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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 have completed the first part of the systematic pyrolysis and gasification study initiated last summer. In this part, we used the Illinois #6 coal from the Argonne collection and investigated the effects of pyrolysis conditions on the macropore structure of coal chars and on their **reactivity** during combustion with oxygen. The variables we considered were (a) the pyrolysis heating rate, (b) the final heat treatment temperature (HTT), and (c) the soak time at HTT. Pyrolysis and gasification experiments were carried out both on our thermogravimetric reactor that provided accurate measurements of volatile evolution and combustion rates and on the microscope hot-stage reactor that allowed **direct observation of pyrolyzing and burning particles under the microscope.** A video timer unit was purchased and integrated in our video microscopy system in order to facilitate the analysis of time-resolved pyrolysis and combustion experiments.

The combination of thermogravimetry and video microscopy allowed us to observe for the first time and interpret some interesting transient phenomena such as **self-ignition** and **fragmentation** of char particles. In agreement with literature data, our results showed that high heat treatment temperatures and longer soak times result in significant declines in reactivity caused by the increased molecular order of the chars. More importantly, however, the preliminary results presented here clearly indicate that the pyrolysis conditions have strong effects on the macropore structure and, consequently, on the reactivity of the produced chars. They also provide some new insights into the transient phenomena associated with **particle ignition** and **macropore opening** during combustion in the diffusion-limited regime of high temperatures.

Task A: Pyrolysis and Macropore Structure

The first coal used in this series of experiments was the Illinois #6 from the Argonne premium coal sample collection. Coal particles in the 28-32 mesh (500-595 μm) range were pyrolyzed in our thermogravimetric reactor (Perkin Elmer TGS-2) with a custom-built furnace and computer-controlled heater. For each run, a coal sample of about 1 mg (**8-10 particles**) was pyrolyzed in nitrogen atmosphere. Pyrolysis experiments were carried out at the following conditions:

- **Heating rates**: 0.1, 1 and 10 °C/s;
- **Final heat treatment temperature** (HTT): 700, 800 and 900 °C; and
- **Soak Time** at HTT: 0 and 3 minutes.

A data acquisition and control computer continuously monitored the weight of the samples during both the pyrolysis stage. The same computer controlled the temperature of the TGA and operated the mass flow controllers that set the gas flow rates. Temperature control was very accurate. During the entire temperature program, the average squared error in temperature was of the order of 1 °C. Raw data (sample weight and temperature vs. time) were stored on a computer disk for later analysis. The weight vs. time data were interpolated with B-splines (using a least squares approximation) and the interpolant was differentiated to obtain the rates of volatile release. The gravimetric capabilities of our reactor were also used to obtain a proximate analysis of the total volatile content of the coal samples.

A microscope hot-stage reactor (Glass and Zygourakis, 1988) was also used for visual observation of the coal particles during the stages of pyrolysis and combustion. The experiments were recorded in video tape and specific images were later digitized on a digital image processor. From the digital images, time resolved measurements of particle swelling were obtained.

The experiments on the microscope hot-stage reactor showed that the coal particles swell considerably and that the swelling increases with increasing heating rates. Although we did not characterize in detail the macropore structure of the chars produced during the experiments reported here, our swelling measurements indicate that the char particles have very open cellular macropore structures similar to those quantified via digital image analysis in our earlier studies with the same parent coal (Zygourakis, 1988). As we expected, the heating rate strongly affected the swelling (and therefore the macroporosity) of the char particles.

By continuously monitoring the weight loss of the pyrolyzing coal samples, the instantaneous volatile release rates were obtained and analyzed to elucidate the effects of heating rate. Figure 1a shows the weight loss rates for several runs at two different heating rates The results for 0.1 and 10 °C/s indicate very good reproducibility and the maximum pyrolysis rate is observed in a rather narrow temperature range for each heating rate. There is, however, a significant shift of this maximum towards higher temperatures as shown in Figures 1a, 1b and Table 1.

Table 1

Temperature Ranges where the Maximum Weight Loss Rate is Observed during Pyrolysis

Heating rate (°C/s)	0.1	1.0	10
Temperature (°C)	410-425	460-480	510-545

This shifting of the maximum to higher temperatures with increasing heating rates suggests that such experiments can be used **to determine the kinetic constants of devolatilization rates.** For example, if we assume that the rate of devolatilization can be described by the following simple model

$$\frac{dV}{dt} = k_0\, e^{-\frac{E}{RT}} \, (V^* - V) \tag{1}$$

where V(t) is the fraction of the original coal sample lost up to time due to the release of volatiles and $V(t) \rightarrow V^*$ as $t \rightarrow \infty$ (see Anthony and Howard, 1976). If we set $\theta = (V^* - V) / V^*$, Equation (1) becomes

$$\frac{d\theta}{dt} = - k_0\, e^{-\frac{E}{RT}} \, \theta \tag{2}$$

At the temperature T_m where the maximum devolatilization rate is observed

$$\frac{d^2\theta}{dt^2} = 0 \;\Rightarrow\; \exp\left[- \frac{E}{RT_m} \right] = \frac{E\, q}{k_0\, R\, T_m^{\,2}} \;\Rightarrow\; \ln\left(\frac{T_m^{\,2}}{q} \right) = \left(\frac{E}{R} \right) \frac{1}{T} + \ln\left(\frac{E}{R\, k_0} \right)$$

where q is the constant pyrolysis heating rate. The semi-log plot of Figure 2 shows an excellent correlation (R=0.9998) and yields E = 43.4 kcal/mole and $k_0 = 2.09 \times 10^{11}$. These numbers are in good agreement with other data in the literature. An analysis of these data using a more detailed pyrolysis model is currently under way. Although the weight loss rate changes significantly during the pyrolysis stage, our data show that most of the weight loss occurs during a period when the pyrolysis rate is almost constant. Since the pyrolysis occurs under nonisothermal conditions, this observation agrees with the previous model.

A final observation (Figure 3) is that the amount of released volatiles appears to increase slightly with increasing heating rates. This observation is in agreement with the theoretical predictions (Fletcher et al., 1989) of the chemical percolation devolatilization (CPD) model and the experimental observations of Gibbins-Matham and Kandiyoti (1987). We should note, however, that video microscopic observations of coal particles pyrolyzing at high heating rates show "vigorous bubbling" as volatiles are emitted from the softened coal. This raises the possibility that the escaping volatiles may carry away small fragments of the coal.

Task B: Char Gasification

After every pyrolysis run on the TGA, the char particles were **immediately** reacted with oxygen. The pyrolyzed samples were rapidly cooled from the HTT to 250 °C and a mixture consisting of 20% oxygen and 80% nitrogen was introduced in the reactor. After a few minutes, the samples were rapidly ramped to the final combustion temperature which varied from 400 °C to 550 °C. Figure 4 shows the reactor temperature and the char sample weight for a run with 1.0 °C/s pyrolysis heating rate and combustion at 550 °C. The raw data (sample weight and temperature vs. time) were stored on a computer disk for later analysis. The weight vs. time data were interpolated with B-splines (using a least squares approximation) and the interpolant m(t) was differentiated to obtain the combustion rates according to the formula

$$r(t) = \frac{1}{m(t)} \frac{dm(t)}{dt} \qquad (3)$$

where m(t) is obviously the interpolated sample weight at time t.

Figures 5a and 5b show the evolution of reaction rates with conversion for several char samples prepared at a heating rate of 1 °C/s and three different heat treatment temperatures (HTT): 700, 800 and 900 °C. Soak time at the HTT for all these samples was 3 minutes. The experimental gasification data at 450 °C show the expected char reactivity pattern. Chars produced at a HTT of 700 °C are more reactive than chars produced at higher HTT (800 and 900 °C) and the char reactivity (as measured by r(t)) increases continuously with conversion. These observations are in agreement with earlier studies on char combustion (see, for example, Serio et. al, 1989) indicating an increase in the molecular order of chars produced at high HTT due to enhanced annealing of the organic and mineral components and the microporosity of the chars. They also agree with theoretical models for gasification in the kinetic control regime where the active surface area associated with the micropores is easily accessible to the reactants (see, for example, Zygourakis and Sandmann, 1988). These and similar models predict that the intrinsic reaction rate will follow an increasing pattern due to the increasing accessibility and specific surface area of the enlarging micropores.

The experimental reactivity curves at 550 °C reveal a different behavior. Figure 5b shows that the reaction rate increases sharply and in a rather "discontinuous" fashion in the early stages of gasification with sharp maxima spanning a conversion range of approximately 10%. After one (or more) such maxima, the reaction rate settles at a fairly constant plateau for the remainder of the reaction. Similar maxima but with smaller amplitude and width can be seen in the reactivity curves of Figure 5a.

We carried out a systematic analysis to make sure that these sharp maxima were not artifacts due to measurement errors or to the interpolation of the numerical data. Figure 6 shows the raw weight and temperature as well as the computed reaction rate for curve A of Figure 5b. By carefully analyzing these and other similar data we concluded that the sudden and sharp drop of the sample weight cannot be due to errors in weight measurements or failures of our controller to maintain constant sample temperature.

We have also carefully analyzed our procedure for obtaining the reaction rates. Usually, our data acquisition system will collect about 300 data points during the pyrolysis stage of each run and 300-3,000 data points during the combustion stage (depending on the reaction temperature). The collected weight vs. time data are interpolated in the least-squares sense (L^2 norm) using B-splines and this polynomial approximation is then differentiated to obtain the observed reaction rate according to Eq. (3). It is essential to determine the appropriate order of polynomials and number of breakpoints to use for the interpolation of the raw weight data. If high order polynomials are used, the reactivity curves will be smoothed out and fine details will be lost. Also, the curves will be very noisy if a large number of breakpoints is used. Our choice of polynomials was dictated by the form of our data that indicated the reaction rate is continuous in time but not necessarily smooth (i.e. it has a discontinuous first derivative). Such behavior has also been observed by Sundback et. al. (1984) who attributed it to particle fragmentation. Our earlier studies (Zygourakis and Sandmann 1988, Zygourakis 1989) indicate that these jumps may also be caused by the opening of large internal pores during combustion in the diffusion-limited regime (high temperatures). Therefore, we decided to use C-1 quadratics for the interpolation instead of the more often used C-2 cubic splines. This assumes that the reaction rate is a linear function of time at each interval and can exhibit sharp maxima and minima which would be smoothed out with a cubic spline. The number of intervals is in most cases larger than 30 and our software allows for dynamic placement of the breakpoints in regions with rapidly changing sample weight, a feature that improves our ability to resolve fine details of the reactivity curve. Since we always have more than 20 data points in each subinterval, any noise disturbances cannot significantly influence our results.

The microscope hot-stage reactor provided the last piece of conclusive evidence that helped us determine the cause of the observed "spikes" in the reactivity curves. Visual observation revealed that some particles **ignited**, usually during the very early stages of gasification at the higher temperatures (e.g. 550 C). Ignited particles were then rapidly consumed. The width of the spikes corresponds to about 10% total conversion and, thus, spike should be attributable to the ignition of one of the 8-10 particles loaded in our reactor for each run.

All this evidence strongly suggest that the sharp spikes in the reactivity curves are due to **particle ignition** After the ignited particles are completely consumed, the reaction rate remains almost constant for a wide range of conversion. This behavior is in (at least qualitative) agreement with our gasification models that assume that the macropore structure is the major rate-determining factor in the regime of diffusional limitations (high temperatures). While at first only the outer macropores are available for reaction, closed macropores open up as the reaction front reaches them and the observed reaction rate remains relatively constant.

The jumps observed during reaction in the kinetic control regime may also be caused by a progressive opening of large macropores that makes previously closed micropores accessible to the reactive molecules and creates sharp maxima in the reaction vs. conversion curves. We should also note here that **char particles treated at lower HTT are more likely to ignite at 550 °C.**

Figures 7a and 7b show that longer soaking times at the HTT decrease the reactivity of the char samples. Our results also strongly indicate that the longer soaking time (3 mins) rendered the chars much less likely to ignite at 550 C.

Finally, Figures 8a and 8b provide the strongest evidence of the significant effects of the macropore structure on char reactivity. As we have previously established (Zygourakis, 1988), high pyrolysis heating rates lead to increased particle swelling, large vesicular macropores and higher macropore surface areas. These structural characteristics should lead to (a) more reactive chars when combustion is carried out at high temperatures and (b) reactivity vs. conversion patterns exhibiting sharply increasing rates followed by regions of slowly decreasing or almost constant gasification rates. Figures 8a and 8b clearly show that the chars produced at 1 and 10 C/s are more reactive, exhibit the reactivity patterns that are clearly attributable to their macropore structure and ignite more easily during combustion at 550 °C (Figure 8b). When combustion takes place at 450 °C, the reaction rates do not appear to be significantly influenced by the pyrolysis heating rate and, therefore, by the macropore structure. Still, the reactivity curve for the char produced at a pyrolysis heating rate of 10 °C/s shows some "jumps" whose small amplitude seems to indicate that they are caused by macropore opening (e.g. cenosphere structures) rather than by particle ignition.

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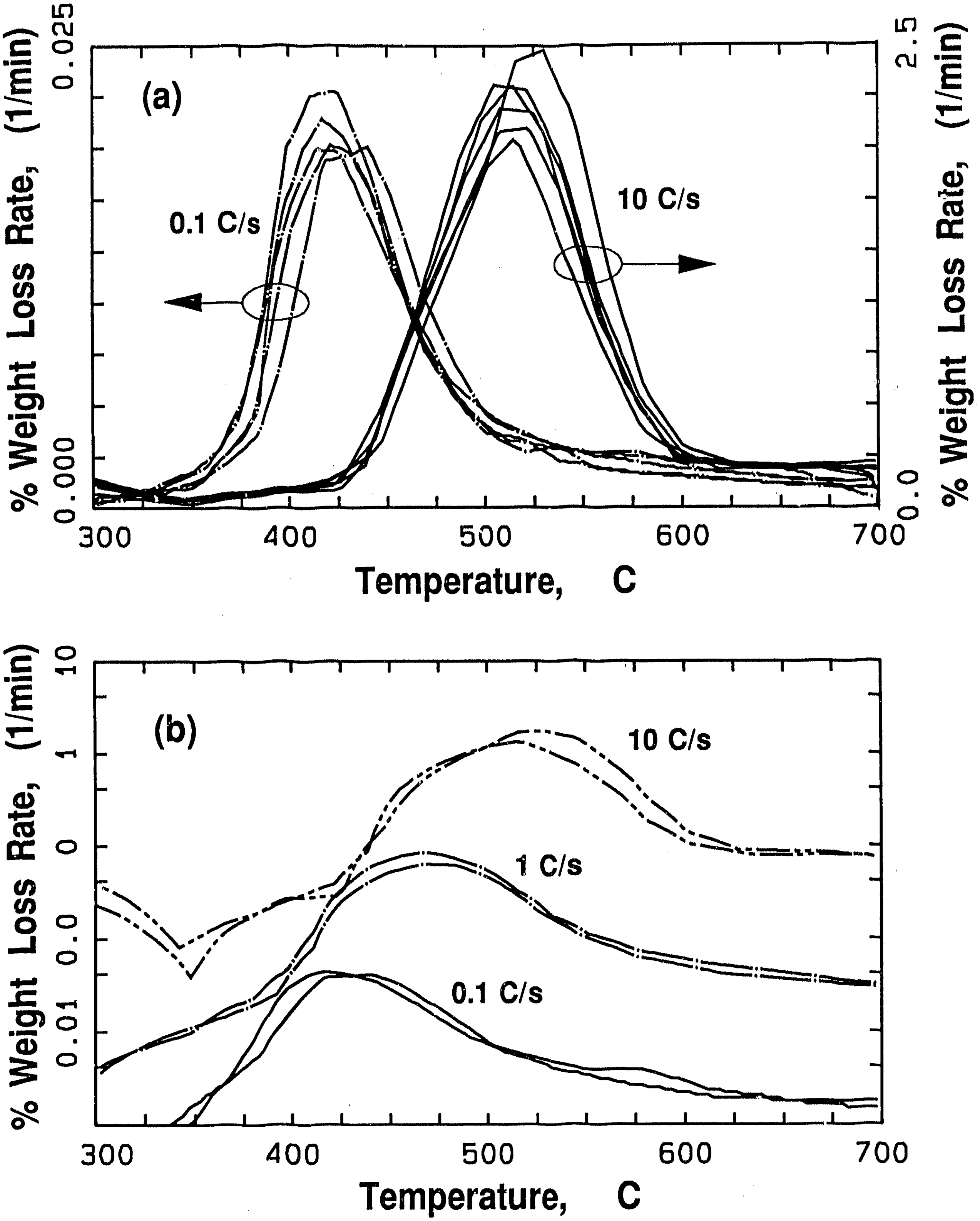

Figure 1: Experimental devolatilization rates for several pyrolysis runs performed at three different heating rates.

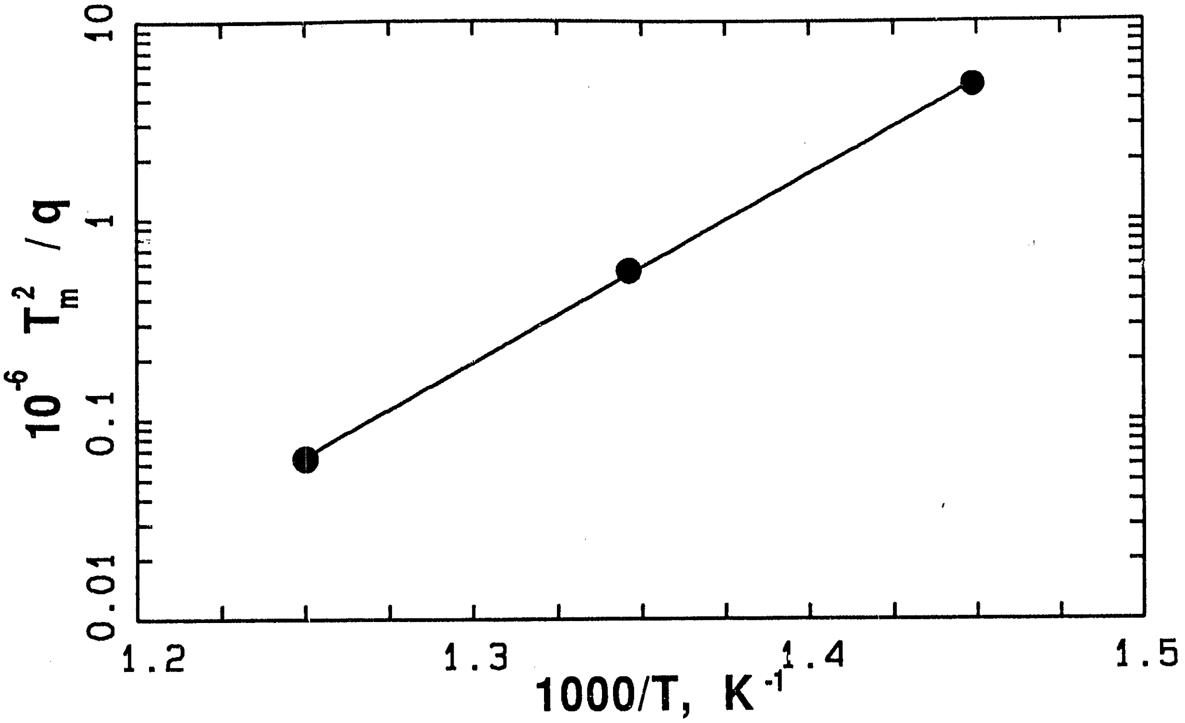

Figure 2: Plot for determining the kinetic constants of the pyrolysis model of Equation (1).

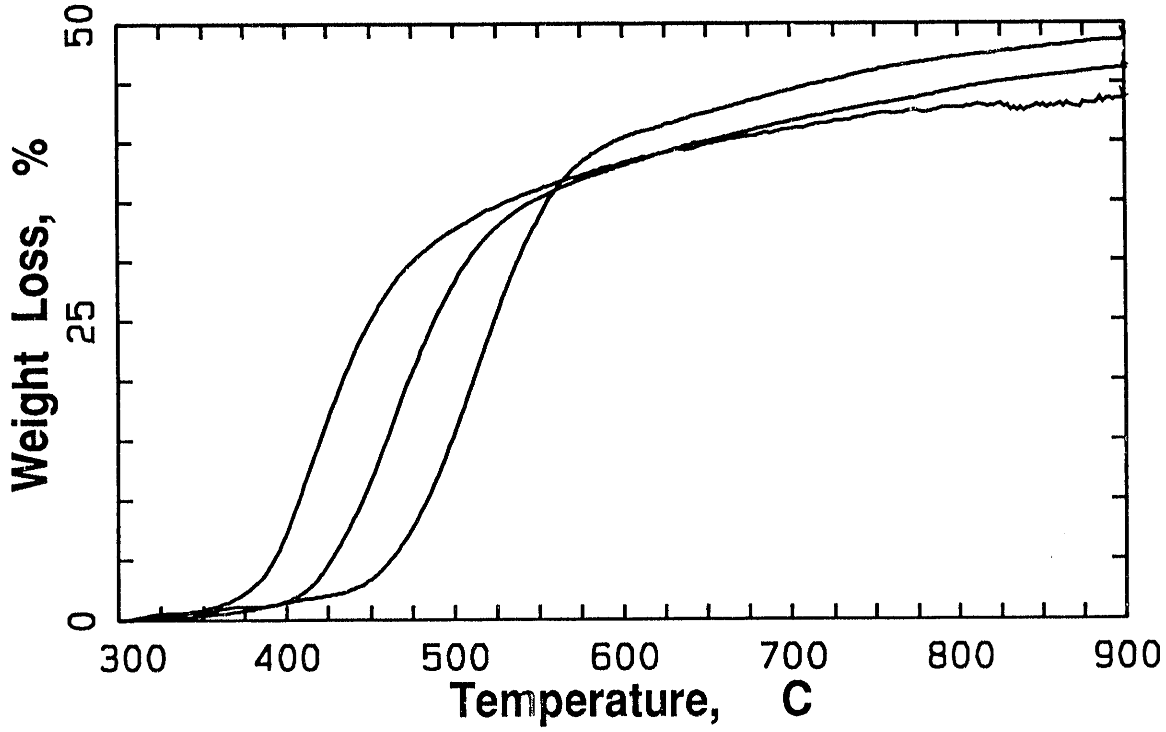

Figure 3: The effect of pyrolysis heating rate on the total amount of released volatiles.

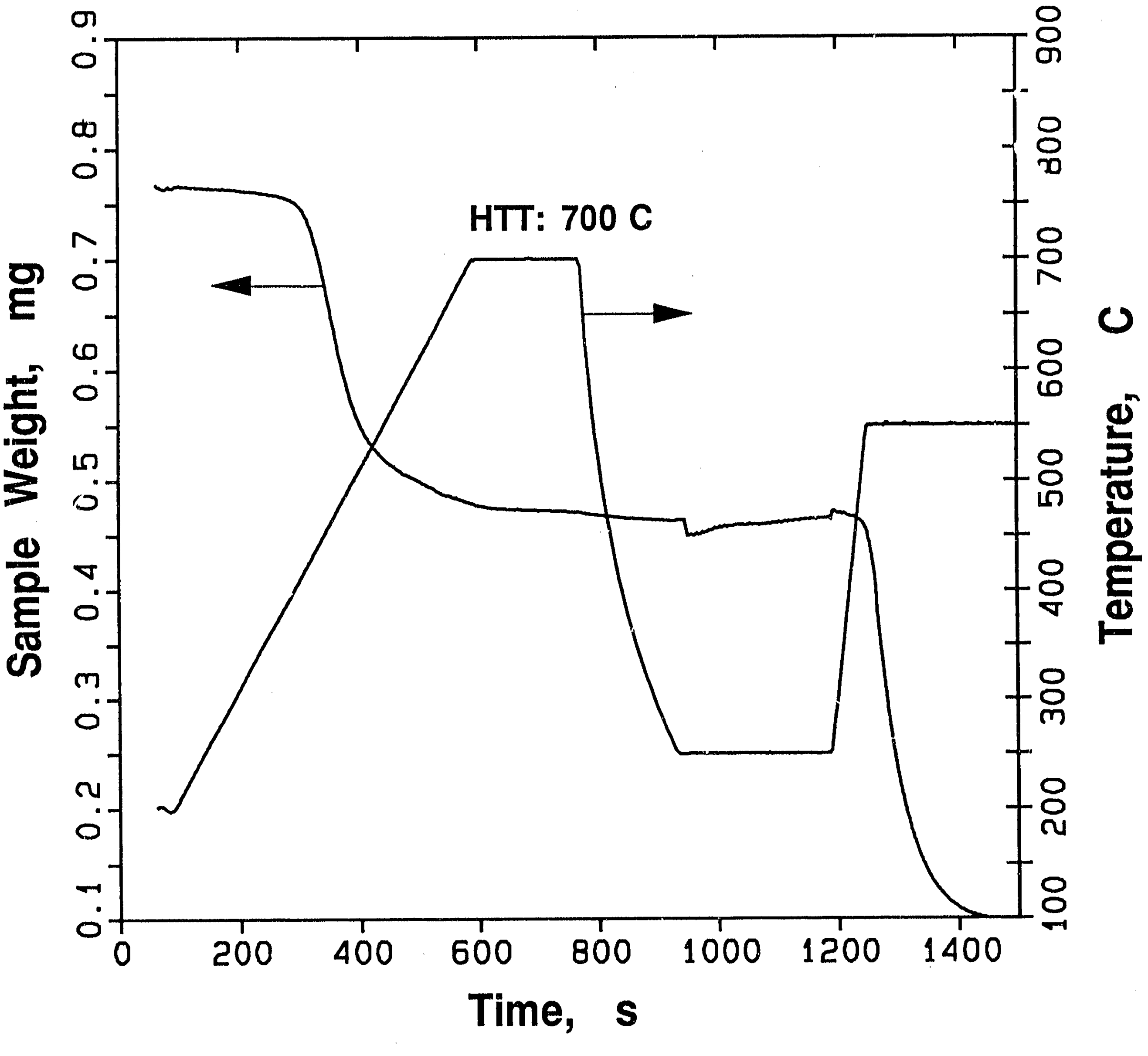

Figure 4: Temperature program and weight vs. time data for a typical run (Pyrolysis heating rate: 1 °C/s; Combustion temperature: 550 °C).

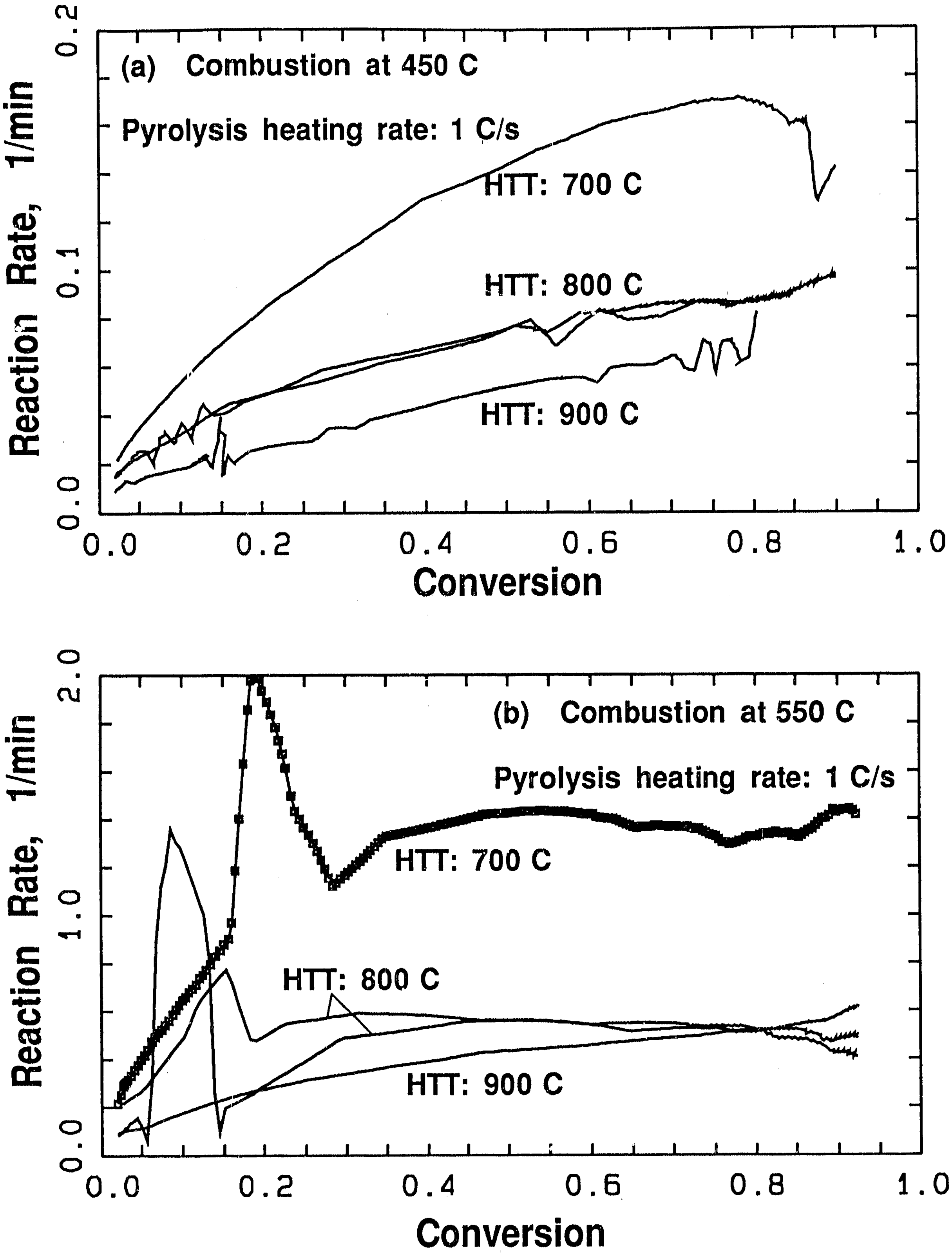

Figure 5: The effect of heat treatment temperature on the reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at (a) 450 and (b) 550 °C (Soaking time at HTT: 3 minutes).

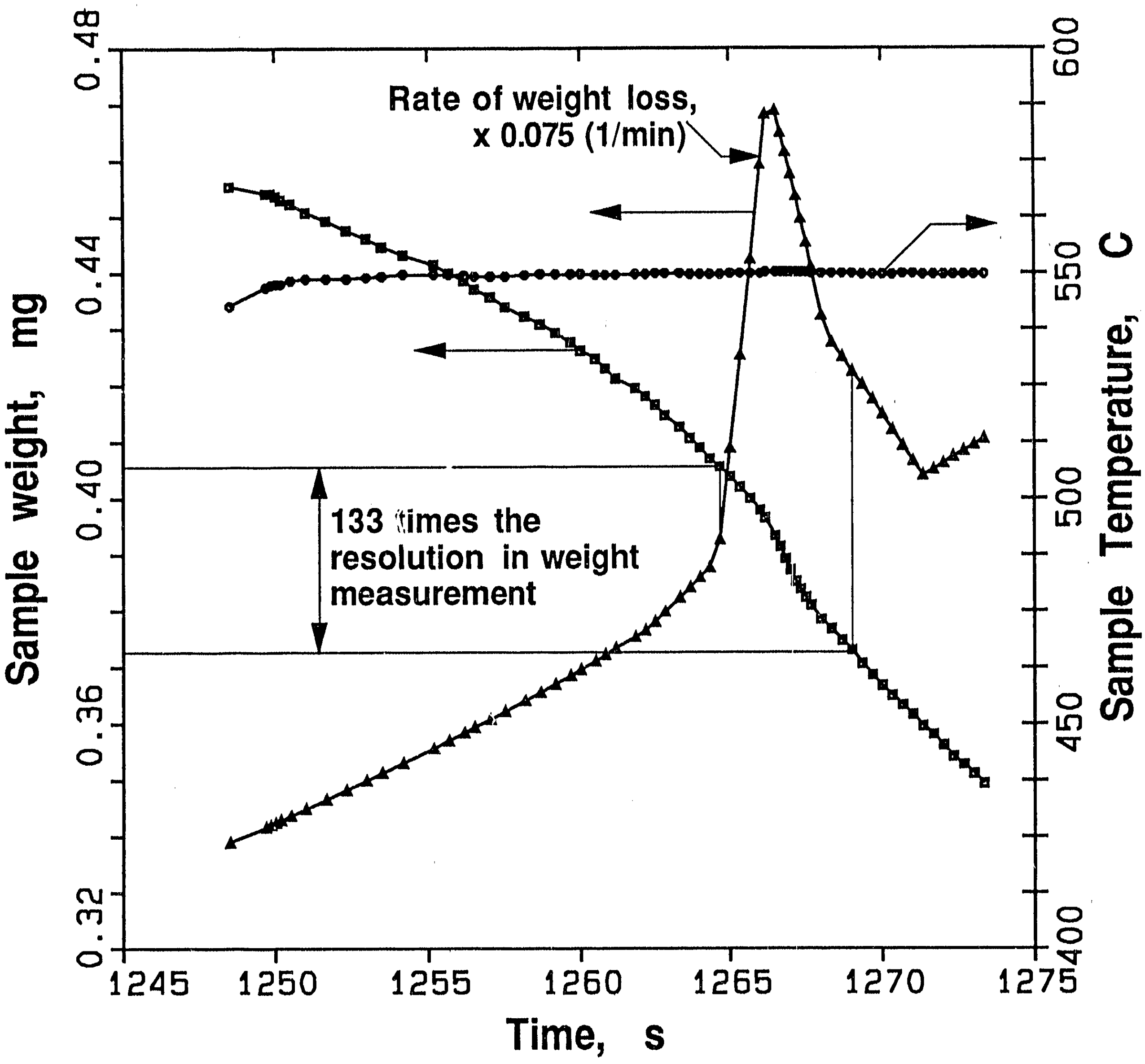

Figure 6: Raw data (sample weight and temperature vs. time) and computed reaction rate for a small part of curve A of Figure 5b.

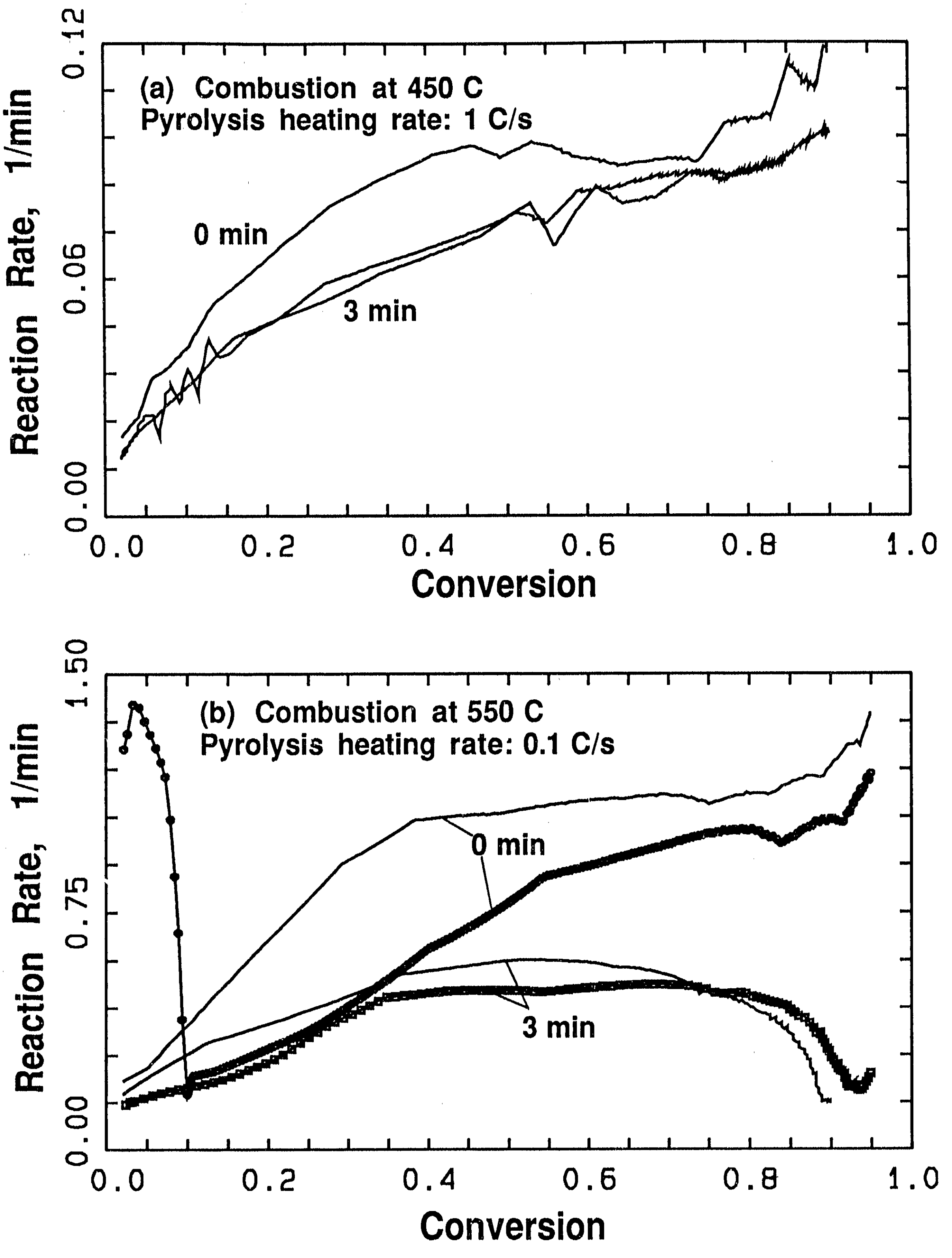

Figure 7: The effect of soaking time on the reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at (a) 450 and (b) 550 °C (Heat treatment temperature: 800 °C).

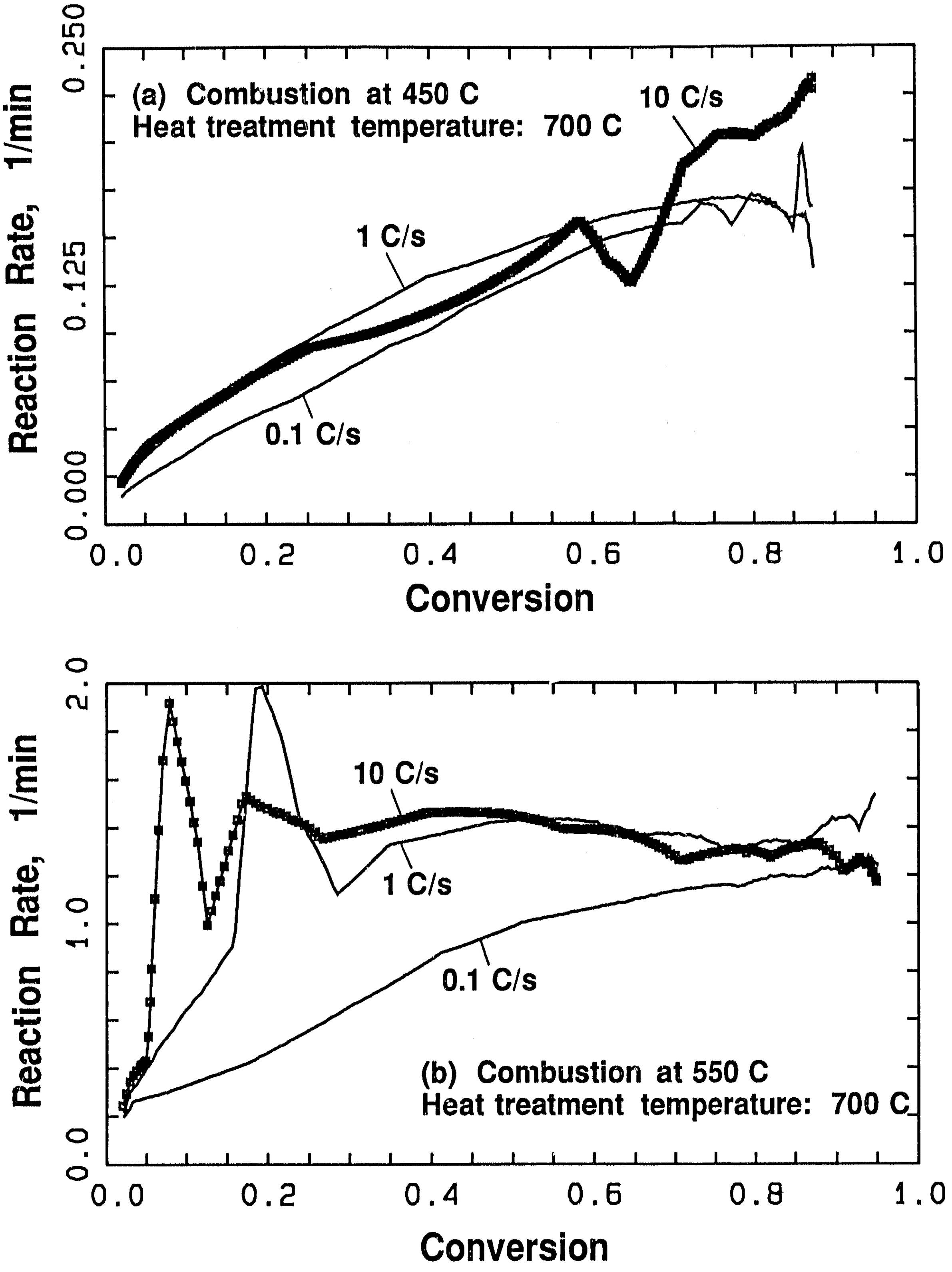

Figure 8: The effect of pyrolysis heating rate on the reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at (a) 450 and (b) 550 °C.

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