Post analysis of the temperature versus time curves shows, however, that the actual heating rate is quite different than 500 ˚C/sec. Figure 2 shows that the actual heating rate in this case varies dramatically and exhibits a maximum of about 1000 ˚C/sec. This is to be expected from the dynamics of our heater (which behaves like a first-order system) and the oscillations of the actual temperature about the setpoint.

4. REACTIVITY MEASUREMENTS

A new procedure was developed to obtain the reactivity of the sample from the measured weight loss data. Sample reactivity was determined using the following formula:

$$R_o = \frac{dx}{dt} = -\frac{1}{m_o}\left(\frac{dm}{dt}\right)$$

where x is the conversion of the solid, m_o is the initial ash free solid weight, and m is the mass of unreacted sample at any time t. Calculating the reactivity of the sample depended on the way in which the weight versus time curve was fit. To achieve a proper fit, the number of curve fit points and the type of curve fit was modified. For samples which did not exhibit ignition, and reactivity was fairly low, a smooth curve fit was used. For samples which ignited, however, sharp changes in weight required a large number of curve fit points and were generally fit with cubic spline interpolates. From this curve fit information, the weight data was regenerated in a new data column. This data was then differentiated and divided by the initial ash free weight to calculate reactivity.

In an attempt to better quantify the reactivity data of samples reacting under a wide range of conditions, average reactivities were calculated from combustion experiments. Reactivity data was averaged over a specified conversion range for each sample and also computed for multiple experiments conducted at each set of conditions. With this data we quantified the differences in reactivity observed experimentally.

5. DIGITAL IMAGE PROCESSING

Digital images with a resolution of 640x480 8-bit pixels were acquired from the video tapes of experiments using a Macintosh computer (Quadra 900) equipped with a frame grabber (Data Translation, Quick Capture). Analysis of digital images obtained allowed for quantification of visual data such as light intensity and particle size.

By acquiring a sequence of images at fixed time intervals, we were able to obtain time-resolved light intensity traces for individual particles or the entire pan. Experiments designed to study particle ignitions were typically conducted with the microscope illumination turned off. Before turning off the illumination, however, digital images were acquired to determine the precise location of each particle in the pan. This allowed us to define regions of interest (ROI), such that each ROI included only one particle (see Figure 3). For each ROI, we monitored the maximum light intensity in order to detect light emissions and, therefore, particle ignitions.

Figure 3 shows a digitized image from an experiment in which 4 particles were placed in the pan. ROI's C and D are centered on particles which cannot be seen because they are not emitting light. ROI's A and B, however, are centered on particles which are in ignited states. Char particles rarely moved during combustion experiments. If particle movement occurs, however, it may be necessary to monitor intensity across the entire pan. All steps of the image analysis procedure developed to obtain light intensity traces were performed using NIH Image, a public-domain image processing software available by anonymous ftp from zippy.nimh.nih.gov. Figure 4 illustrates an example of a light intensity trace for an experiment in which all five particles present in the TGA / VMI reactor ignited.

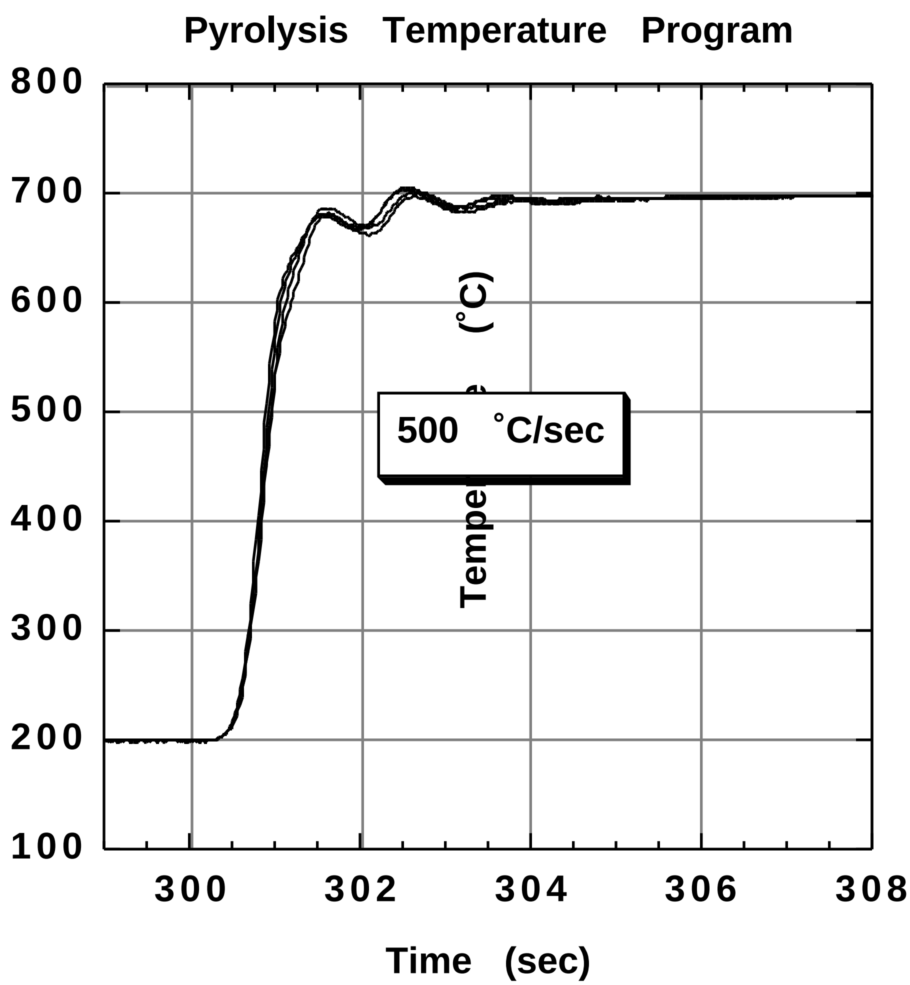

Figure 1: Temperature traces showing the quality of temperature control for repeated pyrolysis runs conducted at 500 ˚C / sec.

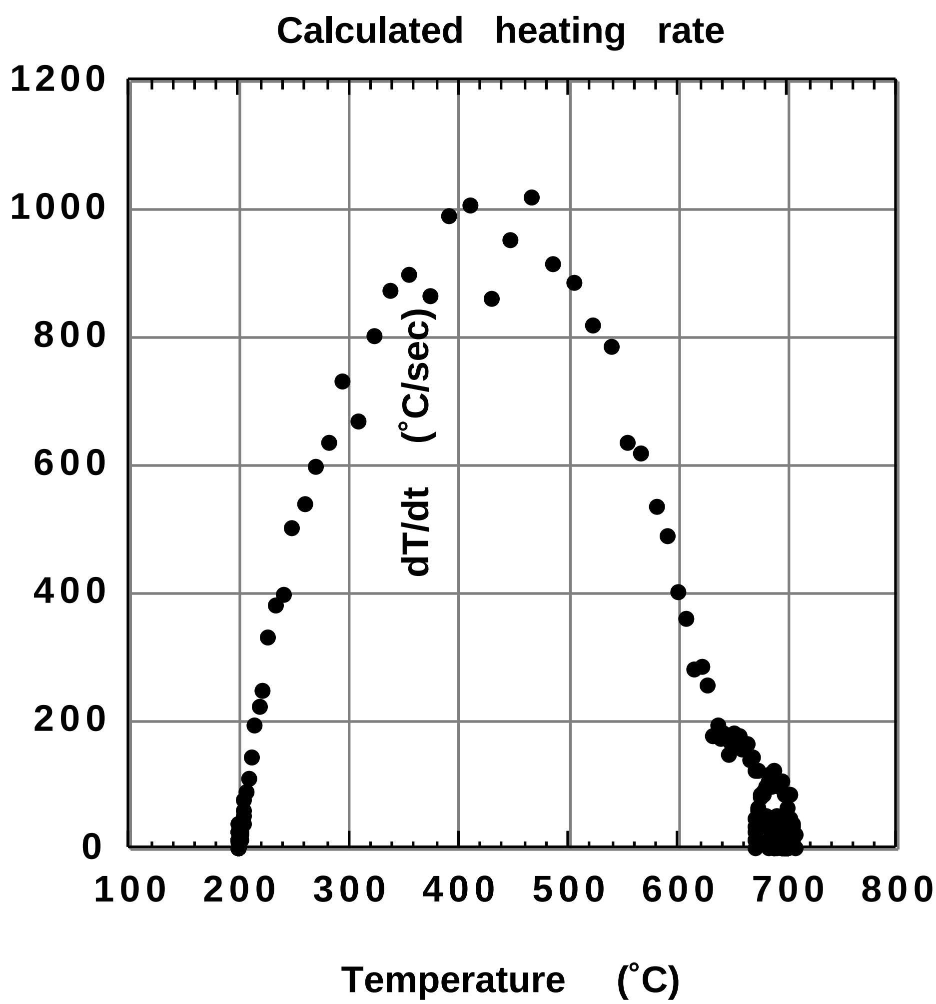

Figure 2: Actual heating rate achieved in the hot-stage reactor for a nominal heating rate of 500 ˚C / sec.

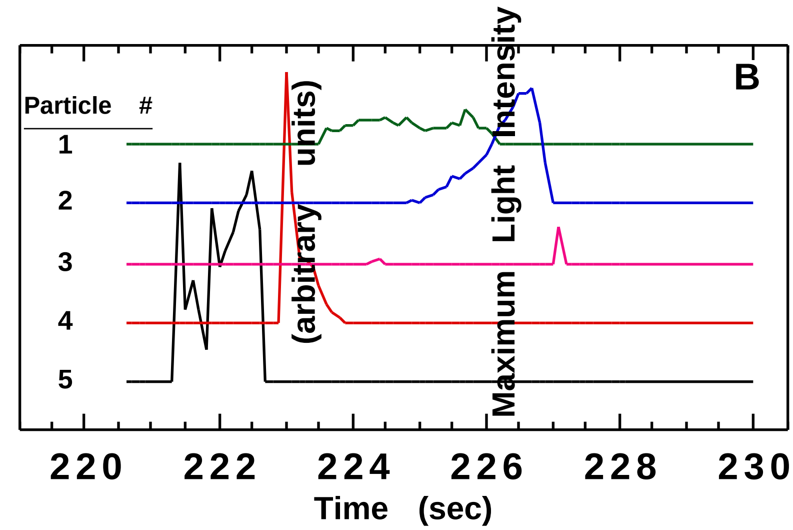

Figure 3: Light intensity trace from a char combustion experiment illustrating the ability to monitor light intensities of individual particles during a multiple particle experiment.