PYROLYSIS AND GASIFICATION OF COAL AT HIGH TEMPERATURES

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QUARTERLY PROGRESS REPORT

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SHORT DESCRIPTION OF TASKS

(A) Effects of Pyrolysis Conditions on Macropore Structure

Coals of different ranks will be pyrolyzed in a microscope hot-stage reactor using inert and reacting atmospheres. The macropore structure of the produced chars will be characterized using video microscopy and digital image processing techniques to obtain pore size distributions. Comparative studies will quantify the effect of pyrolysis conditions (heating rates, final heat treatment temperatures, particle size and inert or reacting atmosphere) on the pore structure of the devolatilized chars.

(B) Gasification Under Strong Intraparticle Diffusional Limitations

The devolatilized chars will be gasified in the regime of strong intraparticle diffusional limitations using O_2/N_2 and $O_2/H_2O/N_2$ mixtures. Constant temperature and programmed-temperature experiments in a TGA will be used for these studies. Additional gasification experiments performed in the hot-stage reactor will be videotaped and selected images will be analyzed to obtain quantitative data on particle shrinkage and fragmentation.

(C) Mathematical Modeling and Model Validation

Discrete mathematical models will be developed and validated using the experimental gasification data. Structural properties of the unreacted chars will be used to generate computational grids simulating the pore structure of the solid. Simulations will then provide the evolution of observed reaction rates with conversion. The size distribution of particle fragments obtained as the reaction front moves through the particle will also be obtained. Proper statistical averaging of the results from these simulations will yield the expected behavior for each char. Comparisons of experimental data and theoretical predictions will identify the fundamental phenomena that must be included in a mathematical description of the process, thus leading to the development of accurate models for the gasification of coal particles.

SUMMARY

We made considerable progress towards developing a thermogravimetric reactor with in-situ video imaging capability (TGA/IVIM). Such a reactor will allow us to observe macroscopic changes in the morphology of pyrolyzing particles and thermal ignitions while monitoring at the same time the weight of pyrolyzing or reacting samples.

The systematic investigation on the effects of pyrolysis conditions and char macropore structure on char reactivity continued. Pyrolysis and gasification experiments were performed consecutively in our TGA reactor and the char reactivity patterns were measured for a wide range of temperatures (400 to 600 °C). These conditions cover both the kinetic and the diffusion limited regimes. Our results show conclusively that chars produced at high pyrolysis heating rates (and, therefore, having a more open cellular macropore structure) are more reactive and ignite more easily than chars pyrolyzed at low heating rates. These results have been explained using available predictions from theoretical models.

We also investigated for the first time the effect of coal particle size and external mass transfer limitations on the reactivity patterns and ignition behavior of char particles combusted in air. Finally, we used our hot stage reactor to monitor the structural transformations occurring during pyrolysis via a video microscopy system. Pyrolysis experiments were videotaped and particle swelling and the particle ignitions were determined and analyzed using digitized images from these experiments.

A. DEVELOPMENT OF A TGA WITH IN-SITU VIDEO IMAGING CAPABILITIES (TGA/IVIM)

We made considerable progress towards developing a thermogravimetric reactor with in-situ video imaging capability (TGA/IVIM). Such a reactor will allow us to observe macroscopic changes in the morphology of pyrolyzing particles and thermal ignitions while monitoring at the same time the weight of pyrolyzing or reacting samples.

Several major alterations were performed on our TGA reactor. The furnace element was lowered by almost 2 cm inside the furnace tube. This was done in order to improve the visibility of the sample during the reaction. A glass side arm was attached to the furnace tube with a tilted flat optical window at its top. This allows us to observe pyrolyzing or reacting samples through the window. The angle of incidence of the image beam and the window surface is close to 90° thus preventing any diffraction and distortion of the image.

The imaging is provided by a high-magnification, extra-long working distance microscope. This unit is currently under evaluation.

PYROLYSIS AND GASIFICATION EXPERIMENTS

Experimental Procedures

The pyrolysis and gasification of our coal samples were carried out in our TGA system. We studied the Illinois #6 coal from the Argonne premium coal sample collection. Two coal particle sizes were used: 28-32 mesh (500-595 μm) and 20-24 mesh (707-841 μm). For each run, the reactor was loaded with less than 1 mg of coal (that is, 8 coal particles for the 28-32 mesh fraction and 2-3 particles for the 20-24 mesh fraction) . The other conditions for the sequential pyrolysis and gasification experiments are listed below.

PYROLYSIS STAGE	
Heating rate:	0.1, 0.3, 1, 3, 10 C/s
Final heat treatment temperature:	700 °C
Soak time at HTT:	0 and 3 minutes
Flowing Gas:	Nitrogen
COMBUSTION STAGE	
Reaction Temperatures:	400 - 600 °C.
Flowing gas:	Air
Gas flow rates :	200 and 300 sccm.

The weight vs time measurements were interpolated with a 2nd order B-splines to obtain the derivative which represents the reaction rate (see procedure described in quarterly report #9).

Results and Discussion

(A) Effect of heating rate on char gasification patterns

Preliminary results on such effects were first reported in a previous Quarterly Report (#9). The conclusion drawn was that chars produced at high pyrolysis heating rates are more reactive in the diffusion-limited regime (high temperatures). Char reactivity in the kinetic-control regime, however, was not significantly influenced by the pyrolysis heating rates. Furthermore, we have observed that the reactivity patterns are different in the two regimes. In the kinetic control regime the reaction vs. conversion curves are monotonically increasing. In the diffusion-limited regime, the reactivity curves reach a plateau after an initial increase.

We also observed that the particles ignited more often when the reaction was carried out in the diffusion-controlled regime. When the particles ignite, the reactivity curve exhibits several maxima, one for each ignition. Additional confirmation that the spikes observed in the reaction rates are due to particle ignitions is provided by the controller feedback power signal we measure during the reaction (see Fig 10). If the reaction rate is high, the controller develops a negative feedback to counterbalance the heat released by the reaction. Note that the reaction rate maxima correspond to the maxima of the feedback power.

The experiments performed during the past quarter have confirmed the earlier preliminary results. Figures 1 through 3 show the reactivity patterns for several char samples reacted with air at 400, 420 and 450 °C. All these chars were heated to 700 °C at various rates and held there for 3 minutes. Clearly, all chars show almost identical reactivity patterns (within the margin of reproducibility) when combusted at 400, 420 and 450 °C.

Figures 4-6 show the reactivity patterns when char samples produced under the same conditions are combusted at higher temperatures (500, 550, 600 C). The chars produced at high pyrolysis heating rates exhibit significantly larger reactivity than chars produced at low heating rates and these differences become more pronounced with increasing reaction temperatures (see, for example, Figures 5 and 6 for the chars produced at 0.1 and 1 °C/s).

Another observation is that after reaching a threshold temperature the particles ignite (see Figure 6). This phenomenon has been predicted by previous investigators (Sotirchos and Amundson 1984a, Sotirchos and Amundson 1984b) who solved the coupled mass and heat transfer equations inside a coal particle and in the boundary layer around it. Sotirchos and Amundson assumed that the macropores form a thoroughly interconnected network of pores and they can be regarded as the main transport arteries of the porous solid. They also assumed that there are not significant concentration gradients in the micropores; that is they considered that the surface of the micropores functions is a local extension of the surface of the macropores from which the micropores emanate. Some of their calculations support the validity of the assumption.

Sotirchos and Amundson predicted that when the ambient temperature exceeds a threshold value, the problem has three solutions and there is a sudden transition to a higher temperature which induces **particle ignition.** This threshold value is lower when Knudsen diffusion in the macropores is not dominant. That is, when the average macropore size of the particle is higher then the diffusional limitations are lower and the ignition temperature is also lower. Furthermore, they found that after the ignition temperature the reaction rate is almost constant with ambient temperature and not affected by the extent of diffusional limitations.

This approach can be used to explain the difference in reactivity of the chars treated at various heating rates. The differences we observe can be attributed to three factors.

(a) The structural changes occurring during the pyrolysis stage due to particle softening and swelling can lead to chars that have a **highly cellular pore structure when the heating rate is relatively high.** Our previous work in this area (Zygourakis 1988) revealed that the average macropore size, particle size, porosity and macropore specific surface area are all monotonically increasing with the pyrolysis heating rate. Therefore, a more open and more accessible macropore network would significantly decrease the Knudsen diffusional limitations in the macropores. Thus, the ignition temperature will be lower for chars treated at higher heating rates.

This is apparent in Figure 6 where only 1 and 10 °C/s treated chars have significant ignition phenomena. In another agreement with the model prediction, chars produced at 1 and 10 °C/s have virtually the same reaction rate since they have both reached the ignition stage.

(b) The decrease of intraparticle diffusional limitations makes the internal surface more accessible to the gaseous reactants. Thus, the concentration of reactants is higher inside the particle and consequently the reaction rate is enhanced.

(c) At ambient temperatures that are high enough (almost 550-600 °C) the reaction rate is high enough to release significant amounts of heat. The heat removal through the boundary layer is not fast enough and intraparticle and boundary layer temperature gradients appear. The heat removal is greater when the particle effective thermal conductivity and the external surface to volume ratio are higher. If we consider that the particles treated with higher heating rates have higher porosity and size then we can conclude that their thermal conductivity and external surface to volume ratio will be lower respectively. Therefore, heat removal is less efficient for these particles that are thus more prone to overheating that leads to ignitions and higher reaction rates.

(B) Effect of particle size on char reactivity patterns

We also reacted with air particles of two different sizes at 450 and 550 °C. The particles we used were in the range of 28-32 mesh (500-595 μm) and 20-24 mesh (707-841 μm). The pyrolysis conditions were the same for both sizes.

As we see in Figures 7 and 8, the reactivity remains the same at 450 °C. This is evidence that at 450 °C we are in the kinetic control regime. At 550 °C, however we observe a dramatic difference. The larger particles are igniting and reacting at rates that are twice as high.. This can also be predicted from the results presented by Sotirchos and Amundson who found that the ignition temperature decreases with particle size. The increased size of the particles makes their external surface to volume ratio lower and heat removal less efficient. Therefore, particle overheating and thermal ignition occur at lower ambient temperatures.

(C) Effect of flow rate on particle overheating

Heat dissipation from the particle is limited when reaction takes place at elevated temperatures. Thus, the heat transfer coefficient determines partially the extent of heat removal and therefore the magnitude of intraparticle temperature gradients. It is expected that a higher gas flow rate will increase the heat transfer coefficient and prevent particle overheating and thermal ignition.

This hypothesis is confirmed by the results of Figure 9. With a flow rate of 200 sccm we observe particle ignitions at a reaction temperature of 550 °C. When the flow rate is increased to 300 sccm, however, particle ignitions are not observed due to the increased rates of heat transfer.

(D) Effect of pyrolysis on macropore structure

Digital images of particles obtained before and after the pyrolysis stage revealed that the coal particles swell by a factor of 1.5 when heated at 10 °C/s. The swelling factor is smaller for heating rates of 1 °C/s and almost unity for chars heated at 0.1 C/s. These measurements are consistent with our earlier results (Zygourakis 1988) and show the large effect of pyrolysis conditions on the char macropore structure.

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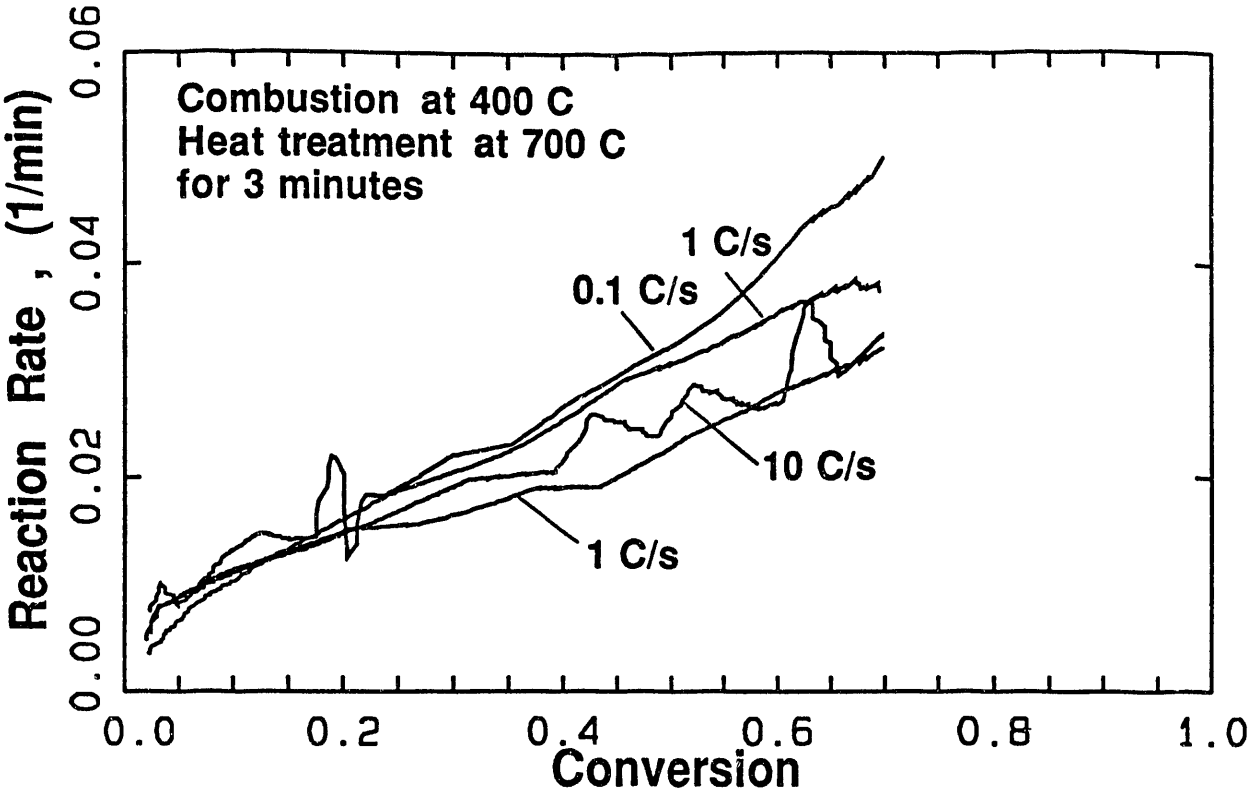
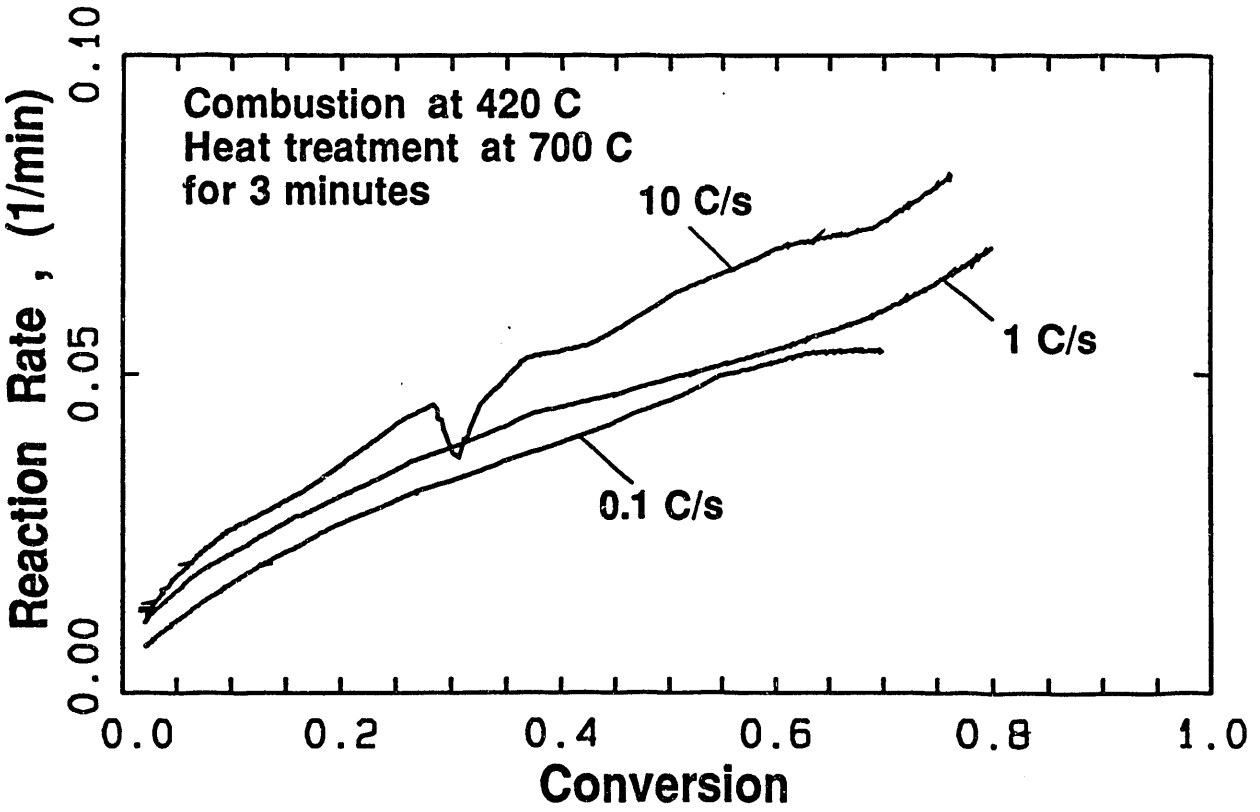
Sotirchos, S, V., and N.R. Amundson. 1984a. Diffusion and Reaction in a Char Particle and in the Surrounding Gas Phase. A Continuous Model. Ind. Eng. Chem. Fundam. 23 (2) : 191-201.

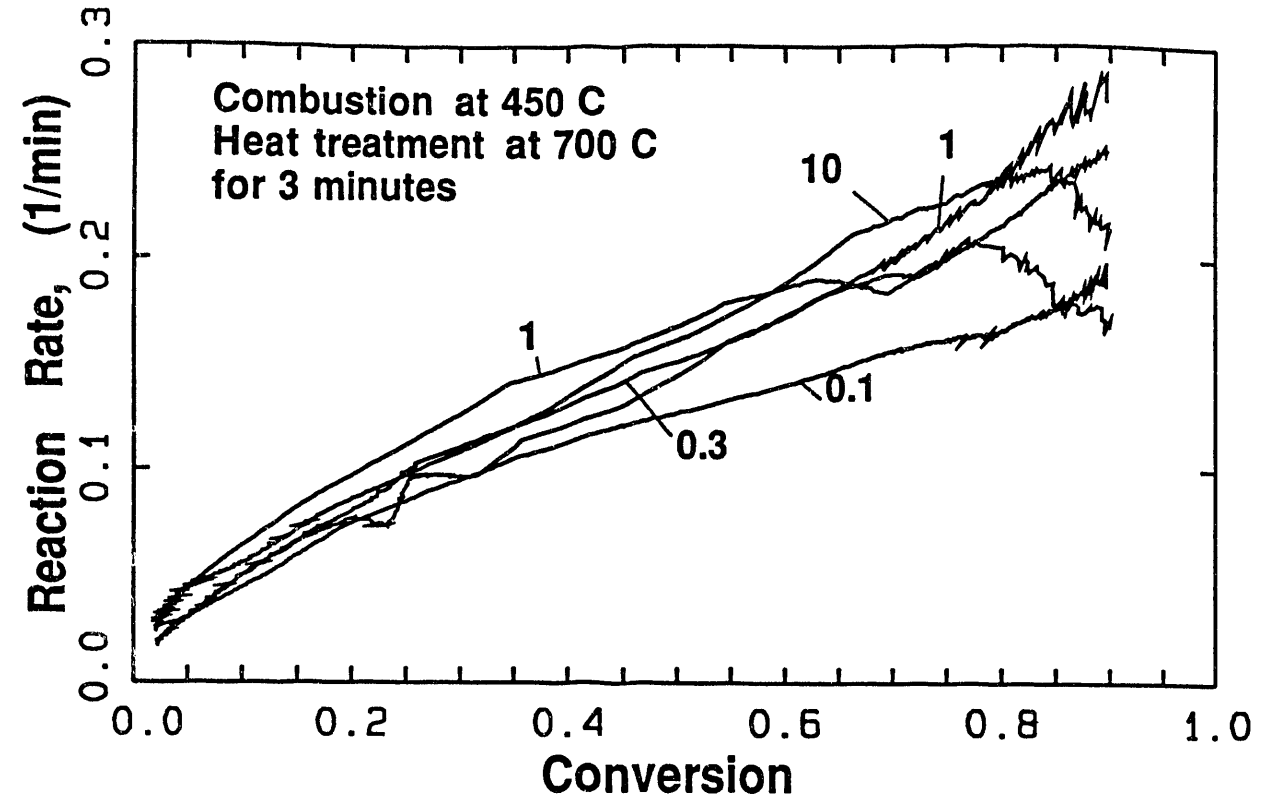
Sotirchos, S, V., and N.R. Amundson. 1984b. Diffusion and Reaction in a Char Particle and in the Surrounding Gas Phase. Two Limiting Models. Ind. Eng. Chem. Fundam. 23 (2) : 180-191.

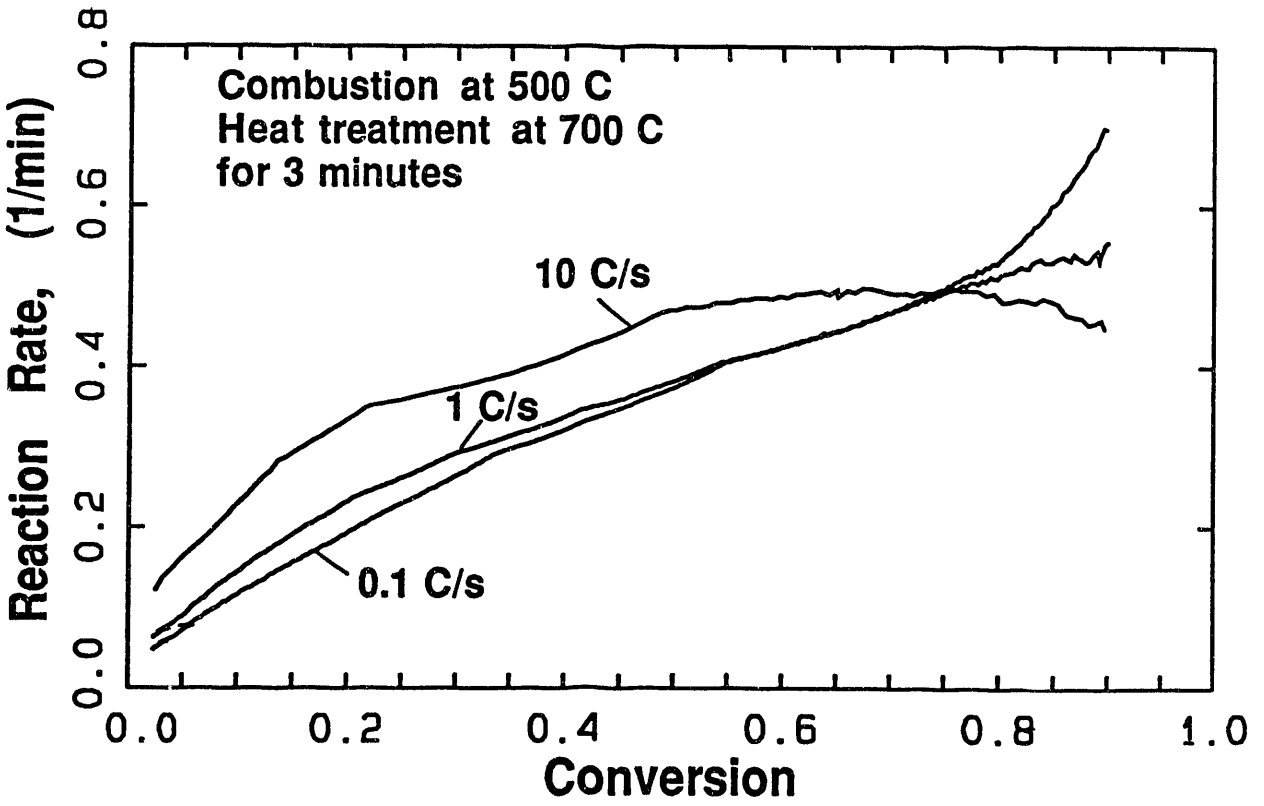
Zygourakis, K. 1988. The Effects of Pyrolysis Conditions on the Macropore Structure of Coal Chars. Amer. Chem Soc., Div. Fuel Chem. Prepr. 33 (4) : 951-959.



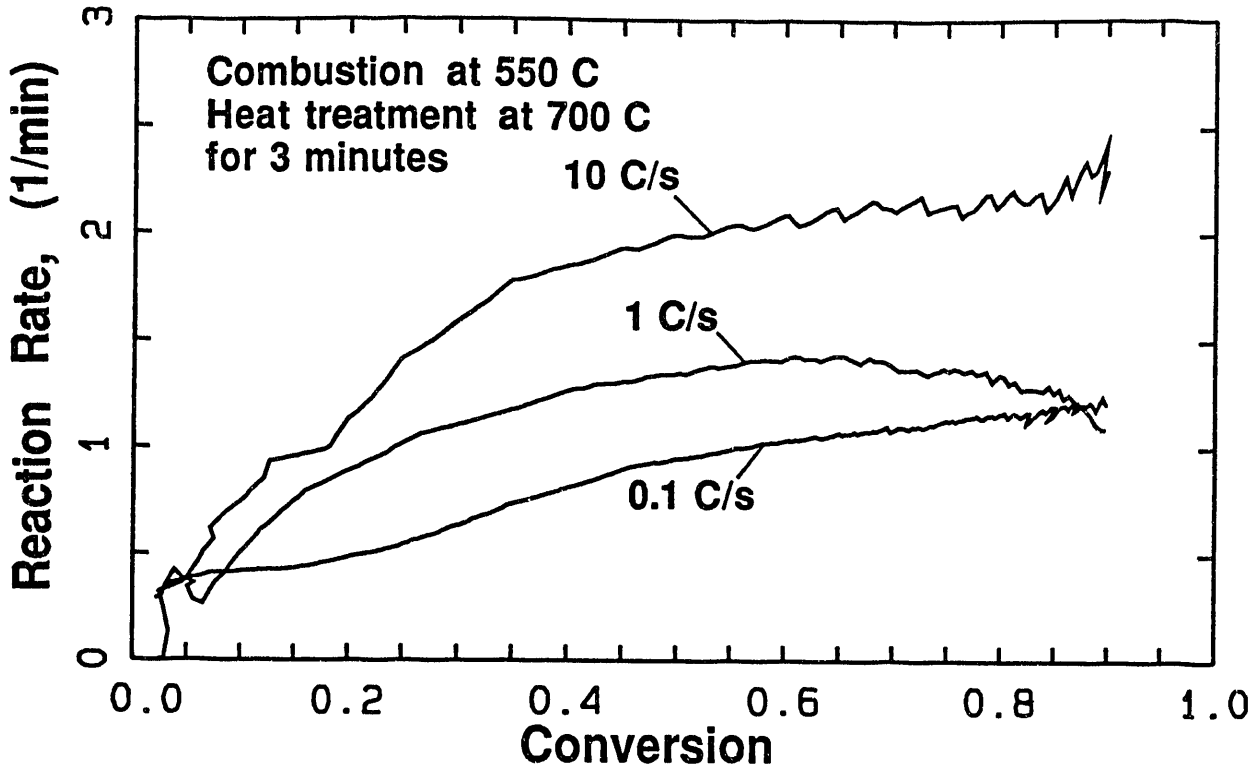


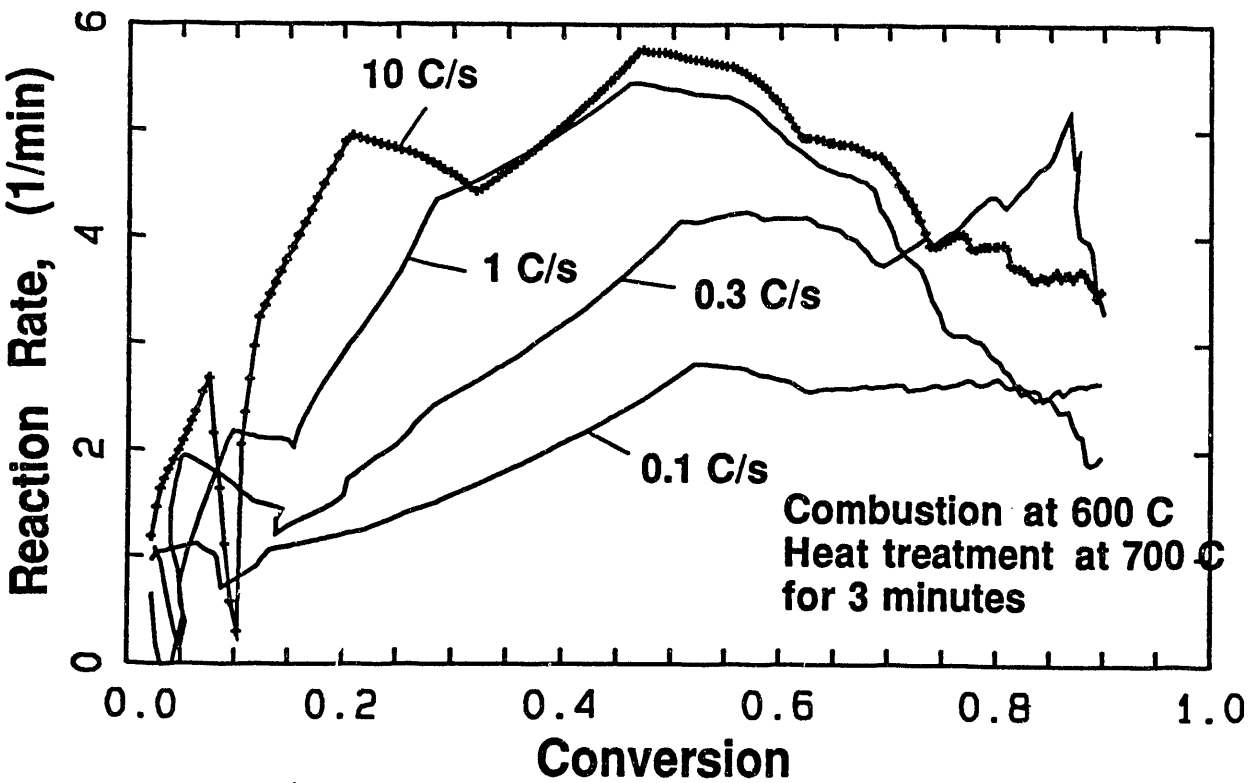
Figures 1 (top) and 2 (bottom): Gasification rate vs. conversion patterns for three Illinois #6 chars produced at different pyrolysis heating rates. The three chars were gasified with air at 400 °C (top) and 420 °C (bottom).



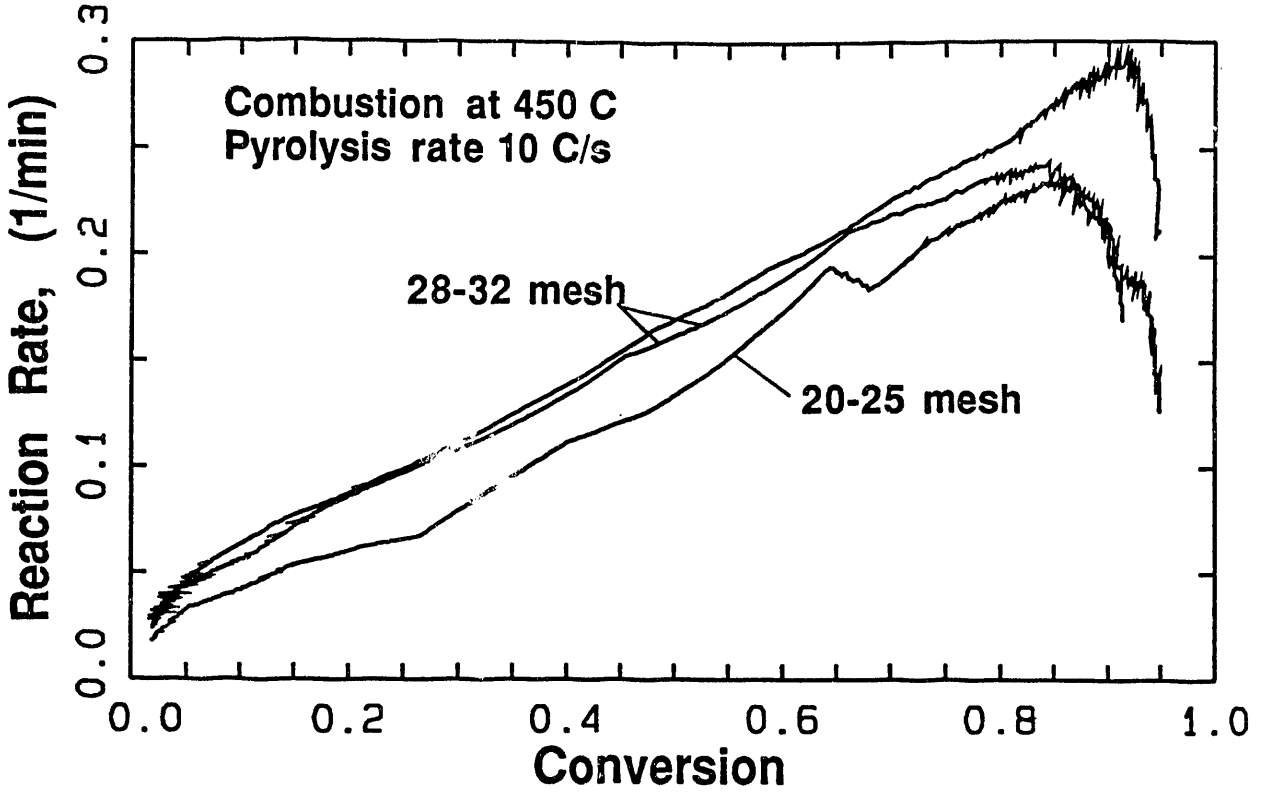


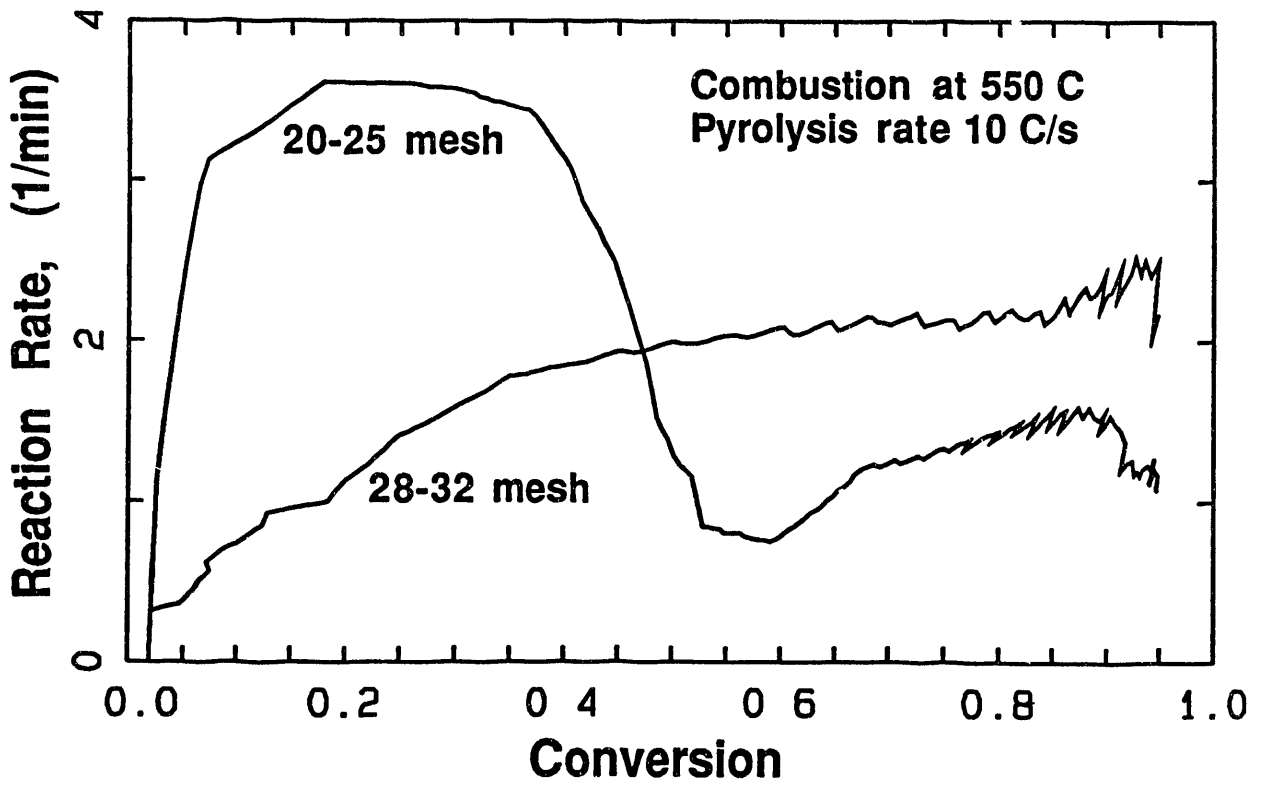
Figures 3 (top) and 4 (bottom): Gasification rate vs. conversion patterns for three Illinois #6 chars produced at different pyrolysis heating rates. The three chars were gasified with air at 450 °C (top) and 500 °C (bottom).





Figures 5 (top) and 6 (bottom): Gasification rate vs. conversion patterns for three Illinois #6 chars produced at different pyrolysis heating rates. The three chars were gasified with air at 550 °C (top) and 600 °C (bottom).





Figures 7 (top) and 8 (bottom): Gasification rate vs. conversion patterns for Illinois #6 chars produced from two different coal particle sizes: 28-32 mesh (500-595 μm) and 20-24 mesh (707-841 μm). The chars were gasified with air at 450 °C (top) and 550 °C (bottom).

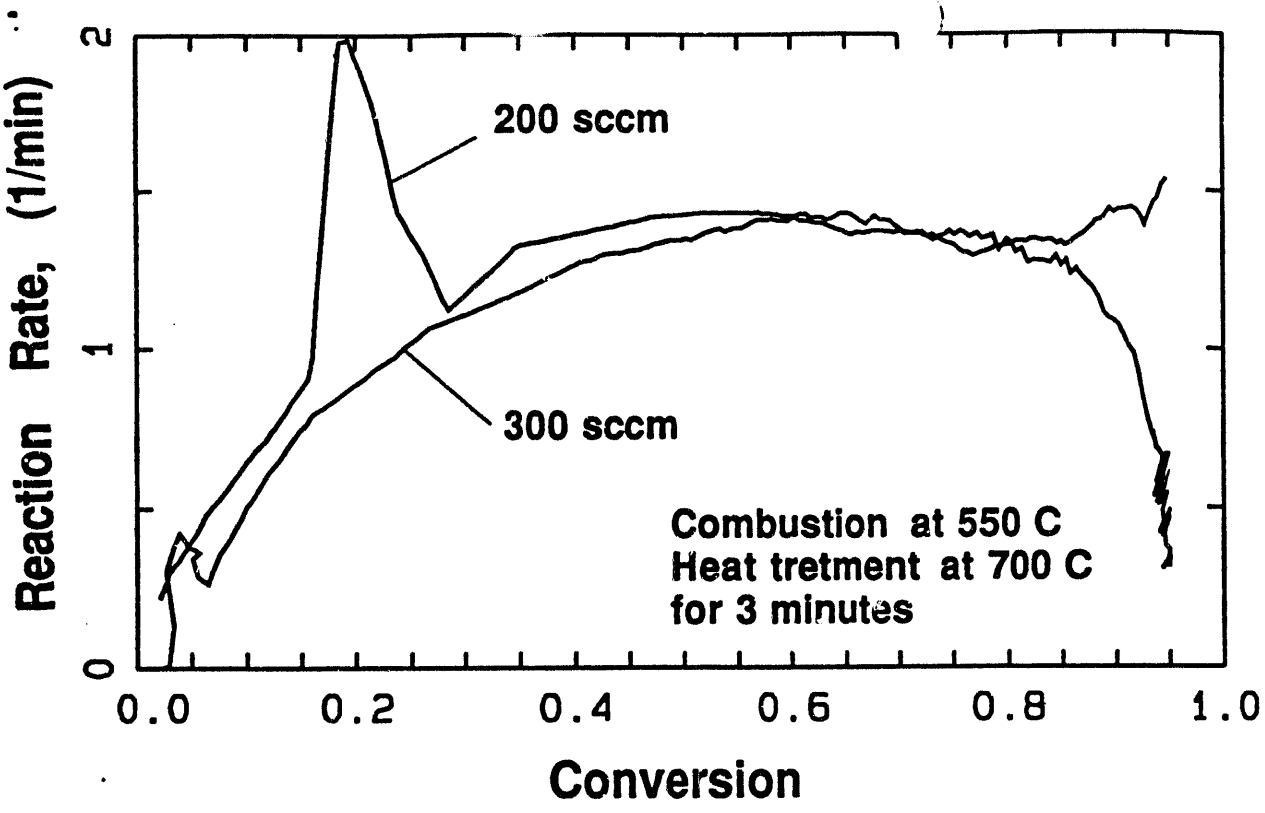


Figure 9: Gasification rate vs. conversion patterns obtained for the same Illinois #6 char reacted with air at 550 °C at two different gas flow rates.

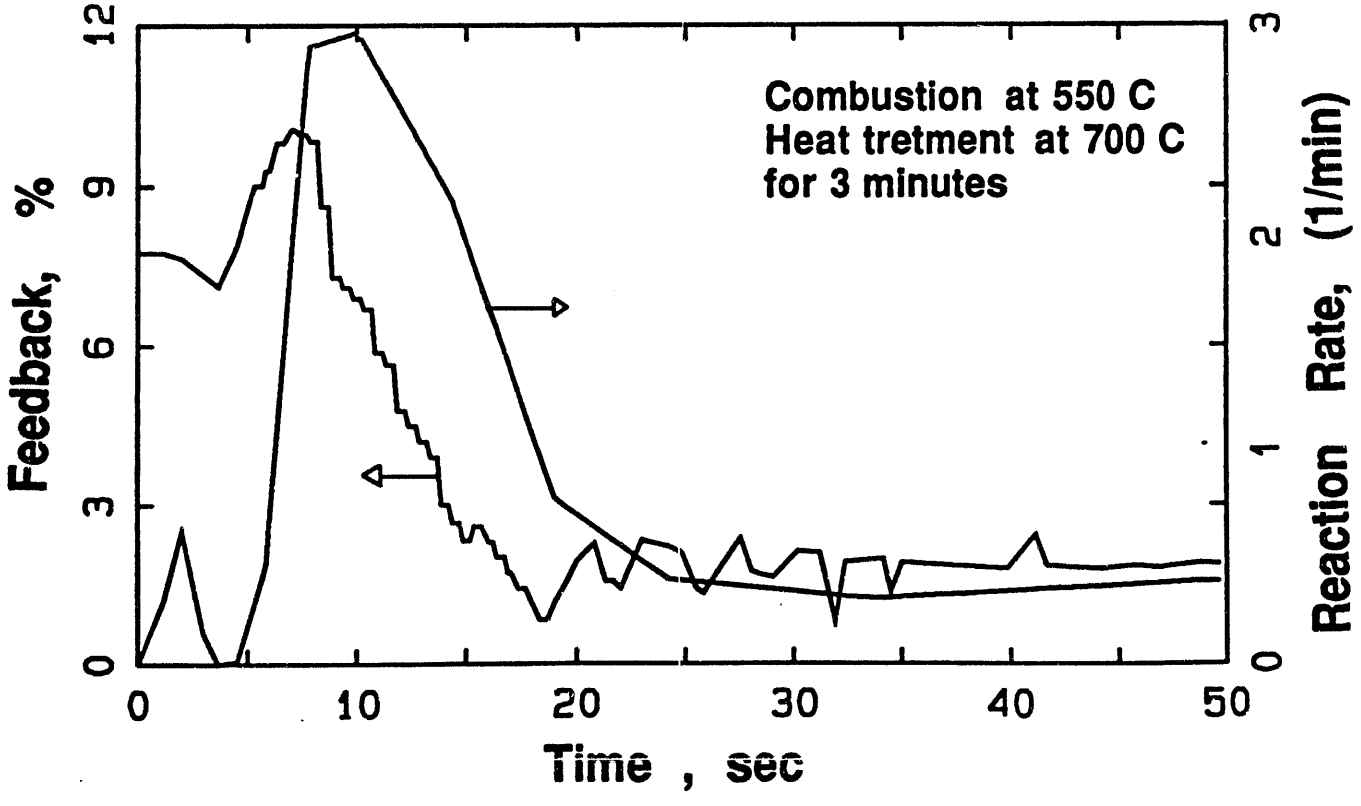


Figure 10: Time histories of feedback control signal and reaction rate for a typical experiment. As discussed in the text, these signals provide additional evicence that the sharp spikes in the reaction rate are due to particle ignitions.

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