1. SUMMARY

The effects of process conditions on the reactivity of Illinois #6 coal in the kinetic and diffusion control regime were studied using new sequential combustion procedures. Reactivity patterns in the kinetic controlled regime were not influenced by the pyrolysis heating rates. Results presented in the previous DOE report have shown, however, that combustion rates were significantly affected by the pyrolysis heating rates at reaction temperatures higher than 550 °C. These results establish the importance of the macropore structure of chars in determining their combustion rates under conditions leading to significant intraparticle diffusional limitations.

2. EXPERIMENTAL PROCEDURE

A new combustion protocol for the TGA/VMI reactor was used to study the reaction of coal with oxygen in the kinetic control regime. Illinois #6 coal particles (from the Argonne collection) were devolatilized in pure nitrogen atmosphere by raising the temperature to 600 °C at heating rates ranging from 0.1 to 10 °C/s. The reactor temperature was maintained at 600 °C (the “heat treatment temperature”) for 10 minutes to ensure substantial completion of the devolutilization (pyrolysis) stage. After this “soak” period, the reactor was cooled to the desired combustion temperature and a mixture of oxygen and nitrogen was introduced to burn the remaining carbonaceous material. Both the reactor temperature and the oxygen concentration remained constant until combustion was complete. Table 1 summarizes the heating rates, combustion temperatures and oxygen concentrations used for this series of experiments.
At least three runs were carried out for each set of conditions. Average reaction rates were then computed from the results of these runs.

### 3. RESULTS AND DISCUSSION

Figure 1 shows the devolatilization rates measured for three different coal samples that were pyrolyzed at 0.1 °C/s. Reactivity differences between the three samples show the magnitude of the variability one should expect from small samples of a highly heterogeneous material like coal. In all four cases, the maximum devolatilization rate was observed when the reactor reached a
temperature of about 450 °C. After a sharp decrease, the devolatilization patterns exhibited a second, smaller peak as the reactor temperature approached 600 °C, indicating the onset of the secondary pyrolysis stage. Note that the secondary pyrolysis peak was larger for the coal samples that exhibited smaller weight losses during the primary pyrolysis stage. Figure 2 shows devolatilization rates for additional coal samples pyrolyzed at the same heating rate of 0.1 °C/s. Differences in the reactivity of the latter three samples were larger than those of Figure 1. Coal samples exhibiting low primary pyrolysis rates, however, again showed high devolatilization rates during the subsequent secondary pyrolysis stage.

The observed differences in devolatilization behavior are not due to differences in the temperature history of the samples. As shown in Figures 1 and 2, the reactor temperature profiles of all runs were virtually identical. The control system of our reactor did an excellent job in producing reactor temperature profiles that were highly accurate and reproducible. Therefore, we may conclude that the observed differences are due to significant property variations among the small samples used for these experiments, due to the highly heterogeneous nature of coal.

Figures 3 and 4 show the devolatilization rates for several coal samples pyrolyzed at 1 °C/s to a final temperature of 608 °C. The rates exhibited a large peak in the same temperature range as before (450-475 °C). That peak was followed by plateau of very low reactivities when the reactor reached the final heat treatment temperature. Devolatilization rates remained very low throughout the 10-minute soak period.
Similar behavior was observed when the samples were pyrolyzed at the fastest heating rate of 10 °C/s (Figures 5 and 7). A very sharp peak was obtained at reactor temperatures between 450 and 500 °C for all samples studied. Figures 6 and 8 show that devolatilization rates were very low during the 10-minute soak period (up to two orders of magnitude smaller than the measured peak values).

Figures 5 and 7 also show that the temperature control for the highest heating rate was not as accurate as in the cases of the lower heating rates (0.1 and 1 °C/s). The actual reactor temperature deviated from the setpoint by as much as 6 - 8 °C during the heating ramp. Note also that the reactor temperature oscillated slightly before settling down to the final heat treatment temperature.

Temperature deviations of this magnitude, however, will not have significant effects on the reactivity behavior. As shown in Figure 9, it takes large differences in the temperature history of the sample to shift the devolatilization peaks or otherwise significantly affect the pyrolysis behavior.

Figure 10 shows the evolution of average combustion rates with conversion for samples pyrolyzed at three heating rates ranging from 0.1 to 10 °C/s. For these runs, combustion took place at 400 °C in a mixture containing 2% oxygen and 98% nitrogen. As mentioned in the previous section, oxygen was introduced after the pyrolyzed samples were cooled down to the combustion temperature. Under these conditions, all three char samples follow the same reactivity pattern with a maximum occurring between 20% and 40% conversion. Since these chars have widely different macropore surface areas and exhibit different reactivities at higher
combustion temperatures, we may conclude that combustion at 400 °C takes place in the kinetic control regime with full utilization of the micropore surface area.

At 420 °C, coal samples pyrolyzed at different heating rates again exhibited similar reactivity patterns (Figure 11). The sample prepared at 1 °C/s appears to be an exception, showing a sharp peak at 10% conversion that is followed by a monotonically decreasing combustion rate. Such a sharp peak, however, appeared in the reactivity pattern of only one of the three samples reacted under these conditions and was probably due to highly catalytic impurities present in this particular sample.

When the temperature was raised to 450 °C, we observed larger deviations in the average reactivity behavior of the three chars (Figure 12). In particular, the reactivity pattern of the char prepared at 1 °C/s exhibited several sudden jumps in reactivity. The differences were probably due to the onset of diffusional limitations in the micropores that resulted in incomplete utilization of the internal surface area. More specifically, the reactivity jumps observed for the 1 °C/s char might have been caused by the sudden opening of internal cavities that were initially inaccessible to oxygen. As combustion proceeded, however, walls blocking the access of oxygen burned away and the reaction rate increases suddenly as the oxygen reached the previously inaccessible cavities and (more importantly) the micropores that branch out from the surface of these cavities.

These trends became more pronounced at higher oxygen concentrations. Figure 12 shows the reactivity pattern measured at 450 °C and 5% oxygen. Differences in the maximum reaction rate were now as high as 50% and the chars
produced at 1 °C/s exhibited more reactivity “spikes” that persisted until conversion reached the 40% level.

When the oxygen concentration increased even further to 21%, chars produced at 1 °C/s exhibited significantly higher reactivity than chars produced at either 0.1 or 10 °C/s. This behavior was a clear indication of significant diffusional limitations in the micropores, as explained in an earlier report to DOE.
Figure 1: Devolatilization rates and reactor temperature profiles measured for four runs with Illinois #6 coal particles. The heating rate was 0.1 °C/s and the chars were then combusted at 400 °C with 5% oxygen. The experimental protocol is described in section 2 of this report.
Figure 2: Devolatilization rates and reactor temperature profiles measured for three runs with Illinois #6 coal particles. The heating rate was 0.1 °C/s and the chars were then combusted at 400 °C with 21% oxygen. The experimental protocol is described in section 2 of this report.
Figure 3: Devolatilization rates and reactor temperature profiles measured for four runs with Illinois #6 coal particles. The heating rate was 1 °C/s and the chars were then combusted at 400 °C with 5% oxygen. The experimental protocol is described in section 2 of this report.
Figure 4: Devolatilization rates and reactor temperature profiles measured for three runs with Illinois #6 coal particles. The pyrolysis heating rate was 1 °C/s and the chars were then combusted at 400 °C with 21% oxygen. The experimental protocol is described in section 2 of this report.
Figure 5: Devolatilization rates and reactor temperature profiles measured for three runs with Illinois #6 coal particles. The heating rate was 10 °C/s and the chars were then combusted at 400 °C with 5% oxygen. The experimental protocol is described in section 2 of this report.
Figure 6: Devolatilization rates and reactor temperature profiles measured during the soak times for the three experiments shown in Figure 5. After a 10 minute soak time at 608 °C, the chars were cooled down and combusted at 400 °C with 5% oxygen. The experimental protocol is described in section 2 of this report.
Devolatilization rates and reactor temperature profiles measured for four runs with Illinois #6 coal particles. The heating rate was 10 °C/s and the chars were then combusted at 400 °C with 21% oxygen. The experimental protocol is described in section 2 of this report.
Figure 8: Devolatilization rates and reactor temperature profiles measured during the soak times for the four runs presented in Figure 7. After a 10-minute soak time at 608 °C, the chars were cooled down and combusted at 400 °C with 21% oxygen. The experimental protocol is described in section 2 of this report.
Figure 9: The effect of reactor temperature profiles on the devolatilization rates of two Illinois #6 coal samples. Note the shift in the devolatilization rate peak induced by differences in the reactor temperature program.
Figure 10: Average combustion rates vs. conversion for Illinois #6 chars produced at different heating rates. Combustion took place at 400 °C in 2% oxygen (balance nitrogen). Section 2 of the report provides the details of the protocol followed for these experiments.
Average combustion rates vs. conversion for Illinois #6 chars produced at different heating rates. Combustion took place at 420 °C in 2% oxygen (balance nitrogen). Section 2 of the report provides the details of the protocol followed for these experiments.
Figure 12: Average combustion rates vs. conversion for Illinois #6 chars produced at different heating rates. Combustion took place at 450 °C in 2% oxygen (balance nitrogen). Section 2 of the report provides the details of the protocol followed for these experiments.
Figure 13: Average combustion rates vs. conversion for Illinois #6 chars produced at different heating rates. Combustion took place at 450 °C in 5% oxygen (balance nitrogen). Section 2 of the report provides the details of the protocol followed for these experiments.
Figure 14: Average combustion rates vs. conversion for Illinois #6 chars produced at different heating rates. Combustion took place at 450 °C in 21% oxygen (balance nitrogen). Section 2 of the report provides the details of the protocol followed for these experiments.