RICE

COAL COMBUSTION: EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

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CHAPTER 1

OBJECTIVES AND SIGNIFICANCE

1.1 STAGES OF COAL UTILIZATION PROCESSES

Coal utilization involves two major stages: coal pyrolysis and char combustion. Figure 1.1 summarizes the steps of these processes. During the pyrolysis stage, heated particles from plastic coals soften, swell and release their volatiles before resolidifying again. During the combustion or gasification stage, char particles may ignite and fragment as the carbon is consumed leaving behind a solid ash residue.

Process conditions such as pyrolysis heating rate, heat treatment temperature, pyrolysis atmosphere, and particle size are shown to chemically and physically affect the coal during pyrolysis and the resulting char. Consequently, these pyrolysis conditions as well as the combustion conditions such as the oxygen concentration and combustion temperature affect the char reactivity and ignition phenomena during the combustion stage.

Better understanding of the fundamental mechanisms of coal pyrolysis and char combustion is needed to achieve greater and more efficient utilization of coal. Furthermore, this knowledge also contributes to the development of more accurate models that describe the transient processes involved in coal combustion.

1.2 PROJECT OBJECTIVES

The primary objective of our project was to quantify the effect of the following pyrolysis conditions on the macropore structure and on the subsequent reactivity of chars:

Figure 1.1: Typical processes in coal utilization.

- (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); and
- (f) coal rank.

To investigate the effect of coal rank, pyrolysis and combustion experiments would 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).

To achieve the project objectives, the following three tasks were identified and successfully implemented.

1.2.1 Task A

We obtained the time histories and followed the fate of single particles during pyrolysis in our TGA/VMI reactor. The experiments were videotaped and digital images at several time instants were acquired and analyzed on the image processor. The following measurements were performed for each run.

- (i) We measured the temporal evolution of the particle size during the pyrolysis stage (transient swelling pattern) as well as the maximum and final particle sizes (maximum and final swelling).
- (ii) From primary measurements, we computed the temporal evolution of particle shape (circularity, elongation etc.) during the pyrolysis stage, as well as the final particle shape.

For selected sets of conditions, several char samples were collected and

polished sections were prepared to accurately analyze the internal structure of the char particles.

1.2.2 Task B

A different set of pyrolysis experiments was immediately followed by combustion experiments. Without removing the particles from the TGA/VMI reactor, the char samples were reacted with O₂ to complete conversion at high temperatures. Different gas flow rates of gases and O₂ concentrations were used to investigate the effect of external mass transfer limitations.

1.2.3 Task C

We developed a steady-state mathematical model for char particle ignitions. All the necessary model parameters were obtained from structural measurements for the Illinois #6 chars. The model predicted that the ignition temperature decreases (a) increasing pyrolysis heating rate, (b) increasing particle size, (c) increasing oxygen concentration and (d) with decreasing gas flow rate. The model was also used to systematically investigate the effect of porosity, macropore surface area, and micropore radius on ignition phenomena. Model predictions were in very good agreement with our experimental data obtained using the thermogravimetric reactor with video microscopy imaging (TGA/VMI).

CHAPTER 2

EXPERIMENTAL EQUIPMENT AND PROCEDURES

2.1 EXPERIMENTAL EQUIPMENT

Experiments were carried out in the thermogravimetric reactor with in-situ video microscopy imaging (TGA/VMI). The advantages and main features of this system are the following.

- 1) The reactor system was interfaced to a microcomputer that performed the data acquisition and control tasks. The weight and reactor temperature were continuously recorded during the experiments. Reactor operation was fully automatic since the computer controlled the furnace heater to achieve the desired furnace temperature as well as the mass flow controllers, the video camera, the video timer, and the video cassette recorder.
- 2) With the TGA/VMI reactor, we observed and recorded the structural transformations of coal particles during pyrolysis. By post-processing the video tapes, we detect the occurrence of transient phenomena like char particle ignition or fragmentation and determine the ash residue for each particle. At the same time, the weight of the sample was recorded by the computer. The experiment video tapes together with the traces of reactor temperature and sample weight provided a complete time-registered record of the history of the particles as they pyrolyzed or burned in the TGA/VMI reactor.
- 3) The experimental setup also allowed us to perform sequential pyrolysis and combustion experiment to investigate the effect of pyrolysis conditions on char reactivity.

The schematic of the TGA/VMI reactor system is shown in Figure 2.1. A detailed description of the TGA/VMI reactor, the computer interfaces, the heater control, the remotely activated mass flow controllers and the digital

computer control algorithm can be found elsewhere (Matzakos 1991; Matzakos and Zygourakis 1993).

The reactor consisted of a Pt sample pan that was suspended from the weighing mechanism with a Pt wire. The balance accuracy is 0.1% and the sensitivity is 0.1 μg . The sample pan was placed inside a cylindrical ceramic furnace that was designed to provide high heating rates. The furnace can withstand temperatures up to 1150 $^{\circ}\text{C}$ and the reactor temperature was measured by a chromel-alumel thermocouple (type K, range: 0-1000 $^{\circ}\text{C}$) located exactly below the sample pan (Matzakos 1991; Matzakos and Zygourakis 1993).

For direct visualization of the particles, a flat optical window was inserted at the top of a glass side tube attached to the main furnace tube. Through this window, the coal sample was imaged by a high magnification, extra-long working distance microscope [JENA, Model 121] mounted outside the reactor facing downwards into the furnace.

Figure 2.2 shows the schematic of video microscopy system for the TGA/VMI reactor. Video images of reacting coal samples were obtained with a CCD color video camera [Javelin , Chromachip II] with 760x485 lines resolution that was attached to the microscope. A video timer [FOR-A, UTG-33] was used to superimpose on the camera signal the time elapsed since the beginning of the experiment. The images were recorded on a Super-VHS video tape recorder [Panasonic, AG-7300] with 400 lines of resolution. The video tape recorder had a video signal sensor (sensor mode) that can start recording whenever a video signal was supplied by the camera. Using this feature, the video camera was remotely controlled so as to record only the important intervals of the experiments.

Images from the videotapes were latter digitized using 640x480 pixel frame grabber (Imaging Technology Inc., FG100) attached to the backplane of a computer workstation (Digital Equipment Corporation, VAXstation-II/GPX). We digitized images for pyrolysis temperatures between 380 $^{\circ}\text{C}$ and 600 $^{\circ}\text{C}$ where the coal particles exhibited their plastic behavior. For the pyrolysis heating rates of 10 and 20 $^{\circ}\text{C}/\text{s}$, we acquired images at a rate of 0.15 sec/image. For the heating rate of 1 $^{\circ}\text{C}/\text{s}$, images were acquired at the rate of 0.7 sec/image. At these acquisition rates, a total of 80, 160, and 200 images were digitized for the heating rates of 20, 10, and 1 $^{\circ}\text{C}/\text{s}$, respectively. The digital images were then transferred to another computer (Apple Computer, Inc.,

Macintosh Quadra 900) for image analysis and data processing.

2.2 EXPERIMENTAL CONDITIONS

Experimental conditions were chosen to systematically study the effect of process conditions on coal pyrolysis and char reactivity.

2.2. Coal rank

We performed pyrolysis and combustion experiments for three coals from the Argonne collection samples (Vorres 1990).

- (a) a high volatile bituminous coal with high ash content (Illinois #6),
- (b) a bituminous coal with low ash content (Utah Blind Canyon), and
- (c) a lower rank sub-bituminous coal (Wyodak-Anderson seam).

2.2.2 Particle size

The effect of particle size was studied using three size fractions:

- (a) 20-25 mesh (710-840 μm),
- (b) 28-32 mesh (500-600 μm), and
- (c) 50-60 mesh (250-300 μm).

To prevent agglomeration during pyrolysis, the particles were placed far away from each other of the pan. Thus, the number of particles used for each run varies with the particle size. We placed on the pan 2-3, 6-7, and 30-35 particles respectively for the 20-25, 28-32, and 50-60 mesh size fractions.

2.2.3 Pyrolysis heating rate, pyrolysis atmosphere and final heat treatment temperature

Four pyrolysis heating rates were used in this study: 0.1, 1.0, 10, and 20 $^{\circ}\text{C/s}$. We chose five final heat treatment temperatures (HTT) for our runs: 550, 625, 700, 800, and 900 $^{\circ}\text{C}$. After reaching the final heat treatment

temperature, the pyrolyzed particles were held at the HTT for 3 minutes.

Coals were pyrolyzed in inert (100% nitrogen) and reactive (5% oxygen; 95% nitrogen) atmospheres to quantify the effect of pyrolysis environment on particle swelling and char reactivity.

2.2.4 Effect of combustion temperature and oxygen concentration

Low combustion temperatures (380-420 °C) were used to investigate the char reactivity in kinetic control regime and to compute the kinetics parameters for the Illinois #6 coal.

To study the reactivity in diffusional limited regime, the char was combusted at higher combustion temperatures (550-625 °C). Two oxygen concentrations (21 and 33%) were used during combustion stage to determine their effects on char particle ignition.

2.3 SEQUENTIAL PYROLYSIS AND GASIFICATION EXPERIMENTS

Our pyrolysis and gasification experiments followed the experimental steps established earlier in our laboratory (Matzakos 1991).

- 1) The coal particles were placed in the sample pan, in a configuration that keeps them away from each other to prevent agglomeration during the plastic phase.
- 2) The flow of the gas (100% nitrogen or 5% oxygen/95% nitrogen) was started. The sample was held at 150 °C for a few minutes to remove any moisture present. Then it was ramped to the starting temperature for pyrolysis, 200 °C.
- 3) When the reactor temperature reached 200 °C, videotaping and counting of elapsed time started. The reactor temperature was increased at a constant pyrolysis heating rate until the final heat treatment temperature (HTT) was reached. Then the temperature was held constant at HTT for a duration of desired soak time (0 or 3 minutes).

- 4) At the end of soak time, videotaping stopped and the reactor was cooled as fast as possible to 250 °C. At that point, the desired oxygen/nitrogen mixture for combustion stage was introduced. The temperature remained at 250 °C long enough to allow the mixture to achieve steady state.
- 5) Videotaping started and the temperature was ramped as fast as possible to the desired combustion temperature. There it was kept constant until coal conversion higher than 90% was achieved.
- 6) Finally, the reactor temperature was raised to 650 °C and the sample was kept there for 5 minutes to burn the remaining carbon and measure the ash content of the sample.

Experiments were also performed by repeating the pyrolysis ramp two and three times to investigate whether all the volatile matters were completely released from the sample during the first devolatilization. These results were useful in proving that heterogeneous (as opposed to homogeneous) ignitions were observed on our video sequences.

2.4 IMAGE ANALYSIS

Image analysis was done on a Macintosh Quadra 900 computer (Apple Computer, Inc.) using the public domain NIH Image image analysis software (written by Wayne Rasband at the U.S. National Institutes of Health and available electronically via Internet by anonymous ftp from zippy.nimh.nih.gov or from Library 9 of the MacApp forum on CompuServe and on floppy disk from NTIS, 5285 Port Royal Rd., Springfield, VA 22161, part number PB93-504868). Our image processing procedure involved the following steps:

- 1) The grayscale raw image (Figure 2.3) was opened and a region of interest (ROI) was defined to process one coal particle at a time due to the nonuniform illumination of the pan. As an example, the lower right particle in Figure 2.3 was chosen to illustrate the steps of the image analysis procedure shown in Figure 2.4.

- 2) Noise reduction and smoothing were first applied to the grayscale image (Figure 2.4i) to obtain a filtered image (Figure 2.4ii).
- 3) A threshold was manually chosen to segment the filtered image and create a binary image (Figure 2.4iii).
- 4) This binary image was smoothed using dilation and erosion steps to obtain the final binary image (Figure 2.4iv).
- 5) The final binary image was analyzed to compute the area and perimeter of the projection of the coal particle. We also computed the length of the major and minor axes of an ellipse fitted around the coal particle. Based on these measurements, other parameters like area-equivalent radius, shape factor, and elongation for the particle were calculated.
- 6) Steps 1 through 5 above were repeated to process all the particles on the original image.
- (7) Steps 1 through 6 were repeated to process all the images obtained at different time levels (and, thus, at different reactor temperatures) for each run.

With these measurements we could follow the temporal evolution of the size and shape of any pyrolyzing particle. Figure 2.5 shows some of the final binary images we obtained for the particle used in this illustration at various temperatures. The images of Figure 2.5 clearly show that the particle expands and contracts several times during the course of pyrolysis.

2.5 DATA ANALYSIS

2.5.1 Reaction rates

The reaction rate R_0 per unit mass of initial solid or the reaction rate R_s per unit mass of remaining solid were used to describe char reactivity. These two reaction rates were calculated from experimental data as follows:

$$R_0(t) = \frac{dx}{dt} = -\frac{1}{m_0} \left(\frac{dm(t)}{dt} \right) \quad (2.1)$$

$$R_s(t) = \frac{1}{1-x} \frac{dx}{dt} = -\frac{1}{m(t)} \left(\frac{dm(t)}{dt} \right) \quad (2.2)$$

where x is the conversion of the solid, m_0 is the initial (unreacted) mass of the solid on an ash-free basis and $m(t)$ is the mass of char remaining unreacted at time t . The first rate R_0 gives the absolute values of char reactivity and exhibits a maximum at 20-40% conversion for reaction with oxygen in the kinetic control regime (Ballal and Zygourakis 1987; Gavalas 1980). The second rate R_s gives specific values of reactivity per mass of remaining solid. In the kinetic control regime, this rate was shown to have a monotonic increase for the conversion range 0 - 90%. When chars reacted in the presence of diffusional limitations, ignition phenomena appeared as "spikes" or sharp changes in R_s for a small interval of conversion indicating rapid consumption of the ignited particle (Matzakos 1991).

2.4.2 Devolatilization rate

The devolatilization rate was calculated using the equation

$$R_o(t) = \frac{dx}{dt} = -\frac{1}{m_o} \left(\frac{dm(t)}{dt} \right) \quad (2.3)$$

where m_o is the initial mass of the solid in ash-free basis and x (for pyrolysis studies) is the fraction of the weight loss. This rate exhibits a maximum at 10-30% weight loss during primary devolatilization.

2.5.3 Particle radius

The radius, r of a coal particle during pyrolysis was computed as the area-equivalent radius of the projected area defined by

$$r = \sqrt{\frac{A}{\pi}} \quad (2.4)$$

where A is the measured projected area given by image analysis. The average

radius of all the particles from several runs was computed to achieve better statistical results and was reported in the plots. The total numbers of particles processed depended on the particle size fraction. At least 12 and 6 particles were used for 28-32 and 20-25 mesh fractions, respectively.

2.6 REPRODUCIBILITY ERROR ASSESSMENTS

Two types of error expressions were used to assess the reproducibility error of our experimental results.

- 1) The relative average error defined by

$$e_{\text{relative}} = \frac{1}{M} \sum_{i=1}^M \frac{1}{N} \sum_{j=1}^N \frac{|f_{ij} - \bar{f}_j|}{\bar{f}_j} \quad (2.5)$$

- 2) and the L₂ error defined by

$$e_{L_2} = \frac{1}{M} \sum_{i=1}^M \frac{1}{\sqrt{N}} \sqrt{\sum_{j=1}^N (f_{ij} - \bar{f}_j)^2} \quad (2.5)$$

where

M is the number of runs,

N is the total number of points used to compute the error,

$\bar{f}_j$ is the average of experimental value at point number j, and

f_{ij} is the experimental value at point number j of run number i.

The plots for a few runs and the average reaction rate of Illinois #6 (20-25 mesh) char gasified at 550 °C are presented in Figure 2.6. The plots show that the reactivity patterns are very reproducible among runs. The reproducibility errors of reactivity curves for three particle size fractions are tabulated in Table 2.1. Two main conclusions can be drawn:

- (a) the average relative error increases with the particle size and
- (b) more runs are required for larger particle sizes to obtain the same

reproducibility error.

TABLE 2.1

Reproducibility Error for Reactivity Curves

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

These results are not surprising because we use fewer particles for each run with larger particles to prevent agglomeration during the pyrolysis stage.

Similar conclusions are reached when we assess the error for the devolatilization rates. Figure 2.7 shows the plots for the rates of Illinois #6 (20-25 mesh) pyrolyzed using 1 °C/s and Table 2.2 presents the computed errors for different particle sizes.

TABLE 2.2

Reproducibility Error for Devolatilization Rates

Particle size fraction	Number of runs	$e_{relative}$ (%)	e_{L_2}
50-60 mesh	3	2.0	0.0081
28-32 mesh	4	2.4	0.0066
20-25 mesh	4	3.4	0.0090

Finally, the errors for the computation of the average particle radius are tabulated in Table 2.3. The average relative error for the 20-25 mesh fraction is higher than that of the 28-32 mesh fraction because again we use fewer

particles for each run with 20-25 mesh particles. The evolution of the average radius and the radii for three individual particles are plotted in Figure 2.8 for the 20-25 mesh fraction.

TABLE 2.3

Reproducibility Error for Particle Radius

Particle size fraction	Number of particles	$e_{relative}$ (%)	e_{L_2}
28-32 mesh	12	7.7	0.042
20-25 mesh	7	9.4	0.090

REFERENCES

- Ballal, G. and K. Zygourakis. 1987. Evolution of Pore Surface Area During Noncatalytic Gas-Solid Reactions: 2. Experimental Results and Model Validation. *Ind. Eng. Chem. Research*. 26: 1787-1796.
- Gavalas, G. R. 1980. A Random Capillary Model with Application to Char Gasification at Chemically Controlled Rates. *AIChE J.* 26: 577-585.
- Matzakos, A. 1991. Fundamental Mechanisms of Coal Pyrolysis and Char Combustion. Ph.D. Dissertation, Rice University.
- Matzakos, A. N. and K. Zygourakis. 1993. Computerized thermogravimetric reactor with video microscopy imaging system for coal pyrolysis and combustion studies. *Rev. Sci. Instrum.* 64: 1541-1548.
- Vorres, K. S. 1990. The Argonne Premium Coal Sample Program. *Energy & Fuels*. 4: 420-426.

Figure 2.1: Schematic showing the TGA/VMI reactor system.

Figure 2.2: Schematic showing the video microscopy system for the TGA reactor.

Figure 2.3: Sample of a grayscale image for the whole pan.

i. Grayscale image

ii. Image after noise reduction
and smoothing

iii. Binary image

iv. Binary image after dilation
and erosion

Figure 2.4: Steps in image processing.

Figure 2.5: Final binary images of the particle at various temperatures.

Figure 2.6: Reaction rates and average reaction rate from a few runs for particle size 20-25 mesh fraction.

Figure 2.7: Devolatilization rates and average devolatilization rate from a few runs for particle size 20-25 mesh fraction.

Size = 20-25 mesh; Heating rate = 20 °C/s

Figure 2.8: A few of individual particle radius and the average particle radius for 20-25 mesh fraction.

CHAPTER 3

EFFECT OF PYROLYSIS CONDITIONS ON PARTICLE SWELLING AND DEVOLATILIZATION RATES

3.1 INTRODUCTION

Devolatilization is the first process taking place when coal particles are heated. At low temperatures (below 370 °C), the loosely bound H₂O and CO₂ is released from the coal. Primary devolatilization occurs in the temperature range of 370-550 °C, where the volatiles are released in the form of low molecular weight gases, liquids, and semisolid tars. The primary devolatilization is essentially complete at 550 °C. At a higher temperature range (600-800 °C), secondary devolatilization occurs producing mostly CH₄ and H₂ ^{1, 2}.

Plastic coals soften as they are heated and behave like highly viscous non-Newtonian fluids during the primary devolatilization stage (370 to 550 °C) ¹. Examples of plastic coals are bituminous and subbituminous coals. Complex morphological changes occur during the plasticity stage and determine the pore structure of the chars produced from these coals. As the thermal decomposition reactions of pyrolysis start to occur, gaseous volatiles are released in the softened particle interior. As bubbles of volatiles grow and coalesce, the softened coal particles may swell considerably. Eventually, the volatile bubbles break through the particle surface releasing their gaseous contents and, as a result, the softened particles contract. Thus, particle swelling and contractions or bubbling may occur several times until most of the volatiles are released and the particle is completely resolidified ^{3, 4}.

The appearance and temperature range of plasticity, the rate of bubbling, and the extent of swelling depend on coal rank, the pyrolysis heating rate, and the pyrolysis atmosphere. Low rank coals (like lignite) and very high rank coals (like anthracites) are non-plastic coals. These coals do not soften

and do not undergo drastic macropore structural changes during pyrolysis ^{3, 4}.

The pyrolysis heating rate has significant effects on coal plasticity and swelling. Higher heating rates broaden the plastic regime and increase the swelling as well as the bubbling rate ⁵. Structural studies, using different methods such as electron or optical microscopy, have also shown that the particle porosity, macropore surface area and macropore size depend on the pyrolysis heating rate. Low heating rates produce char particles exhibiting a few scattered large cavities with thick walls and few cenospheres are observed under these conditions. The term "cenosphere" was introduced by Sinnatt and his coworkers ⁶ to describe the hollow char particles they obtained under various atmospheres in entrained reactors. On the other hand, higher heating rate produces chars with larger cenospheres having thinner walls and significantly higher macroporosity ^{4, 7}. Finally, increasing pyrolysis heating rates widen the temperature range of primary devolatilization ^{4, 7}, increase the devolatilization rates and have a smaller effect on the total weight loss observed during pyrolysis.

Previous investigators also reported that coals become less plastic after pre-oxidation ². This result indicates that an oxygen-containing pyrolysis atmosphere may have similar effects resulting in decreased coal plasticity and particle swelling.

3.2 EFFECT OF PYROLYSIS HEATING RATE

The pyrolysis heating rate has significant effects on particle swelling, devolatilization rate, and the development of the internal structure of coal. Consequently, the pyrolysis heating rate will affect the reactivity of the char in the combustion stage.

Using the thermogravimetric reactor with video microscopy imaging (TGA/VMI), we were able to follow continuously the evolution of the size and shape of each coal particle as well as the weight of the coal sample throughout the pyrolysis stage. Figure 3.1 presents grayscale images showing typical changes in the size and shape of Illinois #6 coal particles pyrolyzed at 20 °C/s. As the temperature of the coal sample was raised at a constant rate,

the particles swelled and started to "bubble." Significant particle swelling was usually followed by a rapid contraction and this "bubbling" pattern continued until resolidification occurred at the end of the plasticity stage.

Using the image analysis procedure described in Chapter 2, we were able to quantify the effect of pyrolysis process conditions on the transient swelling patterns of pyrolyzing particles. Figure 3.2 presents the effect of heating rate on the average transient particle swelling patterns of Illinois #6 coal particles in the 28-32 mesh fraction. The average radius r was computed as the area-equivalent radius of the projected area defined as

$$r = \sqrt{\frac{A}{\pi}} \quad (3.1)$$

where A is the measured projected area.

Because Illinois #6 is a plastic coal, the particles swell considerably when heated and the extent of swelling depend strongly on the heating rate. For the lowest heating rate of 1 °C/s, the particles swell rapidly to their maximum size and stay there as they undergo a series of expansions and contractions ("bubbling") indicated by rapid oscillations of their size on Figure 3.2. When the bubbling has stopped, the particles decrease to their final size that is almost equal to their original size.

For the heating rates of 20 and 10 °C/s, the particles rapidly expand to their maximum size and then start to shrink. Vigorous "bubbling" takes place now as the particles slowly shrink to achieve their final size. The final size of the char particles is substantially larger than the original size.

These results demonstrate that the negligible final particle size increase observed at low heating rates can mask the large transient swelling and vigorous "bubbling" of plastic coal particles. Thus, measurements of the transient particle size are necessary to model the phenomena occurring during pyrolysis even at relatively low heating rates. Also, accurate measurements of the final particle size can be made only if we allow the particles to completely resolidify at the end of plastic stage.

The temperature range of the plastic regime of the Illinois #6 coal depends on the heating rate as shown in Table 3.1. Higher heating rates shift the plastic regime and the maximum swelling radius to higher temperatures.

Figure 3.2 also shows that both the maximum radius and the final radius

of a particle depend on the heating rate. These results (summarized in Figure 3.3) indicate that higher heating rates produce particles with larger final and maximum swelling radii. The final radius measurements are in good agreement with previous results obtained in our lab using as many as 60 particles to achieve 95% confidence level ⁸.

Figure 3.4 shows the average radius for different heating rates as a function of weight loss. The plots clearly show that the particles expand to achieve their maximum size before we observe any substantial weight loss due to devolatilization. This weight loss is smaller than 5% for all heating rates. Close inspection of Figure 3.4 also reveals that particles pyrolyzed at 1 °C/s do not show any weight loss before their average radius increases to about 50% of the maximum swelling radius. Increasing heating rates also shift the maximum swelling radius to higher conversions.

Figures 3.5 and 3.6 present the devolatilization rate as a function of temperature and weight loss, respectively, for different heating rates. Both figures show that high heating rates increase the devolatilization rates and slightly enhance the total weight loss. The devolatilization rate for coal pyrolyzed at 10 °C/s is 10 times higher than the rate obtained at 1.0 °C/s and the rate at 20 °C/s is twice as large as the rate at 10 °C/s. Increasing heating rates also shift the maximum devolatilization rate to higher temperatures as illustrated in Figure 3.5. The plots in Figure 3.6 show that the total weight loss increases slightly with increasing heating rates.

Figure 3.7 compares the average transient swelling pattern to the devolatilization rate of Illinois #6 coal particles pyrolyzed at 10 °C/s. We observe that the peak for maximum swelling radius does not coincide with that of maximum devolatilization rate. Maximum swelling occurs 30 °C below the temperature where the maximum devolatilization rate is observed. Clearly, the particles initially expand to their maximum size without releasing any volatiles. As the pressure builds up in the particle interior, however, the walls of the particles rupture releasing the volatiles and the particles undergo a series of rapid expansions and contractions as volatile bubbles grow in the interior and break through the surface.

The effect of heating rate on particle shape during pyrolysis was also quantified. The particle shape factor s is defined by

$$s = \frac{P^2}{4\pi A} \quad (3.2)$$

where P is the perimeter of the projected area of the particles and A is the projected area of the particles. This shape (or circularity) factor takes the value of 1 when the particle projection is a perfect circle.

The plots in Figure 3.8 reveal that for all heating rates analyzed, the shape factor for Illinois #6 coal increases slightly with temperature indicating increasing deviations of the particles from a spherical shape. This is probably caused by the growth of volatile bubbles in the particle interior that are asymmetrical. The shape factors appear to decrease as the temperature increases and the particles resolidify. Here, the smallest changes in particle shape are observed for the highest heating rate of 20 °C/s.

Figure 3.9 presents changes in the particle elongation defined as the average ratio of the length of major to minor axis of an ellipse fitted to each particle projection. These plots show that for all heating rates the particles become elongated as they go through their series of rapid expansions and contractions. As the particles resolidify, however, they approach a more spherical shape.

The trends of computed particle shape factor and elongation agree very well with the behavior of the swelling particle shown in our recorded video sequences of pyrolysis experiments (see, for example, Figure 3.1).

Table 3.1
Effect of heating rate on plasticity regime of Illinois #6 coal

Heating Rate (°C/s)	Temperature Range (°C)
20	405-565
10	395-525
1.0	385-485

3.3 PARTICLE SIZE

Swelling is caused mainly due to pressure build-up as volatiles are released inside the pyrolyzing particles during their plasticity phase. The original size of the coal particle can influence the rate at which pressure builds up and, hence, the swelling of the particle. Also, larger volatile bubbles can develop inside larger particles.

To study the effect of coal particle size, we measured the transient swelling patterns for Illinois #6 coal particles in the 20-25 mesh fraction. Figure 3.10 shows the average transient swelling patterns computed from these runs for different pyrolysis heating rates. We observe similar trends as with the smaller particles (28-32 mesh) discussed in the previous section. Higher heating rates produce char particles with larger final radius and maximum swelling radius.

To assess the effect of coal particle size, we computed the swelling ratio as follows

$$\text{Swelling Ratio} = \left(\frac{r(t)}{r_0} \right)^3 \quad (3.3)$$

where r_0 is the average initial radius of the particle and $r(t)$ is the average radius at time t . The results presented in Figure 3.11 reveal that the larger particles exhibit higher maximum and final swelling ratios for all heating rates. These results are expected since higher pressures will build-up in larger particles.

Figure 3.12 plots the measured devolatilization rate as a function of temperature for the large particles (20-25 mesh). By comparing these results to the results obtained for the smaller particle size (28-32 mesh) and plotted on Figure 3.5, we observe that the coal particle does not affect the patterns of devolatilization rates at the lower pyrolysis heating rates. For the heating rate of 20 °C/s, however, we observe a shift of the devolatilization rates measured for the larger particles (20-25 mesh) towards higher temperatures.

3.4 PYROLYSIS ATMOSPHERE

Illinois #6 coal particles were pyrolyzed in reactive atmospheres containing 5% O₂ to study the effect of oxygen on particle swelling and devolatilization rate. The lowest heating rate, 1.0 °C/s, was not used for oxygen experiments since the coal would have enough time to react with oxygen and significant coal combustion would take place in this stage.

The plots of Figure 3.13 show that the reactive atmosphere has a profound effect on the trend of particle swelling. Particles pyrolyzed in a 5% O₂ / 95% N₂ atmosphere swell to their maximum size and do not shrink after reaching their maximum radius, as we have observed for the particles pyrolyzed in inert atmosphere.

This is clearly shown in the sequence of images presented in Figure 3.14 where the size and the shape of coal particles pyrolyzed in the two atmospheres are compared. The top two images show the initial particle size before swelling, the middle images show the particles at maximum swelling and the bottom images were taken after all the particles settled down to their final size. Note that the maximum swelling radius and the final radius for particles pyrolyzed in the reactive atmosphere are almost identical. The presence of oxygen during pyrolysis caused the coal to become less plastic and the rate of "bubbling" was significantly reduced.

Although the maximum radius is almost the same when the particles are pyrolyzed either in pure nitrogen or in an oxygen-containing atmosphere, the final radius of particles produced in reactive atmosphere is much higher (Figure 3.13) for both heating rates studied here.

The shape factor plots in Figure 3.15 indicate that there is no significant change in particle shape during pyrolysis in reactive atmosphere (compare this with Figure 3.8 for inert atmosphere). This is due to the absence of vigorous particle "bubbling" as previously discussed. However, there is a slight increase in particle elongation as shown in Figure 3.16 (compare to particles shown in the image sequence of Figure 3.14).

The presence of oxygen also influenced the devolatilization rate as shown in Figure 3.17 for three different oxygen concentrations used during coal pyrolysis. The main conclusion that can be drawn from these results is that the devolatilization rate decreases with increasing oxygen concentration due to decreasing coal plasticity. The weight loss curves in Figure 3.18 lead us

to the same conclusion, namely that increasing oxygen concentrations decrease the total weight loss during pyrolysis.

3.5 COAL RANK

Coal rank is expected to influence the particle swelling since the volatile and carbon contents of a coal vary with its rank. To quantify the effect of coal rank, we also studied the pyrolysis of

- (a) a bituminous coal with low ash content (Utah Blind Canyon) and
 - (b) a lower rank subbituminous coal (Wyodak-Anderson seam)
- in addition to the high-volatile bituminous coal with high ash content (Illinois #6). The proximate analysis for these three coals are given in Table 3.2.

Table 3.2
Proximate Analysis for Illinois #6 , Utah Blind Canyon
and Wyodak Coals

% Content	Illinois #6	Utah	Wyodak
Moisture	8.0	4.6	28.1
Volatile Matter	36.9	43.7	32.2
Fixed Carbon	40.9	52.8	33.0
Ash	14.4	4.5	6.3

The results for particle swelling for the three different coals are presented in Figures 3.19 and 3.20 for the heating rates of 20 and 10 °C/s, respectively. In both cases, the Utah Blind Canyon coal particles rapidly swell to their maximum size in patterns similar to those observed for the Illinois #6 coal. However, the Utah coal particles do not show any vigorous "bubbling" as evidenced by the absence of rapid oscillations in their transient swelling patterns. As expected, Wyodak coal particles do not show plastic behavior and do not swell at all. Figure 3.21 shows representative images for Utah

Blind Canyon and Wyodak coal particles pyrolyzing at a heating rate of 20 °C/s.

The results from Figure 3.20 agree well with the devolatilization rates for the three coals shown in Figure 3.22. Wyodak coal has the lowest devolatilization rate because it has the lowest volatile content and because it is not a plastic coal. The absence of vigorous "bubbling" from the transient swelling pattern of Utah Blind Canyon coal particles explains its lower devolatilization rate when compared to that of Illinois #6.

Figures 3.23 and 3.24 show the evolution of the shape factor and the elongation for the Utah Blind Canyon coal particles. For heating rates of 10 and 20 °C/s, the shape factor increases toward the end of pyrolysis. The changes of the particle elongation are more dramatic and they clearly indicate that the char particles obtained from the Utah coal are very elongated.

On the other hand, the shape factor and the elongation remain fairly constant for the lowest heating rate of 1 °C/s. When Utah coal particles are pyrolyzed at low heating rates, round char particles are obtained.

3.6 REFERENCES FOR CHAPTER 3

- (1) Berkowitz, N. *The chemistry of coal* ; Elsevier: New York, 1985.
- (2) Gorbaty, M. L.;Larsen, J. W.; Wender, I. *Coal Science* ; Academic Press: London, 1982.
- (3) Glass, M. W. *Ph.D. Dissertation*; Rice University; 1987.
- (4) Zygourakis, K. *Energy & Fuels* 1993, 7, 33-41.
- (5) Dulhunty, J.; Harrison, B. *Fuel* 1953, 32, 441-450.
- (6) Sinnat, F.;McCulloch, A.; Newall, H. J. *Soc. Chem. Ind.* 1927, 46, 331-335.
- (7) van Krevelen, D. *Coal: typology, chemistry, physics, constitution* ; Elsevier: New York, 1961.
- (8) Boissiere, F. *M.S. Dissertation*; Rice University; 1993.

380 °C

420 °C

470 °C

490 °C

510 °C

600 °C

Figure 3.1: Sequences of images at various reactor temperatures for Illinois #6 coal (28-32 mesh) pyrolyzed at 20 °C/s. The scale bar is 1 mm.

Figure 3.2: Effect of heating rate on particle swelling of Illinois #6 coal.

Figure 3.3: Effect of heating rate on the final and maximum swelling radii of Illinois #6 coal (28-32 mesh).

Figure 3.4: Average radius vs. weight loss of Illinois #6 coal (28-32 mesh) for various pyrolysis heating rates.

Coal = ILL #6; Size = 28-32 mesh

Figure 3.5: Effect of heating rate on devolatilization rate.

Figure 3.6: Devolatilization rate vs. weight loss.

Figure 3.7: Comparison of radius and devolatilization rate as a function temperature.

Figure 3.8: Effect of heating rate on shape factor for Illinois #6 coal.

Figure 3.9: Effect of heating rate on elongation for Illinois #6 coal.

Figure 3.10 Effect of heating rate on particle swelling for 20-25 mesh (Illinois #6 coal) particles.

Figure 3.11: Swelling ratio for two particle sizes of Illinois #6 .

Figure 3.12: Effect of heating rate on devolatilization rate for 20-25 mesh (Illinois #6 coal) particles.

Figure 3.13: Effect of pyrolysis atmosphere on particle swelling of Illinois #6 coal.

No Oxygen (Temperature=380 °C)

5% Oxygen (380 °C)

No Oxygen (470 °C)

5% Oxygen (500 °C)

No Oxygen (600 °C)

5% Oxygen (600 °C)

Figure 3.14: Sequences of images for Illinois #6 coals pyrolyzed in an inert and reactive atmospheres using heating rate 20 °C/s. The scale bar is 1 mm.

Figure 3.15: The shape factor for Illinois #6 coal (28-32 mesh) pyrolyzed in reactive atmosphere.

Figure 3.16: Particle elongation for Illinois #6 coal (28-32 mesh) pyrolyzed in reactive atmosphere.

Figure 3.17: Effect of pyrolysis atmosphere on devolatilization rate of Illinois #6 coal.

Coal = ILL #6; Rate = 10 °C/s; Size = 28-32 mesh

Figure 3.18: Effect of pyrolysis atmosphere on the weight loss of Illinois #6 coal.

Figure 3.19: Effect of coal rank on particle swelling for pyrolysis heating rate 20 °C/s.

Figure 3.20: Effect of coal rank on particle swelling for pyrolysis heating rate 10 °C/s.

Utah (Temperature=380 °C)

Wyodak (380 °C)

Utah (470 °C) Wyodak (470 °C)

Utah (600 °C) Wyodak (600 °C)

Figure 3.21: Sequences of images for Utah Blind Canyon and Wyodak coals pyrolyzed at 20 °C/s. The scale bar is 1 mm.

Figure 3.22: Effect of coal rank on devolatilization rate.

Figure 3.23: Shape factor for Utah Blind Canyon coal.

Figure 3.24: Elongation for Utah Blind Canyon coal.

CHAPTER 4

EFFECT OF PROCESS CONDITIONS ON CHAR REACTIVITY

4.1 REACTIVITY IN THE KINETIC CONTROL REGIME

4.1.1 Char reactivity in the kinetic control regime is only affected by the final heat treatment temperature and not by pyrolysis heating rate, pyrolysis atmosphere or coal particle size

At low temperatures, the heterogeneous reactions between carbon and oxygen take place in the kinetic control regime. Oxygen can fully penetrate the micropores of the chars and all the internal surface area of the chars (attributed to both macropores and micropores) is available for reaction. Our measurements have shown that chars produced from Illinois #6 coal react with oxygen in the kinetic control regime at temperatures below 420 °C.

Figure 4.1 presents the reactivity patterns of several Illinois #6 chars combusted with 21% oxygen at 420 °C. These chars were produced from coal particles of different sizes pyrolyzed at two heating rates (1 and 20 °C/s). The data presented in this figure clearly show that particle size and pyrolysis heating rate do not affect the reactivity pattern when the chars react in the regime of kinetic control. Since micropore structure is important in this regime and the micropore surface area accounts for most of the total surface area, these results suggest that the chars have similar active micropore surface areas and, therefore, similar intrinsic reactivities. Moreover, the plots show that the char reactivity increases monotonically with conversion.

The effect of pyrolysis atmosphere on char reactivity in the kinetic control regime is shown in Figure 4.2. Since the reactivity patterns are almost identical for chars produced in both inert and reactive (5% O₂) atmospheres and two particle sizes, we can conclude that the pyrolysis atmosphere does not affect the micropore structure of the chars. This is in good agreement with the previous results obtained in this lab ¹.

To determine whether the heat treatment temperature (HTT) affects the reactivity in this regime, Figure 4.3 presents the reactivity patterns for several chars produced using various final heat treatment temperatures. These plots show that the reactivity of the char decreases significantly with increasing heat treatment temperature and this is in good agreement with previous data from the literature ² and our laboratory ¹.

4.1.2 Measurement of kinetic parameters

Figure 4.4 presents the dependence of char combustion rates on the oxygen concentration. Such results can be used to determine the kinetic parameters for char combustion.

Figures 4.5, 4.6, and 4.7 present the results from the kinetic study of Illinois #6 char combustion. The reaction rates used in these plots are the average reaction rates up to a specific conversion defined as follows:

$$\bar{r}_{x_0} = -\frac{1}{t_0} \int_0^{t_0} \frac{1}{m_0} \frac{dm}{dt} dt = \frac{1}{t_0} \frac{m_0 - m_{t_0}}{m_0} = \frac{x_0}{t_0} \quad (4.1)$$

where x_0 is a reference conversion, t_0 is the time to achieve the reference 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 reaction rates are more accurate and statistically more significant than the instantaneous reaction rates. The reference conversion we have chosen for the plots in Figures 4.5, 4.6, and 4.7 is $x_0 = 0.25$.

The following rate expression was used to describe the kinetics of char combustion:

$$R_0 = \frac{1}{m_0} \frac{dm}{dt} = \frac{dx}{dt} = ky^n \quad (4.2)$$

where R_0 is the normalized reaction rate, $\frac{dm}{dt}$ is the instantaneous reaction rate, y is the mole fraction of oxygen, n is the order of reaction, and k is the reaction rate constant that takes the Arrhenius form:

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \quad (4.3)$$

where k_0 is the pre-exponential factor for the reaction, E is the activation energy, T is the absolute temperature, and R is the gas constant

The order of reaction n was determined by plotting the reaction rate R_0 vs. y in log-log scale at three different combustion temperatures (see Figure 4.5). All three curves are straight lines and their slope gives the order of reaction n as:

$$n = 1.0 \pm 0.05$$

We conclude, therefore, that the reaction of Illinois #6 chars with oxygen is first order. Since

$$k = \left(\frac{R_0}{y}\right)$$

for a first order reaction, the activation energy E and the pre-exponential factor k_0 can be calculated from the slope and the intercept of the Arrhenius plot of the rate constant k plotted vs. $(1/T)$. From the data shown in Figures 4.6 and 4.7, the kinetic parameters E and k_0 were found to be equal to

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

and

$$k_0 = 7.30 \times 10^7 \text{ sec}^{-1}$$

for the reaction of Illinois #6 chars with oxygen.

4.2 TRANSITION TO THE REGIME OF DIFFUSIONAL LIMITATIONS

Earlier reports from our laboratory¹ have presented the transition of the reactivity patterns for Illinois #6 chars as we move from the kinetic control

regime to the regime of diffusional limitations by raising the combustion temperature. At a combustion temperature of 450 °C, the Illinois chars react in the kinetic control regime, where the entire micropore surface area is fully accessible to the reactant. The reactivity pattern shows an almost constant increase of the reaction rate for conversions between 10 and 90%.

When the combustion temperature is increased to 500 °C, the reactivity pattern has a large initial slope (at low conversions), but the rate increases more slowly after the char reaches the 25%-30% conversion levels. At a still higher conversion temperature (525 °C), the reactivity patterns exhibit small local maxima at about 20% conversion.

This transition becomes more clear when the absolute reaction rate R_0 is plotted vs. conversion. The reaction rate measured at the highest temperature (525 °C) exhibits a sharp maximum at about 20% conversion. This maximum becomes less pronounced and is shifted to higher conversions (30-40% level) when the combustion temperature is lowered.

4.3 REACTIVITY WITH DIFFUSIONAL LIMITATION

4.3.1 Effect of oxygen concentration

Figure 4.8 shows the effect of oxygen concentration on the reactivity of Illinois #6 chars in the regime of diffusional limitations. Coal particles in the 50-60 mesh size were used to produce these chars. When we used 21% oxygen, all combustion runs at 550 °C gave the characteristic reactivity pattern showing monotonic increases in reaction rates until conversions around 90% were achieved. When the oxygen concentration was increased to 33%, however, particle ignitions were observed. The reactivity patterns for these runs (see Figure 4.8) exhibited a "spike" or sharp increase of reaction rate indicating particle ignitions. Our video sequences showed that the ignited particles were engulfed in luminous flames that lasted for a fraction of a second.

Figure 4.9 shows the reactivity patterns for chars produced from Illinois #6 coal particles in the 28-32 mesh size fraction. No ignitions were observed for combustion at 550 °C with 21% oxygen. The char reactivity patterns from

some (but not all) combustion runs at 625 °C and 21% oxygen concentration showed rapid changes in the reaction rate indicating possible ignitions. The video tapes from these experiments, however, did not show particle ignitions with luminous flames. Only sudden and rapid consumption of char particles was observed in the video sequences. These results indicate that the rapidly consumed particles reacted at temperatures higher than the ambient temperature of 625 °C, but lower than the temperature required to produce a luminous flame. Finally, combustion runs at 550 °C and 33% oxygen gave reactivity patterns with sharp "spikes" indicating particle ignitions. These ignitions were confirmed from the video tapes.

We conclude that high oxygen concentrations increase the reaction rate and, consequently, the rate of heat generation inside the particle. When the rate of heat generation is substantially larger than the rate of heat removal from the particle, the particle temperature increases dramatically leading to thermal ignition. A luminous flame is observed if the particle temperature is high enough.

4.3.2 Effect of pyrolysis heating rate

Since pyrolysis heating rate affects the development of macropore structure of the char, we expect that it also influences the char reactivity in the diffusion limited regime. The results presented in Tables 4.1 and 4.2 show that increasing heating rates during pyrolysis lead to chars with larger macroporosities and higher macropore surface areas. The more open macropore structures of these should lead to decreases in the intraparticle diffusional limitations and increase the likelihood of particle ignition. Also, the results presented in Chapter 3 show that the final radius of the char particles increases with increasing heating rate. Large particle radii decrease the heat removal rates per unit particle volume, thus increasing the likelihood of particle ignition.

Our experimental results confirm these hypotheses. Figure 4.10 shows that chars produced from Illinois #6 coal (50-60 mesh particles) at 0.1 and 1 °C/s pyrolysis rates did not ignite when reacted at 550 °C and 33% oxygen. However, ignitions were observed during runs at the same conditions with chars produced at a pyrolysis heating rate of 10 °C/s.

Figure 4.11 shows the reactivity patterns for chars produced from larger (28-32 mesh) Illinois #6 coal particles. Ignitions are now observed for runs with chars produced at 1 and 10 °C/s pyrolysis heating rates. The run with a 10 °C/s char shows two distinct ignition "spikes", indicating that two particles ignited at different times. This was confirmed from the video images of this run. Still, no ignitions were observed with chars produced at the lowest heating rate of 0.1 °C/s. •

These results prove that macropore structure is a very important parameter in determining char reactivity at elevated temperatures.

Table 4.1
Effect of pyrolysis heating rate on char structure.
Coal particle size: 50-60 mesh ³

Heating rate, °C/s	Average particle radius, μm	Porosity	Macropore surface area, cm ² /cm ³
0.1	168.5	0.33	659
1.0	168.5	0.55	1479
10.0	195.6	0.72	2951

Table 4.2
Effect of pyrolysis heating rate on char structure.
Coal particle size: 28-32 mesh ⁴

heating rate, °C/s	average particle radius, μm	porosity	macropore surface area, cm ² /cm ³
0.1	317.0	0.59	853
1.0	325.0	0.60	1260
10.0	407.0	0.65	1046

4.3.3 Effect of particle size

Particle size is an important parameter in determining the reactivity patterns of chars. Figure 4.12 shows the reactivity patterns for three chars produced from coal particles of three different sizes at a pyrolysis heating rate of 20 °C/s. The plots indicate particle ignitions for all three sizes. When a lower pyrolysis heating rate (1 °C/s) was used, however, we did not observe particle ignitions during runs with the smallest (50-60 mesh) particle size (see Figure 4.13).

4.3.4 Effect of heat treatment temperature

Figure 4.14 presents the effect of heat treatment temperature on the reactivity and ignition of char particles produced from 28-32 mesh coal particles. Ignitions were observed for heat treatment temperatures of 700 and 800 °C. When the HTT was raised to 900 °C, however, no ignitions were observed. This is due to the significant decrease in the intrinsic reactivity of chars produced at HTT due to the thermal annealing of the active sites ⁵.

4.3.5 Effect of pyrolysis atmosphere

Chars produced in reactive pyrolysis atmosphere (5% O₂) are more reactive than chars produced in inert atmospheres as shown in Figure 4.15. Structural measurements ⁴ indicated that chars produced in a reactive pyrolysis atmosphere have higher porosities and macropore surface areas than chars produced in an inert atmosphere.

As seen in Chapter 3, the presence of oxygen during pyrolysis leads to increases in the final radius of char particles. Both these factors increase the likelihood of particle ignitions by decreasing the intraparticle diffusional resistance and the rate of heat removal per particle volume.

4.3.6 Effect of coal rank

Finally, we compared the reactivity of Illinois #6 chars with that of Utah Blind Canyon and Wyodak chars. Our video sequences and the plots of Figure 4.16 for the combustion of Utah Blind Canyon chars show that the particles tend to have multiple ignitions. This is shown by several peaks in the reactivity plots for both heating rates.

When Utah chars produced at different pyrolysis heating rates were reacted in the regime of kinetic control (420 °C and 21% oxygen), they exhibited similar reactivity patterns (see Figure 4.17) indicating that these chars have similar values of active micropore surface area.

Among the three coals we have studied, Wyodak coal yields the most reactive chars. Figure 4.18 shows that Wyodak chars ignited at very low combustion temperatures (around 400 °C) when 33% oxygen was used. When conditions corresponding to the kinetic control regime for the other two chars were used, Wyodak chars still exhibited sharp peaks in their reactivity patterns (see Figure 4.19). In agreement with literature data, earlier results from our laboratory have shown that lower rank coals yield more reactive chars ⁶.

4.4 REFERENCES FOR CHAPTER 4

- (1) Matzakos, A. *Ph.D. Dissertation*; Rice University; 1991.
- (2) Khan, M. R.;Serio, M. A.;Malhotra, R.; Solomon, P. R. *Amer. Chem. Soc., Div. Fuel Chem. Preprints* 1989, 34, 1054-1061.
- (3) Zygourakis, K. *Energy & Fuels* 1993, 7, 33-41.
- (4) Boissiere, F. *M.S. Dissertation*; Rice University; 1993.
- (5) Serio, M. A.;Solomon, P. R.; Bassilakis, R. *Amer. Chem. Soc., Div. Fuel Chem. Prepr.* 1989, 34, 9-21.
- (6) Sandmann, C. W., Jr.; Zygourakis, K. *Chem. Eng. Commun.* 1987, 58, 139-164.

Figure 4.1: Effect of particle size and pyrolysis heating rate on reactivity of Illinois #6 chars in kinetic control regime.

Figure 4.2: Effect of pyrolysis atmosphere on reactivity of Illinois #6 chars in kinetic control regime.

Figure 4.3: Effect of heat treatment temperature on reactivity of Illinois #6 chars in kinetic control regime.

Figure 4.4: Effect of oxygen concentration on reactivity of Illinois #6 chars in kinetic control regime.

Figure 4.5: Arrhenius plot of average reaction rate for Illinois #6 chars gasified using various oxygen concentrations. Reference conversion is 0.25.

Figure 4.6: Average reaction rates vs. oxygen concentration of Illinois #6 chars gasified at various combustion temperatures.

Figure 4.7: Arrhenius plot of the reaction rate constant for Illinois #6 chars.

Size = 50-60 mesh; Rate = 10 °C/s
HTT = 700 °C; Combustion at 550 °C

Figure 4.8: Reactivity patterns for Illinois #6 chars (50-60 mesh) using different oxygen concentrations.

Fig 4.9: Reactivity patterns for Illinois #6 chars (28-32 mesh) using different oxygen concentrations and combustion temperatures.

Figure 4.10: Reactivity patterns for Illinois #6 chars (50-60 mesh) produced using various pyrolysis heating rates.

Figure 4.11: Reactivity patterns for Illinois #6 chars (28-32 mesh) produced using various pyrolysis heating rates.

Figure 4.12: Reactivity patterns for chars of various particle size fractions produced using 20 °C/s.

Figure 4.13: Reactivity patterns for chars of various particle size fractions produced using 1.0 °C/s.

Figure 4.14: Reactivity patterns for Illinois #6 (28-32 mesh) chars produced using different heat treatment temperatures.

Size = 28-32 mesh; HTT = 625 °C; Rate = 10 °C/s
Combustion at 550 °C and 33% O₂

Figure 4.15: Reactivity patterns for Illinois #6 chars produced in inert and reactive atmospheres.

Figure 4.16: Reactivity patterns for Utah Blind Canyon chars gasified at 550 °C and 33% oxygen for different pyrolysis heating rates.

Figure 4.17: Reactivity patterns for Utah Blind Canyon chars gasified at 420 °C and 21% oxygen for different pyrolysis heating rates.

Figure 4.18: Reactivity patterns for Wyodak chars gasified at 420 °C and 33% oxygen for different pyrolysis heating rates.

Figure 4.19: Reactivity patterns for Wyodak chars gasified at 420 °C and 21% oxygen for different pyrolysis heating rates.

CHAPTER 5

A MATHEMATICAL MODEL FOR CHAR PARTICLE IGNITION

5.1 INTRODUCTION

Char particle ignition is an interesting and important phenomenon in coal gasification whose history goes back to Faraday and Lyell ^{1,2}. Coal or char particles can ignite either homogeneously or heterogeneously. Homogeneous ignition occurs in the gaseous phase around the particle when the release of volatiles is faster than the rate of heating of the particle surface. Heterogeneous ignition takes place on the char particle surface and interior when the rate of particle heating is faster than the rate of heat removal. At intermediate conditions, the two mechanisms of ignition may happen simultaneously ³.

Heterogeneous ignition is the dominant mechanism for coal chars because all volatiles have been removed during the pyrolysis stage. This is particularly true in the case where the coal has been pyrolyzed at high heating rate, high heat treatment temperature and long soak time ⁴.

Several investigators have experimentally observed char ignition using different methods ^{2, 5, 6}. When combustion is observed with video microscopy, ignition appears as a luminous flame engulfing the char particle. The duration of the flame is in the order of one second. This phenomenon may appear on the reactivity plot as a "spike" or a sharp and sudden increase in the reaction rate for a small interval of conversion before the extinction happens. During this short time, a large amount of heat is released to the surrounding. Measurement of product gas concentration reveals that the concentration changes rapidly at the time of ignition ⁷.

Another experimental observation is that ignition is initiated in localized reactive spots on the particle surface and then propagates all over the entire surface ⁸. More interestingly, at least two investigators have reported multiple ignitions on one particle. Up to a dozen multiple ignitions

for some particles have been observed in our previous experimental work ⁴. Solomon and coworkers ⁹ have observed a primary and then a more intense secondary ignition of particles injected into a hot gas stream. Until recently, however, few experimental studies attempted to quantify systematically the effects of process conditions (particle size, bulk concentration, and pyrolysis heating rate) on char ignition. Most of the results in this area come from theoretical studies.

The ignition phenomenon has been modeled in several ways. The Thermal Explosion Theory (TET), first formulated by Samenov, has been used to describe both the heterogeneous and homogeneous ignitions ^{2, 10}. Briefly stated, the ignition happens when the heat generation curve (sigmoidal line) and the heat loss curve (straight line) intercept and the surface particle temperature takes the higher stable temperature.

A family of detailed models of coal ignition has been presented by Sotirchos and Amundson ^{11, 12, 13, 14} who developed a comprehensive model to simulate the reaction, mass and heat transfer in the particle and in the surrounding boundary layer. The work of Sotirchos and Amundson predicts that there is a region of ambient temperatures where the solid temperature can take three steady-state values. The first is a stable steady state temperature that is slightly higher than the ambient. This is the situation when the oxygen penetrates the entire particle and reacts uniformly with the solid reactant. The second solution is unstable and the particle temperature is higher than the ambient. The third solution, which is stable, gives a particle temperature that is considerably higher than the ambient. In this case, the particle ignites homogeneously when carbon dioxide reacts with the carbon to produce carbon monoxide that burns in a sheath surrounding the particle. The model also predicts that larger particle size and larger pore radius reduce the ignition temperature.

The main parameters of ignition models are those describing the internal structure of the particles. In the absence of this information, the model may give qualitatively correct predictions but without satisfactory agreement with experiments. Therefore, it is important that we incorporate accurate measurements of the pore structure of chars in any ignition model.

The objective of our studies, then, was to combine our theoretical and experimental results of char particle ignition. A steady-state mathematical model was developed to describe char particle ignitions. Results from

macropore structure measurements of chars produced under different process conditions were used to compute all the model parameters. The model was used to systematically investigate the effect of porosity, particle size, macropore surface area, micropore radius, and the flow rate on ignition phenomena. Model predictions confirmed the effects of process conditions on reactivity we observed experimentally.

5.2 PYROLYSIS AND COMBUSTION EXPERIMENTS

Sequential pyrolysis and combustion experiments were carried out in the thermogravimetric reactor with in-situ video microscopy imaging (TGA/VMI) described in Chapter 2. Three size fractions of Illinois #6 coal from the Argonne premium coal sample collection [Vorres, 1990 #43] were used for the ignition studies: 20-25 mesh (710-840 μm), 28-32 mesh (500-600 μm) and 50-60 mesh (250-300 μm). Ignition experiments are repeated at least three times to check for reproducibility. The experimental conditions for the pyrolysis and combustion stages are as listed in Table 5.1. Since our chars react in the regime of kinetic control at temperatures below 500 $^{\circ}\text{C}$, combustion temperatures for the ignition studies were chosen so that the reaction will take place in the regime where intraparticle diffusional limitations become important.

Table 5.1
Experimental Conditions for Pyrolysis and Combustion Experiments

Pyrolysis Stage	
Heating Rate ($^{\circ}\text{C}/\text{s}$)	0.1, 1.0 and 10.0
Final Heat treatment Temperature or HTT ($^{\circ}\text{C}$)	700
Soak time (min)	3
Pyrolysis Atmosphere	Pure Nitrogen
Combustion Stage	
Reaction Temperature ($^{\circ}\text{C}$)	550 and 625
Oxygen concentration (balance is Nitrogen)	21% and 33%
Gas Flow Rate (std. cm^3/min)	360

5.3 DEVELOPMENT OF MATHEMATICAL MODEL

5.3.1 Heat and mass balances

Let us assume that the concentration of gaseous reactant (oxygen) is uniform throughout a spherical particle with radius R . The steady-state mass balance is then given by

$$4\pi R^2 k_g (C_f - C_s) = \frac{4}{3} \pi R^3 \eta k_o \exp\left(\frac{-E}{R_c T_s}\right) C_s \quad (5.1)$$

where C_f is the concentration of oxygen in the bulk phase, C_s is the concentration of oxygen in the reacting particle, k_g is the mass transfer coefficient, η is the effectiveness factor for the first order reaction, k_o is the pre-exponential factor of the reaction rate expression, E is the activation energy, and R_c is the gas constant.

If we also assume uniform particle temperature, the steady-state heat balance becomes

$$4\pi R^2 h (T_s - T_f) = (-\Delta H_R) \frac{4}{3} \pi R^3 \eta k_o \exp\left(\frac{-E}{R_c T_s}\right) C_s \quad (5.2)$$

where T_s is the particle temperature, T_f is the temperature of the ambient gas, h is the heat transfer coefficient and $(-\Delta H_R)$ is the heat of reaction. The results from our kinetic study reveal that the combustion reaction is first order with respect to oxygen concentration. The values for the activation energy and pre-exponential factor were found to be 34.5 kcal/mol and $7.30 \times 10^7 \text{ sec}^{-1}$, respectively. In this model, only the heterogeneous reaction

is considered^{8, 17}. The reaction is exothermic and the heat of reaction, $(-\Delta H_R)$ at standard conditions equals to 220.0 kJ/mol.

If we solve equation (1) for C_s and substitute this expression in the heat balance (equation (2)), the following algebraic equation is obtained:

$$Q_r = \frac{3h}{Rk_g C_f} (T_s - T_f) = \frac{(-\Delta H_R) \eta k_o \exp(\frac{-E}{R T_s})}{\frac{R}{3} \eta k_o \exp(\frac{-E}{R T_s}) + k_g} = Q_g. \quad (5.4)$$

The left hand side of the above equation gives the rate Q_r of heat removal, while the right hand side gives the rate Q_g of heat generation. A straight line is obtained if we plot the heat removal function Q_r vs. T_s (at a fixed T_f), while a plot of Q_g vs. T_s yields a sigmoidal curve. The intersections of these two curves give the steady state solutions T_s of equation (4). The bisection method was used to solve the algebraic equation (4) for T_s at each T_f . Depending on the operating conditions and the ambient gas temperature T_f , there might exist one, two or three steady state solutions for equation (4).

5.3.2 Estimation of transport properties

Heat and mass transfer coefficients h and k_g are estimated using the correlations¹⁸ for forced convection around a sphere given by

$$\frac{h(2R)}{k_f} = 2.0 + 0.6 \text{Re}^{1/2} \text{Pr}^{1/3} \quad (5.5)$$

and

$$\frac{k_g(2R)}{D_{AB,f}} = 2.0 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad (5.6)$$

where the Reynolds, Prandtl and Schmidt numbers are defined by

$$\text{Re} = \frac{(2R)v_\infty \rho_f}{\mu_f} \quad (5.7)$$

$$\text{Pr} = \left(\frac{C_p \mu}{k} \right)_f \quad (5.8)$$

$$\text{Sc} = \left(\frac{\mu}{\rho D_{AB}} \right)_f \quad (5.9)$$

respectively, and where k_f is the bulk thermal conductivity, $D_{AB,f}$ is the bulk binary diffusion coefficient, v_∞ is the velocity of the ambient gas flowing around the sphere, ρ_f is the bulk density, μ_f is the bulk viscosity, and C_p is the heat capacity at constant pressure for the bulk gas. Using the above correlations, the model will also allow us to investigate the effects of ambient gas flow rates on ignition through the Reynolds number. In the case of stagnant fluid, the Reynolds number vanishes and the Nusselt and Sherwood numbers in equations (5) and (6) respectively reduce to 2.0.

Thermal conductivities of the pure gases are computed using a modified Eucken approximation ¹⁹ and the thermal conductivity of gas mixtures is estimated by a method suggested by Mason and Saxena ¹⁸. Heat capacities are determined using the empirical equation given by Felder and Rousseau ²⁰ and viscosities are calculated using the estimation presented by Thodos and coworkers (Perry, Green et al. 1984). The binary diffusion coefficients are estimated from the Fuller, Schettler, and Giddings relation ¹⁹.

5.3.3 Bimodal Pore Size Distribution and Effectiveness Factor

The effectiveness factor η , must account for diffusional resistances in both the micropores and the macropores, since the pore structure of chars is characterized by a bimodal size distribution. For this purpose, the model proposed by Mingle and Smith ^{21, 22} is used. The mass balance for the micropores can be written as

$$D_\mu \frac{d^2 C_\mu}{dz^2} = \frac{2}{r_\mu} k_s C_\mu \quad (5.10)$$

where C_μ is the oxygen concentration in the micropores, z is the axial coordinate in the cylindrical micropores, D_μ is the diffusion coefficient for micropores, k_s is the surface reaction rate constant and r_μ is the micropore radius. The boundary conditions for equation (10) are

$$\frac{dC_\mu}{dz} = 0 \quad @ z = 0$$

and

$$C_\mu = C_M \text{ @ } z = L_\mu \quad (5.11)$$

where L_μ is the micropore length and C_M is the concentration at the end of the micropore where it opens up into a large macropore. Solving equation (10) with the boundary conditions (11) we obtain the effectiveness factor η_μ for the micropores:

$$\eta_\mu = \frac{\tanh \phi_\mu}{\phi_\mu} \quad (5.12)$$

where the Thiele modulus ϕ_μ is defined by

$$\phi_\mu = L_\mu \sqrt{\frac{2k_s}{r_\mu D_\mu}} \quad (5.13)$$

The size of the micropores, L_μ , is estimated as the ratio of volume to surface area of solid as follows

$$L_\mu = \frac{1 - \varepsilon}{2S_g} \quad (5.14)$$

where S_g is the specific macropore surface area and ε is the macroporosity. This estimate is valid when the average macropore size is large compared to the average micropore size. This is particularly true for the thin-walled chars produced at high pyrolysis heating rates.

The mass balance giving the concentration C_M of oxygen in the macropores becomes

$$D_{eff} \frac{d^2 C_M}{dr^2} = k_o \exp\left(\frac{-E}{R_c T_s}\right) \eta_\mu C_M \quad (5.15)$$

where r is the radial coordinate for the spherical particle and D_{eff} is the effective diffusion coefficient for the macropores. The Thiele modulus in this case is

$$\phi_M = \frac{R}{3} \sqrt{\frac{k_o \exp(\frac{-E}{R_c T_s}) \eta_\mu}{D_{eff}}} \quad (5.16)$$

and the overall effectiveness factor η is

$$\eta = \eta_\mu \frac{\tanh \phi_M}{\phi_M} \quad (5.17)$$

or

$$\eta = \eta_\mu \eta_M \quad (5.18)$$

The diffusion coefficient D_μ in the micropores is calculated assuming Knudsen diffusion and the micropore radius, r_μ , is taken to be 5 Å since this is considered to be the size separating the micropores from submicropores. Our measurements of macropore radius reveal that the macropore radius is larger than 1000 Å. Therefore, the effective diffusion coefficient, D_{eff} , can take the value of the bulk diffusion coefficient.

5.4 EFFECT OF CHAR STRUCTURAL PARAMETERS AND REACTION CONDITIONS ON PARTICLE IGNITIONS

A systematic parametric study was carried out to quantify the effect of different process parameters on the ignition phenomena. Table 5.2 lists the base values of the model parameters used for this study.

5.4.1 The effect of Oxygen Concentration

Typical plots of T_s vs. T_f are shown in Figure 5.1 for various oxygen concentrations. When multiple solutions exist, the plots have the classical hysteresis form and we can define:

- (a) T_L , as the minimum ignition temperature, and
- (b) T_U as the upper temperature limit of the multiplicity region.

Table 5.2

Base values for Structural parameters and
Combustion Conditions

Parameter	Base Value
Particle Diameter	0.39 mm
Macroporosity	0.72
Macropore Surface Area	$2951 \text{ cm}^2/\text{cm}^3$
Micropore Radius	$5 \text{ \AA}$
Oxygen Concentration	33%
Bulk Velocity	0 cm/s (stagnant fluid)

When the ambient temperature is smaller than T_L , we have only one steady-state solution corresponding to a low particle temperature. For ambient temperatures in the range $T_L < T_f < T_U$, we have three steady-state solutions for the particle temperature: a low value (unignited state), a high value (ignited state) and an intermediate value that is unstable. For ambient temperatures above T_U , the particle can exist only in the ignited state characterized by a high solid temperature T_s .

Figure 5.1 shows that the oxygen concentration has a significant influence on the likelihood of particle ignitions. High oxygen concentrations reduce the minimum ignition temperature T_L and broaden the multiplicity region. For a particular ambient temperature in the multiplicity region, the ignited particle temperature increases with increasing oxygen concentration.

The effect of oxygen concentration on the multiplicity region is shown more clearly on Figure 5.2 where the limits of the multiplicity region [T_L, T_U] are plotted as a function of bulk oxygen concentration. As the oxygen concentration decreases, the multiplicity region shrinks and disappears completely for low oxygen concentrations (lower than about 20% for our steady-state model). The minimum ignition temperature increases rapidly as

the oxygen concentration decreases.

5.4.2 Larger Particles Ignite More Easily

The effect of particle size on the multiplicity region is shown in Figure 5.3. These results indicate that larger particles ignite more easily, since the minimum ignition temperature decreases with increasing particle size. No multiple steady states are predicted for particles smaller than 0.1 mm in diameter. As the size decreases, the multiplicity region shrinks as depicted in the plots of T_L and T_U vs. particle diameter of Figure 5.4.

Our model predictions agree with the predictions of the distributed model developed by Sotirchos and Amundson^{11, 12}. These investigators concluded that the minimum ignition temperature decreases with increasing particle size. The larger particles have a lower external surface to volume ratio and the heat removal is less efficient. Therefore, particle overheating and thermal ignition take place at lower ambient temperatures.

5.4.3 Large Values of Macroporosity and Macropore Surface Area Lower Particle Ignition Temperatures

Figure 5.5 shows the effect of particle macroporosity on the multiplicity region. Particles with larger macroporosity will ignite more easily, since their pore surface area is more accessible to the gaseous reactants. The resulting decrease in intraparticle diffusional limitations leads to higher rates of reaction and heat generation. Figure 5.6 shows that the upper temperature limit of the multiplicity region T_U is virtually independent of macroporosity, while the minimum ignition temperature T_L decreases with increasing macroporosity. At very low macroporosity (less than 0.35), only one steady solution is possible.

The macropore surface area has a similar effect on the multiplicity region, since the reaction rate in the regime of diffusional limitations becomes proportional to the surface area of the macropores. Figures 5.7 and 5.8 show the effect of macropore surface area on the multiplicity region. Particles with high macropore surface areas will ignite more easily than

particles with low macropore surface areas. Again, the upper temperature limit T_U of the multiplicity region is virtually independent of the surface area of macropores S_g while the minimum ignition temperature T_L decreases with increasing S_g .

The behavior shown in Figures 5.7 and 5.8 is expected since larger macropore surface areas enhance the reaction rate and increase the rate of heat generation inside the particle.

5.4.4 Micropore Radius Affects Ignition Temperatures

The model also predicts that increases in the average micropore radius will decrease the minimum ignition temperature and widen the multiplicity region. This effect is shown in Figures 5.9 and 5.10. When the average micropore radius is large, diffusional limitations in the micropores will diminish making more surface area available for reaction and increasing the combustion rates.

Figure 5.10 shows that the minimum ignition temperature T_L decreases very rapidly as the micropore radius increases from 1 Å to 6 Å. For micropore radii larger than 6 Å, the minimum ignition temperature is almost independent of the micropore radius. Except for a very small drop for small micropore radii, the upper temperature limit of the multiplicity region T_U remains constant at 740 °C.

5.4.5 Large Gas Flow Rates Quench Char Particle Ignitions

The velocity of the ambient gas flowing around a burning particle has an important influence on the rates of external mass and heat transfer. Until now, only stagnant fluid around the particle was considered. The assumption of stagnant flow is valid for the particles located in the middle of the TGA sample pan. However, particles close to the edges of the pan should experience significant fluid velocities.

Our model was also used to study the effect of fluid velocity. Figures 5.11 and 5.12 present the model predictions for various fluid velocities around the particle. These plots reveal that the minimum ignition temperature increases

with increasing flow rate. High gas flow rates increase the heat transfer coefficient, thus enhancing the heat removal rates and preventing thermal ignition at low ambient temperature. These predictions agree with our earlier experimental results ⁴.

5.4.5 Summary

Our simple steady-state model predicts that the likelihood of particle ignition increases with

- increasing oxygen concentration,
- increasing particle size,
- increasing macroporosity,
- increasing macropore surface area,
- increasing micropore radius, and
- decreasing fluid velocity of the ambient gas.

5.5 COMPARISON WITH EXPERIMENTAL RESULTS

To determine whether our mathematical model is able to predict the ignition behavior we observed experimentally, we computed the multiplicity regions for all the process conditions used for our experimental runs. The values of the particle radius, porosity and macropore surface area used in this study are listed in Table 5.3 for the 50-60 mesh size fraction and Table 5.4 for the 28-32 mesh size fraction respectively. These structural parameters were measured with the methods described in detail elsewhere ^{23, 24}.

Since the data in Tables 5.3 and 5.4 were obtained from direct measurement in our lab, model predictions can be used to explain the experimental observations of the effect of process conditions on char particle ignition. For the subsequent discussion, only stagnant flow is considered and the micropore radius is taken to be 5 Å.

Table 5.3

Effect of pyrolysis heating rate on char structure.
Coal particle size: 50-60 mesh ²³.

Heating rate °C/s	Average particle radius, μm	Macroporosity	Macropore surface area, cm^2/cm^3
0.1	168.5	0.33	659
1.0	168.5	0.55	1,479
10.0	195.6	0.72	2,951

Table 5.4

Effect of pyrolysis heating rate on char structure.
Coal particle size: 28-32 mesh ²⁴.

Heating rate, °C/s	Average particle radius, μm	Macroporosity	Macropore surface area, cm^2/cm^3
0.1	317.0	0.59	853
1.0	325.0	0.60	1,260
10.0	407.0	0.65	1,046

5.5.1 Effect of pyrolysis heating rate

Our experimental results showed that the pyrolysis heating rate significantly affects the radius of the char particles as well as their macroporosity and macropore surface area. These results are tabulated in Tables 5.3 and 5.4 above. Consequently, the pyrolysis heating rate has a profound effect on the likelihood of particle ignitions.

The model predictions showing this effect are presented in Figure 5.13

for the 50-60 mesh particles. In this case, the model predicts that the ignition is only possible for char particles produced at the highest heating rate of 10 °C/s, when the char is gasified at 550 °C with 33% oxygen. Note also that the multiple solution region does not exist for particles produced at the other two pyrolysis heating rates. These results are in excellent agreement with the experimental results presented in Figure 5.14 where we plot the reaction rate defined as follows:

$$R_s(t) = \frac{1}{1-x} \frac{dx}{dt} = -\frac{1}{m(t)} \left(\frac{dm(t)}{dt} \right) \quad (5.19)$$

where x is the conversion of the solid and $m(t)$ is the mass of char remaining unreacted at time t . The plots in Figure 5.14 show that the char ignites only when the highest pyrolysis heating rate 10 °C/s is used to prepare the chars. This is depicted on the curve as a "spike" or sharp increase of the reaction rate for a very short time. The ignition is also observed and recorded in our video sequences as a luminous flame engulfing the char particle. As shown in Table 5.3, high heating rates produce chars with large macroporosities and macropore surface areas. Our parametric study shows that the minimum ignition temperature decreases with increasing macroporosity and macropore surface area due to enhancements in the combustion rates.

The simulation results for 28-32 mesh particles are shown in Figure 5.15. When combustion is carried out at 550 °C with 33% oxygen, model predictions show that ignitions are possible for char particles produced at pyrolysis heating rates of 10 and 1 °C/s. These model predictions agree with our experimental results reported on Figure 5.16.

5.5.2 Effect of particle size

Video tapes from combustion experiments show that larger char particles tend to be more reactive and to ignite more easily. Figures 5.17 and 5.18 present the model predictions on the effect of particle size for two pyrolysis heating rates (10 and 1 °C/s respectively).

For the higher heating rate of 10 °C/s (Figure 5.17), the model predicts that both size fractions will ignite at a combustion temperature of 550 °C with

33% oxygen. The larger particles will achieve a slightly higher solid temperature. On the other hand, Figure 5.18 indicates that only the larger particles (28-32 mesh fraction) may ignite, when the lower heating rate of 1 °C/s is used to prepare the chars. These results confirm our experimental observations of the effect of particle size presented in Figures 5.19 and 5.20.

5.5.3 Effect of oxygen concentration

Some model predictions of the effect of ambient oxygen concentration on particle ignitions are presented in Figures 5.21 and 5.22 for the two mesh fractions chars (50-60 and 28-32 mesh, respectively) produced using 10 °C/s.

In both cases, the model predicts that the minimum ignition temperature decreases with increasing oxygen concentration. There is only one solution (unignited state) when combustion takes place at 550 °C with 21% oxygen concentration. Therefore, we do not expect to observe particle ignitions when these three chars are reacted at these conditions. However, the model predicts three steady-states when these three chars are burned at 550 °C with 33% ambient oxygen concentration. All these predictions are in excellent agreement with our experimental observations presented in Figures 5.23 and 5.24.

Another interesting comparison between model and experiment that should be pointed out here involves the results for the char produced from 28-32 mesh coal particles at 10 °C/s pyrolysis heating rate and combusted at 625 °C with 21% oxygen concentration. Although the experimental reactivity pattern (Figure 5.24) shows some sharp changes in the reaction rate (possibly indicating ignition), no flames were visible on the video sequences for these experiments and only sudden and rapid consumption of the particles was observed. One possible explanation for this behavior can be based on the model predictions shown in Figure 5.24. These predictions show an ignited steady-state solution for 21% oxygen concentration that is a few hundred degrees lower than the ignited particle temperature predicted for 33% oxygen concentration.

5.6 CONCLUSIONS

A simple steady state model was developed to describe the ignition phenomena observed in our experiments. The model parameters are computed using our structural measurements (macropore structure and particle swelling) for chars produced using different pyrolysis conditions.

The results from a parametric study carried out with this model indicate that the minimum ignition temperature decreases with increasing macroporosity, increasing macropore surface area, and decreasing bulk flow rate.

Model predictions of the effect of pyrolysis heating rate, particle size, and oxygen concentration is in excellent agreement with experimental results. Moreover, the model estimates the particle temperature during ignition and the minimum ignition temperature for various process conditions. The minimum ignition temperature decreases with increasing heating rate, particle size, and oxygen concentration.

The model predictions explain the perhaps counter-intuitive experimental results showing that large coal particles react faster than smaller particles in the regime of diffusional limitations. This is because the larger particles ignite more easily and ignitions bring the particle temperature to much higher values.

5.7 REFERENCES FOR CHAPTER 5

- (1) Faraday, M.; Lyell, C. *Philos. Mag.* 1845, 26, 16-21.
- (2) Essenhigh, R. H.; Misra, M. K.; Shaw, D. W. *Combust. Flame* 1989, 77, 3-30.
- (3) Fu, W. B.; Zeng, T. F. *Combust. Flame* 1992, 88, 413-424.
- (4) Matzakos, A. *Ph.D. Dissertation*; Rice University; 1991.
- (5) Tognotti, L.; Malotti, A.; Petarca, L.; Zanelli, S. *Combust. Sci. Technol.* 1985, 44, 15-28.

- (6) Zhang, D.-k.; Hills, P. C.; Wall, T. F.; Tate, A. G. *Fuel* 1992, 71, 1206-1207.
- (7) Gomez, C. O.; Vastola, F. J. *Fuel* 1985, 64, 558-63.
- (8) Levendis, Y. A.; Sahu, R.; Flagan, R. C.; Gavalas, G. R. *Fuel* 1989, 68, 849-55.
- (9) Solomon, P. R.; Chien, P. L.; Carangelo, R. M.; Serio, M. A.; Markham, J. R. *Combust. Flame* 1990, 79, 214-15.
- (10) Semenov, N. Z. *Physik* 1928, 48, 571-582.
- (11) Sotirchos, S. V.; Amundson, N. R. *Ind. Eng. Chem. Fundam.* 1984, 23, 180-91.
- (12) Sotirchos, S. V.; Amundson, N. R. *Ind. Eng. Chem. Fundam.* 1984, 23, 191-201.
- (13) Sotirchos, S. V.; Amundson, N. R. *AIChE J.* 1984, 30, 537-549.
- (14) Sotirchos, S. V.; Amundson, N. R. *AIChE J.* 1984, 30, 549-556.
- (15) Matzakos, A. N.; Zygorakis, K. *Rev. Sci. Instrum.* 1993, 64, 1541-1548.
- (16) Vorres, K. *Energy & Fuels* 1990, 4, 420-426.
- (17) Mitchell, R. E. *Comb. Sci. Tech.* 1987, 53, 165-175.
- (18) Bird, R. B.; Stewart, W. E.; Lightfoot, E. N. *Transport Phenomena*; John Wiley and Sons: New York, 1960; pp 647-648.
- (19) Perry, R. H.; Green, D. W.; Maloney, J. O. *Perry's Chemical Engineers' Handbook*; McGraw-Hill: New York, 1984; pp 3-278 - 3-288.
- (20) Felder, R. M.; Rousseau, R. W. *Elementary Principles of Chemical Processes*; John Wiley and Sons: New York, 1978; pp 535-537.
- (21) Mingle, J. O.; Smith, J. M. *AIChE J.* 1961, 7, 243-249.
- (22) Froment, G. F.; Bischoff, K. B. *Chemical Reactor Analysis and Design*; John Wiley and Sons: New York, 1979; pp 151-165.
- (23) Zygorakis, K. *Energy and Fuels* 1993, 7, 33-41.
- (24) Boissière, F. M.Sc. *Dissertation*; Rice University, 1993.

Figure 5.1: Model predictions of the effect of oxygen concentration on char ignition.

Figure 5.2: Effect of oxygen concentration on the multiplicity region.

Figure 5.3: Model predictions of the effect of particle size on char ignition.

Figure 5.4: Effect of particle size on the multiplicity region.

Figure 5.5: Model predictions of the effect of macroporosity on char ignition.

Figure 5.6: Effect of macroporosity on the multiplicity region.

Figure 5.7: Model predictions of the effect of macropore surface area on char ignition.

Figure 5.8: Effect of macropore surface area on the multiplicity region.

Figure 5.9: Model predictions of the effect of micropore radius on char ignition.

Figure 5.10: Effect of micropore radius on the multiplicity region.

Figure 5.11: Model predictions of the effect of fluid velocity on char ignition.

Figure 5.12: Effect of fluid velocity on the multiplicity region.

Figure 5.13: Effect of pyrolysis heating rate on ignition for 50-60 mesh fraction chars.

Figure 5.14: Reactivity patterns for 50-60 mesh fraction chars produced using various pyrolysis heating rates.

Figure 5.15: Effect of pyrolysis heating rate on ignition for 28-32 mesh fraction chars.

Figure 5.16: Reactivity patterns for 28-32 mesh fraction chars produced using various pyrolysis heating rates.

Figure 5.17: Effect of particle size on ignition for chars produced using 10 °C/s.

Figure 5.18: Effect of particle size on ignition for chars produced using 1.0 °C/s.

Figure 5.19: Reactivity patterns for chars of various particle size fractions produced using 20 °C/s.

Figure 5.20: Reactivity patterns for chars of various particle size fractions produced using 1.0 °C/s.

Figure 5.21: Effect of oxygen concentration for 50-60 mesh fraction chars produced using pyrolysis heating rate 10 °C/s.

Figure 5.22: Effect of oxygen concentration on ignition for 28-32 mesh fraction chars produced using pyrolysis heating rate 10 °C/s.

Figure 5.23: Reactivity patterns for 50-60 mesh fraction chars using different oxygen concentrations.

Figure 5.24: Reactivity patterns for 28-32 mesh fraction chars using different oxygen concentrations and combustion temperatures.

CHAPTER 6

ACCOMPLISHMENTS AND CONCLUSIONS

6.1 COAL PYROLYSIS AND PARTICLE SWELLING

Using the TGA/VMI reactor, we are able to quantify the effect of several process conditions on particle swelling and devolatilization rate of three coals.

One of the most important conclusions of our work concerns the importance of the transient swelling patterns of pyrolyzing plastic coals. Using a novel image analysis procedure, we monitored the transient changes in particle size and shape during pyrolysis. Our results show conclusively that the final size and shape of char particles is not always a good indicator of the structural changes occurring as the particles release their volatiles. Under some conditions, plastic coal particles swell, release their volatiles and then contract again almost back to their original size. We have also observed significant differences in the pattern of volatile release. Illinois #6 coal particles "bubble" vigorously as volatiles are released, while Utah coal particles exhibit a smooth change in particle size without rapid expansions and contractions.

For the two plastic coal we studied (Illinois #6 and Utah Blind Canyon), increasing heating rates produced chars that swelled more and had larger final radii. Also, the devolatilization rate and total weight loss increased when high pyrolysis heating rates were used. These findings agree with earlier structural measurements in our lab that showed char macroporosity and macropore surface area to increase with increasing heating rate.

When the plastic coals were pyrolyzed in reactive atmosphere (5% oxygen; 95% nitrogen), the particles swelled more than when they were pyrolyzed in inert atmosphere (pure nitrogen). However, the presence of oxygen degraded the plasticity characteristics of the coals and less "bubbling"

was observed. The total weight loss and devolatilization rate during pyrolysis stage decreased with increasing oxygen composition.

We measured the swelling ratio for different particle sizes and found that it increases with particle size. The devolatilization rate and total weight loss are not affected by the coal particle size.

The two plastic coals we studied (Illinois #6 and Utah Blind Canyon) have similar maximum swelling and final radii for different pyrolysis heating rates. However, the Utah coal does not exhibit vigorous "bubbling" as the swollen pyrolyzing particles shrink to their final size. The devolatilization rate of the Utah coal is lower than that of Illinois #6 coal. Measurements of particle shape factor and elongation indicate that Illinois #6 char particles produced using different process conditions are spherical while Utah Blind Canyon chars tend to elongate.

The third coal used in this study (Wyodak), is not a plastic coal and therefore it does not swell. Moreover, this coal has the lowest devolatilization rate.

6.2 CHAR REACTIVITY

Our studies confirmed the importance of ignition phenomena and systematically explored the effect of process conditions on char reactivity. The TGA/VMI reactor setup allowed us to perform sequential experiments with char combustion immediately following the pyrolysis stage in order to study the effect of pyrolysis conditions on char reactivity.

At temperatures (less than 420 °C) where Illinois #6 chars react in the regime of kinetic control, the combustion rate R_s and the reactivity pattern were not affected by the pyrolysis heating rate, particle size, and pyrolysis atmosphere. Since the oxygen is expected to fully penetrate the micropores of the chars in this regime, these results indicate that the chars have similar micropore structure and intrinsic reactivity. Our studies confirmed literature results showing that the intrinsic reactivity of chars in this regime decreases with increasing heat treatment temperature.

Char particles ignite at higher combustion temperatures where intraparticle diffusional limitations become important. Char particle ignitions occur appear as "spikes" on the reactivity plots and as luminous flames on the experiment video tapes. The likelihood of particle ignitions increases with increasing particle size and increasing pyrolysis heating rate, since higher pyrolysis heating rates produce chars with higher macroporosity, macropore surface area and larger radius. Chars produced in reactive pyrolysis atmosphere (5% O₂ / 95% N₂) ignite more easily since the particle swelling measurements reveal that these chars achieve larger radius at the end of the pyrolysis stage.

In the regime of kinetic control, Utah Blind Canyon chars show reactivity patterns that are very similar to the patterns of Illinois #6 chars. This result indicates that both types of chars have similar micropore structure and intrinsic reactivity. In the diffusional limited regime, however, Utah Blind Canyon chars tend to have multiple ignitions.

Wyodak chars are the most reactive among the chars that we have investigated. They ignite at low temperatures and low oxygen concentrations.

6.3 STEADY-STATE MATHEMATICAL MODEL OF CHAR PARTICLE IGNITION

A simple steady state model was developed to describe the ignition phenomena observed in our experiments. The model parameters were computed using our structural measurements (macropore structure and particle swelling) for chars produced using different pyrolysis conditions.

The results from a parametric study carried out with this model indicate that the minimum ignition temperature decreases with increasing macroporosity, increasing macropore surface area, and decreasing bulk flow rate.

Model predictions of the effect of pyrolysis heating rate, particle size, and oxygen concentration are in very good agreement with experimental results. Moreover, the model estimates the particle temperature during ignition and

the minimum ignition temperature for various process conditions. The minimum ignition temperature decreases with increasing heating rate, particle size, and oxygen concentration.

The model predictions explain the perhaps counter-intuitive experimental results showing that large coal particles react faster than smaller particles in the regime of diffusional limitations. This is because the larger particles ignite more easily and ignitions lead to much higher particle temperature and, consequently, to much higher combustion rates.

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