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COAL COMBUSTION: EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

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PROJECT OBJECTIVES

The project will quantify the effect of the following pyrolysis conditions on the macropore structure and on the subsequent reactivity of chars: (a) pyrolysis heating rate; (b) final heat treatment temperature (HTT); (c) duration of heat treatment at HTT (or soak time); (d) pyrolysis atmosphere (N_2 or O_2/N_2 mixtures); (e) coal particle size (100 - 1,000 mm in diameter); (f) sulfur-capturing additives (limestone); and (g) coal rank. Pyrolysis experiments will be carried out for three coals from the Argonne collection: (1) a high-volatile bituminous coal with high ash content (Illinois #6), (2) a bituminous coal with low ash content (Utah Blind Canyon) and (3) a lower rank subbituminous coal (Wyodak-Anderson seam).

Task A: We will obtain the time histories and follow the fate of single particles during pyrolysis in our TGA/VMI reactor. The experiments will be videotaped and digital images at several time instants will be acquired and analyzed on the image processor. For each run, we will measure particle swelling and shape, as well as the number and size of volatile bubbles evolving from each particle. For selected sets of conditions, several char samples will be collected and polished sections will be prepared so that we can accurately analyze the internal structure of the char particles. We will pay particular attention to the existence of correlations between particle swelling and macropore surface area as well as to the fate of ash inclusions during pyrolysis.

Task B: A different set of pyrolysis experiments will be immediately followed by combustion experiments. Without removing the particles from the TGA/VMI reactor, the char samples will be reacted with O_2 to complete conversion at high temperatures. Different gas flow rates of gases and O_2 concentrations will be used to investigate the effect of external mass transfer limitations. Issues to be addressed in this study will include the influence of particle swelling and ash content on thermal ignitions.

Task C: We will use mathematical models to simulate combustion of char particles in the regime of strong diffusional limitations. Digitized particle cross-sections obtained from our studies will be used as computational grids for these simulations and the average behavior will be obtained by analyzing a large number of particle cross-sections. The observed reactivity vs. conversion patterns will be analyzed and classified. These patterns will then be used in transient models to describe ignition and extinction phenomena in char combustion.

1. SUMMARY

During the past quarter, we carried out a study of the kinetics of char combustion, assessed the reproducibility error of our experiments, and continued our systematic study of the effects of particle size and oxygen concentration on the reactivity of chars.

The results from the kinetic study indicated that the rate expression for combustion of Illinois #6 chars is first order with respect to the oxygen concentration. The activation energy and the preexponential factor for this reaction were also calculated. The reproducibility error assessment shows that the average relative error increases with increasing particle size. Thus, the number of combustion runs needed for accurate measurements of the reaction rate increases with increasing particle size.

For combustion in the regime of diffusional limitations, our results show the ignition temperature decreases with increasing pyrolysis heating rates, increasing coal particle size, decreasing heat treatment temperatures and increasing oxygen concentrations.

2. EXPERIMENTAL PROCEDURES

The kinetic parameters (activation energy, preexponential rate factor, and order of reaction) for the combustion of Illinois #6 coal were determined using our thermogravimetric reactor with video microscopy imaging (TGA/VMI). In order to obtain a constant slope from the Arrhenius plot, the experiments were performed in the kinetic control regime.

Our previous results demonstrated that in this regime char reactivity is independent of pyrolysis heating rate, heat treatment temperature (HTT), soak time and particle size. For this study therefore, we chose to pyrolyze and combust particles from the 28-32 mesh (500-600 μm) fraction of Illinois #6 coal.

Table 1 gives the experimental conditions for this set of runs.

TABLE 1
EXPERIMENTAL CONDITIONS FOR KINETICS STUDY

PYROLYSIS STAGE	
Rate :	1 $^{o}C/s$
Heat Treatment Temperature (HTT):	550 ^{o}C
Soak Time:	3 min.
Flowing gas:	100% nitrogen
COMBUSTION STAGE	
Reaction Temperature:	380, 400, 420, 440, and 460 ^{o}C
Flowing gas:	21, 27, 33, and 40% oxygen
Gas flow rate:	360 sccm.

Experiments were also done to assess the reproducibility error for our reaction rate measurements. To prevent agglomeration during pyrolysis stage, we place different numbers of particles on the sample pan for runs with different particle sizes. We use 2-3 particles for the 20-25 mesh (710-840 μm) fraction, 7-8 particles for the 28-32 mesh (500-600 μm) fraction, and 20-25 particles for the 50-60 mesh (250-300 μm) fraction.

To determine the error, we repeated several times the combustion experiments for the three size fractions at 550 ^{o}C and 21% oxygen. All other conditions for the reproducibility experiments were the same as those given in Table 1.

Finally, the systematic study of reactivity in the regime of diffusional limitations was continued. We investigated the effects of different oxygen concentrations and particle sizes on the reactivity by performing the set of experiments described in Table 2.

TABLE 2
EXPERIMENTAL CONDITIONS FOR REACTIVITY STUDY IN THE REGIME OF DIFFUSIONAL LIMITATIONS

PYROLYSIS STAGE	
Rate :	1 and 20 °C/s
Heat Treatment Temperature(HTT):	550, 625, and 700 °C
Soak Time:	3 min.
Flowing gas:	100% nitrogen
COMBUSTION STAGE	
Reaction Temperature:	550 °C
Flowing gas:	21 and 33 % Oxygen
Gas flow rate:	360 sccm.

3. RESULTS AND DISCUSSION

Combustion Kinetics for Illinois #6 chars

Figures 1, 2, and 3 present the results from the kinetics study for the combustion of Illinois #6 chars. In these plots, the reaction rates used are the average reaction rates up to a specific conversion defined as follows:

$$\bar{r}_{x_0} = -\frac{1}{t_0}\int_0^{t_0}\frac{1}{m_0}\frac{dm}{dt}\,dt = \frac{1}{t_0}\,\frac{m_0 - m_{t_0}}{m_0} = \frac{x_0}{t_0}$$

where

x_0 is the reference conversion,

t_0 is the time to achieve this conversion x_0,

m_0 is the initial mass of the solid in ash-free basis, and
m_{t_0} is the unreacted mass at conversion x_0.

These average reaction rates are more accurate and statistically more significant that the instantaneous reaction rates. The reference conversion chosen for the plots in Figures 1, 2 and 3 is $x_0 = 0.25$.

We found that the following rate expression can be used to describe the kinetics of char combustion:

$$R_0 = \frac{1}{m_0}\frac{dm}{dt} = \frac{dx}{dt} = ky^n$$

where

R_0 is the normalized reaction rate,
$\frac{dm}{dt}$ is the instantaneous reaction rate,
y is the mole fraction of oxygen, and
n is the order of reaction.

Also, k is the reaction rate constant that takes the Arrhenius form:

$$k = A\exp(\frac{-E}{RT})$$

where

A is the preexponential factor for the reaction,
E is the activation energy,
T is the absolute temperature, and
R is the gas constant.

The plots of $\ln(R_0)$ vs. $\ln(y)$ at different combustion temperatures in Figure 2 give a constant slope of $n = 1.0 \pm 0.05$. Therefore, we can conclude that the reaction is first order.

The activation energy and the preexponential factor can be calculated from the slope and the intercept of the Arrhenius plot of the rate constant ($k = \frac{R_0}{y}$ for first order reaction) shown in Figure 3. The activation energy is found to be

$$E = 34.5 \text{ kcal/mol}$$

and the preexponential factor is

$$A = 7.30 \times 10^{7} \text{ sec}^{-1}.$$

Reproducibility Errors

Figures 4, 5, and 6 show some of the experimental results used to assess the reproducibility errors for combustion of char particles from the 50-60, 28-32, and 20-25 mesh fractions respectively. The reaction rates used in these plots are defined as follows:

$$R_s = \frac{1}{m(t)} \frac{dm}{dt}$$

where

$m(t)$ is the mass of char remaining unreacted at time t

$\frac{dm}{dt}$ is the instantaneous reaction rate.

Two types of error expressions were used in the error calculations:

1) The relative average error defined by

$$e_{relative} = \frac{1}{M} \sum_{i=1}^{M} \frac{1}{N} \sum_{j=1}^{N} \frac{\left| f_{ij} - \bar{f}_j \right|}{\bar{f}_j}$$

and

2) the L_2 error defined by

$$e_{L_2} = \frac{1}{M} \sum_{i=1}^{M} \frac{1}{\sqrt{N}} \sqrt{\sum_{j=1}^{N} \left(f_{ij} - \bar{f}_j \right)^2}$$

where

M is the number of combustion runs,

N is the total number of points for each combustion rate curve,

$\bar{f}_j$ is the average reaction rate at the j-th point of the curve, and

f_{ij} is the instantaneous reaction rate at point number j of the i-th run.

From the results summarized in Table 3, we can draw the following two conclusions. The average relative error increases with the particle size and, thus, one should carry out more combustion runs to accurately determine the reactivity of the larger particles. These results are not surprising because we use fewer particles during each run with the larger particle size fraction to prevent agglomeration during the pyrolysis stage.

TABLE 3
Results for Reproducibility Error Calculations

Particle size fraction	Number of runs	$e_{relative}$ (%)	e_{L_2}
50-60 mesh	2	2.7	0.0208
28-32 mesh	3	3.7	0.0355
20-25 mesh	4	4.9	0.0331

Char Reactivity in the Regime of Diffusional Limitations

The last four Figures (7, 8, 9, and 10) present our most recent results from the reactivity studies in the regime of diffusional limitations.

Figures 7 and 8 show the results for combustion with 33% oxygen concentration and for different particle size fractions. When the heating rate of 20 °C/s is used (Figure 7), the particles from all three different size fractions ignite. These ignitions are indicated by the sharp peaks in the reactivity plots and they were visible in our video sequences. When the heating rate of 1 °C/s is used (Figure 8), only the particles from the larger 20-25 and 28-32 mesh fractions ignite. Therefore, the effect of particle size and pyrolysis heating rates on the reactivity can be summarized as follows.

(A) As the coal particle size increases, the produced char particles are more reactive and they ignite at lower temperatures.

(B) High pyrolysis heating rates will produce more reactive chars that ignite more easily.

The effect of oxygen concentration on the reactivity can be seen from Figures 9 and 10. Figure 9 shows that the 20-25 mesh particles pyrolyzed at 1 $^{o}C/s$ ignite when 33% oxygen concentration is used. It is also interesting to notice the effect of the heat treatment temperatures (HTT) on the ignition phenomena shown in Figure 9. The particles treated at lower HTT tend to ignite at lower conversion. This provides additional evidence that lower HTT increases the reactivity of the chars.

Figure 10 compares the reactivity at two different oxygen concentrations of 50-60 mesh char particles pyrolyzed at 1 $^{o}C/s$. Under these conditions, the particles do not ignite. The results of Figure 10 indicate that the reactivity increases with oxygen concentration. This is consistent with our result from the kinetics study that the rate of char combustion is first order with respect to the oxygen concentration.

4. FUTURE WORK

In the next quarter, the investigation of the effect of process conditions on char reactivity will continue. We will also develop a simple model to simulate the ignition and extinction phenomena observed in our experiments using our measurements for the macropore structure of chars.

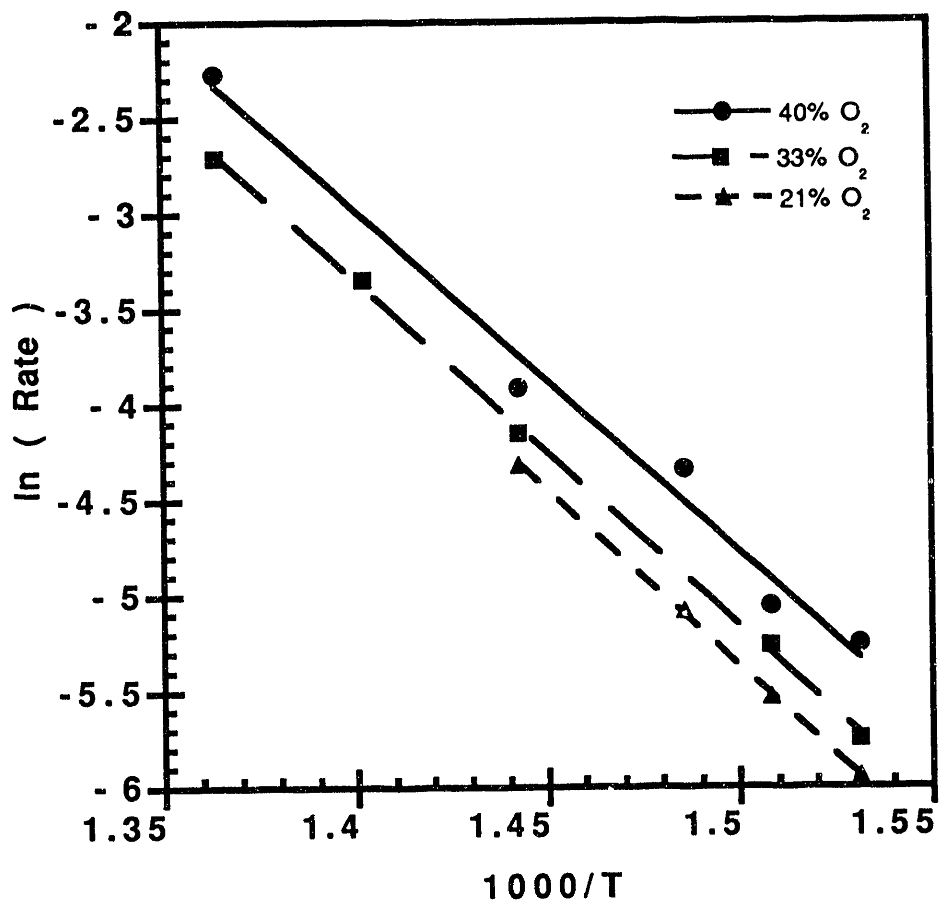

Figure 1: Arrhenius plots for the average combustion rates of Illinois #6 chars at various oxygen concentrations. Reference conversion for calculating the average reaction rates is 0.25.

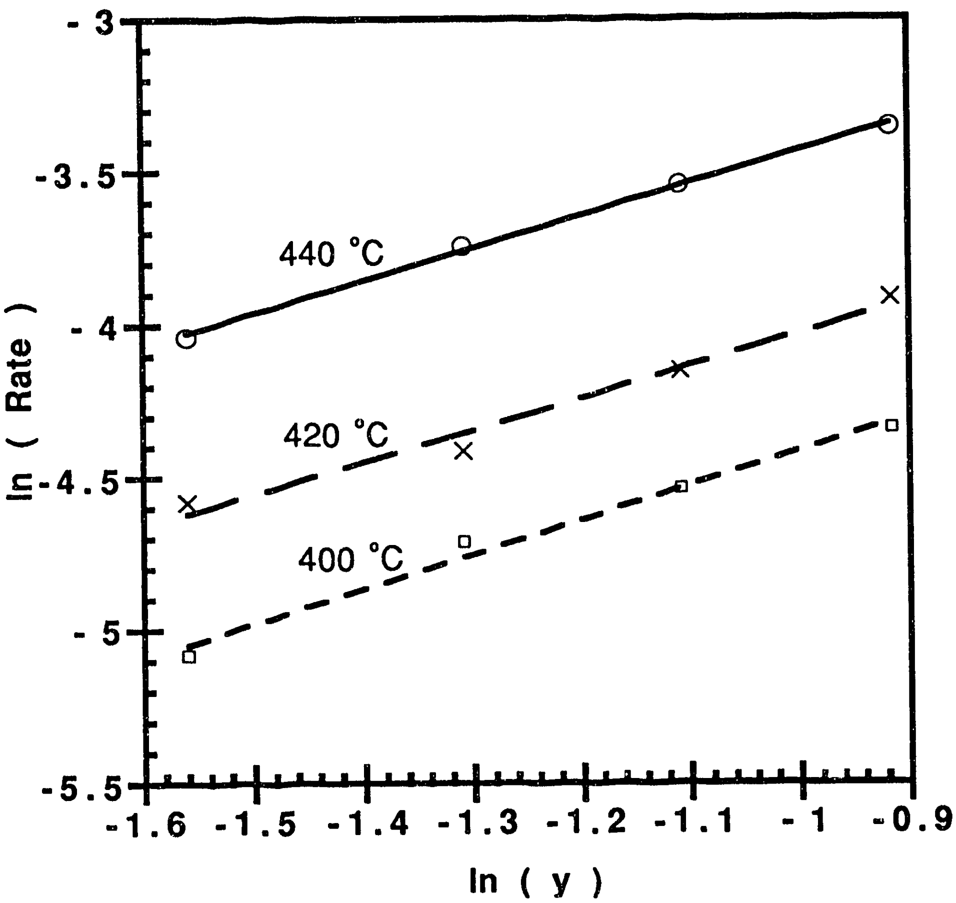

Figure 2: Reaction rates vs. oxygen concentrations at various combustion temperatures.

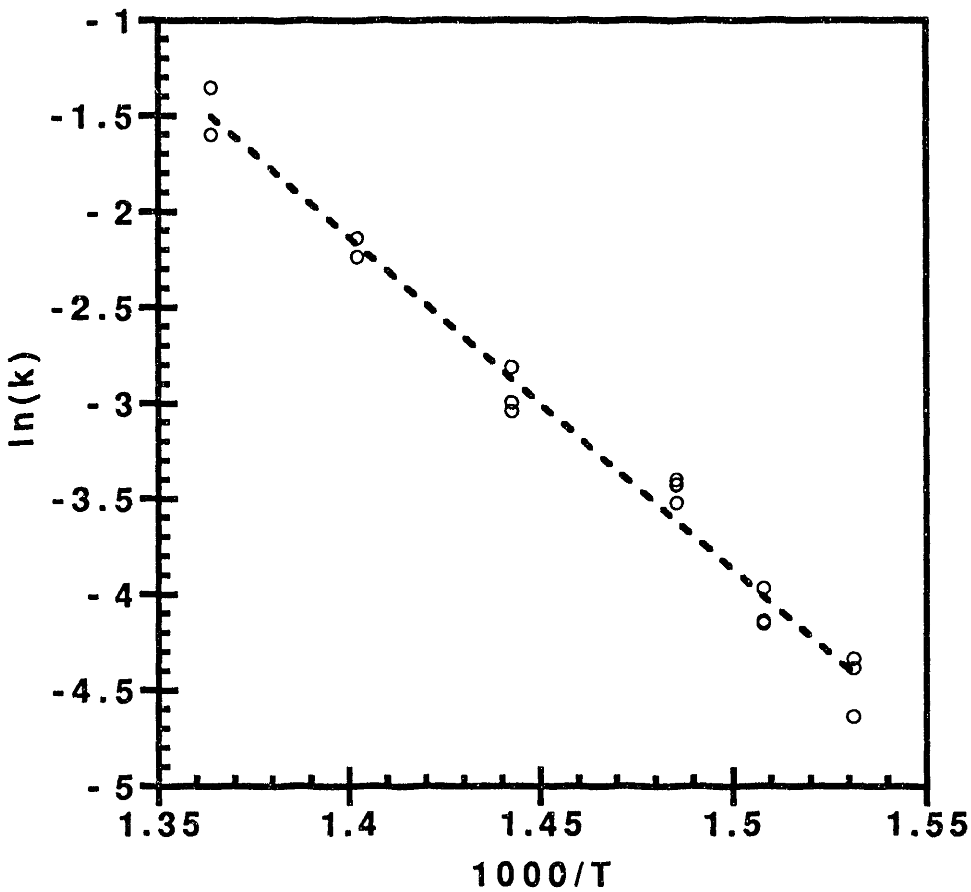

Figure 3: Arrhenius plot of the reaction rate constant for combustion of Illinois #6 chars

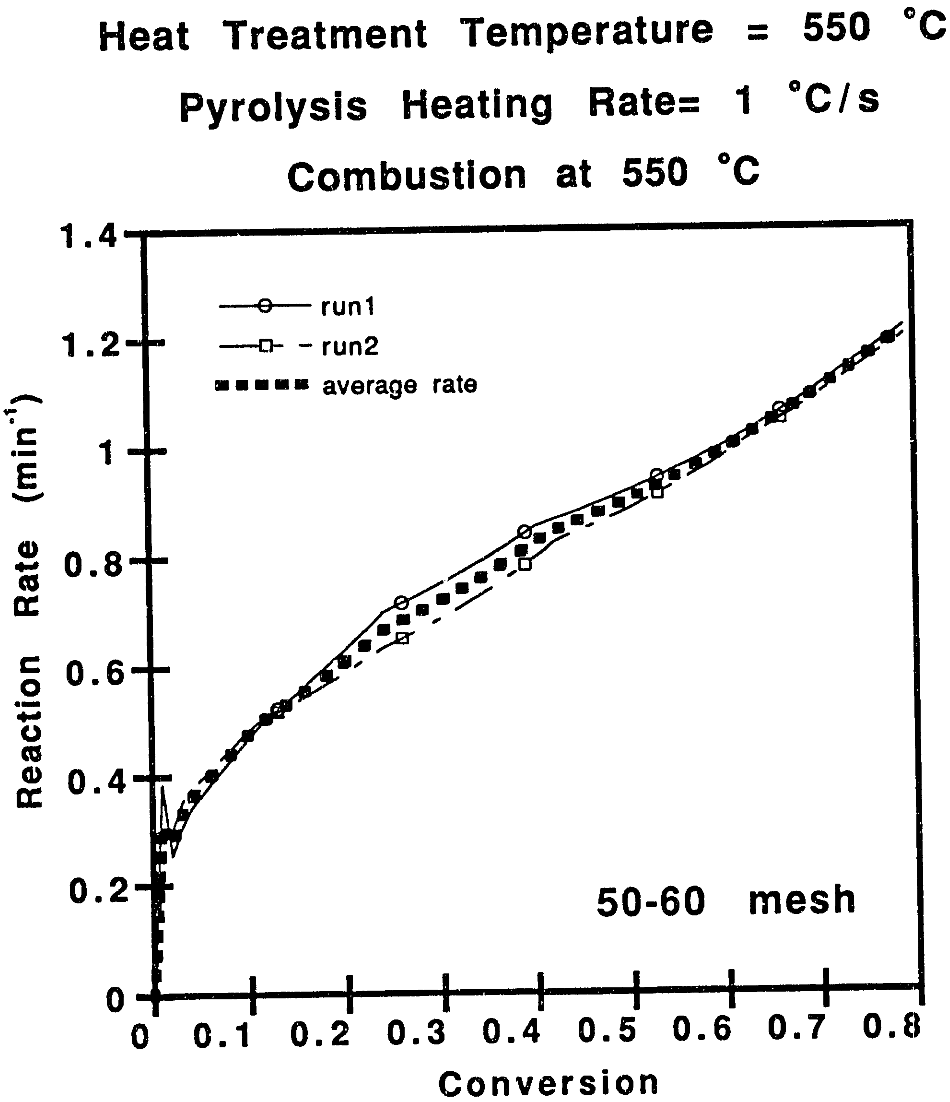

Figure 4: Reaction rates from several combustion runs (21% oxygen) with char particles from the 50-60 mesh fraction.

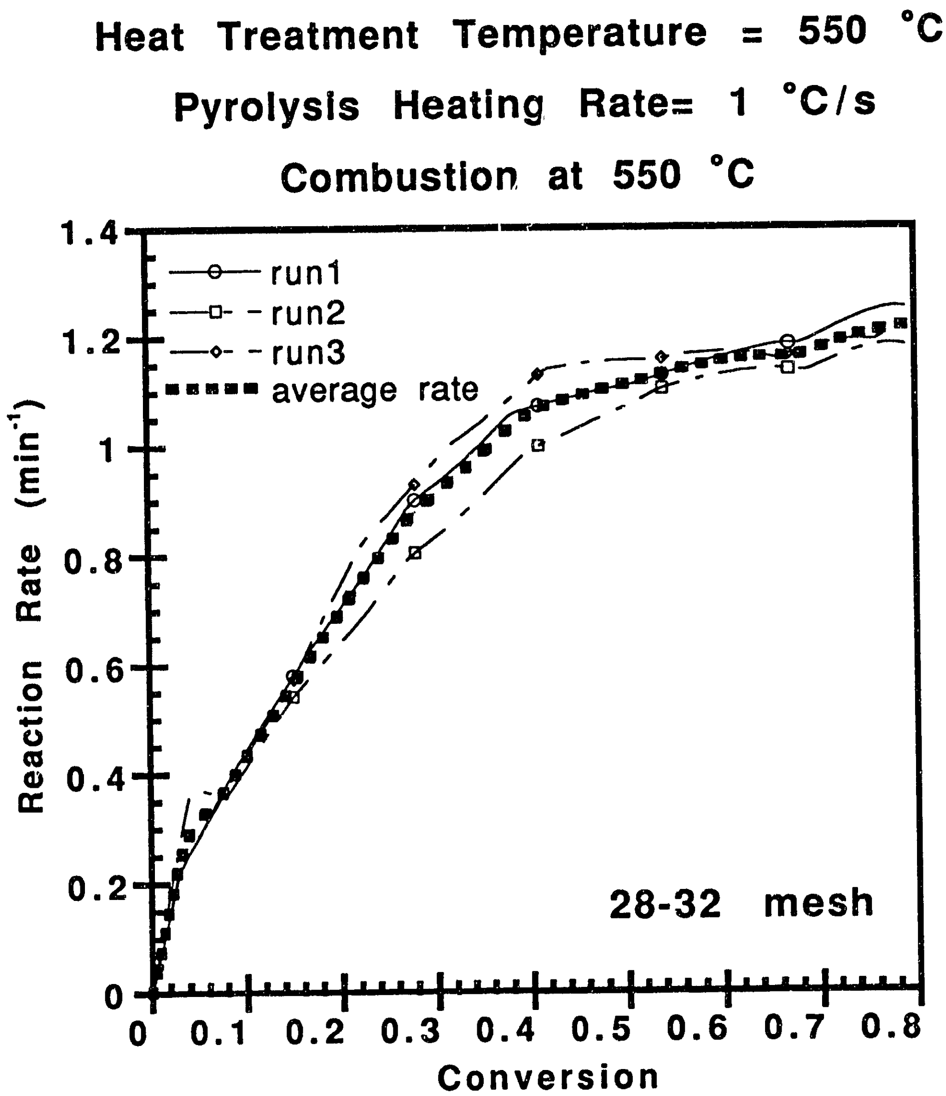

Figure 5: Reaction rates for several combustion runs (21% oxygen) with char particles from the 28-32 size fraction.

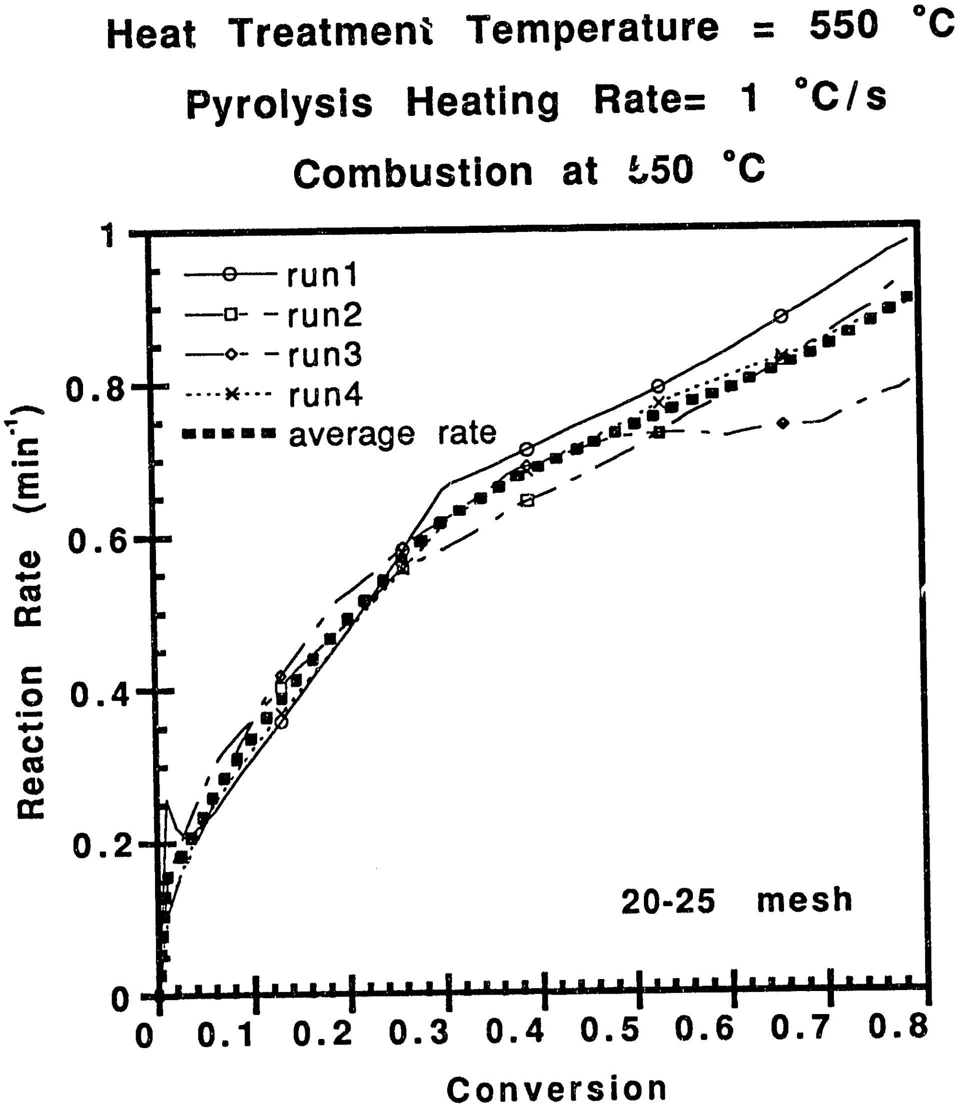

Figure 6: Reaction rates for several combustion runs (21% oxygen) with char particles from the 20-25 mesh fraction.

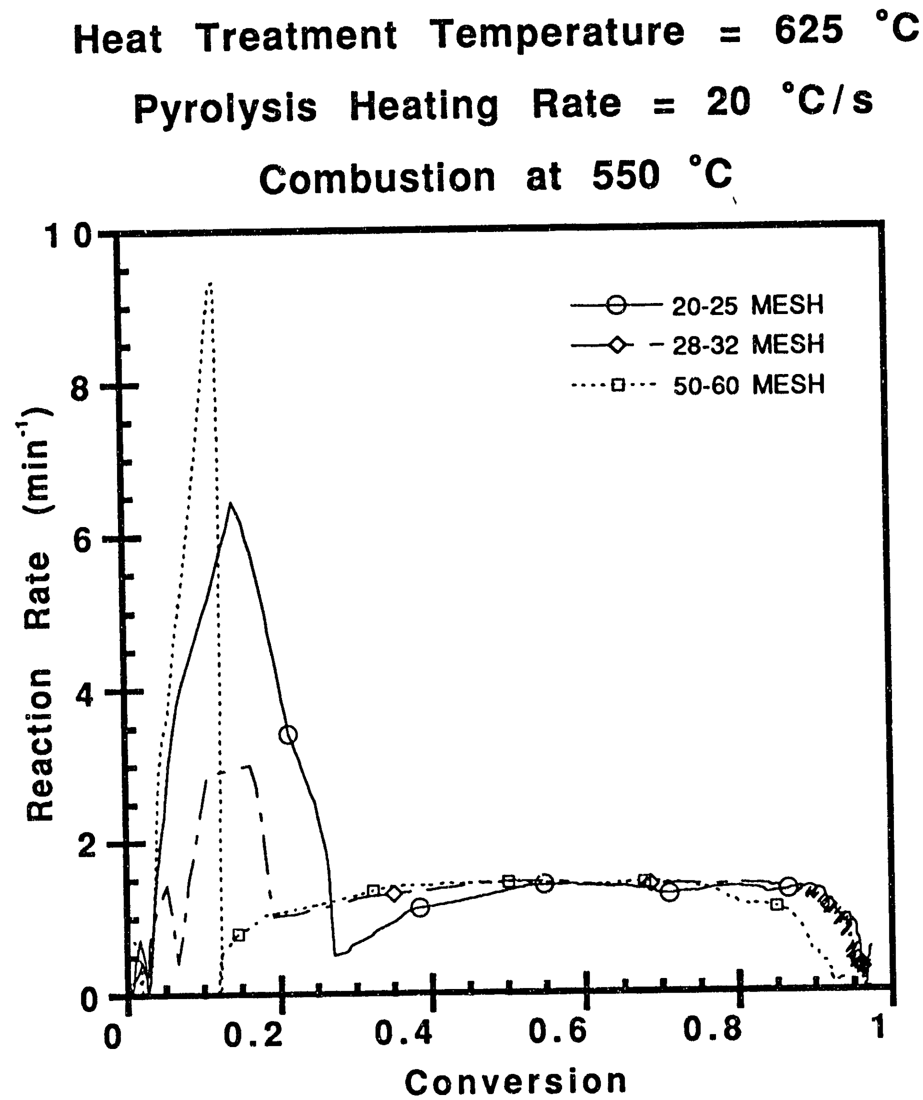

Figure 7: The effect of particle size on the reactivity and ignition patterns of Illinois #6 chars reacted with 33% oxygen.

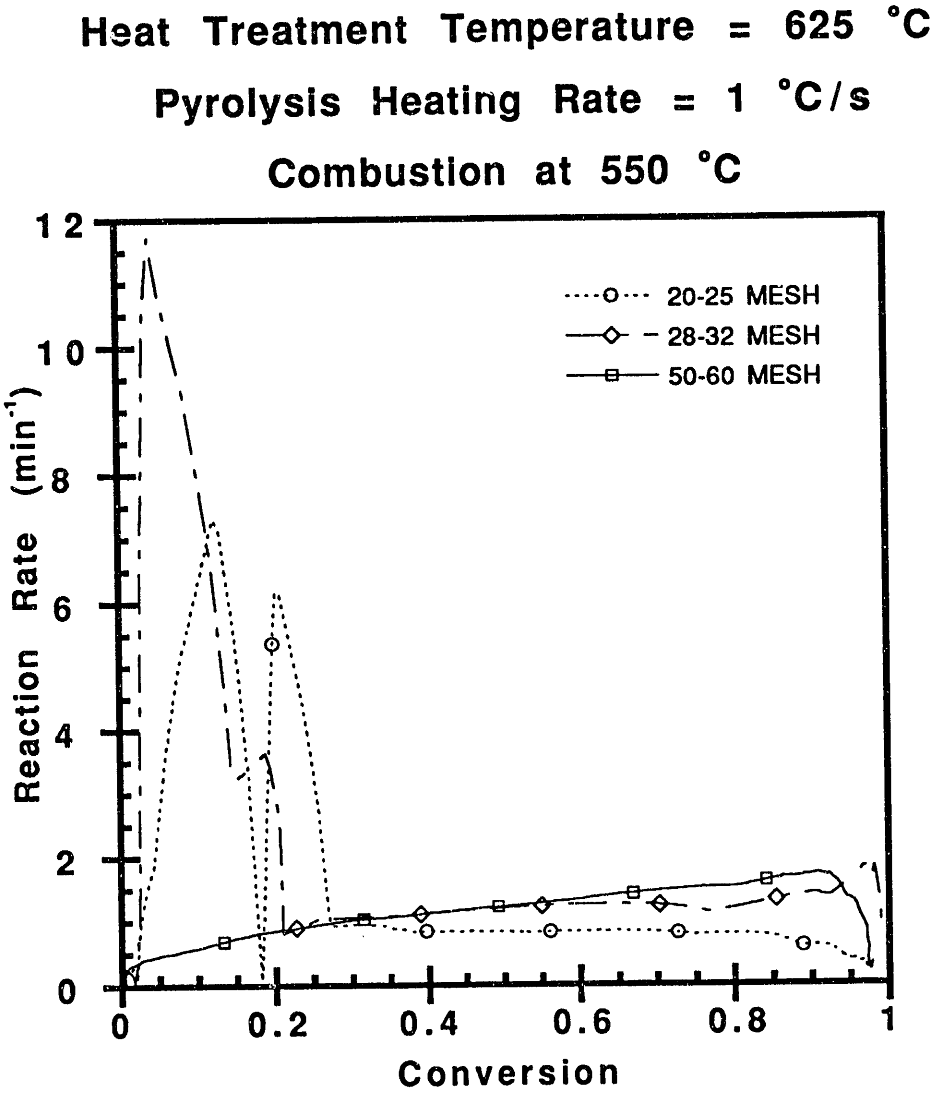

Figure 8: The effect of particle size on the reactivity and ignition patterns of Illinois #6 char particles.

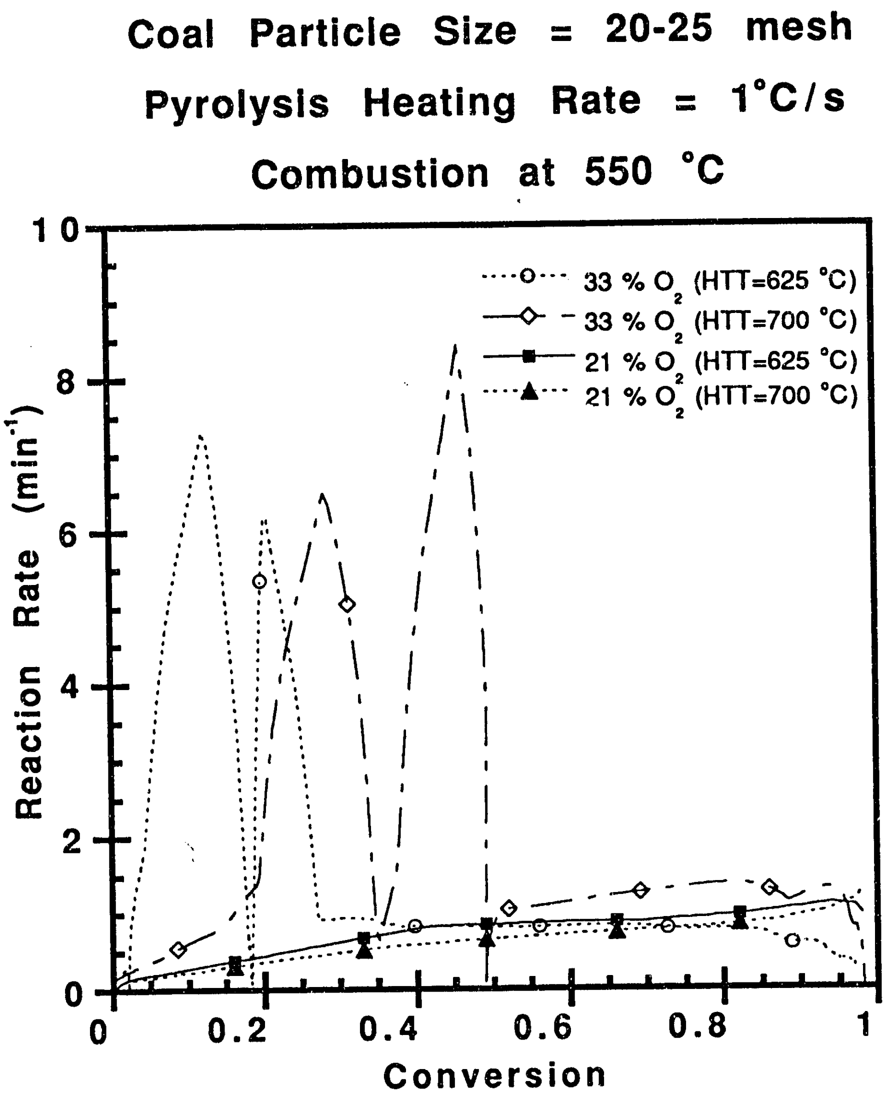

Figure 9: The effect of oxygen concentration on the reactivity rates of char particles from the 20-25 mesh fraction. Note the particle ignitions shown as sharp peaks in reactivity.

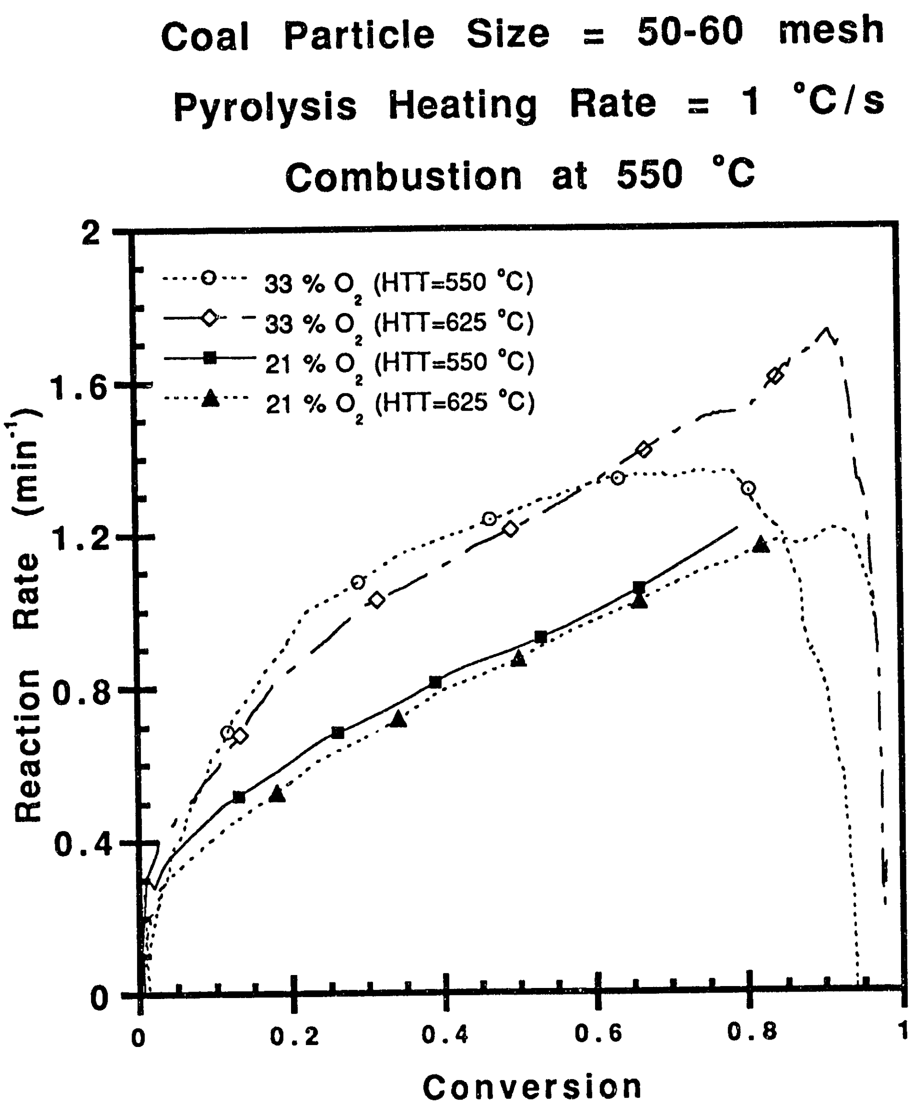

Figure 10: The effect of oxygen concentration on the reactivity rates of char particles that do not exhibit ignitions.

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