RICE

DOE/PC/91307--T7

DE93 013613

COAL COMBUSTION: EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

Quarterly Technical Report

Performance Period: 12/1/92 -3/1/93 (Quarter #6)

Submitted to the

Department of Energy

Grant Number DE-FG22-91PC91307

Grant Period: 9/1/1991 to 8/31/1994

PRINCIPAL INVESTIGATOR

Kyriacos Zygourakis

Department of Chemical Engineering

Rice University

Houston, Texas 77251-1892

DOE Technical Project Officer

Kamalendu Das

Morgantown Energy Technology Center

*"U.S. DOE Patent Clearance is not required prior to the
publication of this document"*

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

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 μm 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 developed the image analysis procedure for obtaining the transient swelling patterns of pyrolyzing coal particles. Pyrolysis experiments were videotaped and a sequence of digital images was acquired from each experiment tape at rates of 1.5 to 6 images per second. These digital images were then processed to measure the size and shape of pyrolyzing particles as a function of pyrolysis temperature. A systematic analysis of the transient swelling patterns showed significant differences among runs carried out at different heating rates. At low heating rates ($1\text{ }^{\circ}\text{C/s}$), the particles swelled rapidly to their maximum size. This initial swelling was followed by a "bubbling" phase during which the particles underwent a rapid sequence of expansions and contractions as bubbles of volatiles grew in the particle interior and broke through their surface. The particle size then decreased to show a small final swelling. At higher heating rates, the particle size decreased significantly during the "bubbling" phase and the final swelling was higher. A systematic comparison of particle swelling and devolatilization rates is also presented.

2. EXPERIMENTAL PROCEDURES

Using the thermogravimetric reactor with *in situ* video microscopy imaging (TGA/VMI), we followed the fate of single particles of Illinois #6 coal during the pyrolysis stage under experimental conditions listed in Table 1. To prevent agglomeration (especially at high heating rates), 6 particles of 28-32 mesh (500-600 μm) fraction were placed on the sample pan for each run. The heat treatment temperature of $625\text{ }^{\circ}\text{C}$ was chosen after we observed that all particles

(for all heating rates chosen) had resolidified (after they became plastic) well before reaching this heat treatment temperature.

All the experiments were videotaped and the tapes from two runs for each heating rate were processed as follows. Using a frame grabber, we acquired a sequence of digital images from each tape. The sequence covered the pyrolysis temperature ranges from 380 °C to 525 °C when the coal particles exhibit their plastic behavior. For the heating rates of 10 and 20 °C/s, the images were acquired at intervals of 0.15 sec. For the 1 °C/s experiments, we acquired a digital image every 0.7 sec. A total of 80, 120, and 160 digital images were acquired for the heating rates of 20, 10, and 1 °C/s, respectively. The digital images were then analyzed to measure the size and shape of pyrolyzing particles as a function of pyrolysis temperature.

Table 1
Experimental Conditions for Pyrolysis

Rate :	1, 10 and 20 °C/s
Heat Treatment Temperature (HTT):	625 °C
Soak Time:	3 min.
Flowing gas:	100% Nitrogen

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the average devolatilization rate from several runs for different heating rates as a function of reactor temperature and conversion respectively. The devolatilization rate is defined as

$$Rate = \frac{1}{m_0} \left(\frac{dm}{dt} \right) \quad (1)$$

where m_0 is the initial mass of the coal and $\left(\frac{dm}{dt} \right)$ is the instantaneous devolatilization rate. The conversion x is defined as

$$x = \frac{m_0 - m(t)}{m_0} \quad (2)$$

where $m(t)$ is the mass of the coal remaining at time t after the start of the experiment.

Figures 1 and 2 indicate that the maximum devolatilization rate for the heating rate 10 °C/s is 10 times higher than that of 1 °C/s and the maximum rate of 20 °C/s is twice the rate of 10 °C/s. Notice in Figure 1 that the maximum devolatilization rates for higher heating rates occur at higher reactor temperatures: 450, 500, and 535 °C for 1, 10, and 20 °C/s respectively. Similarly, Figure 2 shows that the maximum devolatilization rate is shifted towards higher conversions as the pyrolysis heating rate increases. These results are in agreement with our earlier experimental findings.

Figures 3 through 8 present the information for the transient swelling pattern of coal particles when they are pyrolyzed under various heating rates. In these figures, the computed equivalent radius of the projected area of the pyrolyzing particles is plotted against the reactor temperature.

At the lowest heating rate of 1 °C/s, Figure 3 shows that the particles swell in an almost monotonic fashion until they reach their maximum size. This swelling phase is followed by a phase of alternating expansions and contractions that may be rapid (see top plot of Figure 3) or slower (bottom plot of Figure 3). The particle expansions correspond to the formation and growth of big bubbles due to the release of gas volatiles in the particle interior. These bubbles then break through the particle surface and the particle contracts. The pattern of contraction/expansion we observe is related to the plasticity of the particle and the fluidity of its

outer shell. Finally, the particles contract to almost their original size as they resolidify. The pyrolyzed particles exhibit only a small degree of swelling. Figure 4 shows the transient swelling patterns of all six coal particles from a pyrolysis run. All particles show the same pattern with a rapid monotonic swelling, a period with alternating expansions and contractions and a final decrease in size as the particles resolidify.

We observed different swelling patterns at the higher heating rates. At 10°C/s , some particles swelled rapidly to reach their maximum size. Their size then started to decrease as the particles underwent a series of rapid expansions and contractions (see Figure 5). Other particles showed a gradual increase in size followed by a phase characterized by fast expansions and contractions (see Figure 6). The particles had swelled considerably when they resolidified (Figure 6).

Figures 7 and 8 show similar behavior for the particles pyrolyzed at 20°C/s . At this heating rate, however, the particles swelled more. Both their maximum and final sizes were the highest among the three cases considered here. The swelling patterns of particles pyrolyzed at high heating rates, however, showed large variability. Figure 7 (bottom), for example, shows the swelling pattern for a particle whose size increased very little without the characteristic expansion/contraction pattern of other particles.

Note also that for higher heating rates, the particles settle at their final sizes at higher reactor temperatures compared to that of lower heating rates. For example, the particles contract to their final size at about 525°C for a heating rate 20°C/s and at less than 500°C for a heating rate of 1°C/s . If accurate measurement of final swelling is required, size measurements must be performed only for particles heated above this temperature.

We also computed the evolution of the average particle size from two runs each with 5-6 coal particles (10-12 total particles). Figure 9 shows the average particle size plotted together with the devolatilization rate for a pyrolysis heating rate of 1°C/s . After swelling rapidly to their maximum size, the average coal particle size fluctuates about a constant value while the particles undergo a series of expansions and contractions. As expected, we do not observe much weight

loss as the particles expand to their maximum size. The maximum rate of weight loss occurs towards the end of the "bubbling" phase. When this phase is over both the particle size and the devolatilization rate decrease rapidly.

Figure 10 shows the same results from two pyrolysis runs at 10°C/s . Again the average particle size increases rapidly to its maximum value while the rate of devolatilization remains fairly low. The average particle size then decreases as the particles pass through the "bubbling" phase, while the devolatilization rate continues to increase reaching its maximum at about the middle of the bubbling phase. We are in the process of acquiring and analyzing more digital images to complete the average transient swelling pattern for this heating rate.

FUTURE WORK

In the next quarter we will complete the analysis of the previous set of experiments and compare the transient swelling patterns to devolatilization rates for all the heating rates. We will also compute the average swelling ratios and the transient patterns of particle shape factors that will tell us how the particle shape evolves with pyrolysis. We will also start experiments with a new coal (Utah Blind Canyon, Argonne Collection) to determine its transient particle swelling patterns and devolatilization rates.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Figure 1: Devolatilization rate as a function of temperature for three different heating rates.

Figure 2: Devolatilization rate as a function of conversion for three different heating rates.

Figure 3: Transient swelling pattern of two coal particles pyrolyzed at 1 °C/s.

Figure 4 : Transient swelling patterns for six coal particles from the same pyrolysis run at a heating rate of 1 °C/s.

Figure 5: Transient swelling patterns for two individual coal particles from the same pyrolysis run at a heating rate of 10 °C/s

Figure 6: Transient swelling patterns for six coal particles from the same pyrolysis run at a heating rate of 10 °C/s

Figure 7: Transient swelling patterns for two individual coal particles from the same pyrolysis run at a heating rate of 20 °C/s

Figure 8: Transient swelling patterns for six coal particles from the same pyrolysis run at a heating rate of 20 °C/s

Figure 9: Average transient swelling pattern and devolatilization rate for particles pyrolyzed at a heating rate of 1 °C/s. Average size and devolatilization rates computed from two pyrolysis runs (12 particles).

Figure 10: Average transient swelling pattern and devolatilization rate for particles pyrolyzed at a heating rate of 10 °C/s. Average size and devolatilization rates computed from two pyrolysis runs (12 particles).

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

END

**DATE
FILMED**

6 / 10 / 93