DOE/PC/79930--T17

PYROLYSIS AND GASIFICATION OF COAL AT HIGH TEMPERATURES

DOE/PC/79930--T17

DE93 007683

Grant Number DE-FG22-87PC79930

QUARTERLY PROGRESS REPORT

(Quarter #11: 3/15/1990 to 6/15/90)

PRINCIPAL INVESTIGATOR: Prof. Kyriacos Zygourakis
Department of Chemical Engineering
Rice University
Houston, Texas 77251-1892
Tel. (713) 527-8101 Ext. 3509.

PROJECT MANAGER: Dr. James R. Longanbach
Morgantown Energy Technology Center
P.O. Box 880
Collins Ferry Road
Morgantown, West Virginia 26505

GRANT PERIOD: 9/15/1987 to 9/14/1990

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 completing the development of a thermogravimetric reactor with video microscopy imaging capabilities (TGA/VMI). The video microscopy components were designed, installed and are currently under testing. With the newly developed TGA/VMI apparatus we can **directly** observe macroscopic changes in the morphology of pyrolyzing particles and thermal ignitions of burning particles while **simultaneously** monitoring 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 (400-600 °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 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 have completed the process of installing and testing the video imaging apparatus attached to the thermogravimetric reactor (TGA/IVIM). As mentioned in our previous report (QR#10), a special microscope with video camera attached was installed beside the reactor. Through an optical glass window attached to the

furnace tube, the camera can image the entire sample pan. The high magnification possible with this microscope allows us to image an area as small as 2.8 x 2.1 mm. This gives a pixel size of 4.3 μm for our 640x480 pixel digital image acquisition board. Illumination of the sample pan is provided by a fiber optic bundle connected to a light source providing 50,000 ft. candles of light.

A color video camera with 760x485 lines resolution was attached to the microscope. The signal from a video timer is superimposed on the images from the video microscope, so that the elapsed time for each experiment is shown on the TV monitor and recorded on tape. Sequences from pyrolysis and gasification experiments are recorded on a S-VHS video tape recorder (400 lines of resolution). The computer is capable of activating the VTR recording function whenever it is necessary (during pyrolysis and gasification). This way we avoid recording unimportant stages of the experiment (e.g. preheating, feed of oxygen etc).

Digital images of pyrolyzing or burning particles are later acquired from the experiment videotapes. Our digital image processing software can be used for further processing of the images. Thus, image enhancement techniques may be applied to increase the contrast and quality of the images. Furthermore, we can measure the structural properties of the particles observed (like size, area of cross-section, swelling factor etc).

We also improved considerably the furnace of our thermogravimetric reactor. Up to now, power was supplied by a heating element made of Kanthal A-1 wire of 0.008" diameter (32 AWG). This element was supplied with 110 VAC giving a total power of about 210 Watts. We recently made a major alteration in the furnace. The ceramic element supporting the wire was redesigned and built of machinable ceramic manufactured by Aremco. This ceramic can withstand temperatures up to 2100 °F (1150 °C) which is sufficient for our experiments. The ceramic was designed to carry wire of larger diameter and shorter length. This way the resistance of the heating element was decreased and the power increased. The heating element is now a Ni-Cr wire of 0.013" diameter (28 AWG) and the power of the furnace has reached 950 Watts.

We hope that with the new furnace we will be able to achieve higher heating rates, possibly up to 100 °C/s. There are inherent problems however, associated with these high rates. Fast and accurate temperature control is highly needed. Excessive temperature gradients between the furnace exterior and interior can create overheating of the ceramic or the wire and cause melting. We are

currently working on these problems. The highest heating rate that we have achieved easily with our new furnace is 20 °C/s.

The biggest advantage of the new TGA/VMI reactor is that, for the first time, we can **simultaneously**

- observe and record on tape the macroscopic changes in the morphology of pyrolyzing particles and thermal ignitions of burning particles and
- monitor the weight of pyrolyzing or reacting samples.

PYROLYSIS AND GASIFICATION EXPERIMENTS

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. Pyrolysis experiments were videotaped and particle swelling and the particle ignitions were determined and analyzed using digitized images from these experiments.

Experimental Procedures

The pyrolysis and gasification of our coal samples were carried out in our TGA system. We began to study of another coal from the Argonne premium coal sample collection. This is the Blind Canyon that was studied along with the Illinois #6 coal. One particle size was used for both coals: 28-32 mesh (500-595 μm). For each run, the reactor was loaded with less than 1 mg of coal (about 8

coal particles for the 28-32 mesh fraction). The other conditions for the sequential pyrolysis and gasification experiments are listed below.

PYROLYSIS STAGE

Heating rate:	1, 10, 20 C/s
Final heat treatment temperature:	700 °C
Soak time at HTT:	3 minutes
Flowing Gas:	Nitrogen

COMBUSTION STAGE

Reaction Temperatures:	450 - 600 °C
Flowing gas:	Air
Gas flow rates :	300 sccm

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

Images obtained from the pyrolyzing and reacting particles were videotaped and later inspected. With this methodology, we analyzed and correlated the morphological and chemical transformations of the particles to the experimental conditions. For example, we managed to correlate the maxima in the observed reaction rate with the particle ignitions observed in the video sequences. We also investigated the connection between the pyrolysis heating rate and the phenomena of particle swelling and bubbling.

Results and Discussion

(A) Effect of ignition on reaction rate patterns

In previous reports, we have observed sharp maxima or **spikes** in the reactivity vs. conversion curves during combustion at high temperatures. Our explanation at that time, based on visual observations, was that these spikes were caused by particle ignition. With our experimental setup, however, we could not prove beyond any doubt that the spikes in the reactivity curves corresponded to

particle ignitions. Our new TGA/VMI setup has removed this difficulty and allowed us to directly observe particle ignitions while monitoring at the same time the char sample weight to obtain the reaction rates.

The images of particle ignitions gave us some fresh insights into the ignition mechanism. One type of particle ignition, which we will call from now on **global ignition**, involves the generation of an orange or yellow flame engulfing the particle. The particle surface changes from shiny black to rough, grey with many cavities and fissures. Most of the particle mass is consumed at that time. The light emission is strong and is easily distinguishable from the background. Gas is released rapidly carrying away small fragments and sometimes providing momentum for the particle to move. The duration of the flame is between 1-3 secs.

We also observed, however, another type of ignition. This is a localized, short ignition lasting only a few tenths of a second. The flame is less bright and is visible only when the background illumination is low. Only a part of the surface is covered by the flame and the flame color is more orange, an indication of lower ignition temperatures than those prevailing during global ignitions (yellow is emitted by hotter objects). The local ignitions are much harder to detect with the weight measurements since their effect on the total reaction rate is small. Furthermore, our data acquisition computer is only able to collect 2-4 weight measurements during a short ignition (our temperature control algorithm runs about every 0.1 sec). With so few weight measurements, it is impossible to detect a maximum in the reaction rate. These arguments strongly support the use of a video imaging device if every ignition is to be detected.

Figure 1 shows the reaction rate measurements from a combustion experiment. The reaction rate pattern exhibits three spikes (local maxima). A careful analysis of the video sequence for this run clearly showed that the first two rate spikes (at -2 and 2 secs) were attributed to ignition of one particle each time. This confirms our hypothesis concerning the connection between particle ignitions and local maxima in the reactivity curve. A third maximum in the reactivity pattern was observed at 10 seconds but it did not correspond to a particle ignition. This is a maximum we often observe at high conversions when very little mass of solid is left. If we plot the reaction rate per unit mass of initial solid the maximum disappears.

The correspondence between ignitions and reactivity maxima is not as simple however. If many particles ignite at the same time or if the ignitions are short and localized, the reaction rate curve may not show any sharp spikes. This is

demonstrated in Figure 2 that shows a very smooth reaction rate pattern. Although we would expect no ignition to occur during that time, the video sequence showed that there were 4 ignitions in the -5 to 0 sec period. Three of the ignitions occurred in the same particle: first a massive ignition and, later, two localized ones. The fourth ignition was also a massive one and occurred at time zero. The effect of this ignition on the reaction rate was probably masked, however, by the two localized ignitions occurring exactly before and after the massive one.

Similar observations were made for the Blind Canyon coal (see Figure 3). There were almost 12 localized ignitions and a few massive ones during the period -5 to 15 secs, but only two were detected at time 8 and 12 sec. The same was true for the run of Figure 4 where about 14 ignitions occurred but only one was detected by the thermogravimetric method.

Our conclusion is that although some ignitions can be detected by the thermogravimetric method, their majority cannot be detected. That is why a video microscopy system is necessary to detect all particle ignitions.

(B) Effect of heating rate on char gasification patterns

Preliminary results on such effects were first reported in earlier Quarterly Reports (#9,10). The conclusion drawn was that Illinois #6 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. This was confirmed again with experiments performed with a pyrolysis heating rate of 20 °C/s. As seen in Figure 5, the reactivity of chars at 450 °C is the same for chars pyrolyzed between 0.1 and 20 °C/s. The slightly higher reactivity for the 20 °C/s chars may be due to several factors. First, the total exposure of these chars to high temperatures during the ramp is shorter although it is compensated by the 3 min soak time. This means that the 20 °C/s chars are kept in the 500-700 C range 10 seconds less than the chars produced at 10 °C/s. We are not yet certain whether this difference is important or not. The bubble formation is very localized and occurs in small generation sites that are dispersed throughout the particle mass. If these small bubbles are not given enough time to diffuse and coalesce then they may be frozen at their initial small size after the plasticity stage ends. This

phenomenon may create a more fine and dispersed network of mesopores that have some important surface area.

At the temperature of 600 °C, however, the reactivity of the chars produced at 20 °C/s is significantly higher than that of other chars (Figure 6). This is another confirmation of the hypothesis that **higher heating rates produce chars that are more reactive in the diffusion limited regime.**

(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.

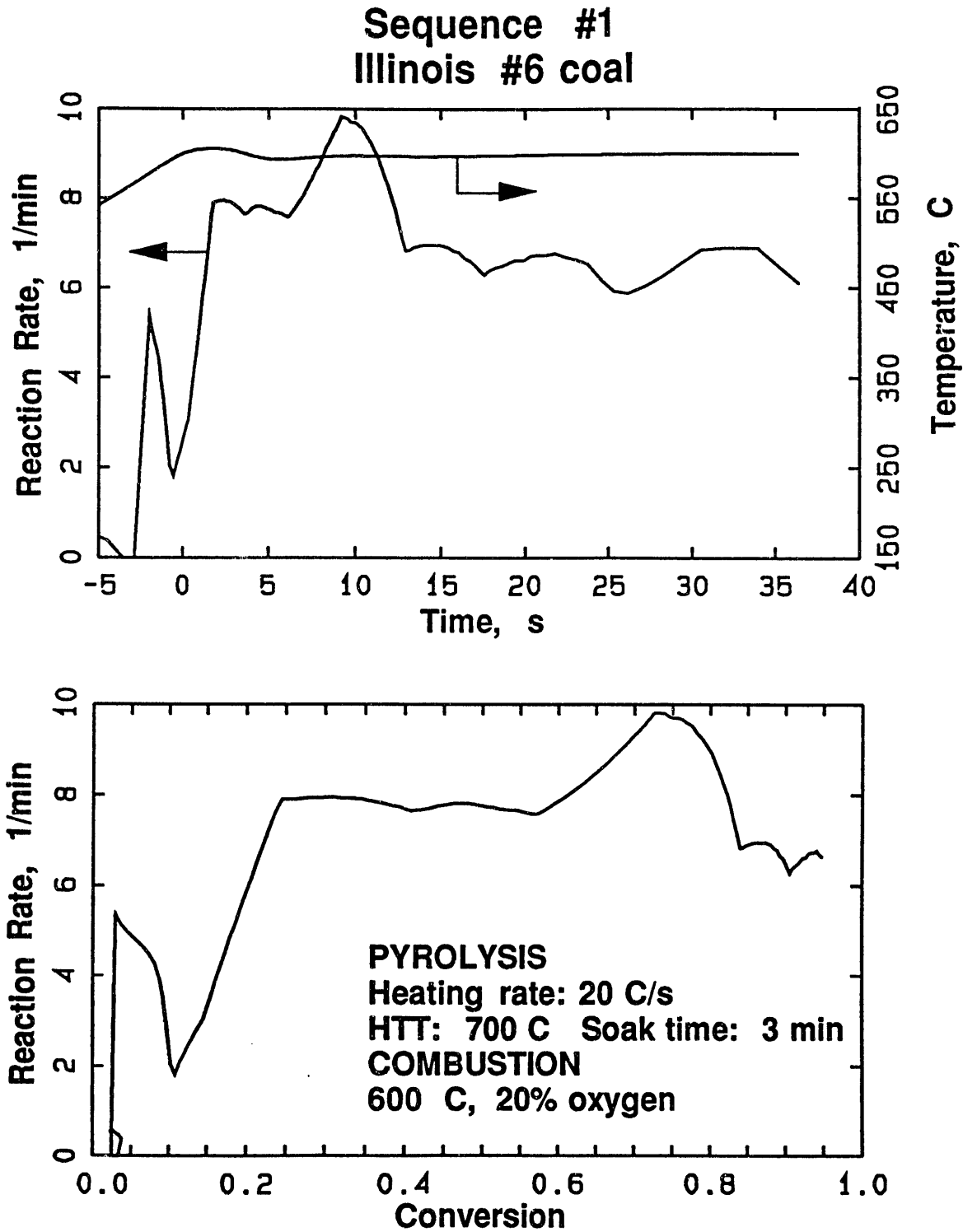

Figure 1: Reaction rate measurements obtained during the combustion of an Illinois #6 char. The top graph also presents the sample temperature along the right axis.

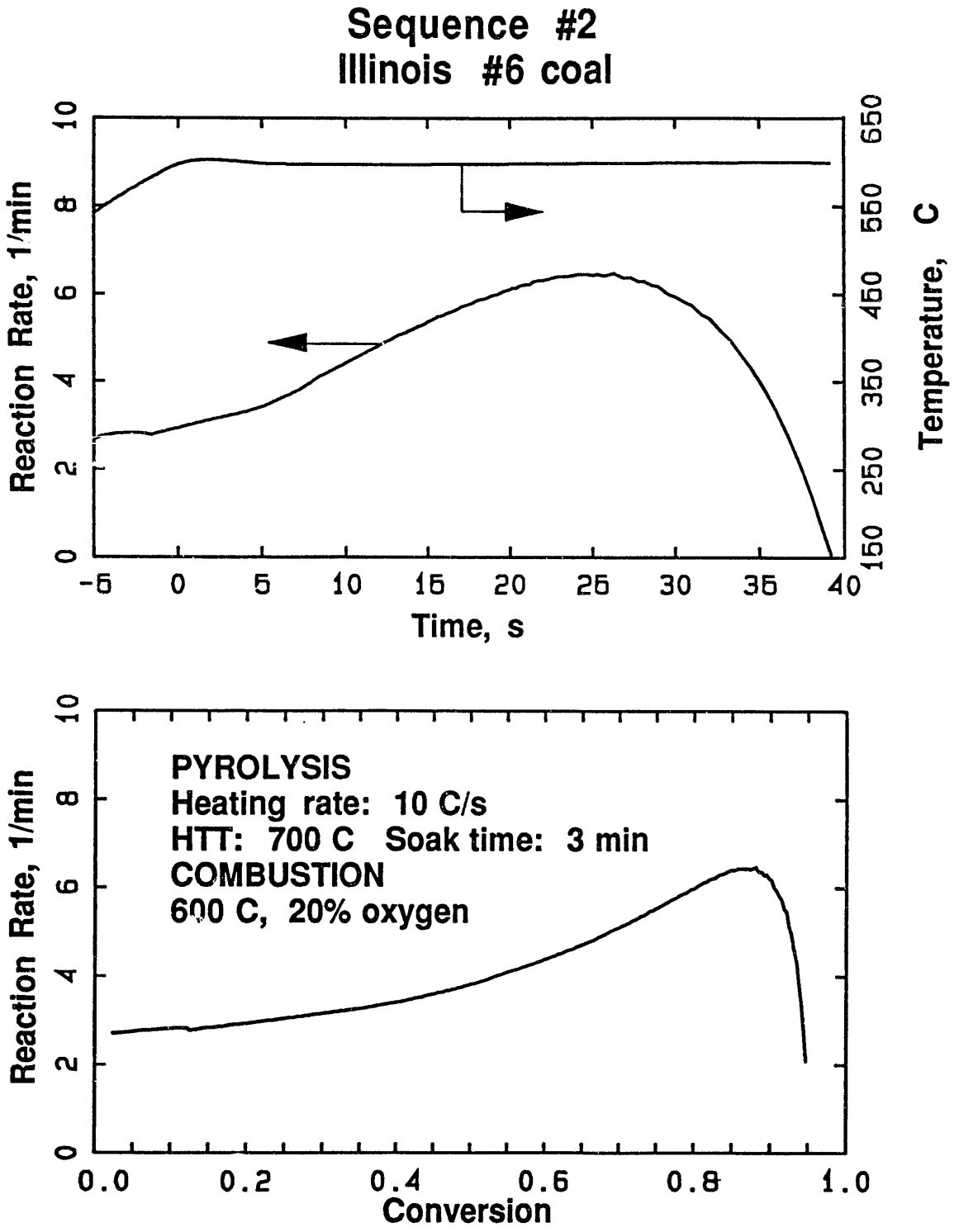

Figure 2: Reaction rate measurements obtained during the combustion of another Illinois #6 char. The top graph also presents the sample temperature along the right axis.

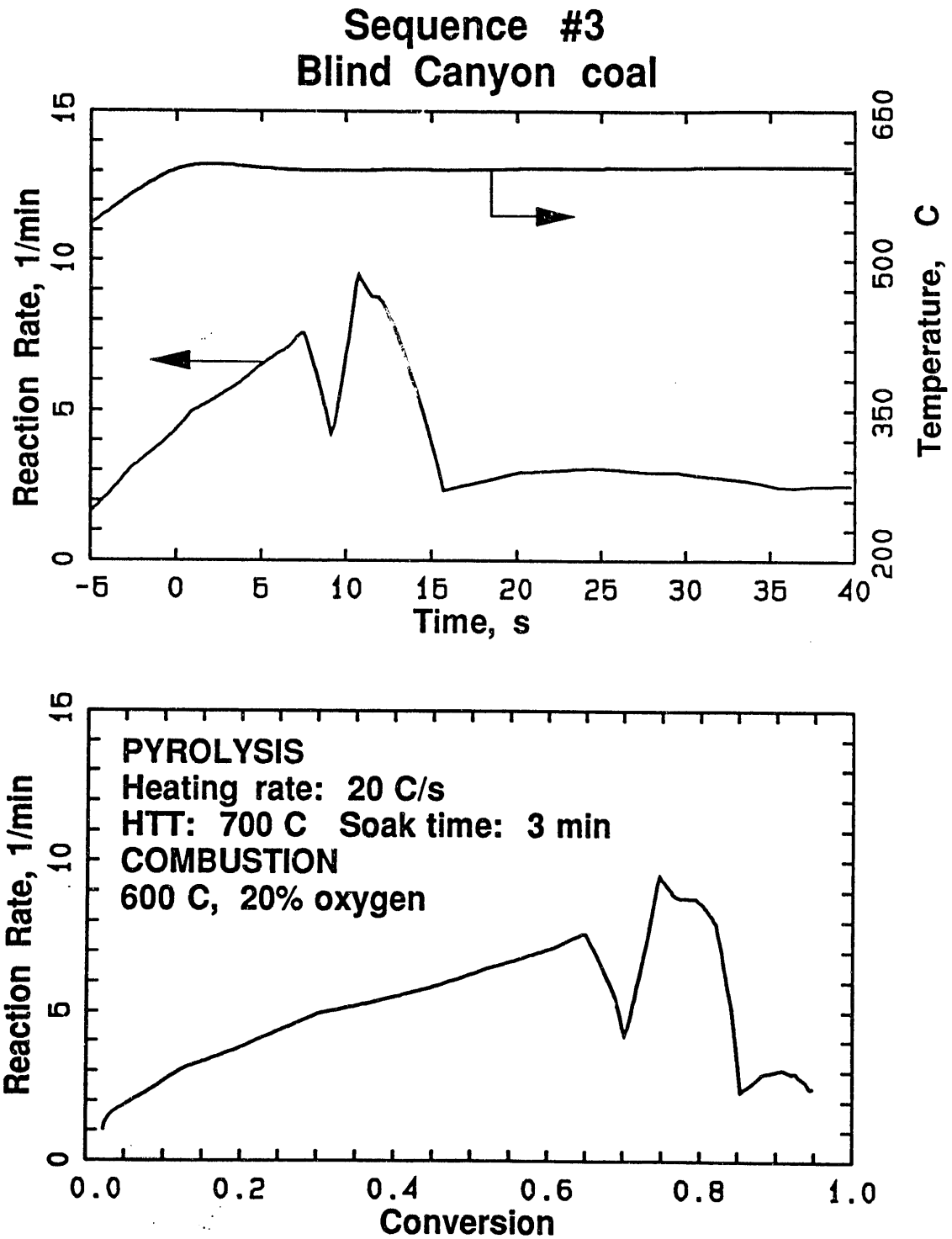

Figure 3: Reaction rate measurements obtained during the combustion of a Blind Canyon char. The top graph also presents the sample temperature along the right axis.

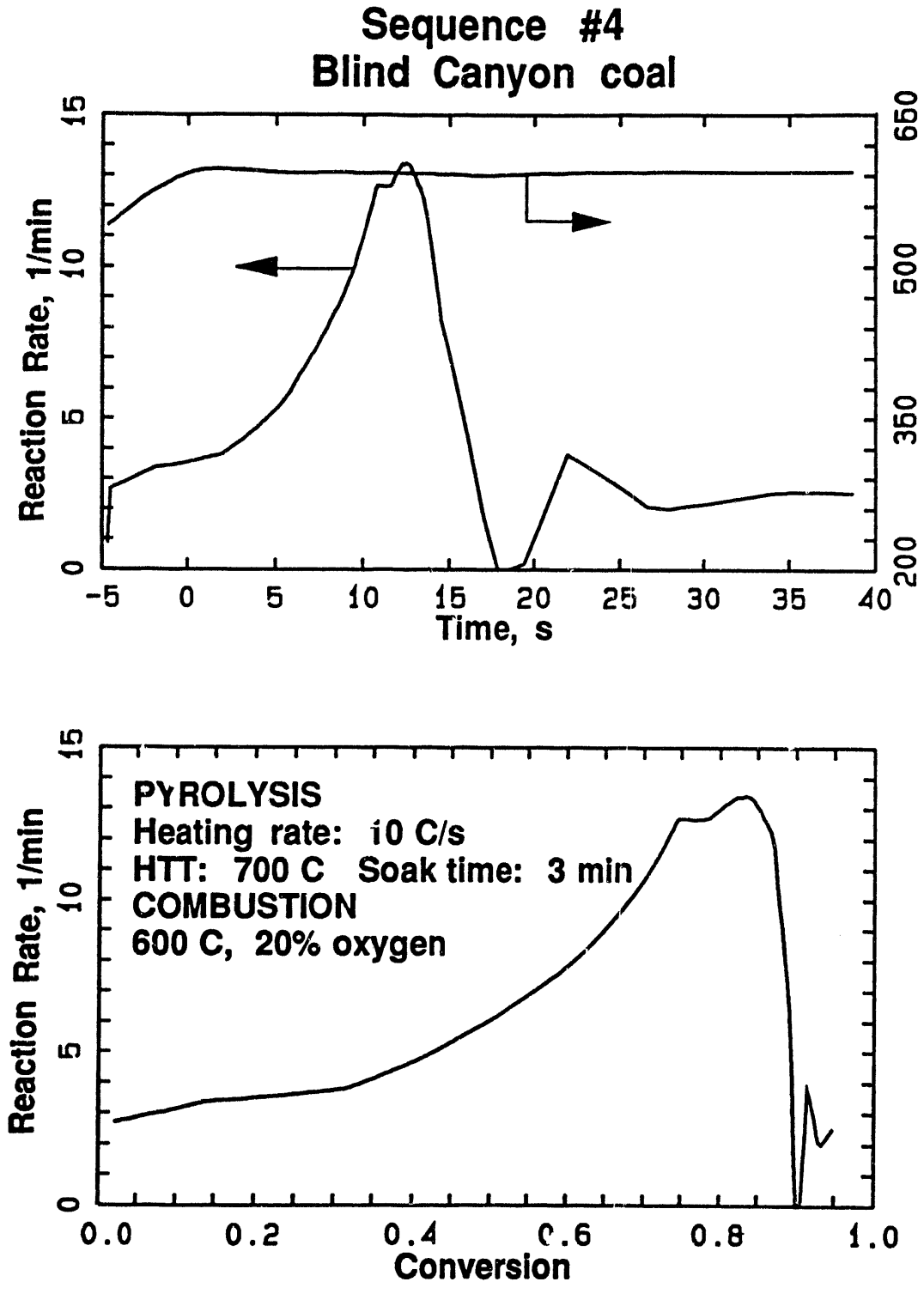

Figure 4: Reaction rate measurements obtained during the combustion of another Blind Canyon char. The top graph also presents the sample temperature along the right axis.

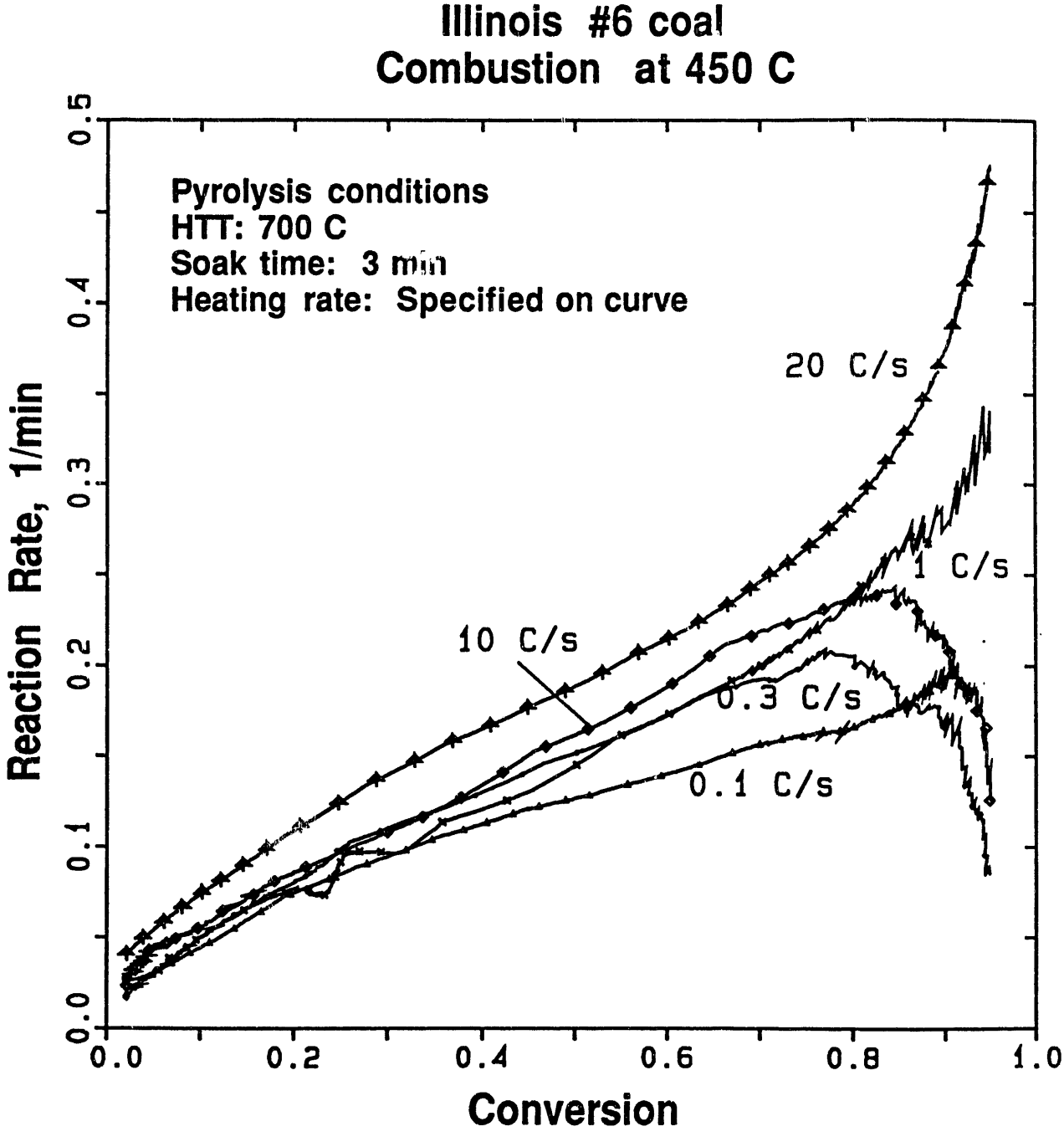

Figure 5: Reactivity patterns for combustion at 450 °C of five Illinois #6 chars produced with different pyrolysis heating rates. Combustion takes place here in the regime of kinetic control.

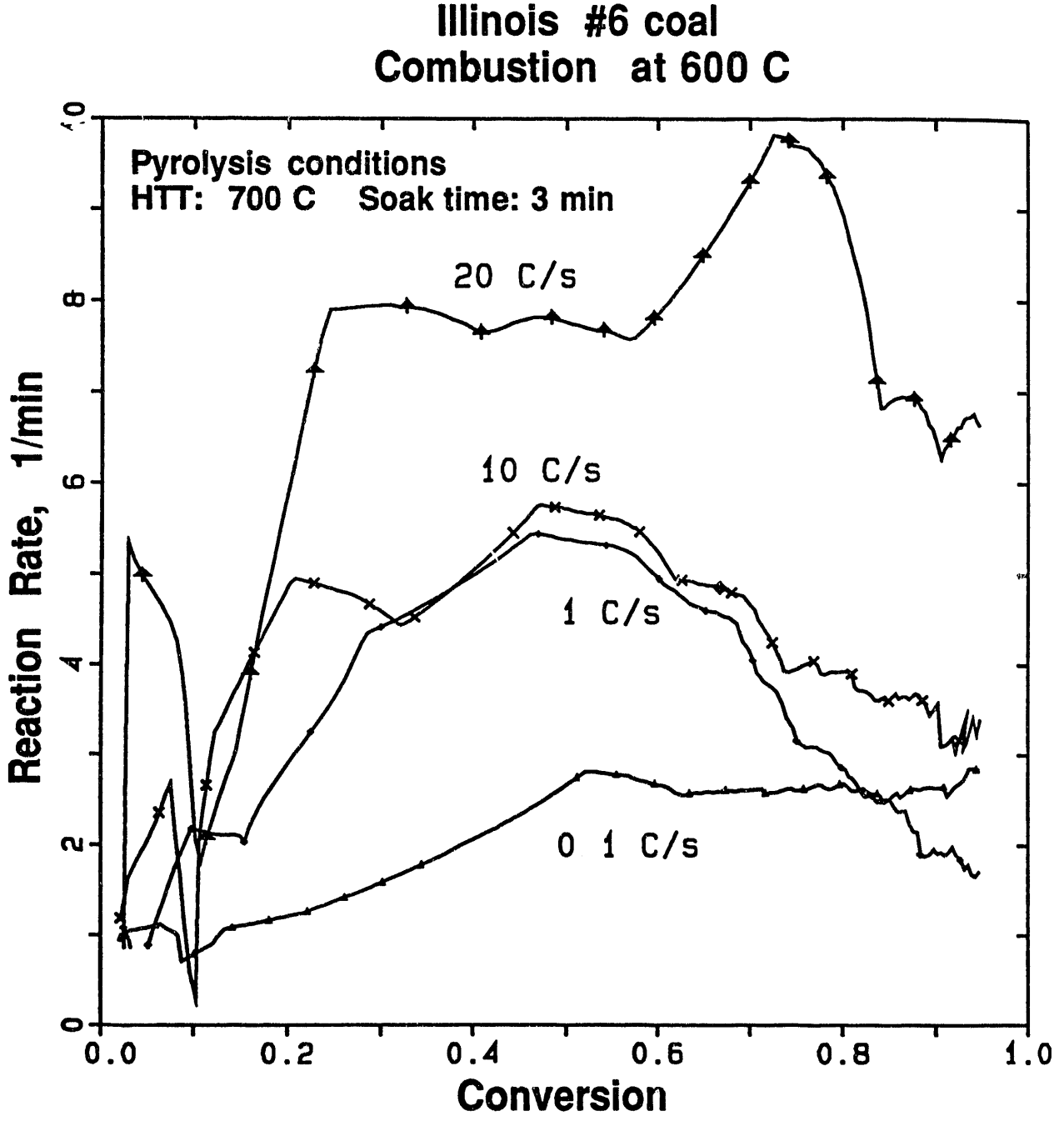

Figure 6: Reactivity patterns for combustion at 600 °C of five Illinois #6 chars produced with different pyrolysis heating rates. Combustion takes place here in the regime of significant intraparticle diffusional limitations.

END

DATE
FILMED
2/19/93