**DOE/PC/79930-T8
(DE92013241)**

PYROLYSIS AND GASIFICATION OF COAL AT HIGH TEMPERATURES
Final Technical Report for the Period September 15, 1987–September 14, 1991

**By
Kyriacos Zyggourakis**

Work Performed Under Contract No. FG22-87PC79930

**For
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
Rice University
Houston, Texas**

DISCLAIMER

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

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615)576-8401, ~~800-547-8401~~.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

PYROLYSIS AND GASIFICATION OF COAL AT HIGH TEMPERATURES

Final Technical Report

Submitted to the

Department of Energy

Grant Number DE-FG22-87PC79930

Grant Period: 9/15/1987 to 9/14/1991

PRINCIPAL INVESTIGATOR

Kyriacos Zygourakis

**Department of Chemical Engineering
Rice University
Houston, Texas 77251-1892**

DOE Technical Project Officer

James R. Longanbach

Morgantown Energy Technology Center

TABLE OF CONTENTS

CHAPTER 1

PROJECT OBJECTIVES AND SUMMARY OF ACCOMPLISHMENTS.....	1.1
1.1 Project Objectives	1.1
1.2 Importance of Solving the Problem Addressed by the Research	1.1
1.3 Highlight Accomplishments.....	1.4

CHAPTER 2

MACROPORE STRUCTURE OF COAL-DERIVED CHARS	2.1
2.1 Summary	2.1
2.2 Pyrolysis and Char Micropore Structure.....	2.1
2.3 Experimental Procedures.....	2.5
2.3.1 Hot-stage Pyrolysis Reactor	2.5
2.3.2 Image Processing and Analysis.....	2.6
2.4 Pyrolysis of a Plastic Coal.....	2.9
2.4.1 The Effect of Heating Rate.....	2.9
2.4.2 Characterization of the Macropore Structure	2.10
2.4.3 Effects of Coal Particle Size.....	2.15
2.5 Pyrolysis of a Non-Plastic Coal	2.18
2.6 Conclusions	2.20
2.7 References for Chapter 2.....	2.21

CHAPTER 3

PYROLYSIS AND COMBUSTION IN A THERMOGRAVIMETRIC REACTOR SYSTEM WITH VIDEO MICROSCOPY IMAGING (TGA/VMI).....	3.1
3.1 Introduction	3.1
3.2 Development of a TGA Reactor with Video Microscopy Imaging Capabilities (TGA/VIM).....	3.2

3.2.1	Microcomputer Hardware	3.4
3.2.2	Temperature measurement	3.4
3.2.3	Heater control	3.5
3.2.4	Mass flow controllers-Remotely activated devices.....	3.5
3.3	Computer control.....	3.6
3.3.1	Digital control algorithm	3.6
3.3.2	Process model.....	3.6
3.3.3	Performance of control algorithm	3.9
3.4	Experimental Procedures.....	3.11
3.4.1	Sample preparation.....	3.11
3.4.2	Experimental protocol	3.12
3.4.3	Data processing	3.14
3.5	Coal Plasticity and Swelling	3.15
3.6	Devolatilization Rates	3.17
3.7	Macropore structure measurements	3.18
3.8	References for Chapter 3.....	3.19

CHAPTER 4

FUNDAMENTAL MECHANISMS OF COAL COMBUSTION		4.1
4.1	Pore Structure and Coal Char Reactivity	4.1
4.2	Transient Patterns of Char Reactivity	4.3
4.3	Mechanism of Particle Ignitions	4.5
4.3.1	Case I: Particles Exhibit Single Ignitions.....	4.6
4.3.2	Case II: Particles Exhibit Multiple Ignitions.....	4.7
4.4	Particle Ignitions and Reactivity Patterns	4.8
4.5	Effect of flow rate on particle ignitions	4.9
4.6	References for Chapter 4.....	4.9

CHAPTER 5

EFFECT OF PYROLYSIS CONDITIONS ON CHAR REACTIVITY		5.1
5.1.	Effect of heat treatment temperature (HTT) on char reactivity	5.1
5.2.	Effect of soak time on char reactivity	5.2
5.3.	Effect of heating rate on char reactivity	5.3
5.4.	Effect of pyrolysis on combustion	5.4

5.5.	Kinetic measurements	5.6
5.6.	Statistical significance of our results.....	5.9
5.7.	References for Chapter 5.....	5.10

CHAPTER 6

COAL PARTICLE SIZE AND CHAR REACTIVITY.....		6.1
6.1.	Effect of size on intrinsic reactivity	6.1
6.2.	Effect on ignition temperature.....	6.2
6.3	Effect of size on macropore structure	6.2
6.4	Reactivity dependence on heating rate - The role of particle size	6.3
6.5	References for Chapter 6.....	6.5

CHAPTER 7

MODELING OF CHAR GASIFICATION IN THE DIFFUSION- CONTROLLED REGIME.....		7.1
7.1	Summary	7.1
7.2	Model Development.....	7.1
	7.2.1 Cellular Arrays and Reaction Rules	7.2
	7.2.2 Estimating Reaction Rates from Discrete Simulations	7.6
7.3	Computer Implementation.....	7.11
7.4	Reaction in Regime A	7.12
7.5	Reaction in Regime B	7.14
7.6	References for Chapter 7.....	7.16

CHAPTER 1

PROJECT OBJECTIVES AND SUMMARY OF ACCOMPLISHMENTS

1.1 Project Objectives

The macropore structure of chars is a major factor in determining their reactivity during the gasification stage. The major objectives of this contract were to (a) quantify by **direct measurements** the effect of pyrolysis conditions of the macropore structure, and (b) establish how the macropores affected the reactivity pattern, the ignition behavior and the fragmentation of the char particles during gasification **in the regime of strong diffusional limitations**.

Results from this project provide much needed information on the factors that affect the quality of the solid products (chars) of coal utilization processes (for example, mild gasification processes). The reactivity data will also provide essential parameters for the **optimal design** of coal gasification processes.

1.2 Importance of Solving the Problem Addressed by the Research

Pyrolysis is the first stage of direct coal utilization processes. As coal particles are heated, they release most of their volatile constituents in the form of gases and tars. The chemical transformations characterizing the pyrolysis stage are accompanied by complex

morphological transformations that determine the pore structure and, consequently, the reactivity of the produced chars during the subsequent combustion or gasification stage.

Coals can be broadly categorized as **plastic** or **non-plastic** according to their behavior during pyrolysis. Plastic coals soften as they are heated up and behave as highly viscous non-newtonian fluids over a broad temperature range. The volatile gases form bubbles that grow and coalesce swelling the coal particles and leading to the formation of highly cellular internal pore structures that are characteristic of chars derived from plastic coals. Non-plastic coals, on the other hand, do not soften and do not undergo drastic macropore structure transformations during the pyrolysis stage. Bituminous and subbituminous coals are generally considered to be plastic, while lignites and other low rank coals belong to the non-plastic category.

Although several experimental studies reported that the macropores play an important role in determining combustion rates and burning times of char particles, there exist very little quantitative data on macropore structure characterization. Most investigators have focused their attention on characterizing the micropore structure, measuring the total and active surface area of the micropores and correlating such measurements with char reactivity.

Combustion processes, however, are usually diffusion-limited since the various heterogeneous reactions take place at elevated temperatures. Under such conditions, we expect low utilization of the surface area associated with micropores and transitional pores. Since the larger pores are the main arteries for reactant transport to the smaller ones, reaction in micropores (and transitional pores) should occur only in a small region where these smaller pores intersect a macropore. As the surface of the macropores recedes due to the chemical reaction, new micropore and transitional pore area is exposed. Thus, it becomes reasonable to assume that the smaller pores make a constant contribution to the reaction rate when the rate is expressed per unit area of the macropores.

As temperatures increase and reaction rates become faster, diffusional limitations appear in pores of continuously increasing size. Reactions should occur mostly in the larger macropores that are close to the particle exterior, since internal pores may be inaccessible to reactants. As the reaction continues, however, walls of closed pores will burn away exposing surface area previously unavailable for reaction and leading to substantial particle fragmentation.

The opening of closed porosity, the formation of a progressively more tortuous particle exterior and the fragmentation of the original particles can lead to large enhancements of the observed gasification rates. Since these mechanisms affect the particle burning time and, thus, the carbon load for commercial reactors, they must be understood and analyzed.

It is important, therefore, that we

- **characterize the macropore structure of coal-derived chars;**
- **determine how the pyrolysis conditions affect its development; and**
- **quantify the effect of macropore structure on the reactivity of chars in the regime of strong intraparticle diffusional limitations.**

The above list presents the major contributions of this project. Most of the presented results are new since previous investigations offer little quantitative information on these issues.

The data presented here can provide guidelines about the **optimal heat treatment** of coal that will maximize the reactivity of the produced solid fuels (chars). This is particularly important for mild gasification processes. Highly reactive chars will allow the use of smaller, more economical reactors operating at lower combustion temperatures.

1.3 Highlight Accomplishments

All three tasks outlined in the original proposal for this contract were successfully completed. These are tasks 1, 2 and 4 from the list below. During the contract performance period we also defined and successfully completed an additional task (Task 3) that involved the development of a novel experimental system.

The major accomplishments are presented in the following list of contract tasks.

TASK 1: Coals of different ranks (Illinois #6 and a lignite) were pyrolyzed in a microscope hot-stage reactor. The macropore structure of the produced chars was characterized using video microscopy and digital image processing techniques and essential structural parameters were measured. Careful data analysis quantified the effect of pyrolysis conditions (heating rates, final heat treatment temperatures, and particle size) on the pore structure of the devolatilized chars.

TASK 2: Sequential pyrolysis and gasification experiments were carried out to study the effects of pyrolysis conditions on the macropore structure of coal chars and on their reactivity during combustion with oxygen. The variables we considered were (a) the pyrolysis heating rate, (b) the final heat treatment temperature (HTT), and (c) the soak time at HTT. Sequential pyrolysis and gasification experiments were carried out both on our thermogravimetric reactor and on a hot-stage reactor that allowed **direct observation of pyrolyzing and burning particles under an optical microscope**. The combination of thermogravimetry and video microscopy allowed us to observe for the first time and interpret some interesting transient phenomena such as **self-ignition and fragmentation** of char particles.

TASK 3: To further investigate the transient phenomena occurring during pyrolysis and gasification, we developed a novel reactor system consisting of a thermogravimetric apparatus (TGA) with a special video microscopy imaging (VMI) attachment. The biggest advantage of the new TGA/VMI reactor is that, for the first time, we can **simultaneously**

- observe and record on tape the macroscopic changes in the morphology of pyrolyzing particles and thermal ignitions of burning particles and
- monitor the weight of pyrolyzing or reacting samples.

TASK 4: We developed and tested discrete mathematical models of char gasification. Structural properties of the unreacted chars were used to generate the initial computational grids modeling the pore structure of the solid and the simulations provided the evolution of observed reaction rates with conversion. Averaging of the results from these simulations yielded the expected behavior for each char. Comparisons of experimental data and theoretical predictions identified the fundamental phenomena that must be included in a mathematical description of the process and the development of accurate models for the gasification of coal particles.

CHAPTER 2

MACROPORE STRUCTURE OF COAL-DERIVED CHARs

2.1 Summary

In this section, we present and analyze the effects of pyrolysis heating rate and coal particle size on the macropore structure of chars produced from an Illinois #6 coal and a lignite. The coal particles were pyrolyzed in a captive-sample heated-grid reactor at heating rates ranging between 0.1 and 1,000 °C/s. Image processing and analysis procedures were developed to measure the macroporosity of the char samples, the total surface area and the shape of the macropores. The results for the Illinois #6 coal showed that high pyrolysis heating rates produced chars with larger macroporosities, more open pore structures and larger macropore surface areas. The coal particle size did not affect the sample porosity, but changed the shape of the macropores. Pyrolysis heating rates had only minor effects on the macropore structure of lignite chars. These results indicate that the macropore structure may be a significant factor in determining char reactivity in the regime of strong intraparticle diffusional limitations.

2.2 Pyrolysis and Char Micropore Structure

Pyrolysis is the first stage of direct coal utilization processes. As coal particles are heated, they release most of their volatile constituents in the form of gases and tars. The chemical transformations characterizing the pyrolysis stage are accompanied by complex

morphological transformations that determine the pore structure and, consequently, the reactivity of the produced chars during the subsequent combustion or gasification stage.

Coals can be broadly categorized as plastic or non-plastic according to their behavior during pyrolysis. Plastic coals soften as they are heated up and behave as highly viscous non-newtonian fluids over a broad temperature range. Three phases are found to coexist during this plasticity stage: a viscous (but optically isotropic) coal melt, an anisotropic liquid crystalline phase and a gaseous phase. The volatile gases form bubbles that grow and coalesce swelling the coal particles and leading to the formation of highly cellular internal pore structures that are characteristic of chars derived from plastic coals. Non-plastic coals, on the other hand, do not soften and do not undergo drastic macropore structure transformations during the pyrolysis stage. Bituminous and subbituminous coals are generally considered to be plastic, while lignites and other low rank coals belong to the non-plastic category.

Sinnatt and his co-workers (1924, 1926) were the first to study the internal structure of devolatilized coal particles and they introduced the term "cenosphere" to describe the hollow char particles they obtained under various atmospheres in entrained reactors. Essenhigh and Yorke (1965) used direct photography to measure the particle swelling and the evolution of particle diameter during combustion. After analyzing their measurements with the Nusselt "square law" relationship, they concluded that their particles did not form cenospheres and that combustion occurred only on the exposed outer surface with no significant internal reaction.

Lightman and Street (1968) and Street et. al. (1969) used electron and optical microscopy to study the internal structure of coal particles pyrolyzed in drop furnaces, shock tubes and typical pulverized coal flames. These studies identified four types of devolatilized particles: thin-walled hollow cenospheres, thick-walled hollow cenospheres, "lacy" cenospheres with many internal partitions, and solid particles with very few large pores. The same investigators reported that the internal structure affected the burning rates

and they described a char combustion mechanism that involved irregular erosion of the outer surface of the particle and internal burning, with the particle structure growing progressively more open until it broke up. Mason and Schora (1969, 1970) also investigated petrographically the internal structure of coal chars at various stages of a hydrogasification process. Street et. al. (1969) reported that the macropore structure of the chars produced in nitrogen was more open than that of chars produced in air. In a recent study, however, Tsai and Scaroni (1987) observed exactly the opposite trends and they reported increased particle swelling when the coal was pyrolyzed in an oxidative atmosphere.

Shibaoka (1969) modified the hot-stage microscope first developed by Ivanova and Babii (1966a, b) to obtain via a cine camera direct measurements of the coal/char transformations occurring during combustion of stationary single coal particles. His main conclusions were that (a) the degree of swelling of a coal particle affected its combustion behavior, (b) the combustion of coal particles takes place not only at the surface but also in their interior and (c) the different petrographic components exhibit different combustion rates. Shibaoka also observed that particle swelling increases with increasing heating rate and that smaller particles expand more than larger ones. Bailey et. al. (1990) have also shown that the macropore structure influences the reactivity of chars and they proposed a classification system of char morphology based on the characteristics that affect combustion reactivities.

Although several experimental studies reported that the macropores play an important role in determining combustion rates and burning times of char particles, there exist very little quantitative data on macropore structure characterization. Most investigators have focused their attention on characterizing the micropore structure, measuring the total and active surface area of the micropores and correlating such measurements with char reactivity.

Combustion processes, however, are usually diffusion-limited since the various heterogeneous reactions take place at elevated temperatures. Under such conditions, we expect low utilization of the surface area associated with micropores and transitional pores. Since the larger pores act as the main arteries for reactant transport to the smaller ones, reaction in micropores (and transitional pores) should occur only in a small region where these smaller pores intersect a macropore. As the surface of the macropores recedes due to the chemical reaction, new micropore and transitional pore area is exposed. Thus, it becomes reasonable to assume (see also Gavalas, 1980) that the smaller pores make a constant contribution to the reaction rate when the rate is expressed per unit area of the macropores.

As temperatures increase and reaction rates become faster, diffusional limitations appear in the macropores. Under such conditions, reactions should occur mostly in the larger macropores that are close to the particle exterior, since internal pores may be inaccessible to reactants. As the reaction proceeds, walls of "closed" pores will burn away exposing surface area previously unavailable for reaction and leading to substantial particle fragmentation. The opening of closed porosity, the formation of a progressively more tortuous particle exterior and the fragmentation of the original particles can lead to large enhancements of the observed gasification rates. Since these mechanisms affect the particle burning time and, thus, the carbon load for commercial reactors, they must be understood and analyzed.

It is important, therefore, that we quantitatively characterize the macropore structure of coal-derived chars and determine how the pyrolysis conditions affect its development. Existing literature data offer little quantitative information on the effect of pyrolysis conditions on macropore structures, since past studies have mainly studied the kinetics of pyrolysis reactions and product distributions.

The main objective of this study is to examine and quantify the effect of the

- (a) pyrolysis heating rate and

(b) coal particle size

on the macropore structure of chars produced from two parent coals: a bituminous Illinois #6 and a lignite (Wilcox, Texas). Coal rank, the pyrolysis heating rate and the coal particle size are all expected to have a strong influence on the macropore structure of chars (Hamilton, 1981; Howard, 1981), since these factors govern the kinetic and transport processes occurring during pyrolysis (such as the rate of volatile release, the diffusion of volatiles into the bubbles, the transport of volatiles to the particle exterior etc.). The pyrolysis atmosphere (inert or reactive) may be another important factor (Street et. al., 1969; Tsai and Scaroni, 1987) and it will be considered in a future study.

We will estimate the parameters of the macropore structure using measurements obtained via optical microscopy and digital image processing. Direct microscopic measurements can quantify structural features that cannot even be detected by porosimetry methods (Zygourakis and Glass, 1988). This approach, however, can only be used to characterize pores whose diameters are larger than 2 microns. Porosimetry and gas adsorption techniques must be used to characterize smaller macropores and micropores.

2.3 Experimental Procedures

2.3.1 Hot-stage Pyrolysis Reactor

We carried out pyrolysis experiments in the captive-sample heated-grid reactor described in a previous communication (Glass and Zygourakis, 1988). While incorporating most of the desirable features of earlier reactors with electrically heated grids, our pyrolysis reactor offers two significant advantages.

1. The reactor has a quartz window that allows it to operate as a **high-temperature microscope hot-stage**. This allows us to observe the pyrolysis process under an

optical microscope equipped with video camera. Process information such as elapsed time and reactor temperature are superimposed in alphanumeric form on the video signal. We can thus store complete histories of pyrolysis experiments on videotape for post-processing and analysis of transient phenomena.

2. A sophisticated digital algorithm combining model control and feedback control is used to program and control the reactor temperature. The algorithm runs on a microcomputer equipped with custom-built analog/digital interfaces. This reactor can achieve heating rates ranging from 0.1 °C/s (typical of coking ovens) to 1,000 °C/s (approaching the rates encountered in pulverized coal gasifiers) with very good reproducibility.

For each pyrolysis run, 2 mg coal samples were placed in the wire-mesh holder. The reactor was then purged with nitrogen at a flow rate of 150 ml/min and the pyrolysis experiments were carried out in this inert atmosphere. In order to remove the moisture of the coal sample, the temperature was first raised to 150 °C and kept there for 20 min. The reactor temperature was then ramped at the specified rate to a final heat treatment temperature of 950 °C. At that point, power to the grid was cut off and the reactor was allowed to cool down. Char particles collected from ten runs at each set of conditions were embedded in an epoxy-resin block, and one side of the block was polished to reveal random cross-sections.

2.3.2 Image Processing and Analysis

We used a video microscopy system to analyze the polished section samples. Reflected-light microscopy was performed on an optical microscope (Jena Pol) equipped with a video camera. The video signal was routed to a frame grabber (FG-100, Imaging Technology Inc) attached to the backplane of our image processing computer (VAXstation-

II/GPX, Digital Equipment Corp.). For each char sample, we acquired digitized grey-level (black and white) images of 40 to 60 particle cross-sections. The resolution of each image was 640x480 pixels and the pixel size was equal to 1.08 μm .

The grey-level images were segmented to obtain binary images where the pixels corresponding to the char matrix show up as black, while all other pixels (pores or epoxy) are set to white. Image analysis procedures were then applied to the binary images to identify the macropores and measure their statistics. Figure 2.1A shows a binary image of an entire particle cross-section (left) and a blow-up image (right) of a small area of the same cross-section. Note again that the black areas of these images correspond to the char matrix, while the internal white areas are the cross-sectional profiles of macropores.

The pore profiles identified on the original binary images have very jagged edges due to pixelization errors introduced during the digitization and segmentation steps. Such pixelization errors are evident in Figure 2.1A, both in the original binary image of the entire cross-section and the blow-up image that shows some pore profiles at higher magnification. In order to eliminate possible artifacts introduced by the pixelization errors, we developed and evaluated two procedures for smoothing the pore profile boundaries.

Smoothing Procedure A: Each 640x480 image is first converted to an artificial grey-level image with only two intensity levels (black and white). The sharp boundaries of this grey-level image are then "blurred" by applying a filter with a 3x3 kernel. Finally, the filtered image is segmented and magnified by a factor of 4 to obtain a 2560x1920 pixel binary image with smooth pore profiles and particle boundaries.

Figure 2.1B shows the smoothed image obtained by applying this procedure on the original binary image of Figure 2.1A. Also, the blow-up image of Figure 2.1B shows exactly the same part of the cross-section shown in Figure 2.1A. This blow-up image, in particular, shows that the smoothing procedure eliminated the pixelization that led to boundary jaggedness. In addition, the smoothing procedure filtered out several small pores

that were only one or two pixels wide. This is another desirable result of the smoothing operation, since pores with only a few pixels may be due to noise in the original image.

Smoothing procedure A, however, is very CPU-intensive since it creates and analyzes binary images with 2560x1920 pixels (i.e. 16 times more pixels than the original binary image). We must also note that a large internal macropore profile in the original image of Figure 2.1A opened to the exterior. The smoothing operation broke the wall of this pore profile at a point where it was only one pixel wide.

Smoothing Procedure B: In order to speed up the computation of the structural parameters, we developed and evaluated another smoothing procedure that works on the original 640x480 binary images. An isotropic dilation operation is first applied to the raw images. This operation enlarges the solid part of the binary images and, consequently, shrinks the pores in an isotropic fashion (i.e. the pores shrink by the same amount in all directions). The dilation is followed by an erosion operation. The operations that enlarge and erode pores in an isotropic fashion are special cases of the cellular automata models we presented elsewhere (Zygourakis and Markenscoff, 1990). Figure 2.1C shows the effect of smoothing procedure B on the particle cross-section image of Figure 2.1A. Although the pore profiles of Figure 2.1C appear considerably smoother, they still have a jagged appearance since these binary images have the same spatial resolution as the original ones. Smoothing procedure B also filtered out many small pores.

After identifying the char matrix and the pore profiles for each particle cross-section, we used our image analysis software to obtain the following primary measurements:

- (a) the area of each macropore profile;
- (b) the perimeter (or length) of the boundary of each macropore profile;

- (c) the length of the longest and smallest chords that can fit in each pore profile (these are measurements that provide information on the elongation of pore profiles);
- (d) the total area of each particle cross-section (solid plus pores); and,
- (e) the number of pore profiles per particle cross-section.

Further processing of these primary measurements yielded cumulative statistics for each char sample. Among the parameters we calculated were the total cross-sectional area A_m of two-dimensional macropore profiles, the total area A_p of char particles (pores plus char matrix), and the total length B_m of pore profile boundaries (perimeters). Unbiased estimates of the macroporosity and the macropore surface area were then calculated from these parameters.

2.4 Pyrolysis of a Plastic Coal

2.4.1 The Effect of Heating Rate

A plastic coal (Illinois #6) was studied first. Coal particles in the 50-60 mesh (250-300 μm) range were pyrolyzed in the heated-grid microreactor at five different heating rates: 0.1, 1.0, 10, 100 and 1000 $^{\circ}\text{C/s}$. Figure 2.2 shows binary images of some representative particle cross-sections from each of these five char samples.

The lowest heating rate (0.1 $^{\circ}\text{C/s}$) produced char particles exhibiting a few scattered large cavities with thick walls and several smaller cavities. This is consistent with the accepted pyrolysis mechanism involving formation and growth of volatile gas bubbles. Note that most of the particles shown in Figure 2.2A have retained their angular shape and only a few cenospheres were observed. Calculations indicated a moderate pressure buildup

in the particle interior, since the volatile production rates are slow enough to let the gas escape before the bubbles can grow to a large size.

At faster heating rates, however, the volatile production rates increase substantially leading to considerably higher pressures in the particle interior and, thus, to larger bubble sizes and more particle swelling. At a heating rate of 1 °C/s, the formation of several thin-walled cavities was observed (Figure 2.2B) and several pyrolyzed char particles started exhibiting a distinct cellular internal structure. At still higher heating rates, the cellular internal structure was dominant. Chars pyrolyzed at 100 and 1000 °C/s showed exclusively thin-walled cellular structures with a few large cavities and a group of smaller secondary vesicles formed in the thin walls of the larger ones.

One should note also that large particle swelling occurs at the higher heating rates leading to particles with very high porosity. This is in agreement with results from earlier studies (see, for example, Shibaoka, 1969; Hamilton, 1981).

2.4.2 Characterization of the Macropore Structure

Using image analysis measurements on the two-dimensional pore profiles, we can accurately estimate two important properties of the three-dimensional char structure: the macroporosity ϵ and the macropore surface area density S_v (defined as macropore surface area per unit volume of char particle). We must emphasize that these two properties can be estimated from two-dimensional pore profiles without any restricting assumptions concerning the geometrical shape of the macropores (DeHoff, 1983).

Unbiased estimates of the macroporosity ϵ_m can be obtained (Weibel, 1980) from the two-dimensional particle cross-sections according to the formula

$$\epsilon_m = \frac{A_m}{A_p} \quad (2.1)$$

where A_m is the total cross-sectional area of two-dimensional macropore profiles and A_p is the total area of char particles (pores plus char matrix). An unbiased estimate of the macropore surface area density S_v (expressed in cm^2 of pore surface area per cm^3 of char particle) is given by

$$S_v = \frac{4}{\pi} \frac{B_m}{A_p} \quad (2.2)$$

where B_m is the total length of the boundary length (or perimeter) of pore profiles (Weibel, 1980). We must emphasize again the generality of the above formulae that can provide estimates of ϵ and S_v without any restricting assumptions concerning the geometrical shape of the pores. This is unfortunately not the case with the computation of other pore structure statistics. For example, the size distribution of the macropores can be estimated only if we assume that the macropores have a specific shape (e.g. spherical).

Figure 2.3 quantifies the effect of the pyrolysis heating rate on the char sample porosity. As expected, the macroporosity increases sharply with increasing heating rates. These increases, however, tend to level off at the higher heating rates. The average porosity (middle line in Figure 2.3) was computed from 40 to 60 cross sections for each of the five heating rates. The dashed lines on Figure 2.3 indicate the scatter region for the computed particle macroporosities. Note that the macroporosities computed from the smoothed pore profiles obtained with either smoothing procedure (A or B) were virtually indistinguishable from the macroporosities obtained from the original (raw) images.

In order to quantify the effect of pyrolysis heating rates on particle swelling, we computed the average radius $\bar{r}_p$ of particle cross-sections according to the formula

$$\bar{r}_p = \sqrt{\frac{\sum_{i=1}^N A_i}{N \pi}} \quad (2.3)$$

where N is the total number of analyzed cross-sections ($N = 40 - 60$ for each char sample) and A_i is the total area (solid plus pore profiles) of the i -th cross-section. The average particle radius $\bar{R}_p$ was computed from $\bar{R}_p$ according to the formula

$$\bar{R}_p = \frac{4}{\pi} \bar{r}_p \quad (2.4)$$

(Weibel, 1980). The results are plotted on Figure 2.4 which shows that the Illinois #6 particles swell very little when pyrolyzed at low heating rates (0.1 to 1 °C/s). High heating rates, however, result in considerable particle swelling. These observations agree with the trends reported by Shibaoka (1969) and Hamilton (1981).

We have also computed the average macropore radius $\bar{R}_m$ for each char sample. First, the area-equivalent radius r_j for each pore profile was calculated by the formula

$$r_j = \sqrt{\frac{a_j}{\pi}} \quad (2.5)$$

where a_j is the area of the j -th pore profile. These data were then analyzed to obtain the frequency distribution functions $n(r)$ and $s(r)$ defined as follows.

$n(r) dr$ = fraction of pore profiles with area-equivalent radii between r and $r+dr$; and
 $s(r) dr$ = fraction of total area attributable to pore profiles with area-equivalent radii
 between r and $r+dr$.

Figure 2.5 presents the frequency distributions $n(r)$ and $s(r)$ for the Illinois #6 char obtained at 0.1 °C/s. The two plots show that most of the identified pore profiles are small (note the peak of the top graph at 30 μm^2), but the largest fraction of the area (and consequently most of the porosity) is associated with the largest macropores. The plot giving the $s(r)$ frequency distribution has a maximum at about 10,000 μm^2 .

Since the overwhelming majority of the identified pore profiles are very small, a number average radius would severely underestimate the size of the macropores. Thus, we used the following area-weighted formula to calculate the average radius $\bar{r}_m$ of the macropore profiles

$$\bar{r}_m = \frac{\sum_{j=1}^M a_j r_j}{\sum_{j=1}^M a_j} \quad (2.6)$$

where M is the total number of pore profiles for each char sample. The average macropore radius was then computed by

$$\bar{R}_m = \frac{4}{\pi} \bar{r}_m \quad (2.7)$$

Average pore size calculations assumed that the macropores are spherical cavities and the validity of this assumption (at least for the larger pores) was confirmed via microscopic observations. Figure 2.4 (lower curve) shows the evolution of average macropore radius $\bar{R}_m$ with the pyrolysis heating rate. The average macropore size curve is almost parallel to the curve showing the evolution of the average char particle size with pyrolysis heating rate (upper curve of Figure 2.4).

We must note here that the size distribution of the three-dimensional macropores can be unfolded from the frequency distribution $s(r)$ of the two-dimensional pore profiles according to the procedure we described in a earlier study (Zygourakis and Glass, 1988). That procedure assumes, however, that the macropores are spherical objects. In this study, we will focus our attention on the calculation and analysis of macropore structural properties that do not require any assumptions about the geometric shape of the pores.

Figure 2.6 shows the macropore surface area densities S_v computed from the raw and smoothed images. As the pyrolysis heating rate was raised from 0.1 to 10 °C/s, the

surface area densities computed for the Illinois #6 char samples increased monotonically. At still higher heating rates, however, S_v decreased due to the appearance of very large pore cavities in the highly-swollen char particles (see Figs 2.2D and 2.2E). The property of interest for reaction engineering calculations, however, is the specific macropore surface area S_g expressed in (cm² pore surface)/(cm³ microporous char). Since the macroporosity ϵ_m is known, S_g can be easily calculated from S_v according to the formula

$$S_g = \frac{S_v}{(1 - \epsilon_m)} \quad (2.8)$$

As shown on Figure 2.7, S_g increased monotonically with increasing heating rates. This is an important result since it indicates that chars produced at high pyrolysis heating rates and, therefore, having more open macropore structures may be more reactive during combustion (or gasification) in the regime characterized by significant diffusional limitations in the micropores and transitional pores.

Figures 2.6 and 2.7 show that (as expected) the smoothed images yielded macropore surface areas that were lower (by an almost constant amount) than those computed from the raw (original) images. We believe, however, that the values obtained from the smoothed images are more representative of the true macropore surface areas since the smoothed images should be free from artifacts introduced by video noise and segmentation errors. Note also that the two smoothing procedures A and B gave virtually identical macropore surface areas. Smoothing according to procedure B, however, requires only a small fraction of the CPU time required to implement the smoothing procedure A.

Finally, Figure 2.8 shows a plot of the specific surface area S_g vs. the average particle radius for the five Illinois #6 chars. At least for the coal and the pyrolysis procedure used here, these two quantities appear to be highly correlated. This is not be an unexpected result. Using image analysis techniques, however, we can now obtain the amount of experimental measurements required to develop good correlations based on particle

swelling (an easily measurable property even under process conditions). These correlations can be used to predict (a) the total specific macropore surface area and (b) the char reactivity in the regime where significant diffusional limitations appear in the micropores.

2.4.3 Effects of Coal Particle Size

Heat transfer in pyrolyzing coal particles can be significantly affected by the particle size (Howard, 1981). In order to quantify the effects of particle size on the macropore structure of chars produced from the Illinois #6 coal, two additional size fractions of coal particles were pyrolyzed at 10 °C/s: 25-28 mesh (589-710 μm particle diameter) and 100-120 mesh (125-149 μm particle diameter). Thus, the mass of individual particles varied by about two orders of magnitude for the pyrolysis runs at 10 °C/s. This heating rate was selected in order to facilitate the detection of differences in the pore structure possibly caused by changes in the internal heating rate of the particles.

Fig. 2.9 presents representative cross-sections of char particles produced from the pyrolysis runs at 10 °C/s. A comparison of particle cross-sections revealed different pore structures for the three chars. For the smallest size fraction, we observed that many particles developed cenosphere structures with only few and large spherical cavities per particle. On the other hand, the largest size fraction had only a few particles with very large pores, the pore profiles had very tortuous boundaries and most particles exhibited the characteristic cellular pore structure with small pores embedded in the walls separating the larger cavities.

Differences in the morphology of the pore boundaries were only observed among the three char samples produced from particles of different sizes. In order to characterize the pore morphology, we used the pore shape factor σ defined as follows

$$\sigma = \frac{P^2}{4 \pi A} \quad (2.9)$$

where P is the perimeter of a pore profile and A is its area. The value of the shape factor reflects the complexity of the pore boundary. A perfect circle yields the minimum value $\sigma = 1$ for the shape factor, while complex cross-sectional shapes yield values of σ substantially higher than unity.

Shape factor analysis of the two-dimensional pore profiles identified significant differences among the three Illinois #6 chars produced from different particle sizes. Our analysis was based on the frequency distribution function $f(\sigma)$ defined as follows:

$f(\sigma) d\sigma$ = fraction of total pore area attributed to pore profiles with shape factors between σ and $\sigma+d\sigma$.

The computed distributions $f(\sigma)$ for the three char samples are presented on Fig. 2.10. Most of the macroporosity in the 100-120 mesh sample is attributed to pores with shape factors between 1 and 3 with the maximum occurring around 1.5. A distinct shift to larger values of shape factors is observed with increasing particle size. The corresponding distribution for the 25-28 mesh sample (bottom plot on Figure 2.9) shows a distinct second peak with a substantial fraction of macroporosity now attributed to pores with boundary shape factor greater than 3.0.

Table 2.1 summarizes the measurements for the macropore properties. The interesting result here is that the macroporosity of the particles was not affected by their size. Since macroporosity is strongly influenced by the heating rate, this result indicates that particle size did not significantly affect the internal heating rate and it points out that external heat transfer is not limiting for our pyrolysis reactor.

Table 2.1
Effects of Coal Particle Size on the Macropore Structural Properties of
Illinois #6 Chars

Particle Size		Porosity	Surface Area	Specific Surface
mesh	μm		Density S_v	Area S_g
			cm^2/cm^3 particle	cm^2/cm^3 solid
100-120	125-149	0.684	1,773	5,614
50-60	250-300	0.716	826.3	2,913
25-28	589-710	0.680	651.7	2,035

The average macropore size increased from a radius of 27 μm for the 100-120 mesh sample, to a radius of 81 μm for the 50-60 mesh sample and a radius of 122 μm for the 25-28 mesh sample. Larger macropore sizes lead to lower values of macropore surface area per unit volume of char particle. The increasing tortuosity of the pore boundaries observed in the large char particles, however, partially offsets the decrease in macropore specific areas due to the increasing pore size. Thus, one would expect that char samples produced from large coal particles will exhibit higher reactivities (in the regime of diffusional limitations) than those predicted on the basis of macroporosity only.

We must note, however, that maceral segregation may complicate the determination of particle size effects on the macropore structure of chars produced from plastic coals (Jones et. al, 1985). Due to differences in the mechanical properties of the various coal macerals, grinding and sifting procedures may lead to enrichment of certain macerals in certain size fractions (i.e. small size fractions may contain more exinite). Thus, the well-known

differences in the plastic behavior and volatile content of coal macerals can affect the macropore structure of different size fractions.

2.5 Pyrolysis of a Non-Plastic Coal

In order to study the effect of pyrolysis heating rate on the macropore structure of chars obtained from non-plastic coals, we pyrolyzed 50-60 mesh particles from a lignite coal (Wilcox, Texas) at three heating rates: 0.1, 10 and 1,000 °C/s. Figure 2.11 shows representative images of the polished char sections taken for each sample. A comparison of particle sections obtained from the pyrolyzed chars and the parent coal revealed that several large fractures and cracks were formed during the pyrolysis stage. In contrast to the Illinois #6 chars, however, the cross-sections of lignite char particles show almost no visible change as the heating rate is increased.

The measurements obtained via image analysis (see Tables 2.2 and 2.3) show only small increases of the macroporosity and the macropore surface area with increasing pyrolysis heating rates.

Since the lignite char pores are in general smaller than the pores of the Illinois #6 chars, the smoothing procedures resulted in a measurable reduction of the macroporosity. Also, the average reduction in the macropore surface area caused by pore profile smoothing was 3 times higher for the lignite chars than for the Illinois #6 chars (average reductions were 11% for the Illinois #6 chars and 34% for the lignite chars). Another interesting trend is the observed decrease in average particle radius size with increasing heating rate, indicating possible fragmentation of the devolatilizing particles. This set of data, however, is too small to draw general conclusions from and a more detailed study of videotapes from pyrolysis experiments is required to resolve this issue.

TABLE 2.2
Structural Properties of Lignite Chars Produced at Different Pyrolysis
Heating Rates Measurements Obtained from Original Digital Images

Pyrolysis Heating Rate °C/s	Macroporosity	Surface Area Density cm ² / cm ³ particle	Specific Surface Area cm ² / cm ³ solid	Average Particle Radius μm
0.1	0.139	1,012	1,176	128
10	0.152	1,105	1,303	115
1000	0.194	1,375	1,705	99

TABLE 2.3
Structural Properties of Lignite Chars Produced at Different Pyrolysis
Heating Rates Measurements Obtained from Digital Images Smoothed
According to Procedure B

Pyrolysis Heating Rate °C/s	Macroporosity	Surface Area Density cm ² / cm ³ particle	Specific Surface Area cm ² / cm ³ solid	Average Particle Radius μm
0.1	0.118	681	773	128
10	0.129	740	850	115
1000	0.165	935	1,119	99

2.6 Conclusions

Direct measurements obtained via image analysis show that the pyrolysis heating rates have a significant effect on the macropore structure of chars produced from plastic coals. High pyrolysis heating rates lead to chars with larger porosities and more open pore structures. The calculated values of specific macropore surface areas suggest that the chars produced at high pyrolysis heating rates may be more reactive at elevated temperatures where low utilization of the micropores is expected. This agrees with the experimental reactivity data we have recently reported (Matzakos and Zygourakis, 1990).

The particle size did not affect the computed macroporosities. Pore shape analysis, however, shows subtle but important changes in the macropore structure of chars produced from coal particles of different sizes. The larger coal particles lead to chars with more tortuous macropore boundaries. Our experimental reactivity data again show some interesting trends with large char particles being more reactive than smaller particles in the regime where diffusional limitations in the macropores should become important (Matzakos and Zygourakis, 1990).

The results we presented here clearly show that the macropore structure is a significant factor in determining char reactivity under conditions that lead to strong intraparticle diffusional limitations. This study also demonstrates that optical microscopy and digital image processing can form the basis of analytical techniques that can help us analyze and gain a quantitative understanding of fundamental coal pyrolysis and gasification mechanisms.

2.7 References for Chapter 2

Bailey, J. G., A. Tate, C. F. K. Diessel and T. F. Wall. (1990). "A char morphology system with application to char combustion." *Fuel*. 69(2): 225-239.

DeHoff, R. T. (1983). "Quantitative serial sectioning analysis: preview." *J. Microscopy*. 131(3): 259-263.

Essenhugh, R. H. and G. C. Yorke. (1965). "Reaction Rates of Single Coal Particles: Influence of Swelling, Shape, and Other Factors." *Fuel*. 44: 177-189.

Gavalas, G. R. (1980). "A Random Capillary Model with Application to Char Gasification at Chemically Controlled Rates." *AIChE J.* 26(4): 577-585.

Glass, M. W. and K. Zygourakis. (1988). "A Computerized Captive-Sample Microreactor for Video Microscopy Studies of Rapid Coal Pyrolysis." *Rev. Sci. Instr.* 59(4): 580-587.

Hamilton, L. H. (1981). "Char morphology and behaviour of Australian vitrinites of various ranks pyrolyzed at various heating rates." *Fuel*. 60(10): 909-913.

Howard, J. B. (1981). "Fundamentals of Coal Pyrolysis and Hydropyrolysis." In Chemistry of Coal Utilization, M. A. Elliott, Ed. John Wiley, New York, NY.

Ivanova, I. P. and V. L. Babii. (1966a). "A study of the burn-out mechanism of coal particles." *Therm. Eng.* 13(4): 70-76.

Ivanova, I. P. and V. L. Babii. (1966b). "A study of the burn-out of anthracite p.f. particles." *Therm. Eng.* 13(5): 100-107.

Jones, R. B., C. B. McCourt, C. Morley and K. King. (1985). "Maceral and rank influences on the morphology of coal char." *Fuel*. 64(10): 1460-1467.

Lightman, P. and P. J. Street. (1968). "Microscopical Examination of Heat Treated Pulverized Coal Particles." *Fuel*. 47: 7-28.

Mason, D. M. (1970). "Coal and Char Transformation in Hydrogasification of Coals Ranging in Rank from Lignite to Low-volatile Bituminous." *Ind. Eng. Chem. Process Des. Develop.* 9(2): 298-303.

Mason, D. M. and F. C. J. Schora. (1967). "Coal and Char Transformation in Hydrogasification." In Fuel Gasification, F. C. J. Schora, Ed. American Chemical Society, Washington, D.C.

Matzakos, A. and K. Zygourakis. (1990). "Pyrolysis of Plastic Coals: Pore Structure Development and Reactivity." *Amer. Chem. Soc., Div. Fuel Chem. Prepr.* 35(1): 505-515.

Newall, H. E. and F. S. Sinnatt. (1926). "The Combustion of Particles of Coal in Air. The Study of Cenospheres. - II." *Fuel*. 5(8): 335-339.

Newall, S. E. and F. S. Sinnatt. (1924). "The Carbonisation of Coal in the Form of Fine Particles. - I. The Production of Cenospheres." *Fuel*. 3: 424-434.

Shibaoka, M. (1969). "An investigation of combustion processes of single coal particles." J. Inst. Fuel. 42(2): 59-66.

Street, P. J., R. P. Weight and P. Lightman. (1969). "Further Investigation of Structural Changes Occurring in Pulverized Coal Particles during Rapid Heating." Fuel. 48: 343-365.

Tsai, C.-Y. and A. W. Scaroni. (1987). "The structural changes of bituminous coal particles during the initial stages of pulverized coal combustion." Fuel. 66(2): 200-206.

Weibel, E. R. (1980). Stereological Methods. New York, Academic Press.

Zygourakis, K. and M. W. Glass. (1988). "Macropore Size Analysis Using Digital Image Processing and a Stereological Model." Chem. Eng. Commun. 70: 39-55.

Zygourakis, K. and P. Markenscoff. (1990). "Parallel Iterations and Cellular Automata Models for Simulating Pore Structure Transformations." Procs. ACM Computer Science Conference, in press.

Figure 2.1: Binary image of a particle cross-section for an Illinois #6 char and a blow-up of a small area. (A) Raw (unprocessed) images. (B) Image smoothed according to procedure A (see text). (C) Image smoothed according to procedure B.

Figure 2.2: Binary images of representative particle cross-sections for Illinois #6 char samples produced at different pyrolysis heating rates. Coal particle size: 50 - 60 mesh.

Figure 2.3: Effect of pyrolysis heating rate on the macroporosity of five Illinois #6 char samples. Coal particle size: 50 - 60 mesh.

Figure 2.4: Effect of pyrolysis heating rate on the average char particle radius (top curve) and on the average macropore radius (bottom curve) of five Illinois #6 char samples. Coal particle size: 50 - 60 mesh.

Figure 2.5: Frequency distribution functions $n(r)$ (top graph) and $s(r)$ (bottom graph) showing the size distribution of macropore profiles for the Illinois #6 char sample produced at a pyrolysis heating rate of 0.1 °C/s. Coal particle size: 50 - 60 mesh.

Figure 2.6: Effect of pyrolysis heating rate on the macropore surface area density of five Illinois #6 char samples. Coal particle size: 50 - 60 mesh.

Figure 2.7: Effect of pyrolysis heating rate on the specific macropore surface area S_g of five Illinois #6 chars. Coal particle size: 50 - 60 mesh.

Figure 2.8: The dependence of specific macropore surface area S_g on the average char particle size computed for five Illinois #6 char samples produced at different pyrolysis heating rates. Coal particle size: 50 - 60 mesh.

Figure 2.9: Binary images of representative particle cross-sections for Illinois #6 chars produced from coal particles of different size at a pyrolysis heating rate of 10 °C/s.

Figure 2.10: Frequency distribution functions $f(\sigma)$ for the macropore shape factors calculated for the three Illinois #6 chars produced from particles of different size at a pyrolysis heating rate of 10 °C/s.

Figure 2.11: Binary images of representative particle cross-sections for lignite chars produced at different pyrolysis heating rates. Coal particle size: 50 - 60 mesh.

CHAPTER 3

PYROLYSIS AND COMBUSTION IN A THERMOGRAVIMETRIC REACTOR SYSTEM WITH VIDEO MICROSCOPY IMAGING (TGA/VMI)

3.1 Introduction

In order to meet some of the main project objectives, we developed a novel thermogravimetric reactor system with in-situ video microscopy imaging capabilities (TGA/VMI). An optical microscope equipped with a video camera, video tape recorder and monitors was attached to our thermogravimetric analyzer. The TGA/VMI setup allowed for direct viewing and tape recording of pyrolyzing and reacting particles. This system was interfaced to a microcomputer that performed data acquisition and control tasks (see Figure 3.1). We improved the computer control algorithm and replaced the original TGA reactor furnace with an improved version that allowed us to achieve heating rates as high as 50 °C/s with excellent reproducibility. Finally, we installed a gas-feed system with mass flow controllers interfaced to the microcomputer. This allowed us to automate the entire experimental procedure.

With the TGA/VMI reactor system we could obtain real time reaction rates while simultaneously recording on video tape the structural changes that coal particles undergo during pyrolysis or combustion. Since we could also achieve heating rates as high as 50 °C/s, we exposed our coals to a wider range of pyrolysis conditions that are closer to the conditions encountered in practical applications.

The advantages of the TGA/VMI system are summarized in the following list.

- 1) This system allowed us to perform **sequential** pyrolysis and gasification experiments that revealed the influence of pyrolysis conditions on char reactivity.
- 2) With the TGA/VMI reactor, we could observe and record for post-processing the structural transformations that coal particles undergo during pyrolysis.
- 3) It also helped us detect and monitor the occurrence of transient combustion phenomena like particle ignition, fragmentation and macropore opening.

3.2 Development of a TGA Reactor with Video Microscopy Imaging Capabilities (TGA/VIM)

Figure 3.1 shows the thermogravimetric reactor setup. The thermogravimetric analyzer (TGS-2, Perkin-Elmer) was interfaced to a microcomputer (PDP 11/23+, Digital Equipment Corp.) that performs the data acquisition and control tasks.

The coal sample was placed in a Pt pan and suspended from the weighing mechanism with a Pt wire. The balance accuracy was 0.1% and the sensitivity 0.1 μg . The sample weight was continuously monitored and recorded by the computer.

The sample pan was placed inside a cylindrical ceramic furnace that we designed and custom-built to achieve high heating rates. This furnace was made of machinable ceramic (Aremco) that can withstand temperatures up to 2100 °F (1150 °C). The furnace heating element consisted of Ni-Cr wire (28 AWG, 0.013" diameter) wrapped around the outside of the furnace and it is supplied with 110 VAC giving our furnace a total power output of 950 Watts. The temperature was measured by a chromel-alumel thermocouple (type K, 0-1000 °C range) located exactly below the pan.

We purchased and installed three mass flow controllers (MFC) to feed the reactor with the desired mixture of nitrogen, oxygen and carbon dioxide. The MFC set points were set by the computer that is interfaced to the MFC readout and control unit. Two gas streams were fed to the reactor. The first stream was pure nitrogen and it entered the furnace tube from the top. This stream continuously purged the weighing mechanism located on top of the TGA. The second stream entered through the side of the furnace tube (see Figure 3.2) and contained either nitrogen or nitrogen/oxygen mixture. Overall gas feed rates to the reactor were between 240-360 cm³/min and the velocity of the gas stream inside the tube between 0.8-1.2 cm/s. The location of the sample was almost 3.3 cm below the point where the two streams mix. Since the feed gases needed 2.8-4.2 seconds to reach the sample, we estimate that the two gas streams were adequately mixed before reacting with the sample.

A flat optical window was inserted at the top of a glass side tube attached to the main furnace tube (Fig. 3.2). Through this window, the coal sample was imaged via a high-magnification, extra-long working distance microscope mounted outside the reactor and facing downwards into the furnace. The surface of the optical window was perpendicular to the line of view of the microscope to minimize diffraction and image distortion. We illuminated the sample pan with a bifurcated fiber optic bundle connected to a light source (Dolan-Jenner) providing 50,000 ft. candles of light.

Video images of reacting coal samples were obtained with a color camera (Javelin, 760x485 lines resolution) attached to the microscope. A video timer (FOR-A) superimposed on the camera signal an alphanumeric field containing the time elapsed since the beginning of the experiment. Complete records of pyrolysis and combustion experiments were obtained by recording the images on a S-VHS video tape recorder (Panasonic) with 400 lines of resolution (see Figure 3.5). The video tape recorder had a video signal sensor that can start recording whenever a video signal is supplied by the camera. By remotely activating the video camera, we could record only the important stages

of the experiment and ignore the rest. Images from experiment videotapes were later digitized using a 640x480 pixel frame grabber (Imaging Technology Inc.) attached to the backplane of a microcomputer (VAXstation II/GPX, Digital Equipment Corporation). At its highest magnification, our microscope could image an area as small as 2.8×2.1 mm. This gave a pixel size of $4.3 \mu\text{m}$ for our 640x480 pixel digital image acquisition board. Digital techniques were used to provide image enhancement and analysis.

3.2.1 Microcomputer Hardware

The requirements for an accurate and versatile control and data acquisition system were met by interfacing the TGA/VMI system to a microcomputer. A digital control algorithm was implemented to program the reactor temperature and to automate the operations needed during the pyrolysis-gasification sequence. The micro-computer system used in our studies consisted of: i) a LSI 11/23+ CPU (Digital Equipment Corp.) with floating point hardware; ii) 256 kbyte memory; iii) 10 Mbyte hard disk storage capability; iv) dual floppy disk drives; v) four serial communications ports; vi) eight-channel (0-10 V) 12-bit A/D converter; and vii) eight-channel (0-10 V) 12-bit D/A converter. The computer operated under the RT-11 V5.1 real time operating system.

3.2.2 Temperature measurement

The temperature signal was conditioned, amplified, and linearized by an isolated thermocouple module (Analog Devices, Model 3B47). This module had a gain equal to $10 \text{ mV}/^\circ\text{C}$ which brought the thermocouple signal into the range of 0-10 V for a 0-1000 $^\circ\text{C}$ temperature range. Temperature measurement accuracy was ± 1.0 $^\circ\text{C}$ including the combined effects of repeatability, hysteresis and linearity. The response time to a step change was equal to 0.2 s for 90% of the span. The variations in ambient temperature were

very small and did not affect the output signal significantly (0.0025% of reading for every °C variation). Zero and span adjustments were also available for further calibration. The 12-bit microcomputer A/D converter read the output voltage and converted it to an integer value between 0 and 4095. Thus, the resolution of the A/D converter is 0.24 °C.

3.2.3 Heater control

A phase-fired heater controller circuit was used to regulate the power supplied to the heating element (Glass and Zygourakis 1988). The power supplied to the furnace (110 VAC @10 A) varied between 0 and 100% full power when the control signal coming from the computer D/A converter ranged from 0 to 10 V. With the available power of 950 Watts, the furnace could reach final temperatures as high as 950 °C with heating rates up to 100 °C/s. Due to computer limitations, however, we could not use heating rates higher than 50 °C/s. A faster computer would be necessary to implement heating rates between 50 and 100 °C/s without significant deviations from our temperature program.

3.2.4. Mass flow controllers-Remotely activated devices

The three mass flow controllers (MFC) were interfaced to the microcomputer via their readout/control unit. Three D/A channels provided the set points for the gas flow rates, while 3 TTL signals were used to turn the MFC's on and off. This configuration allowed for complete control of the total flow rate and composition of the gas mixture. For example, it allowed us to use pure nitrogen during pyrolysis and switch to an oxygen/nitrogen mixture with the same total flow rate at the beginning of the combustion stage.

The control computer could also activate several other devices during an experiment. For instance, the reactor is equipped with a cooling fan that needs to be turned on whenever fast cooling is desired (i.e. after the end of pyrolysis) or temperature overshoot occurs. The

fan is connected to an 110 VAC outlet that is in series with a solid state relay . A TTL signal triggered the relay to start the fan when the computer program determined that extra cooling was desirable. The same configuration was used for remote control of the operation of other AC powered devices like the video camera and the solenoid valve that allows the premixing of nitrogen and oxygen before entering the reactor. Finally, a TTL logical signal was directly connected to the remote port of the video timer to trigger its START function. Thus, the computer program could start the timer at exactly the beginning of each experiment.

3.3 Computer control

3.3.1 Digital control algorithm

The digital control algorithm was a combination of a predictive technique (based on a convolution model) and a standard proportional-integral (PI) feedback control. We used an improved version of the algorithm previously developed for this purpose in our laboratory (Sandmann 1986). A system model was experimentally obtained experimentally and it was used to implement the desired temperature program. To compensate for the inaccuracies of the model and the temperature dependence of the process parameters, a feedback controller was also employed based on the deviations of the reactor temperature from the set point.

3.3.2 Process model

The process model is a discrete convolution model that accounts for the system lag time. The system transfer function in the Z-domain can be represented by a polynomial of negative powers of z .

$$G(z) = \sum_{i=0}^{\infty} h_i z^{-i} \quad (3.1)$$

where h_i are the discrete model coefficients

The discrete model coefficients h_i were experimentally obtained by applying power impulses (approximated as pulses of very short duration) and measuring the temperature changes at fixed time intervals (Seborg, Edgar et al. 1989). These coefficients were normalized so that their sum equaled unity. We obtained three different sets of model coefficients for the temperature ranges 25-400 °C, 400-710 °C, and 710-950 °C by performing pulse tests at the midpoint of each range. This is necessary, because furnace dynamics are non-linear due to radiation and process model parameters vary significantly with temperature.

The temperature dependence of the heat losses $Q_{out}(T)$ was found by supplying known power inputs to the furnace and measuring the steady state temperature it would achieve. This function was interpolated with a 4th-order polynomial. The furnace heat capacity $\alpha(T)$ was measured by stepwise increasing by a known amount the power provided to the furnace. At each temperature

$$\alpha(T) = \frac{Q_{in}(T) - Q_{out}(T)}{\left(\frac{dT}{dt}\right)} \quad (3.2)$$

where Q_{in} is the input power, Q_{out} are the heat losses and (dT/dt) is the rate of temperature increase.

Figure 3.4 shows a block diagram of the computer algorithm. Execution of the algorithm starts at fixed sampling instants 1, 2, ..., r, r+1 corresponding to time levels t^1 ,

$t^2, \dots, t^r, t^{r+1}, \dots$ where $t^r = t^{r-1} + \Delta t$, $r=1,2,\dots$. Figure 3.5 shows in pictorial form the computations performed by the feedforward (model-based) part of the algorithm

At each time level t^r , $r=1, 2, \dots$:

- (1) Measure the current reactor temperature T^r .
- (2) Compute the temperature set point $T_f = T_{sp}^{r+N}$ at $t = t^r + N \Delta t$ (i.e the set point N sampling intervals in the future as shown in Fig. 3.5). This temperature T_f is called *prediction horizon*.
- (3) Calculate the power input needed for achieving T_f at the specified time $t = t^r + N \Delta t$. This power is found as the sum of the heat losses and the ramp power.

$$Q_{sum}^r = Q_{out}(T) + \alpha(T) \left| \frac{dT}{dt} \right|_{t=t^r} \quad (3.3)$$

where Q_{sum}^r is the power input prediction at time t^r , T is the temperature at time t^r , $Q_{out}(T)$ are the heat losses, $\alpha(T)$ is the furnace heat capacity and $(dT/dt)_{t=t^r}$ the slope of the curve connecting the future set point T_f with the present temperature T .

- (4) After finding Q_{sum}^r , apply the convolution theorem to all previous power inputs to make sure that their total sum together with the present input will all be equal to the desired power.

$$Q_{sum}^r = Q_{in}^r h_1(T) + \sum_{j=2}^r Q_{in}^{r+1-j} h_j(T) \quad (3.4)$$

where $h_i(T)$ the model coefficients (from Eq. 3.1) and Q_{in}^r is the present input necessary to achieve the set point after N sampling intervals. Equation (3.4) is used to calculate Q_{in}^r .

- (5) Advance to next time level t^{r+1} .

As shown in Figure 3.5, this control scheme is inherently underdamped which is desirable to avoid overshoot when the temperature set point moves from the ramp to the constant steady-state value. The time horizon $N \times \Delta t$ depends on the system lag time and is adjusted for best response. The behavior shown by Figure 3.5 is for a perfect model and zero lag.

To correct for model inaccuracies, our algorithm also implements a proportional-integral (PI) feedback controller (see Figure 3.4). The deviation of the reactor temperature from the current set point is used for feedback control.

There are two kinds of model errors: (a) errors in predicting heat losses and (b) errors in estimating the heat capacity. Therefore, the integral of the error accumulated during a temperature ramp may be meaningless when we move to a steady state. The computer algorithm computes and stores independently two error integrals: (a) the steady-state integral computed while the set point is constant that accounts for errors in calculating heat losses; and (b) the ramp integral computed while the set point is in a ramp that accounts mainly for errors in heat capacity predictions. The algorithm does not accumulate the error integral at the corners when transition between ramp and constant set point occurs. The PI feedback controller, however, uses both integrals during all three stages (ramp, transition, constant set point).

The control algorithm is executed every 0.5 seconds. Shorter sampling times are not advisable since instabilities due to thermocouple and system lags may arise. Also, the computer used is not fast enough to execute the control loop more often. However, temperature and weight measurements can be performed between executions of the algorithm with frequency up to 12 times per sec. Data logging can also be performed with the same frequency.

3.3.3 Performance of control algorithm

The controller's performance is very important since we want to achieve good reproducibility between experiments with accurate linear temperature ramps and stable steady state temperatures. This controller is very good at fulfilling these requirements (see Table 3.1). When the set point is constant (steady-state) and far from corners (ramp to steady-state transitions), the error is at most 0.2 °C (equal to the resolution of the A/D board). During ramps with slopes equal from 0.1 to 1.0 °C/s, the L_1 norm of the error (i.e. the average absolute error) is of the order of 0.3 °C. During ramps of 10 °C/s the L_1 norm of the error is at the order of 1 °C.

Table 3.1
Temperature Error Norms During a Typical Pyrolysis Run
 (Temperature is ramped from 200 °C to a final steady-state of 700 °C)

	Temperature Ramp		Transition to Steady State		
Heating Rate (°C/s)	L_1 (°C)	L_∞ (°C)	L_1 (°C)	L_∞ (°C)	Time (sec)
1	0.3	3.4	0.1	1.1	8.0
10	1.1	5.0	0.6	3.8	19.2
20	2.0	7.3	1.3	4.3	29.2
30	4.7	13.1	0.8	5.0	24.0

During ramp/steady-state transitions, the maximum error (L_∞ norm) observed for a 10 °C/s ramp is 3-5 °C and such errors persist for 1-3 secs. For 30 °C/s heating rates, the maximum error is 13 °C at the corners, but it decays very fast (within a few seconds). The norm of the error at this case is about 4.7 °C.

Figure 3.6 shows a ramp of 20 °C/s. As we see, the control is very good especially for a controller with sampling interval of 0.5 secs.

From process dynamics theory we would expect a minimum error of 10 °C that for a 20 °C/s ramp and a feedback controller with 0.5 sec sampling interval. But our predictive technique suppresses the error to a much lower value. Note also that overshoot is avoided at the end of the temperature ramp. As shown in Figure 3.6, the overshooting is only 2 °C (error -2 °C) and lasts one second.

3.4 Experimental Procedures

3.4.1 Sample preparation

We studied the Illinois #6 coal from the Argonne premium coal sample collection (Vorres 1989). Three coal particle sizes were used: 50-60 mesh (250-297 μm), 28-32 mesh (500-595 μm) and 20-24 mesh (707-841 μm). The sample was received in sealed ampoules containing nitrogen to prevent slow oxidation. After opening the ampoules, we sieved the sample in standard sieves ranging from 20 to 100 mesh fractions. The sample was then stored in a vacuum desiccator at room temperature (21 °C) to prevent oxidation or transformation of the coal pore structure.

For each run, the reactor was loaded with about 1 mg of coal (that is, 30-40 coal particles for the 50-60 fraction, 8 particles for the 28-32 mesh fraction and 2-3 particles for the 20-24 mesh fraction). A sample weight close to 1 mg was necessary for accurate,

noise-free weight measurements. The particles were placed in the pan far from each other to prevent agglomeration during pyrolysis. However, we could not always prevent particle agglomeration during experiments with the 50-60 mesh fraction. Although we tried to place the 30-40 small particles as far as possible from each other, the swelling during pyrolysis forced some particles to coalesce and stick together. We consider that this is not a problem for rate measurements in the kinetic control regime. It could create additional diffusional resistances though, for the particles of interest in the diffusion-limited regime.

The weighing mechanism was constantly purged with nitrogen to prevent intrusion of air in it. The microscope was focused on the sample and the illumination was adjusted to get the best image quality. The video cassette recorder was put in "video sensor" mode so that recording could start each time the camera provided a video output signal. The video timer was zeroed and put in the stand-by mode that awaits for a remote signal to start time counting.

3.4.2 Experimental protocol

Table 3.2 gives the range of conditions used for pyrolysis and gasification experiments. A typical pyrolysis-combustion experiment consists of the following stages. Figure 3.7 shows the sample weight and reactor temperature histories for one experiment.

- a) The sample is held at 150 °C in nitrogen (or 5% oxygen / 95% nitrogen) flow for a few minutes to remove any moisture present. We then raise the reactor temperature to 200 °C, that is the starting point of the pyrolysis ramp.
- b) Videotaping and counting of elapsed time start when the reactor temperature reaches 200 °C. The reactor temperature is ramped at a constant rate (0.1 to 20 °C/s) until the final heat treatment temperature or HTT is reached (500 to 900 °C). The

temperature is then held constant at the HTT for a period equal to the desired soak time (0 or 3 minutes).

- c) At the end of the soak time, videotaping stops and the reactor is cooled as fast as possible to 250 °C. At that point, the desired oxygen/nitrogen mixture is introduced to the reactor and is allowed enough time to achieve a steady state concentration.
- d) Videotaping starts and the temperature is ramped fast to the desired combustion temperature (400-600 °C). There, it is kept constant long enough to achieve coal conversions higher than 90%.
- e) Finally, the reactor temperature is raised to 650 °C and the sample is kept there for 5 minutes to burn any remaining coal in order to measure the sample ash content.

Table 3.2
EXPERIMENTAL CONDITIONS

Pyrolysis Stage

Heating rate:	0.1, 0.3, 1, 3, 10, 20 °C/s
Final heat treatment temperature:	500-900 °C
Soak time at HTT:	0 and 3 minutes
Flowing Gas:	Nitrogen or 5% oxygen

Combustion Stage

Reaction Temperatures:	400 - 600 °C.
Flowing gas:	33% oxygen
Gas flow rates :	240 and 360 sccm.

3.4.3. Data processing

After the end of each experiment, the data file containing the complete histories of sample weight, reactor temperature and control signal is transferred from the microcomputer to the VAXstation for post- processing. We have carefully analyzed our procedure for obtaining the reaction rates. Usually, our data acquisition system will collect about 300 data points during the pyrolysis stage of each run and 300-3,000 data points during the combustion stage (depending on the reaction temperature). The collected weight vs. time data are interpolated in the least-squares sense (L^2 norm) using B-splines and this polynomial approximation is then differentiated to obtain the observed reaction rate per unit mass of initial or unreacted solid. Two reaction rates are calculated according to Equations (3.5) and (3.6).

$$r_0(t) = \frac{dx}{dt} = -\frac{1}{m_0} \left(\frac{dm(t)}{dt} \right) \quad (3.5)$$

$$r_m(t) = \frac{1}{1-x} \frac{dx}{dt} = -\frac{1}{m(t)} \left(\frac{dm(t)}{dt} \right) \quad (3.6)$$

where x is the conversion of the solid, m_0 is the initial mass of the solid in ash-free basis, and $m(t)$ is the mass of the unreacted solid at time t . The first rate r_0 gives absolute values of the reactivity and exhibits a maximum at 20-40% conversion for reaction with oxygen in the kinetic control regime (Ballal and Zygourakis 1987; Bhatia and Perlmutter 1980; Gavalas 1980). The second rate r_m gives specific values of the reactivity per mass of remaining solid. Our experimental data show that r_m follows a monotonic increase in the conversion range of 0-90%. In this report, we will follow the convention of plotting r_m in our figures as most investigators do.

In our numerical differentiation procedure, it is essential to determine the appropriate order of polynomials and the number of breakpoints to use for the interpolation of the raw weight data. If high order polynomials are used, the reactivity curves will be smoothed out and fine details will be lost. Also, the curves will be very noisy if a large number of breakpoints are used. Our choice of polynomials was dictated by the form of our data that indicated the reaction rate is continuous in time but not necessarily smooth (i.e. it has a discontinuous first derivative). Such behavior has also been observed by Sundback et al. (1984) who attributed it to particle fragmentation. Our earlier studies (Zygourakis 1989; Zygourakis and Sandmann 1988) indicate that these jumps may also be caused by the opening of large internal pores during combustion in the diffusion-limited regime (high temperatures). Therefore, we decided to use C-1 quadratics for the interpolation instead of the more often used C-2 cubic splines. This assumes that the **reaction rate is a linear function of time at each interval and can exhibit sharp maxima and minima** which would be smoothed out with a cubic spline. The number of intervals is in most cases larger than 30 and our software allows for dynamic placement of the breakpoints in regions with rapidly changing sample weight, a feature that improves our ability to resolve details of the reactivity curve. Since we always have more than 20 data points in each subinterval, any noise disturbances cannot significantly influence our results. Standard plotting software allows direct visualization of the reaction patterns as a function of conversion or time.

3.5 Coal Plasticity and Swelling

Many experiments were performed on the TGA/VMI reactor with Illinois #6 coal particles in the 28-32 mesh range. An analysis of the video-taped histories of these experiments showed that the coal particles swell considerably and that the swelling

increases with increasing heating rates. We also observed vigorous bubbling during this stage, as the particles expanded and contracted in rapid succession.

Figures 3.8, 3.9 and 3.10 illustrate the dramatic shape and size changes of coal particles observed within a few seconds. The images of Figure 3.8 present the temporal evolution of specific particles during a pyrolysis run with a 10 °C/s heating rate. For this run, the platinum pan of the TGA/VMI reactor was covered with a platinum wire mesh to prevent the particles from agglomerating. The elapsed time is shown on the bottom left part of the screen. Time zero corresponds to the beginning of the heating ramp at 200 °C.

The images of Figure 3.9 are blow-ups from the corresponding images of Figure 3.8 showing in more detail the transformations of two specific particles. One particle starts with a triangular shape (Figure 3.9A), swells and becomes elongated (Fig. 3.9C). After a few contractions and expansions, it ends up with a rounded shape (Fig. 3.9F). Rapid particle expansions and contractions occurred within time intervals as short as 1.5 s. Figure 3.10 shows the images of Figure 3.2 enhanced with an artificial illumination technique. The digitally enhanced images clearly show bubbling effects on the particle surface.

The mechanism of expansion and contraction is as follows. Bubble formation inside the particle induces an internal pressure build-up that forces the particle to expand. The surface tension of the bubble film increases and when it exceeds a limit value the film breaks releasing to the particle exterior the volatile gases contained in the bubble. The particle contracts again until new bubbles start forming in the particle interior and the internal pressure starts building up again.

After the plasticity stage, the resolidified particles have a macropore structure consisting of either many spherical cavities or one large cenosphere created by the coalescence of several bubbles. As the pyrolysis heating rates increase, we expect that the volatile bubbles formed in the particle interior will not have time to coalesce. The macropore structure of particles produced at high heating rates will therefore be more tortuous with many spherical macropores separated by thinner walls.

3.6 Devolatilization Rates

The TGA/VMI reactor allowed for continuous monitoring of the weight loss of the pyrolyzing coal samples. By processing the weight-loss data, we obtained the instantaneous volatile release rates and analyzed it to explain the effects of heating rate on the devolatilization rates.

Figure 3.11 shows the weight loss rates for several runs at two different heating rates. The results for each heating rate show very good reproducibility and the maximum pyrolysis rate is observed in a narrow temperature range. A comparison of the results for 0.1 and 10 °C/s, but, shows a significant shift of the range of maximum devolatilization rates toward higher temperatures as the heating rate increases (see Figure 3.11 and Table 3.2).

Figure 3.12 compares the weight loss curves obtained for three different pyrolysis heating rates: 0.1, 1.0 and 10 °C/s. The important result here is that the amount of released volatiles increases slightly with increasing heating rates (Figure 3.12 and Table 3.2). This observation agrees with the theoretical predictions (Fletcher, Kerstein et al. 1989) of the chemical percolation devolatilization (CPD) model and the experimental observations of Gibbins-Matham and Kandiyoti (Gibbins-Matham and Kandiyoti 1988; Gibbins-Matham and Kandiyoti 1989a; Gibbins-Matham and Kandiyoti 1989b).

We also compared the volatile evolution rates as a function of initial particle size. The gravimetric analysis showed that the weight loss patterns and yield of pyrolyzing coals do not change with particle size, in the range 250-800 µm. This means that there are neither kinetic effects related to the pressure of volatiles in the particle interior nor thermal effects resulting in a non-uniform temperature distribution throughout the particle.

Table 3.2
Temperature Ranges for Maximum Weight Loss Rate
and Average Weight Loss during Pyrolysis

Pyrolysis Heating Rate	0.1 °C/s	1.0 °C/s	10.0 °C/s
Temperature Range for Maximum Weight Loss Rate	410-425 °C	460-480 °C	510-545 °C
Average Weight Loss (%)	36.5	42.4	46.2

Finally, we compared the volatile evolution rates in two different pyrolysis atmospheres: (a) 100% N₂ and (b) 5% O₂ / 95% N₂. The gravimetric analysis showed that the weight loss patterns and yield of pyrolyzing coals are very similar, both in the presence and absence of oxygen. This means that by keeping the oxygen concentration and HTT low (5% oxygen and 500 °C respectively), we have minimized the extent of carbon/oxygen reactions. Otherwise, if some of the carbon combusted with the oxygen, the weight loss patterns and total yield would change.

3.7 Macropore structure measurements

Measurements on the macropore structure of chars produced with the TGA/VMI reactor showed that the particles had very open cellular macropore structures similar to those quantified via digital image analysis in an earlier stage of our project as discussed in Chapter 2 of this report (Zygourakis 1988). The main conclusions from the structural measurements can be summarized as follows.

1. The final particle size, the average macropore size, the macropore specific surface area and the macroporosity of a char particle increase as the pyrolysis heating rate increases.
2. The macroporosity does not depend on the initial particle size.
3. The macropore specific surface area decreases as the initial particle size increases.
4. The heat treatment temperature (500 or 700 °C) does not influence the particle swelling at the low heating rates (0.1 and 1.0 °C/s). However, the chars treated with 10 °C/s have lower swelling when they are ramped to 500 °C. This is because the particles do not reach their maximum devolatilization rate that occurs at around 520 °C under these conditions.

3.8 References for Chapter 3

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(9): 1787-1796.

Bhatia, S. K. and D. D. Perlmutter. (1980). "A Random Pore Model for Fluid-Solid Reactions: I. Isothermal, Kinetic Control." *AIChE J.* 26(3): 379-386.

Fletcher, T. H., A. R. Kerstein, R. J. Pugmire and D. M. Grant. (1989). "A chemical percolation model for devolatilization: temperature and heating rate effects." *Amer. Chem. Soc., Div. Fuel Chem. Preprints.* 34(4): 1272-1279.

Gavalas, G. R. (1980). "A Random Capillary Model with Application to Char Gasification at Chemically Controlled Rates." *AIChE J.* 26(4): 577-585.

Gibbins-Matham, J. and R. Kandiyoti. (1988). "Coal Pyrolysis Yields from Fast and Slow Heating in a Wire-Mesh Apparatus with a Gas sweep." *Energy Fuels.* 2(4): 505-511.

Gibbins-Matham, J. and R. Kandiyoti. (1989a). "The effect of variations in time-temperature history on product distribution from coal pyrolysis." *Fuel.* 68(7): 895-903.

Gibbins-Matham, J. and R. Kandiyoti. (1989b). "Experimental study of coal pyrolysis and hydropyrolysis at elevated pressures using a variable heating rate wire-mesh apparatus." *Energy Fuels.* 3(6): 670-677.

Glass, M. W. and K. Zygourakis. (1988). "A Computerized Captive-Sample Microreactor for Video Microscopy Studies of Rapid Coal Pyrolysis." *Rev. Sci. Instr.* 59(4): 580-587.

Sandmann, C. W., Jr. (1986). Fundamental studies on gas-solid reactions: pore structure and reactivity of coal chars. Ph.D. Dissertation, Rice University.

Seborg, D. E., T. F. Edgar and D. A. Mellichamp. (1989). Process dynamics & control. John Wiley & Sons.

Vorres, K. S. (1989). "Users Handbook for the Argonne Premium Coal Program." Argonne National Laboratory Report.

Zygourakis, K. (1988). "The Effects of Pyrolysis Conditions on the Macropore Structure of Coal Chars." Amer. Chem. Soc., Div. Fuel Chem. Prepr. 33(4): 951-959.

Zygourakis, K. (1989). "A New Discrete Simulation Method for Modeling Char Gasification in the Diffusion-Controlled Regime." Amer. Chem. Soc., Div. Fuel Chem. Prepr. 34(1): 202-211.

Zygourakis, K. and C. W. J. Sandmann. (1988). "Discrete Structural Models and Their Application to Gas-Solid Reacting Systems." AIChE Journal. 34(12): 2030-2040.

Figure 3.1: Schematic showing the TGA reactor and the flow control system interfaced to the computer.

Figure 3.2: Schematic showing the TGA reactor with the side window that allows direct observation of the sample.

Figure 3.3: Video imaging and recording system.

Figure 3.4: Block diagram for control algorithm that combines a feedforward model-based controller with a PI feedback controller.

Figure 3.5: Schematic showing the implementation of the digital algorithm for controlling the temperature of the TGA/VMI reactor. Note that the reactor temperature approaches the final steady-state without overshoot.

Figure 3.6: A typical temperature ramp showing the performance of the control algorithm. The temperature plotted is the actual. Notice the error magnitude on the right axis.

Figure 3.7: Temperature program and weight vs. time measurements for a typical run (Pyrolysis heating rate: 1.0 °C/s; Combustion temperature: 550 °C).

Figure 3.8: Sequence of images showing eight particles pyrolyzing in the hot-stage reactor at various temperatures. Heating rate is 10 °C/s. The grid separates the particles to prevent agglomeration.

Figure 3.9: Sequence of images showing two pyrolyzing particles at various temperatures. Note the large variations of both the shape and the size of the lower particle. This is the detail of the image sequence on Fig. 3.8.

Figure 3.10: Processed images showing the three-dimensional contours of the outside surface of pyrolyzing particles. Note growing bubbles on the surface of the lower particle at images for T=537 and T=552 °C

Figure 3.11: Experimental devolatilization rates for several pyrolysis runs performed at two different heating rates

Figure 3.12: Weight loss curves obtained for three different heating rates (HTT=900 °C)

CHAPTER 4

FUNDAMENTAL MECHANISMS OF COAL COMBUSTION

4.1 Pore Structure and Coal Char Reactivity

The pore structure of coal chars is a major factor in determining their reactivity and rates of intraparticle mass transport.

In the kinetic control regime (low temperatures), the reactant gases penetrate all the internal pores and the entire micropore and macropore surface area is utilized for the heterogeneous reactions. Figure 4.1 is an idealized sketch of a porous char solid showing cross-sections of a few large macropores and smaller micropores emanating from the macropore surfaces. Since the micropore surface area $S_{\mu g}$ of char solids is usually much larger than the macropore surface area S_{mg} , the micropore surface area determines the intrinsic reactivity of a char (i.e its reaction rates in the kinetic control regime).

At higher reaction temperatures, concentration gradients appear in the micropores, while gas concentrations may remain uniform in the larger macropores. Due to diffusional limitations, gas reactants penetrate the micropores to a constant depth below the macropore surface (see the reaction zone depicted in Figure 4.2) and a large fraction of the micropore surface area is not utilized. The average micropore size and length determine the extent of diffusional limitations. Since the smaller pores make now a constant contribution to the reaction rate when the rate is expressed per unit macropore surface area S_{mg} (Gavalas 1980), S_{mg} significantly affects the reaction rates.

At still higher reaction temperatures, concentration gradients develop also in the macropores. Thus, the average macropore size and length become important in determining the reaction rates in the regime of strong diffusional limitations.

We should finally note that the average macroporosity influences the effective thermal conductivity of the porous char solids. The effective thermal conductivity may be estimated by the following formula:

$$k_{\text{eff}} = (1 - \epsilon_M)^2 k_m + \epsilon_M^2 k \quad (4.1)$$

where k_{eff} is the effective thermal conductivity, ϵ_M is the macroporosity of the solid, and k_m and k are the thermal conductivities of the microporous solid and the gas mixture respectively. Since the gas thermal conductivity k is much lower than the solid conductivity k_m , large values of solid macroporosity result in very small values of effective thermal conductivity.

The above observations prepare us to expect the following behavior.

- i) Char particles prepared at high pyrolysis heating rates should exhibit high intraparticle transport rates of the gaseous reactants. The combined increase of macropore size and specific surface area will lead to an increased apparent reactivity of those chars in the diffusion limited regime. These chars will have lower gas concentration gradients in their macropores and thus higher effectiveness factors. Besides, they will probably have fewer pores trapped inside the solid and thus increased macropore accessibility.
- ii) Intraparticle temperature gradients should be more pronounced in chars with high porosity and thus, with lower effective thermal conductivity. Thus, the chars will

react with higher reaction rates than those expected at the given ambient temperature. This may lead to effectiveness factors larger than unity.

In order to test these hypotheses, we performed experiments for a wide range of pyrolysis conditions and combustion temperatures. The reaction rate measurements at low combustion temperatures (kinetic control regime) provided us information about char intrinsic reactivity associated with the micropore structure. Measurements of apparent reactivity at high temperatures (diffusion limited regime), provided information on the significance of the macropore structure of chars.

4.2 Transient Patterns of Char Reactivity

One of the main objectives of this study was to study the mechanisms of char combustion in the diffusion-limited regime. After determining the char intrinsic reactivity with experiments in the kinetic control regime, our efforts focused on determining how the intrinsic reactivity and the macropore structure affect the observable combustion rates.

The temporal evolution of reactivity can provide the initial information on the mechanism of combustion. The reaction rate vs. conversion curve at 450 °C (kinetic control regime) is shown in Figure 4.3a. Char reactivity as measured by the rate $r_m(t)$ defined by Eq. (3.6) increases continuously with conversion. This reaction pattern agrees with theoretical models for gasification in the kinetic control regime where the active surface area associated with the micropores is easily accessible to the reactants (see for example, (Ballal and Zygorakis 1987; Bhatia and Perlmutter 1980; Bhatia and Perlmutter 1981; Cavallas 1980; Sandmann and Zygorakis 1987; Zygorakis and Sandmann 1988)). These and similar models predict that the intrinsic reaction rate will follow an increasing

pattern due to the increasing accessibility and specific surface area of the enlarging micropores.

The experimental reactivity curve at 550 °C (diffusion limited regime), however, revealed a different behavior. For the experiment shown in Figure 4.3b, the reaction rate increased sharply and in a rather "discontinuous" fashion in the early stages of gasification with a sharp maximum spanning a conversion range of approximately 10%. Since 8 particles were loaded in our reactor for each run, each "spike" in the reaction rate was caused by **ignition and rapid burn-off of one particle**. Many experiments with different samples showed very similar behavior.

After one (or more) sharp maxima at low conversions, the reaction rate would settle at a fairly constant plateau for the remainder of the reaction. This behavior was in (at least qualitative) agreement with the gasification models that assume that the macropore structure is the major rate-determining factor in the regime of diffusional limitations (high temperatures). While at first only the outer macropores are available for reaction, closed macropores open up as the reaction front reaches them and the observed reaction rate remains relatively constant (Zygourakis 1989).

The violent emissions of hot gas and small particle fines from an ignited particle to the surroundings would often induce ignitions in neighboring particles. At high oxygen concentrations, chain ignitions of neighboring particles were observed.

Ignitions did not always lead to rapid and complete burn-out of the particle. Often, ignited particles continued to shrink in size and deform even after the disappearance of the flame.

We carried out a systematic analysis to make sure that these sharp maxima were not artifacts due to measurement errors or to the interpolation of the numerical data. This analysis showed that the sudden and sharp drop of the sample weight was not due to errors in weight measurements or failures of our controller to maintain constant sample

temperature. Figure 4.4 presents a blow-up of the "spike" of Figure 4.3b to support the proposition that the spikes are not artifacts introduced by measurement errors.

The video microscopy apparatus provided conclusive evidence on the cause of the observed "spikes" in the reactivity curves. Video tapes of experiments showed that some particles ignited usually during the very early stages of gasification at the higher temperatures (e.g. 550 °C). Particle ignitions as shown on the video monitor occurred when the reaction rate increased sharply. A digital image sequence of combusting particles is shown in Figure 4.5, as obtained from the video microscopy apparatus. Note that this figure corresponds to the same sample that was presented in Figures 3.8-3.10. We note that in the middle image one of the particles becomes very bright as it ignites and moves to a new steady state with higher temperature. We can also see the ash skeleton remaining after complete combustion of the carbon. This sequence (and many others) show that there is very little particle fragmentation.

Additional confirmation that the spikes observed in the reaction rates are due to particle ignitions is provided by the controller power signal (see Figure 4.6). When the reaction rate was high, the controller cut down the power it provided to the furnace to balance the heat released by the reaction. Note that the reaction rate maxima corresponded to the maxima of the power control signal.

4.3 Mechanism of Particle Ignitions

Ignition is a thermal phenomenon caused by an imbalance between (a) the rate of heat generation inside the particle due to chemical reaction and (b) the rate of heat removal from the particle due to convection and radiation. When the reaction rate increases and the generated heat cannot be removed fast enough, the particle temperature can rise rapidly leading to even faster reaction rates and higher particle temperatures. Ignited particles

appear to be engulfed in a bright flame that facilitates the detection of ignitions via video microscopy.

Video tapes of particle ignitions provided new insights into the ignition mechanism. With the hot stage reactor, we obtained video sequences of particles under high magnification where one particle of 500-595 μm diameter was occupying the entire screen. We reacted the particles with oxygen concentrations as high as 100% to increase combustion rates and enhance ignition phenomena. The videotapes were then played back in slow motion (as low as 10 times slower than real-time speed) to observe the mechanism through which the ignitions occurred.

4.3.1 Case I: Particles Exhibit Single Ignitions

During one type of particle ignition, an orange or yellow flame would engulf the entire particle (global ignition). The particle surface changed from shiny-black to rough-grey with many cavities and fissures. Light emission was strong and easily distinguishable from the background. Gas was released rapidly carrying away small fragments and sometimes providing momentum for the particle to move.

Ignition started from a localized area on the particle surface and the flame front propagated rapidly over the entire surface (within 30-100 msec). The duration of the flame was between 1-3 secs reaching a maximum emission intensity and yellow color at an intermediate time.

At high temperatures the ignition started at very low conversions and ended with almost complete conversion of the particle. The flame front shrank towards the center of the particle which was probably experiencing lower reaction rates at the early stages of ignition, due to complete consumption of oxygen on the surface (diffusional limitations).

At moderate temperatures the particle ignited at intermediate conversions. The extinction also left some of the particle unreacted. The particle continued to react in the unignited steady-state with lower reaction rate.

These observations agree with the predictions of Sotirchos and Amundson (Sotirchos 1982; Sotirchos and Amundson 1984a; Sotirchos and Amundson 1984b; Sotirchos, Srinivas et al. 1984) of the transient combustion behavior of a char particle. When the particle reacts at low conversions it may have low micropore surface area and therefore lie in the unignited branch of the solution locus. As reaction proceeds and the micropores grow, the pore surface area increases and the reaction rates are enhanced. The particle obtains a new solution locus shifted to lower temperatures. Therefore, the ignition temperature may decrease and may become smaller than the ambient. As the reaction proceeds, the micropores coalesce and the micropore specific surface area drops. The ignition temperature increases exceeding at some point the ambient, and the particle moves to the extinction state.

4.3.2 Case II: Particles Exhibit Multiple Ignitions

In several cases we observed multiple ignitions in the same particle. They were mostly occurrences of a second type of ignition. This type was a localized, short ignition lasting only a few tenths of the second (30-300 msec). The flame was less bright, was visible only when the background illumination was low and its color was orange, another indication of lower ignition temperatures than those prevailing during global ignitions (yellow light is emitted by hotter objects).

Local ignitions were much harder to detect with the weight measurements since their effect on the total reaction rate was small. Furthermore, our data acquisition computer was only able to collect 1-4 weight measurements during a short ignition (our data collection is performed every 87 msec). With so few weight measurements, it is impossible to detect a

maximum in the reaction rate. These arguments strongly support the use of a video imaging device if every ignition is to be detected.

Multiple ignitions of the same particle have rarely been mentioned in the literature (Solomon, Chien et al. 1990) and no models have been proposed to explain them. A possible explanation of multiple ignitions is that the structural inhomogeneity of the char particles exposes different fractions of the surface area as the conversion increases. Another possibility is that large macropores that are initially inaccessible to the gas open-up causing sudden increases of the reaction rate.

4.4 Particle Ignitions and Reactivity Patterns

Figure 4.7 shows the reaction rate measurements from a combustion experiment. The reaction rate pattern exhibits three spikes (local maxima). A careful analysis of the video sequence for this run clearly showed that the first two rate spikes were attributed to ignition of one particle each time. This confirms our hypothesis concerning the connection between particle ignitions and local maxima in the reactivity curve.

A third maximum in the reactivity pattern was observed at time 10 seconds but it did not correspond to light emission. However, at this instant a particle shrunk rapidly leaving back a sponge-like structure composed of its ash skeleton. This maximum was observed at higher conversions when very little mass of solid is left. If we plot the reaction rate per unit mass of initial solid (r_0) the maximum is less prominent.

Particle ignitions, however, do not necessarily lead to spikes in the rate vs. conversion curves. If many particles ignite at the same time or if the particles exhibit multiple ignitions that are short and localized, the reaction rate curve may not show any sharp spikes. This is demonstrated in Figure 4.8 that shows a very smooth reaction rate pattern. The video sequence showed that there were 4 ignitions in the -5

to 0 sec period. Three of the ignitions occurred in the same particle: first a global ignition and, later, two localized ones. The fourth ignition was also a global one and occurred at time zero. The effect of this ignition on the reaction rate was probably masked, however, by the two localized ignitions occurring exactly before and after the global one.

Our conclusion is that although some ignitions can be detected by the thermogravimetric method, this is not always true. This is the reason why a video microscopy system is necessary to detect all particle ignitions.

4.5 Effect of flow rate on particle ignitions

Particle ignitions occur when heat generation rates are higher than heat removal rates. Heat removal depends on the magnitude of the heat transfer coefficient. It is expected that a higher gas flow rate will increase the heat transfer coefficient and also prevent intraparticle temperature gradients and ignition.

This hypothesis was confirmed by the results of Figures 4.9 and 4.10. Under a flow rate of 240 sccm, the particles ignited at 550 °C. When the flow rate was increased to 360 sccm, however, particle ignitions were less frequent. Several experiments showed similar behavior suggesting that the particles at the flow rate of 240 sccm are more external heat transfer limited.

4.6 References for Chapter 4

Ballal, G. and K. Zygourakis. (1987). "Evolution of Pore Surface Area During Noncatalytic Gas-Solid Reactions: 1. Model Development." Ind. Eng. Chem. Research. 26(5): 911-921.

Bhatia, S. K. and D. D. Perlmutter. (1980). "A Random Pore Model for Fluid-Solid Reactions: I. Isothermal, Kinetic Control." *AIChE J.* 26(3): 379-386.

Bhatia, S. K. and D. D. Perlmutter. (1981). "A Random Pore Model for Fluid-Solid Reactions: II. Diffusion and Transport Effects." *AIChE J.* 27(2): 247-254.

Gavalas, G. R. (1980). "A Random Capillary Model with Application to Char Gasification at Chemically Controlled Rates." *AIChE J.* 26(4): 577-585.

Sandmann, C. W., Jr. and K. Zygorakis. (1987). "Pore Structure Evolution During Noncatalytic Gas-Solid Reactions: 4. Studies with Demineralized Chars." *Chem. Eng. Commun.* 58: 139-164.

Solomon, P. R., P. L. Chien, R. M. Carangelo, M. A. Serio and J. R. Markham. (1990). "New Ignition Phenomenon in Coal Combustion." *Combust. Flame.* 79(2): 214-15.

Sotirchos, E. V. (1982). Diffusion and reaction in a char particle and in the surrounding gas phase. Ph.D. Dissertation, University of Houston, Houston, TX.

Sotirchos, S. V. and N. R. Amundson. (1984a). "Diffusion and reaction in a char particle and in the surrounding gas phase. A continuous model." *Ind. Eng. Chem. Fundam.* 23(2): 191-201.

Sotirchos, S. V. and N. R. Amundson. (1984b). "Diffusion and reaction in a char particle and in the surrounding gas phase. Two limiting models." *Ind. Eng. Chem. Fundam.* 23(2): 180-91.

Sotirchos, S. V., B. Srinivas and N. R. Amundson. (1984). "Modeling of the combustion of single char particles." *Rev. Chem. Eng.* 2(3-4): 175-236.

Zygourakis, K. (1989). "A New Discrete Simulation Method for Modeling Char Gasification in the Diffusion-Controlled Regime." *Amer. Chem. Soc., Div. Fuel Chem. Prepr.* 34(1): 202-211.

Zygourakis, K. and C. W. J. Sandmann. (1988). "Discrete Structural Models and Their Application to Gas-Solid Reacting Systems." *AIChE Journal.* 34(12): 2030-2040.

Figure 4.1: Reaction in the regime of kinetic control. Both the macropores and the entire network of micropores that emanate from the larger pores participate in the heterogeneous reactions.

Figure 4.2:

Reaction in the regime of diffusional limitations. A large portion of the micropore network (darkened areas) does not participate in the reaction. The reaction zone includes the macropore surface and a fraction of the micropores located at a constant depth below the macropore surface.

Figure 4.3: Representative reactivity patterns for combustion of an Illinois #6 char in the kinetic control and the diffusion-limited regimes. Note the different y scales.

Figure 4.4: Measurements of weight and temperature vs. time and computed reaction rate for the "spike" of Figure 4.3b.

(A) END OF PYROLYSIS

(B) IGNITION AT 570 C

(C) END OF COMBUSTION

Figure 4.5:

Video image sequence of eight reacting particles before, during and after combustion. Note the ignition at the center image and the ash content at the bottom one.

Figure 4.6: Controller feedback power and particle reaction rate as functions of time.

Figure 4.7: Reaction rate measurements during combustion of Illinois #6 char at 600 $^{\circ}\text{C}$ (Pyrolysis heating rate: 20 $^{\circ}\text{C/s}$; HTT: 700 $^{\circ}\text{C}$; Soak time: 3 min).

Figure 4.8: Reaction rate measurements during combustion of Illinois #6 char at 600 °C (Pyrolysis heating rate: 10 °C/s; HTT: 700 °C; Soak time: 3min;).

Figure 4.9: Effect of gas flow rate on ignition phenomena during combustion at 550 °C (Pyrolysis heating rate: 1 °C/s, HTT: 700 C; Soak time: 3 min).

Figure 4.10: Effect of gas flow rate on ignition phenomena during combustion at 550 °C (Pyrolysis heating rate: 10 °C/s; HTT: 700 °C; Soak time: 3 min).

CHAPTER 5

EFFECT OF PYROLYSIS CONDITIONS ON CHAR REACTIVITY

5.1. Effect of heat treatment temperature (HTT) on char reactivity

The heat treatment temperature (HTT) is an important parameter for reactor design and influences the swelling of the particles. In order to investigate the effect of HTT on the transient reactivity patterns, we pyrolyzed coal particles at several heating rates and HTT's and measured the char reactivity at both the kinetic control and diffusion-limited regimes.

Figure 5.1 shows the reaction rate patterns at 450 and 550 °C for char samples prepared at the heating rate of 1 °C/s and four different heat treatment temperatures (HTT): 500, 700, 800 and 900 °C. Soak time at the HTT for all these samples was 3 minutes.

The experimental gasification data at 450 °C (kinetic control regime) show temporal patterns exhibiting the gradual increase of char reactivity described in Chapter 4. However, chars produced at higher HTT (e.g. 800 and 900 °C) are less reactive than chars produced at low heat treatment temperatures (500 and 700 °C). Since this decline in reactivity is observed in the kinetic control regime (where macropore structure has no effect), we conclude that high heat treatment temperatures lower the intrinsic reactivity of the chars.

These observations of declining reactivity with increasing HTT are in agreement with earlier studies on char combustion (Serio, Solomon et al. 1989). The molecular order of chars produced at high HTT increases due to enhanced annealing of the organic and mineral components and the microporosity of the chars. In other words, the high treatment temperatures cause sintering of the active carbon sites and a decrease of the intrinsic

reactivity. This observation strongly supports the basic premise of *mild gasification* processes that treat coals to relatively low temperatures so that they produce highly reactive solid fuels.

The experimental gasification data at 550 °C show the char reactivity pattern that we found to correspond to particle ignitions (Chapter 4). A decline in reactivity with increasing heat treatment temperatures can still be observed. This is expected, since intrinsic reactivity affects observable reaction rates in the entire temperature range (except in the case of strong external mass transfer limitations). Another important observation is that **char particles produced at lower HTT's are more likely to ignite**. For example, the chars treated at 700 and 800 °C exhibit ignitions (as indicated by the "spikes" in the reactivity curves), while the chars treated at 900 °C do not ignite. This agrees with the theoretical models that predict low ignition temperatures for very reactive solids.

We should note, however, that the effect of HTT on macropore structure can not be deduced from these experiments since it is screened by the substantial changes in the intrinsic reactivity.

5.2. Effect of soak time on char reactivity

Soak time is the time the pyrolyzing coal sample is kept at the heat treatment temperature. The effect of soak time on char reactivity was studied for the entire range of HTT's. Figure 5.2a shows the effect of soak time at the HTT of 800 °C. Longer soak times decrease the intrinsic reactivity of the chars as measured by the reaction rate at 450 °C. The sample that was quenched immediately after it reached the 800 °C HTT (i.e. zero soak time) was about 40% more reactive than the sample that was kept at 800 °C for 3 minutes.

Figure 5.2b presents the combustion data at 550 °C. As expected, the char that experienced the shorter soak times (0 mins) was more likely to ignite. One of the two runs with chars that experienced zero soak time exhibited ignition phenomena. This is again consistent with the argument that increased reactivity results to lower ignition temperatures.

The effect of soak time, however, diminishes at lower heat treatment temperatures. Our experiments with HTT of 500 °C showed that **prolonging the pyrolysis for 3 minutes did not significantly affect the reactivity.** This is reasonable to expect since the active site sintering is an activated reaction that is much slower at low HTT. This may mean that **prolonged heating at mild temperatures does not deteriorate char reactivity.**

5.3. Effect of heating rate on char reactivity

The reactivity of chars prepared at various heating rates was measured in a wide range of combustion temperatures (400 to 600 °C) covering both the kinetic and the diffusion-limited regimes. For these runs, the chars were heated in nitrogen up to 700 °C and held there for 3 minutes.

Figures 5.3 through 5.8 demonstrate the relative reactivity of chars prepared at heating rates from 0.1 °C/s to 20 °C/s. At low combustion temperatures (400 to 450 °C) where chars react in the kinetic control regime, we observe that **chars prepared at different pyrolysis rates have approximately equal reactivities and burn-off times** (i.e. times required to achieve a specific conversion level). The transient reactivity patterns are also similar. This is a conclusive evidence that:

- (i) **the micropore surface area of chars is not affected by pyrolysis heating rates, and**

- (ii) **the chemical nature and concentration of the reactive sites is not altered by the different heating rates.**

On the other side, as the combustion temperature increases above 550 °C, we observe a progressive divergence of the reactivities. The chars produced at 1 and 10 °C/s are more reactive although they exhibit reactivity patterns without sharp maxima. Finally, at the combustion temperature of 600 °C the chars exhibit the reactivity patterns that are clearly attributable to ignition (Figure 5.8). When the particles ignite, the reactivity curve exhibits several "spikes", one for each ignition that resulted in rapid consumption of a char particle. It is clear that the chars pyrolyzed at higher heating rates are igniting more frequently. This results to a significantly higher reaction rate.

Therefore, chars produced at high pyrolysis heating rates exhibit higher observable reaction rates in the diffusion-limited regime and lower ignition temperatures. Since the heating rates did not affect reaction rates in the kinetic control regime, we can conclude that the intrinsic reactivity was not affected. The cause of the reactivity differences in the diffusion-limited regime must be the macropore structure. Note also that chars prepared at higher heating rates have a more open macropore structure (see Chapter 2 of this report). That should allow for higher intraparticle transport rates for the reactants and, consequently, higher reaction rates at high temperatures.

5.4. Effect of pyrolysis on combustion

An interpretation of these results is now necessary so that we can determine the optimal pyrolysis treatment to produce the most reactive chars.

The experimental results we presented so far in this report agree in principle with the earlier theoretical predictions mentioned earlier (Sotirchos and Amundson 1984a; Sotirchos

and Amundson 1984b; Sotirchos, Srinivas et al. 1984). Sotirchos and Amundson predicted that particle ignition will occur when the ambient temperature exceeds a certain threshold value. The ignition temperature is lower when Knudsen diffusion in the macropores is less dominant. That is, when the average macropore size of the particle is higher then the diffusional limitations are lower and the ignition temperature is also lower.

We will use similar arguments to explain the differences in high-temperature reactivity we measured with chars produced at different heating rates.

- (a) Low heat treatment temperatures and short soak times during the pyrolysis stage lead to the production of chars with high intrinsic reactivity. Highly reactive chars are more likely to ignite and burn faster at all temperatures. Chars that ignite may exhibit observable reaction rates as much as 10 times larger than non-igniting chars.
- (b) The structural changes occurring during the pyrolysis stage due to particle softening and swelling can lead to chars that have a **highly cellular pore structure when the heating rate is relatively high**. As mentioned earlier, the average macropore size, particle size, porosity and macropore specific surface area are all monotonically increasing with the pyrolysis heating rate. Therefore, a more open and more accessible macropore network would significantly decrease the diffusional limitations in the macropores and also increase the available macropore surface for reaction. The decrease of intraparticle diffusional limitations makes the internal surface more accessible to the gaseous reactants. Thus, their concentration is higher inside the particle and consequently the reaction rate is enhanced.
- (c) The ignition temperature will be lower for chars with lower macropore diffusional limitations (i.e. chars produced at high heating rates). This is apparent in Figure 5.8a where only the chars produced at 1, 10 and 20 °C/s show significant ignition

phenomena. On the other hand, chars produced at 0.1 and 0.3 °C/s did not ignite since their ignition temperature is probably higher than the highest combustion temperature (600 °C) we used in these experiments. The increased temperature of the ignited particles induces a much higher reaction rate that is detectable by a sharp peak in the reactivity curves.

- (d) At high ambient temperatures (about 550-600 °C) the reaction rate is high enough to produce high heat generation rates. The heat removal through the particle and its boundary layer is not fast enough and intraparticle and boundary layer temperature gradients appear. As mentioned earlier, the particles treated with higher heating rates have higher porosity and thus lower effective thermal conductivity. Therefore, heat removal is less efficient for these particles and they are more prone to external temperature gradients that lead to ignitions and higher reaction rates. We believe though, that this effect is not as important as the previous ones.

5.5. Kinetic measurements

Reactivity measurements in a wide range of combustion temperatures can be used to determine kinetic parameters of coal combustion, that is the *activation energy*, *preexponential rate factor* and *effectiveness factor*.

Activation energies are determined by measuring the reaction rates at a specific conversion x and various temperatures. An Arrhenius plot should give a straight line in the kinetic control regime whose slope yields the activation energy. One should not use instantaneous reaction rates for activation energy calculations. Sample weight curves always have small local peaks and dips (probably attributed to structural inhomogeneities) that may lead to significant variations in derivatives and instantaneous rates. On the other

hand, these small temporal variations will disappear if we use average reaction rates up to a specific conversion. The average reaction rate can be obtained as following:

$$\bar{r}^* = -\frac{1}{t^*} \int_0^{t^*} \frac{1}{m_0} \left(\frac{dm}{dt} \right) dt = \frac{1}{t^*} \frac{(m_0 - m^*)}{m_0} = \frac{x^*}{t^*} \quad (5.1)$$

where x^* is the reference conversion, t^* is the time to achieve this conversion x^* , m_0 is the initial mass of the solid in ash-free basis and $m(t^*)$ is the unreacted mass at conversion x^* . Therefore it is only sufficient to know the burn-off time at a specific conversion to determine the average reaction rate from the onset of reaction up to this conversion.

Figure 5.9 shows an Arrhenius plot of the average reaction rates computed at three reference conversions: 10%, 25% and 50%. The combustion temperatures used for this plot are 400, 420, 430 and 450 °C. The experimental data are very well fitted by straight lines with correlation coefficients 0.9991, 0.9998 and 0.9973 respectively. This linearity confirms our claims that this temperature range belongs to the kinetic control regime. The slope of the three curves was very similar giving the following values of the activation energy: 32.6, 32.6 and 31.4 Kcal/mol. Although the difference in activation energies is smaller than the experimental error, we will use the value of 32.6 Kcal/mol for subsequent computations since the average rate is more reliable at the early stages of reaction where the error is smaller and the temporal char reactivity patterns more similar.

The preexponential factors are different for each reference conversion. This is expected since the reaction rate changes with conversion. Their values are $1.742 \cdot 10^8$, $2.536 \cdot 10^8$, $1.440 \cdot 10^8 \text{ min}^{-1}$ for reference conversions 10%, 25% and 50% respectively. Actually, this preexponential factor includes the intrinsic reaction kinetics (kinetic constant and order of reaction), the concentration of active sites and the specific surface area. Since none of these quantities is easily measurable, we cannot draw any further conclusion from the value of the preexponential factor.

In Figures 5.13 through 5.15 we see the effectiveness factors as a function of combustion temperature for chars treated with three different heating rates. The effectiveness factors were calculated as

$$\eta = \frac{r_{obs}(T)}{r_{kinetic}(T)} \quad (5.2)$$

where $r_{obs}(T)$ is the average rate observed at the combustion temperature T (and the appropriate conversion level x^*) and $r_{kinetic}(T)$ is the average rate calculated by neglecting intraparticle diffusional resistances and intraparticle or external temperature gradients. The kinetic control regime rates $r_{kinetic}(T)$ were calculated with the previously derived values of activation energy and pre-exponential constants at the appropriate conversion level ($x^*=0.10$, $x^*=0.25$ and $x^*=0.50$ for Figures 5.13 to 5.15 respectively).

We can clearly see that the chars treated with 10 °C/s have effectiveness factors larger than unity at 500 °C ($\eta \approx 1.2$ to 1.3). This is due to the external temperature gradients. Although the reactivity patterns at 500 °C did not exhibit any ignition "spikes", the results suggest that the particles were reacting at temperatures larger than the ambient. The visual observations did not suggest any ignition phenomena either. Thus, the particles react in a regime of moderate temperature gradients (first steady state). From the figures we can see also that the chars treated at lower heating rates are more diffusionally limited since they have lower effectiveness factors.

Another observation is that the effectiveness factor at high temperatures (600 °C) increases as the conversion increases, while this does not happen at lower temperatures (500 °C). The reason of the increase of the effectiveness factor with conversion is the enlargement of the macropores that decreases their diffusional resistances and increases their accessibility. In other words, the progressive growth of the macropores reveals more surface area to the gaseous reactants that was previously closed and inaccessible. Since the

macropore diffusion is more prominent at high temperatures this decrease in the effectiveness factors is more likely to occur at these temperatures. At lower temperatures though, macropore diffusion and accessibility are not as important. The thermal effects control the rate primarily and diffusion is not yet as a limiting factor. At 500 °C the ignition at low conversions (10%) makes the effectiveness factor larger than in the higher conversions (50%) where extinction has occurred probably.

5.6. Statistical significance of our results

We should note that not all the particles in the same sample behave the same. Their slightly different pore structures, ash content and particle size produce a slightly different behavior for each one under the same conditions. For example, not all particles treated at 20 °C/s ignite as seen in Figure 5.8a. Only two of them ignited and the others did not show any light emission. This is caused by the fact that ignition is a thermal phenomenon that depends on whether the ambient temperature exceeds or not the particle ignition temperature. Therefore, only the particles in the batch that have ignition temperature slightly lower than 600 °C will ignite, while the others will not. But even then, the non-ignited particles still contribute to a reaction rate that is larger than that of the chars treated with lower heating rates. In other words, even in the non-ignited portions of the experiment the total reactivity is larger for the chars treated with higher heating rates. By repeating the combustion experiments, we saw that a small number of particles ignited during every run. **Overall burn-off times were very similar for different runs with produced under the same conditions** due to the averaging of the rates of the eight particles in each run. This indicates we can obtain statistically significant results even with three runs for each set of conditions.

The statistical analysis of the burn-off times was performed with the usual t-test. The standard deviation of the experimental measurements was found and the error margin was calculated using the t-coefficient from the T distribution. Our calculations showed that the error achieved in three runs is about 25-30 % with 95% level of confidence.

5.7. References for Chapter 5

Serio, M. A., P. R. Solomon and R. Bassilakis. (1989). "The effect of minerals and pyrolysis conditions on char gasification rates." Amer. Chem. Soc., Div. Fuel Chem. Prepr. 34(1): 9-21.

Sotirchos, S. V. and N. R. Amundson. (1984a). "Diffusion and reaction in a char particle and in the surrounding gas phase. A continuous model." Ind. Eng. Chem. Fundam. 23(2): 191-201.

Sotirchos, S. V. and N. R. Amundson. (1984b). "Diffusion and reaction in a char particle and in the surrounding gas phase. Two limiting models." Ind. Eng. Chem. Fundam. 23(2): 180-91.

Sotirchos, S. V., B. Srinivas and N. R. Amundson. (1984). "Modeling of the combustion of single char particles." Rev. Chem. Eng. 2(3-4): 175-236.

Figure 5.1: The effect of heat treatment temperature on reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at 450 and 550 °C (Heating rate 1 °C/s, soak time 3 min).

Figure 5.2: The effect of soak time on reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at 450 and 550 °C (Heat treatment temperature: 800 °C; Heating rate: 0.1 °C/s).

Figure 5.3: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 400 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.4: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 420 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.5: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 450 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.6: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 500 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.7: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 550 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.8: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 600 °C (HTT: 700 °C; soak time: 3 minutes).

Figure 5.9: Arrhenius plot for the kinetic control regime 400-450 C for Illinois #6 chars (HIT: 700 C; soak time: 3 minutes).

Figure 5.10: Arrhenius plot for the entire temperature range (400-600 C) for Illinois #6 chars (HTT: 700 C; soak time: 3 min). Reference conversion is 10%.

Figure 5.11: Arrhenius plot for the entire temperature range (400-600 °C) for Illinois #6 chars (HTT: 700 °C; soak time: 3 min). Reference conversion is 25%.

Figure 5.12: Arrhenius plot for the entire temperature range (400-600 °C) for Illinois #6 chars (HTT: 700 °C; soak time: 3 min). Reference conversion is 50%.

Figure 5.13: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 C; soak time: 3 minutes). Reference conversion 10%.

Figure 5.14: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 C; soak time: 3 minutes; Reference conversion 25%)

Figure 5.15: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 °C; soak time: 3 minutes; Reference conversion 50%)

CHAPTER 6

COAL PARTICLE SIZE AND CHAR REACTIVITY

6.1. Effect of size on intrinsic reactivity

In this Chapter we present some preliminary experimental findings on the effect of initial coal particle size on the char reactivity patterns.

We used two particle size fractions for our experiments:

- 1) 20-25 mesh (707-841 μm), and
- 2) 28-32 mesh (500-595 μm).

The pyrolyzed char particles were reacted in both the kinetic control regime and the diffusion limited regime to determine the effect of particle size on the reactivity or burn-off times.

The effect of heating rate on the intrinsic reactivities of chars of the 28-32 mesh fraction was presented earlier (Chapter 4). We found that the heating rate did not influence the intrinsic reactivity as measured in the kinetic control regime. Here, we investigate the effect of increasing particle size from 500-595 to 707-841 μm on intrinsic reactivity. We pyrolyzed both samples at 700 °C for 3 min and with heating rate of 10 °C/s. Their reactivity is quite similar at 450 °C (see Figure 6.1a). This is another indication that at this temperature we are in the kinetic control regime since the larger particles should react slower in the presence of intraparticle diffusional limitations).

6.2. Effect on ignition temperature

At the combustion temperature of 550 °C the 20-25 mesh particles exhibit a dramatic difference from the 28-32 mesh. The larger particles are reacting at rates that are twice or three times as high as the rates of the 28-32 mesh particles (Figure 6.1b).

At first this seems counter-intuitive, since we would expect that the larger particles would react slower in the presence of diffusional limitations. The phenomenon is solely attributed to thermal particle ignitions. The rate enhancement is due to the ignition of one of the two large particles that were loaded in the sample pan. Note that ignition "spike" covers the range of 0-50% conversion. We are confident that these ignitions are not artifacts since repeated runs with 20-25 mesh particles showed thermal particle ignitions. After the ignition though, the other large particle reacted with a rate lower than the rate of the smaller particles. Here is where the diffusional limitations determine the reaction rate.

The above observations are in agreement with experimental and theoretical results like the ones presented by Sotirchos and Amundson (Sotirchos and Amundson 1984a; Sotirchos and Amundson 1984b; Sotirchos, Srinivas et al. 1984). They predicted that the ignition temperature decreases with increasing particle size (the large particles have lower external surface to volume ratio). For our experimental conditions and a combustion temperature of 550 °C, several of the 20-25 mesh particles (at least one in each run) had ignition temperature lower than 550 °C while all the 28-32 mesh particles had ignition temperature higher than 550 °C.

6.3. Effect of size on macropore structure

The effect of particle size on the development of macropore structure during pyrolysis was discussed earlier in Chapter 2. We have mentioned that the smaller particles have

higher macropore specific surface areas although they have the same macroporosity with the larger ones (Zygourakis 1988; Zygourakis and Glass 1988). Intraparticle diffusional resistances will be lower in the smaller particles than the resistances of the larger particles at the same temperature since the Thiele modulus is proportional to the particle size).

6.4 Reactivity dependence on heating rate - The role of particle size

The effect of heating rate on reactivity is examined for coal particles in the 20-25 mesh size. Figure 6.2 shows the reaction rates and burn-off times of these large particles in the diffusion limited regime (550 °C). The experimental results lead to the same conclusions we arrived at in Chapter 5 regarding the effect of pyrolysis heating rate on char reactivity.

For the large particles we see again that increasing heating rates make the particles more reactive. The results of Figure 6.2 show in addition that the difference of reactivities between particles pyrolyzed at 0.1 and 10 °C/s is larger for the larger particle size. In other words, if we compare the ratio of reactivities between the 0.1 and 10 °C/s we will notice that this ratio is larger for the large particles. The larger differences can be attributed to the following three reasons.

- (A) Large particles may ignite at lower ambient temperatures due to less effective heat removal rates. A qualitative explanation for this behavior can be obtained from a steady-state analysis. The particle temperature T_p can be found from a simple energy balance that has the following form

$$h(4\pi R^3)(T_s - T_f) = \left(\frac{4}{3}\pi R^3\right)(-\Delta H)k_0 \exp\left(-\frac{E}{RT_s}\right)c_s \quad (6.1)$$

where h is the heat transfer coefficient, R is the particle radius, T_f is the ambient temperature, $(-\Delta H)$ is the heat of reaction, k_0 is the pre-exponential coefficient and c_s is the reactant concentration in the particle. After some rearrangement. Equation (6.1) becomes

$$Q_I(T_s) \equiv \frac{3h}{Rc_s}(T_s - T_f) = (-\Delta H)k_0 \exp\left(-\frac{E}{RT_s}\right) \equiv Q_{II}(T_s) \quad (6.2)$$

The steady-state particle temperature T_s will be found as an intersection of the straight line $Q_I(T_s)$ that represents the left-hand-side of equation (6.2) and the sigmoidal curve $Q_{II}(T_s)$ that represents the right-hand-side of equation (6.2).

When the particle radius R increases, the slope of the straight line $Q_I(T_s)$ decreases. As a result of increasing particle size, the particle temperature may move from an unignited, low-temperature steady-state to the ignited, high-temperature steady state even when everything else (solid reactivity, heat transfer coefficient etc.) remains constant.

- (B) Since the large particles will exhibit stronger intraparticle diffusional resistances, the macropore structure becomes even more important. The more open pore structure of particles produced at high heating rates will result to large decreases of the diffusional limitations.

- (C) Large particles have larger swelling indices (see previous Chapters). Thus, the larger particles will be more affected by the heating rates.

As a conclusion, we believe that the difference in reactivities and heat transport behavior among different particle sizes is important but also complicated. Experimental findings have demonstrated that the ash and sulfur content and the specific surface area of coals vary with the particle size (for sizes less than 1 mm) (Palmer, Cheng et al. 1990). Such variations may further complicate our analysis. A more detailed investigation is needed that will include measurements of surface area and macropore size for different size fractions.

6.5 References for Chapter 6

Palmer, A. D., M. Cheng, J.-C. Goulet and E. Furimsky. (1990). "Relation between particle size and properties of some bituminous coals." *Fuel*. 69(2): 183-188.

Sotirchos, S. V. and N. R. Amundson. (1984a). "Diffusion and reaction in a char particle and in the surrounding gas phase. A continuous model." *Ind. Eng. Chem. Fundam.* 23(2): 191-201.

Sotirchos, S. V. and N. R. Amundson. (1984b). "Diffusion and reaction in a char particle and in the surrounding gas phase. Two limiting models." *Ind. Eng. Chem. Fundam.* 23(2): 180-91.

Sotirchos, S. V., B. Srinivas and N. R. Amundson. (1984). "Modeling of the combustion of single char particles." *Rev. Chem. Eng.* 2(3-4): 175-236.

Zygourakis, K. (1988). "The Effects of Pyrolysis Conditions on the Macropore Structure of Coal Chars." Amer. Chem. Soc., Div. Fuel Chem. Prepr. 33(4): 951-959.

Zygourakis, K. and M. W. Glass. (1988). "Macropore Size Analysis Using Digital Image Processing and a Stereological Model." Chem. Eng. Commun. 70: 39-55.

Figure 6.1: Reaction rate measurements for Illinois #6 chars of two different sizes (28-32 mesh and 20-25 mesh) at combustion temperatures of: a) 450 °C and b) 550 °C (HTT: 700 °C; Soak time: 3 min; Heating rate: 10 °C/s).

Figure 6.3: Effect of heating rate on reactivity and burn-off times of Illinois #6 chars of size 20-25 mesh at 550 °C (HTT: 700 °C; Soak time: 3 min).

CHAPTER 7

MODELING OF CHAR GASIFICATION IN THE DIFFUSION-CONTROLLED REGIME

7.1 Summary

We developed a new modeling and simulation method to solve gas-solid reactions problems. This approach is based on cellular automata and discrete iterations and overcomes many of the limitations of earlier models since it can handle heterogeneous systems with multiple porous reactants and arbitrary pore/solid geometries. The new models were used to simulate the gasification of porous char particles under conditions leading to strong intraparticle diffusional limitations and to low utilization of the micropores. In order to accurately account for the effects of the macropore structure on char reactivity, the new models employed computational grids obtained by digitizing images of actual char particle cross-sections using an optical microscope equipped with a video camera and an image processing computer. Simulation results are presented from multiple runs performed on several char samples that were prepared in our laboratory by pyrolyzing two parent coals under various operating conditions. Model predictions are compared and analyzed in order to elucidate the effects of the macropore structure on the gasification rates and particle burn-out times.

7.2 Model Development

The discrete models we developed consider porous solids that react with one or more gaseous reactants to produce one or more gaseous products. Thus, these models can be applied to all the important coal gasification and combustion reactions.

Discrete models employ rectangular arrays of usually square cells to simulate the temporal evolution of pore structures in reacting systems. In our earlier studies (Zygourakis and Sandmann 1988) we defined the pores of a solid reactant (char) by randomly distributing on the grid overlapping regular geometrical entities (circles, spheres or cylinders) of a given size distribution. Direct microscopic measurements, however, revealed that char particles exhibit highly irregular pore structures (Zygourakis 1988; Zygourakis and Glass 1988).

7.2.1 Cellular Arrays and Reaction Rules

In order to overcome the computational complexities introduced when considering heterogeneous reactions in system with arbitrary pore/solid geometries and multiple porous reactants, we had to develop a new simulation technique. The new approach is based on cellular automata and discrete iterations.

The evolving pore structure of multicomponent systems is again modeled on rectangular arrays of cells. Each cell can exist in one of several possible states. It can represent, for example, a small volume element of (a) solid reactant, or (b) pore that is accessible to the gaseous reactants.

The important thing to notice about our simulation approach is that **the initial configurations of the cellular arrays are obtained directly from the digitized images of actual char particle cross-sections**. Figure 7.1A shows an example of an initial configuration of a computational grid. This is a binary image of an

actual char particle cross-section and it was obtained with our image processor. Black pixels correspond to the char matrix, while the particle exterior and the profiles of the internal macropores are denoted by white.

The number of possible states for each cell depends on the assumed reaction regime. In our studies we considered the following two cases.

Regime A: The operating assumptions for this regime are as follows:

- (A-1) There are strong diffusional limitations in the micropores. This implies that the micropore surface area is not fully utilized and reaction occurs mostly around the pore mouths where the micropores open into the large macropores (see also Figure 4.2).
- (A-2) There are no diffusional limitations in the macropores. Thus, the entire macropore surface area is available for reaction and there are no reactant concentration gradients in the macropores.

For simulations in Regime A, each cell of the computational grid can exist in one of two possible states. It can represent

- (1) a volume element of solid reactant (cell is black), or
- (2) a volume element of pore void (cell is white).

The evolution of the pore structure is modeled by updating the initial cellular array at equally spaced time instants $t^1, t^2, \dots, t^r, t^{r+1}, \dots$ as follows:

- (a) Reaction occurs only in the cells located at the surface of the macropores (thin reaction zone).

- (b) If at time t^r a solid reactant cell is adjacent to one or more gaseous reactant cells (i.e. the solid cell is located at the surface of a macropore), then this solid cell may be changed to a pore void cell (or reacted) at the next time level $t^{r+1} = t^r + \Delta t$.
- (c) The solid cells react according to a probabilistic algorithm that guarantees isotropic consumption of the solid reactant. This algorithm erodes a single layer of pixels from the entire surface area exposed to gaseous reactants during each iteration step Δt .

An initial computational grid for reaction in Regime A is shown in Figure 7.1A. Figures 7.1B through 7.1D show the computational grid of Figure 7.1A after several iteration steps that correspond to solid conversions of $x=0.200$, $x=0.394$ and $x=0.632$. These images show (a) growth of all the internal macropores and (b) erosion of the particle external surface due to the chemical reaction occurring on the solid surface. As the macropores grow and coalesce with either adjacent pores or the receding particle exterior, the total surface area decreases driving the reaction rate down. The predicted reaction rate for this run is shown as a function of solid conversion in Figure 7.3. After a small initial rise, the reaction rate decreases monotonically with conversions. Figures 7.1 and 7.3 show that our model successfully captures the essential features of gas-solid systems reacting in this regime.

Regime B: The operating assumptions for this regime are as follows:

- (A-1) There are strong diffusional limitations in the micropores.
- (A-3) There are also diffusional limitations in the macropores. The model assumes that chemical reaction takes place only at the surface of "open" macropores, i.e. the macropores that are directly connected to the particle exterior. Internal macropores are not initially accessible to the gaseous reactants. When the

reaction front "opens" these interior pores, however, their surface area may become available for reaction.

The new rules are implemented by allowing each cell of the computational grid to exist in one of three possible states (see Figure 7.2A). It can be

- (1) a solid reactant cell (**black**),
- (2) a cell occupied by gaseous reactants or "open pore cell" (**white**), or
- (3) a cell belonging to a "closed macropore" (**gray**).

The initial cellular array is updated according to the following rules:

- (a) A solid reactant (black) cell may "react" (changing its state to white), if its immediate neighborhood contains one or more gaseous reactant (white) cells.
- (b) A solid reactant (black) cell will not change its state, if it is surrounded only by solid (black) or "closed pore" (gray) cells.
- (c) If "closed pore" (gray) cells get exposed to gaseous reactant (white) cells, their state may change to gaseous reactant (white).

Figures 7.2B through 7.2D show the configuration of the cellular array at three different conversion levels. In the early stages, reaction occurs on the external surface of the particle. As the reaction front moves, "closed" macropores become accessible to the reactants and the surface area available for reaction increases. Macropore openings thus lead to sudden increases of the reaction rate. The predicted reaction rate for this run is shown as a function of solid conversion in Figure 7.3.

In general, gaseous reactant cells "consume" solid or closed pore cells at different rates. These rates can be appropriately adjusted to account for **different degrees of**

diffusional limitations in the macropores opening up for reaction. If there are no diffusional limitations in the macropores, when the reaction front reaches a previously closed pore the model will make the entire area of this macropore available for reaction immediately. But if there are significant diffusional limitations in the macropores, when the reaction front reaches a previously closed pore the model will not make the entire area of the macropore available for reaction immediately but it will do so progressively.

7.2.2 Estimating Reaction Rates from Discrete Simulations

The simulation results can be related to experimental gasification data as follows. If $m(t)$ is the mass of solid remaining at time t , the specific rate R_m of the heterogeneous reaction can be expressed as

$$R_s = \frac{1}{m(t)} \frac{dm}{dt} = S_g(X) r_s(c, T; a) \quad (7.1)$$

where S_g is the specific pore surface area available for reaction (expressed in m^2 of surface area per kg of solid), $r_s(c, T; a)$ is the intrinsic reaction rate expressed in (kg of solid)/(s)(m^2 of surface area), c denotes the gaseous reactant concentrations, T is the temperature and $a(X)$ is a measure of the surface activity. Since the porous solid is consumed during the reaction, the surface area S_g changes drastically with the solid conversion X defined by

$$X = \frac{m_0 - m(t)}{m_0} \quad (7.2)$$

where m_0 is the mass of the unreacted solid. Intraparticle diffusional limitations are accounted by equation (7.2), since such limitations (in the micropores, for example) may dramatically decrease the total surface area S_g available for reaction.

Let dV be the volume of solid consumed by the heterogeneous reaction over a time period equal to dt . Then

$$\rho_s \frac{dV}{dt} = m(t) S_g r_s (c, T; a) \quad (7.3)$$

where ρ_s is the density of the solid reactant. If the reaction rate is uniform over the entire surface area S_g , a layer of solid with uniform thickness dz will be consumed over the time period dt . Thus,

$$dV = S_g m(t) dz$$

and equation (7.3) becomes

$$\frac{dz}{dt} = \frac{r_s (c, T; a)}{\rho_s} \quad (7.4)$$

The previous equations can be used to normalize the reaction rates predicted by the discrete models. At every simulation step, we erode a single layer of pixels from the solid surface area available for reaction. Thus, **every erosion step corresponds to a time interval Δt that equals the time required to convert a solid layer of uniform thickness Δz , where Δz is the pixel size.** From equation (7.4)

$$\frac{\Delta z}{\Delta t} = \frac{r_s (c, T; a)}{\rho_s} \quad (7.5)$$

and if two simulations are carried out on images with different pixel sizes Dz and Dz^* , their time steps will be related according to the formula

$$\frac{\Delta z}{\Delta t} = \frac{\Delta z^*}{\Delta t^*} \quad (7.6)$$

The measured reaction rates are most often normalized with respect to the mass m_0 of the unreacted solid or

$$R_0 = \frac{1}{m_0} \frac{dm}{dt} = (1 - X) R_s \quad (7.7)$$

Let now N_0 be the number of solid reactant pixels on the initial computational grid and let $(\Delta N)^r$ be the number of solid pixels that react in the time interval $[t^r, t^{r+1}]$. The specific rate $R_0(r)$ for this step can be computed as

$$R_0(r) \Delta t = \frac{(\Delta N)^r}{N_0} \quad (7.8)$$

Let Δz be the pixel size (in μm) for this image and let Δt^* be the time required to react a layer of solid with uniform thickness equal to $\Delta z^* = 1 \mu\text{m}$. Equations (7.8) and (7.6) yield

$$R_0(r) \Delta t^* = \frac{(\Delta N)^r}{N_0} \frac{\Delta z^*}{\Delta z} \quad (7.9)$$

Thus, equation (7.9) provides specific reaction rates that are independent of the pixel size of the digitized images used in the simulations.

Using equation (7.5), the value of Δt^* can be computed from the value of the intrinsic rate $r_s(c, T; a)$ at the appropriate conditions. Most often, however, the reactivity data obtained at various temperatures and reactant concentrations are normalized so as to obtain

master curves that yield (within experimental error) the dependence of the active surface area on conversion. Such master curves can be obtained directly from the simulations by plotting the dimensionless rate

$$R_0^*(r) = R_0(r) \Delta t^*$$

vs. either the conversion or a dimensionless time θ where

$$\theta = \frac{t}{\Delta t^*} = \frac{t r_s(c, T; a)}{\Delta z^* \rho_s} \quad (7.10)$$

The predictions of observed reaction rates assume, of course, that the surface activity and the intrinsic reaction rate R_s do not change appreciably with conversion. Since several simulations are performed for each char sample, the average rate $R_0^*(r)$ is computed by the formula

$$R_0^*(r) = \frac{\sum (\Delta N)^r \Delta z^*}{\sum N_0 \Delta z} \quad (7.11)$$

where the summations are taken over all simulation runs performed for different particle cross-sections from the same char sample. The reaction rates computed according to Equation (7.11) can be directly compared regardless of the amount of solid in each sample or the magnification used when acquiring the digitized images. Similarly, the dimensionless rate per unit mass of unreacted solid $R_s^*(r)$ can be calculated as

$$R_s^*(r) = R_s^r \Delta t^*$$

The simulations described here are performed on two-dimensional cellular arrays that are discrete approximations of cross-sections of actual char particles. At each iteration step, heterogeneous reactions occur at the boundaries (perimeter) of the two-dimensional pore profiles (see Figs. 7.1 and 7.2). Results from two-dimensional simulations, however, can be used to obtain accurate estimates of reaction rates occurring on our three-dimensional structures. If we assume that the cross-sections used for our simulations form a "random plane section" (Weibel 1980) through our population of char particles, unbiased estimators of the macroporosity ϵ and of the macropore surface density S_v (in (cm² pore surface)/(cm³ particle)) are given (Weibel 1980) by

$$\epsilon = \frac{A_a}{A_c} \quad (7.12)$$

$$S_v = \frac{4}{\pi} \frac{B_a}{A_c} \quad (7.13)$$

where A_a is the total area of pore profiles, B_a is the total pore profile boundary length and A_c is the total area of particle cross-sections. Note that S_v can be estimated from two-dimensional sections without any restricting assumptions concerning the geometrical shape of the pores (DeHoff 1983). The three primary quantities A_a , A_c and B_a can be easily obtained from the particle cross-sections via image processing techniques, and the total specific macropore surface area S_t (expressed in m² per kg of solid) can be easily computed as

$$S_t = \frac{S_v}{(1 - \epsilon) \rho_s} \quad (7.14)$$

When reaction takes place in Regime A, there are no diffusional limitations in the macropores and the entire macropore surface area reacts at the same rate ($S_g = S_t$). If we

assume that the evolving cross-sections continue to constitute "random sections" for our char particle population, the discrete simulations provide accurate estimates of the changing surface area of the three-dimensional macropores and, consequently, of the temporal evolution of reaction rates in Regime A (see equations (7.1) or (7.7)). Although these arguments do not hold in the general case of reaction in Regime B (where the internal macropores are assumed to be "closed" and $S_g = S_t$), approximate estimates of reaction rates can be obtained if we assume that the internal pores for any cross-section do not become available for reaction due to burn-through occurring at planes above or below the studied one. This assumption can be relaxed by carrying out discrete simulations in three-dimensional cellular arrays. Such a model extension, however, would require information (or assumptions) about the connectivity of the three-dimensional macropores, information that is not currently available.

7.3 Computer Implementation

In Chapter 2 we presented the results from microscopic investigations on the macropore structure of coal chars prepared under different pyrolysis conditions. Char particles collected from several runs at each set of conditions were embedded in an epoxy-resin block, and one side of the block was polished to reveal random cross-sections. Digitized images of particle cross-sections were then acquired and segmented on an image processing computer to identify the char matrix and macropores with diameter greater than $1 \mu\text{m}$.

The original binary images had a resolution of 640×480 pixels. Many char samples, however, exhibited macropores with very thin walls that were consumed in only a few iterations. In order to increase the accuracy of the simulations, each 640×480 image was first magnified by a factor of 4. The magnified 2560×1920 images were smoothed to

remove the edge "jaggedness" that is introduced by simple magnification operations. Several runs were also carried out by magnifying the original images by a factor of 8 and smoothing them. Results obtained from simulations with 5120x3840 images showed only small differences from those obtained from simulations with 2560x1920 images. For each char sample, 48 runs were performed with different particle cross-sections and the results were averaged as previously discussed.

7.4 Reaction in Regime A

We simulated first a gas-solid reaction taking place in Regime A, where there are no diffusional limitations in the macropores and the entire macropore surface area reacts at the same rate. Fig. 7.4 presents the reactivity patterns (R_s^* vs. conversion) predicted for the 48 runs with cross-sections from Illinois #6 particles pyrolyzed at 0.1 °C/s. Each of the 6 thin lines of Figure 7.4 was computed by averaging the results from 8 runs with different cross-sections. The thick line in Figure 7.4 shows the average for this sample of 48 particles. There are significant differences among the six 8-particle averages ($\pm 25\%$ for conversions between 0.2 and 0.8), variations that reflect the different pore structures observed in this char sample. As the representative particle cross-sections of Figure 7.5 show, this sample contained

- (a) particles with a few, large, thick-walled cavities,
- (b) cenospheres with one large cavity, and
- (c) "lacy structure" particles with large cavities separated by thin walls.

Figure 7.6 shows the conversion vs. time results for five char samples produced at 0.1, 1, 10, 100 and 1,000 °C/s. As expected from the macropore surface areas reported in Chapter 2, chars produced at high heating rates react much faster than chars produced at low pyrolysis heating rates. Figure 7.7 shows different reactivity patterns R_s^* vs. conversion for these five chars. Although the specific reactivity increases in a monotonic

fashion for the char produced at 0.1 °C/s, R_s^* seems to reach a plateau for the chars produced at 1 and 10 °C/s. The char produced at 1000 °C/s has a third type of reactivity pattern. However, the temperature control during the 1000 °C/s pyrolysis runs was not as good as during the runs with rates from 0.1 to 10 °C/s (Glass and Zygourakis 1988). Therefore, there is some uncertainty regarding the actual pyrolysis conditions (temperature error, HTT) for the 1000 °C/s sample.

We should note here the similarity between Figure 7.7 and the experimental data for three chars (produced at 0.1, 1 and 10 °C/s) presented in Figures 5.6 and 5.7 for combustion at temperatures just below the level where global particle ignitions were prevalent. The experimental and simulation results show very similar trends in the reactivity patterns.

Figure 7.8 presents the alternative form of the reactivity patterns (R_0^* vs. conversion) for the five chars produced from an Illinois #6 coal at different pyrolysis heating rates. Model predictions reflect the wide differences in the pore structure of these chars. All chars exhibit an initial increase in reactivity caused by macropore growth. Such a behavior cannot be predicted by shrinking-core models. Since the chars produced at high heating rates (10 and 1000 °C/s) have almost exclusively large thin-walled cavities (Chapter 2), **the predicted rates drop dramatically when the thin walls separating the macropores are consumed.** The rate vs. conversion patterns exhibit a small maximum that is shifted towards higher conversion levels for the chars produced at high heating rates.

Figure 7.9 shows the predicted R_s^* vs. conversion pattern for three chars produced at a pyrolysis heating rate of 10 °C/s from different size fractions of Illinois #6 coal particles: 100-120 mesh, 50-60 mesh and 25-28 mesh. Small coal particle sizes lead to chars with larger macropore surface areas and, hence, with higher reactivity. When we normalize the reactivities with their initial value, we note that the reactivity ratios $R_s^*(x)/R_s^*(x=0)$ shift

from monotonic functions of conversion x for the smallest particles to functions with maxima for the larger particles (see Figure 7.10).

Figure 7.11 shows the predicted reactivity behavior for two chars produced from a lignite coal at 0.1 and 1000 °C/s. Small differences in char reactivity can be seen from these graphs, an observation consistent with the pyrolysis mechanism and the pore structure of these chars (see Chapter 2).

7.5 Reaction in Regime B

Drastically different reactivity patterns were obtained when the same particle cross-sections were "reacted" in Regime B, where the internal macropores are not initially accessible to the gaseous reactants. Figure 7.12 presents the reactivity patterns (R_0^* vs. conversion) obtained with the four particle cross-sections of Figure 7.5. All reactivities decrease initially as reaction occurs mainly on the receding particle exterior. When "closed" macropores open up, however, new surface area becomes available for reaction and the rate "jumps" to higher values (see, for example, the curve for run 101 where the jump corresponds to the opening of the large interior cavity). Such jumps in the reaction rate have been observed during single-particle gasification experiments (Sundback, Beer et al. 1984). Note also the characteristic pattern exhibited by the cenosphere in Figure 7.12 (run 106). The reactivity decreases slowly until the front reaches the interior cavity. At that point the reactivity jumps to high values and decreases rapidly as the remaining thin cavity walls are consumed.

Figure 7.13 presents the 48-particle average reactivities R_0^* obtained by simulating reaction of the five chars produced at different pyrolysis heating rates in Regime B. The sudden "jumps" observed in the single particle runs have been smoothed out. Due to the progressive opening of internal macropores, however, the reactivity patterns exhibit distinct maxima at conversions between 0.3 and 0.5. Although the differences among the five char

samples seem large, the plots of the reaction rate ratios $R_0^*(x)/R_0^*(x=0)$ shown in Figure 7.14 reveal that the patterns of the samples produced at 10, 100 and 1000 C/s are virtually identical. These observations reflect the similarities of the macropore structures of the three char samples (see Chapter 2).

The reactivity patterns of chars produced at high pyrolysis rates (e.g. 1000 °C/s) show more than one local maxima that correspond to the opening up of the smaller secondary vesicles formed in the walls separating the larger macropores (see Chapter 2).

Figure 7.15 presents the 48-particle average reactivities R_s^* obtained by simulating reaction of the five chars produced at different pyrolysis heating rates in Regime B. It is interesting to note that the reactivity patterns of Figure 7.15 are rather similar to the patterns obtained by simulating reaction of the same chars in regime B. This is an indication that R_s is not sensitive to the pore structural differences studied here.

Figure 7.16 presents the average reactivity ratios $R_0^*(x)/R_0^*(x=0)$ obtained by simulating reaction of three chars obtained from different coal particle sizes. We observe only small differences in the shape of the three reactivity patterns. Of course the smaller particles are substantially more reactive due to their higher values of specific macropore surface area.

We have finally carried out a series of simulation runs that considered diffusional limitations in the macropores. As mentioned above, macropore openings did not lead to immediate utilization of the previously inaccessible surface area. Diffusional limitations in the macropores resulted in significant decreases of the predicted reaction rates. The average R_s^* patterns are plotted in Figure 7.17 for the five chars produced at different pyrolysis heating rates. Since Figure 7.17 has the same scale with Figure 7.15, it is easy to see the drastic drop in reactivity caused by the diffusional limitations. **The decrease in reactivity is more pronounced for the chars produced at high pyrolysis heating rates.** Clearly, the diffusional limitations have compensated for the higher macropore surface areas of these chars. The shape of the reactivity chars has also changed

with all chars now showing a monotonic increase of R_s^* with conversion (compare to patterns of Figure 7.15).

Finally, Figure 7.18 shows how the reaction rate R_0^* is influenced by diffusional limitations in macropores. Diffusional limitations have eliminated the maximum in the reactivity curve, since macropore openings now do not result in large increases in macropore surface area available for reaction. The effect of diffusional limitations is again more dramatic for chars produced at high pyrolysis heating rates since these chars have a more open macropore structure.

We must note here that if we assume strong diffusional limitations in the macropores, our model predictions equal the predictions obtained by a shrinking core model. This desirable asymptotic behavior is another indication that **the discrete models presented here are suitable for simulating gas-solid reactions in the diffusion-limited regime.**

7.6 References for Chapter 7

DeHoff, R. T. (1983). "Quantitative serial sectioning analysis: Preview." *Journal of Microscopy*. 131(3): 259-263.

Glass, M. W. and K. Zygourakis. (1988). "A Computerized Captive-Sample Microreactor for Video Microscopy Studies of Rapid Coal Pyrolysis." *Rev. Sci. Instr.* 59(4): 580-587.

Sundback, C. A., J. M. Beer and A. F. Sarofim. (1984). "Fragmentation behavior of single coal particles in a fluidized bed." *Procs. 20th International Symposium on Combustion*, pp. 495-503.

Welbel, E. R. (1980). Stereological Methods. New York, N.Y., Academic Press.

Zygourakis, K. (1988). "The Effects of Pyrolysis Conditions on the Macropore Structure of Coal Chars." Amer. Chem. Soc., Div. Fuel Chem. Prepr. **33**(4): 951-959.

Zygourakis, K. and M. W. Glass. (1988). "Macropore Size Analysis Using Digital Image Processing and a Stereological Model." Chem. Eng. Commun. **70**: 39-55.

Zygourakis, K. and C. W. J. Sandmann. (1988). "Discrete Structural Models and Their Application to Gas-Solid Reacting Systems." AIChE Journal. **34**(12): 2030-2040.

Figure 7.1: Images showing a particle cross section at four different levels of conversion. They were obtained from a run simulating coal combustion in Regime A (no diffusional limitations in macropores). Reaction takes place on the entire gas/solid area (white/black interface).

Figure 7.2: Images showing a particle cross section at four different levels of conversion. They were obtained from a run simulating coal combustion in Regime B (diffusional limitations in macropores). The gray areas represent "closed" macropores that are not available for reaction. Note the "opening" of the large macropore between images (B) and (C).

Figure 7.3:

Evolution of reaction rate R_0^* with conversion for the particle of Figures 7.1 and 7.2 for two runs simulating reaction in regime A and regime B. Note the "jumps" in R_0^* indicating macropore "openings" during reaction in Regime B.

Figure 7.4: Reactivity patterns obtained from 48 runs simulating reaction in Regime A with char particles pyrolyzed at 0.1 °C/s. Each thin lines is the average from 8 runs with different cross-sections. Coal particle size: 50-60 mesh.

Section 101

Section 102

Section 106

Section 105

Figure 7.5: Representative cross-sections showing the various macropore structures of Illinois #6 char particles pyrolyzed at 0.1 °C/s.

Figure 7.6: Average conversion vs. time curves for five Illinois #6 char samples produced at different pyrolysis heating rates. Char particle size: 50-60 mesh.

Figure 7.7: Average reactivity patterns for five Illinois #6 char samples produced at different pyrolysis heating rates. Char particle size: 50-60 mesh.

Figure 7.8:

Average reactivity patterns (R_0^* vs. conversion) curves for five Illinois #6 char samples produced at different pyrolysis heating rates. Char particle size: 50-60 mesh.

Illinois #6 Coal

Figure 7.9: Average reactivity patterns for three Illinois #6 chars produced from different coal particle sizes. Pyrolysis heating rate: 10 °C/s.

Figure 7.10: Reaction rate ratio ($R_s^*(x) / R_s^*(x=0)$) vs. conversion patterns for three Illinois #6 chars produced from different coal particle sizes. Pyrolysis heating rate: 10 °C/s.

Figure 7.11: Reactivity patterns ($R_0^*(x)$ vs. conversion) predicted for three lignite chars produced at different pyrolysis heating rates. Coal particle size: 50-60 mesh.

Figure 7.12: Reactivity patterns for the four cross-sections of Figure 7.5 obtained from runs simulating reaction in Regime B (diffusional limitations in the macropores).

Figure 7.13: Average reactivity patterns (R_0^* vs. conversion) obtained by simulating reaction in Regime B of the five Illinois #6 chars produced at different pyrolysis heating rates. Coal particle size: 50-60 mesh.

Figure 7.14: Reaction rate ratio ($R_0^*(x) / R_0^*(x=0)$) vs. conversion for the five Illinois #6 chars produced at different pyrolysis heating rates. The computer runs simulated reaction in regime B. Coal particle size: 50-60 mesh.

Figure 7.15: Average reactivity patterns (R_s^* vs. conversion) obtained by simulating reaction in Regime B of the five Illinois #6 chars produced at different pyrolysis heating rates. Coal particle size: 50-60 mesh.

Figure 7.16: Average reactivity ratio ($R_0^*(x) / R_0^*(x=0)$) patterns obtained by simulating reaction in Regime B of the three Illinois #6 chars obtained from different coal particle size fractions. Pyrolysis heating rate: 10 °C/s.

Figure 7.17: Average reactivity patterns obtained from runs simulating reaction in Regime B but with substantial diffusional limitations in the macropores. The five Illinois #6 chars were produced at different pyrolysis heating rates. Coal particle size: 50-60 mesh.

Figure 7.18: Comparison of reactivity patterns obtained from runs simulating reaction in Regime B **without** and **with** diffusional limitations in the macropores. The two char samples were produced from Illinois #6 coal at 0.1 and 10 °C/s pyrolysis heating rates. Coal particle size: 50-60 mesh.

END

**DATE
FILMED**

6 / 19 / 92