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Stereological analysis of the macropore structure of chars produced under various pyrolysis conditions and the influence of macropore structure on char gasification rates in the presence of strong diffusional limitations

Glass, Micheal Walter, Ph.D.

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STEREOLOGICAL ANALYSIS OF THE MACROPOROUS STRUCTURE OF CHARS PRODUCED UNDER VARIOUS PYROLYSIS CONDITIONS AND THE INFLUENCE OF MACROPOROUS STRUCTURE ON CHAR GASIFICATION RATES IN THE PRESENCE OF STRONG DIFFUSIONAL LIMITATIONS

by

MICHAEL WALTER GLASS

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DOCTOR OF PHILOSOPHY

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STEREOLGICAL ANALYSIS OF THE MACROPORTE STRUCTURE OF CHARS PRODUCED UNDER VARIOUS PYROLYSIS CONDITIONS AND THE INFLUENCE OF MACROPORTE STRUCTURE ON CHAR GASIFICATION RATES IN THE PRESENCE OF STRONG DIFFUSIONAL LIMITATIONS

by

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ABSTRACT

The effects of pyrolysis heating rates, particle size and ash upon the macropore structure of coal-derived chars were investigated for an Illinois #6 and a lignite coal. A new direct method was used to characterize the macropore structure of the chars. Polished cross-sections of char particles were analyzed with an integrated video microscopy/digital image processing system. Pore size analysis combined a stereological model and digital image processing techniques to overcome the limitations of indirect methods. Obtained results were used to investigate the effects of the macropore structure on global gasification rates under conditions of strong intraparticle diffusional limitations. Simulations employed a two-dimensional discrete model and image processing techniques to treat the reaction of the complex pore structures observed.
The coals were pyrolyzed in nitrogen to 900°C with a microcomputer-controlled, heated wire-mesh reactor at heating rates between 0.1°C/s and 1000°C/s. The Illinois #6 char showed an increasingly complex macropore structure as the heating rate was increased. Measurements revealed a definite shift toward the formation of cellular structures with thin-walled large and small cavities. Pyrolysis heating rates had virtually no effect on the macropore structure of lignite chars. Three fractions of Illinois #6 coal with different particle sizes were also pyrolyzed at 10°C/s. The char from the smallest size fraction exhibited a few large primary cavities but very little secondary pore formation was present. In contrast, the chars from the larger size fraction contained a large amount of secondary pores. The presence of ash during the pyrolysis process appeared to have very little effect on the development of the macropore structure.

Discrete modeling of char gasification with strong diffusional limitations showed that the wide variation of macropore structure exhibited by the Illinois #6 chars had a marked effect on the global gasification rates. An increase in the amount of secondary pores formed at the higher
heating rates and larger particle sizes produced much more pronounced maxima in the rate vs conversion curves.
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CHAPTER I

INTRODUCTION

Direct coal utilization processes consist of two basic steps: the pyrolysis (or devolatilization) stage and the gasification stage. As coal particles are heated in a gasifier (or combustor), the pyrolysis reactions take place first and most of the volatile constituents of the parent coal are released in the form of gases and tars. Devolatilization thus leads to the formation of coal chars that contain mainly fixed carbon and the inorganic material (ash) present in the original coal. The short pyrolysis stage is followed by gasification (or combustion) of the chars, either to produce gaseous chemical feedstocks (synthesis gas) or for energy recovery.

The pyrolysis step is of major importance since the complex series of chemical and morphological transformations occurring during this stage determine the chemical nature and the pore structure of the produced chars. It is during this short devolatilization stage that the entire pore structure of the chars, ranging from submicropores whose
diameters are only a few angstroms to large macropores whose sizes may exceed a hundred microns, is determined.

Actual gasification rates for the devolatilized char particles are among the most important parameters for the design of reactors. This points out the practical importance of accurate characterization of the pore structure since numerous previous investigations have established that the reactivity of the chars is determined to a large extent by their pore structure (Gavalas, 1980; Bhatia and Perlmutter, 1980, 1981; Zygourakis et al., 1982; Ballal and Zygourakis, 1985, 1987; Sandmann and Zygourakis, 1986a, 1986b). The micropore structure will determine the observed reaction rates in the kinetic-controlled regime, but the larger macropores and internal cavities present in many chars will govern the observed reaction rates in the diffusion-controlled regime.

Most coal utilization processes involve high temperature gasification of coal chars (McCullough, et al., 1982; Smoot and Smith, 1985 for example). Under these conditions, gasification reactions take place in the presence of strong intraparticle diffusional limitations, utilizing only a small fraction of the internal pore surface area that is readily accessible to reactants via the particle's macropore
network. Initially a large portion of the surface area may be closed off from the exterior and it will become accessible only after adjoining pore walls have reacted away exposing the previously unavailable surface area to reactants. The fraction of surface area available for reaction will therefore vary with solid conversion and, as a result, the global reaction rates measured will also vary significantly with conversion. Preliminary modeling results for char gasification in this diffusion-controlled regime (Sandmann and Zygourakis, 1986a,b) have confirmed that the char macropore structure will greatly influence the global gasification rates.

In summary, the development of predictive models for char gasification under actual process conditions (that invariably lead to strong diffusional limitations) necessitates an accurate characterization of the macropore structure of the coal char. Since the pore structure is formed during the pyrolysis stage, one should also know how the pyrolysis conditions affect the pore structure and hence the reactivity of chars.

The above conclusions describe in essence the scope and significance of the study presented here. Its main objectives were to:
(a) develop an analytical technique for the accurate characterization of the macropore structure of coal-derived chars;

(b) study the effect of some crucial pyrolysis conditions on the macropore structure of the devolatilized chars, and

(c) study the effect of the macropore network on the observed global reaction rates of the chars when they are gasified under conditions leading to strong intraparticle diffusional limitations.

It should be emphasized again that almost all the past studies on coal pyrolysis have focused on elucidating the chemical kinetics of the process and paid little attention to the morphological transformations occurring during this stage. This study, however, aims primarily at describing and analyzing the pore structural transformations brought about by the pyrolysis process and at determining how the macropore structure of chars affects their reactivity.

Emphasis is placed on plastic coals since they exhibit the most dramatic macropore transformations during
pyrolysis. A bituminous Illinois #6 coal is used here and its behavior is compared to a non-plastic Texas lignite coal. When plastic coals are pyrolyzed, they pass through a stage of semifluidity (hence their name) during which a liquid crystalline phase, termed the carbonaceous mesophase, appears from the isotropic melt. At the same time, gas bubbles form by the volatiles released from the pyrolysis reactions and grow, stirring and deforming the mesophase regions. However, as the pyrolysis reactions proceed, the coal melt and the mesophase resolidify to yield a solid char.

Char particles resulting from the pyrolysis of plastic coals exhibit a complex pore structure. Their macropores are large spherical vesicles interconnected via smaller neck pores. The large spherical cavities are clearly the result of the gas bubbles being present in the coal melt as it resolidifies. The size of these vesicles can often be of the same order of magnitude as the particle diameter. In contrast, char particles produced by pyrolyzing nonplastic coals do not exhibit large spherical cavities. Instead, their pores are smaller and resemble fissures or cracks.

As with any other porous solid, modeling of char gasification requires an accurate characterization of the pore
structure. The micropore structure of the chars can be characterized by conventional methods such as nitrogen and carbon dioxide adsorption techniques (Mahajan et al., 1978). Considerable errors are introduced, however; when conventional indirect methods such as mercury porosimetry are used to characterize the macropore structure, especially in the case of chars derived from plastic coals. Since the macropores are of the aperture-cavity type, mercury porosimetry will only detect the smaller neck pores which interconnect the larger vesicles. Thus, the macropore size distribution obtained from this method will not reveal the larger pores (Dullien and Batra, 1970) which are known to exist from optical microscopy observations (Glass et al., 1986; Otto et al., 1984; Hamilton, 1981; Lightman et al., 1968; Woods et al., 1963).

The macropore size distribution can be obtained from direct measurements using quantitative optical microscopy. In this study, polished sections of char particles are analyzed using a digital image processor and the three-dimensional macropore size distribution is extracted using stereological methods. Various stereological theories and methods exist to relate two-dimensional measurements to three-dimensional structural properties of solids. Their original use was for particle size analysis, but they have
also been applied to pore size analysis of porous materials. Such methods, however, have not been widely used because the required measurements are extremely time consuming when done manually and a large number of samples must be analyzed to produce a statistically significant result. By using a digital image processor, the time required for object identification and analysis can be drastically reduced and the process can be automated to a large degree.

The rate at which coal particles are heated in a reactor during the pyrolysis stage is one of the most important parameters in determining the pore structure of the produced char particles. Indeed, a qualitative study by Hamilton (1981) indicated that the heating rate during pyrolysis produced dramatic differences in the morphology of chars.

In order to study the effect of pyrolysis heating rates, a captive sample pyrolysis reactor was developed that allowed us to cover a range of heating rates from 0.1°C/s (typical for coke ovens) to 1000°C/s (approaching pulverized coal gasifiers). This reactor was used to produce coal chars at various heating rates to determine its effect on the macropore structure. The effect of particle size was also investigated using this reactor. Raw and demineralized coal chars available from previous studies by Ballal (1985)
and Sandmann (1986) were used for our studies, allowing us also to carry out a preliminary study on the effect of the inorganic impurities (ash) of the parent coal on the macropore structure of the devolatilized chars.

The importance of the macropore structure of chars on their global gasification rates in the presence of strong intraparticle diffusional limitations was investigated using a two-dimensional discrete gasification model. Sandmann and Zygourakis (1986a,b) demonstrated the applicability of discrete models to modeling gas-solid reactions. According to their approach, a computational grid consisting of a large number of discrete cells is used to model the porous solid. Regions corresponding to pore voids or solid reactant are defined by setting the cells to appropriate values and these regions are then grown or shrunk according to simple rules simulating gas-solid reactions. The original discrete models considered only regions defined by overlapping regular geometrical entities (circles or spheres) of uniform size or having a given distribution of sizes.

However, it is rather difficult to approximate highly irregular pore cross-sections observed directly under the microscope by a collection of overlapping regular entities (e.g. circles). For this reason, new discrete models are
developed here to allow using the actual digitized images of char particle cross-sections to represent the pore structure of unreacted chars. Discrete models offer the only alternative for quantitatively assessing the effects of complex macropore structure of chars on their gasification rates in the regime of strong intraparticle diffusional limitations. The digitized char images obtained from the macropore structure analysis mentioned earlier were used for our studies and predicted reaction rates are compared to elucidate the effect of structural parameters and of pyrolysis conditions on the important process of char gasification under actual process conditions.
CHAPTER II

COAL PYROLYSIS

Coals can be broadly categorized as being plastic or nonplastic depending upon their behavior during the pyrolysis process. During the pyrolysis stage, plastic coals soften and behave like highly viscous non-newtonian fluids over a broad temperature range. Bituminous coals are generally considered to be plastic. Nonplastic coals, on the other hand, do not display any softening during the pyrolysis stage and lignites are examples of coals belonging to this category.

During the pyrolysis of nonplastic coals, the initial macropore network of the coal essentially remains intact (Gavalas and Wilks, 1980). Some enlargement and coalescence of pores is observed as volatiles are released, but the primary change occurs in the micropore network leaving the macropore network essentially intact. The macropore network for nonplastic coals is often described using a pore tree type of model (Gavalas and Wilks, 1980). In this case, the
mechanism for mass transport of the volatiles out of the particle is diffusion through the combined micro/macropore network. A considerable amount of work has been done in this area with good results. Much of the work for modeling the pore growth and the diffusion process already exists from past work on general gas-solid reaction systems. By combining pore diffusion results with the appropriate pyrolysis kinetics, very good models for nonplastic coals have been developed (Russel et al., 1979; Chen and Wen, 1979; Gavalas and Wilks, 1980; Simons, 1983 and 1984).

Plastic coals, however, undergo drastic morphological changes during pyrolysis which completely destroy the original pore structure of the coal. As previously mentioned, the pyrolysis process is characterized by a transition zone in which the coal behaves like a highly viscous non-newtonian plastic fluid allowing for deformation, swelling and coalescence. The original pore network that existed prior to pyrolysis is completely destroyed at this time.

A short discussion of the chemical and morphological transformations occurring during pyrolysis is in order here. During the heat-up process, a complex reaction sequence is triggered. The primary pyrolysis reactions occur in the temperature range of 350 - 550°C. The onset of plastic
behavior is caused by thermal mobilization of the micelles forming the poorly aligned lamellae of the major coal macerals (Neavel, 1982; Berkowitz, 1960). Indigenous low-molecular hydrogen-rich compounds solvate the micelles increasing their mobility, while at the same time stabilizing the free radicals produced by thermal rupturing of bonds. Plasticity is, however, a transient phenomenon. The hydrogen-donor compounds escape as volatiles while the pyrolytic formation of free radicals continues. Thus, the aromatic condensation reaction rates increase leading to the resolidification of the plastic coal.

A nematic liquid crystalline phase appears as the pyrolyzing mass begins to congeal to semicoke (Brooks and Taylor, 1968). It is known as carbonaceous mesophase and consists of planar polyaromatic molecules (MW = 1500 - 2000) aligned parallel to each other. The carbonaceous mesophase regions exhibit optical anisotropies similar to those of the better known nematic and smectic liquid crystals formed by rod-like molecules. This transient period is characterized by the coexistence of three phases: isotropic coal melt, liquid crystalline carbonaceous mesophase and gaseous volatiles present in the form of bubbles. It is the interaction of these phases which determines the final macropore structure of the char. As the carbonaceous mesophase
regions grow, rotational and translational defects form and propagate in their interior giving rise to characteristic mesophase microstructures (Zimmer and White, 1976). The mesophase regions also coalesce and deform under the stresses imposed by the motion of the volatile gas bubbles through the medium. As additional volatiles diffuse into the existing bubbles, these bubbles will grow in size often coalescing with other bubbles. As the bubbles grow and break through to the surface, their contents are released to the exterior and the ruptured walls recollapse upon themselves. Finally as the pyrolysing mass congeals into solid char, the gas bubbles present within the coal melt are frozen into place, forming a unique macropore structure.

Optical microscopy and gas adsorption studies of resolidified char particles confirm that their micropore and macropore structures reflect the morphology imposed by the mesophase regions and the growth of volatile gas bubbles. The particles exhibit many large vesicles interconnected via smaller neck pores and open to the exterior (Ballal and Zygorakis, 1985; Hamilton, 1981). The cavities are the remnants of gas bubbles that were present within the coal melt as it resolidified and they give the appearance of a very cellular macropore network. Detailed gas adsorption studies with N₂, CO₂ and CO (Ballal and Zygorakis, 1985) also established that the chars have an extended network of
micropores whose diameters approach in many cases the molecular dimensions of the gaseous adsorbants.

II.A FACTORS AFFECTING THE MACROPORE STRUCTURE

The major factors influencing the pyrolysis process are: (1) coal type and (2) operating conditions. As mentioned previously, coal type pertains mainly to plastic and nonplastic coals. Within each classification, operating conditions effect the pyrolysis process differently. The operating conditions thought to have the most influence on the pyrolysis process are heating rate, particle diameter, and pressure. Existing literature data offer very little information on the effect of operating conditions on macropore structures, since the majority of past studies have concentrated on studying the kinetics of pyrolysis reactions and the distributions of the obtained products.

Careful examination of the literature does give a basic outline of the effects of operating conditions on the structure of the resulting chars. The macropore structure of chars produced from lignite coals (nonplastic) have been found to remain unaffected by changes in pressure and particle diameter (Anthony and Howard, 1976; Gavalas, 1982; Suuberg et al., 1979). The effect of particle diameter on
plastic coals is difficult to ascertain for two main reasons. Maceral segregation is likely to occur as smaller particles are used and it is a well known fact that different macerals display different plastic properties (van Krevelen, 1961; Howard, 1963). Also, different macerals have different mechanical properties so grinding and sifting procedures may lead to enrichment of certain macerals in certain size fractions (Parks, 1963). Variations in heat transfer conditions can also accompany variations in particle diameter. At high heating rates and large particle size, temperature gradients may exist within the particle affecting the pyrolysis kinetics, making it difficult to separate particle size and heat transfer effects. Unpublished data from the Massachusetts Institute of Technology (MIT) indicate a critical particle size of 100-1000 μm for a heating rate of 600°C/s (Howard, 1963). For plastic coals, variation in heating rate shifts the softening and resolidification points (Howard, 1963). As the heating rate increases, both points also increase but not to the same extent thus widening the plastic region.

As mentioned previously, the presence of the carbonaceous mesophase along with the formation and growth of gas bubbles produces the striking macropore structure in plastic coals. The properties of the gas bubbles, such as growth
rate and size, will be influenced by several factors such as the rate of volatile release, diffusion of the volatiles into the bubbles and the viscosity of the coal melt. These kinetic and transport processes will be governed by the time-temperature history of the coal particle during the pyrolysis stage. Hence, varying the heating rate of the pyrolysis process will produce the most change in the macropore structure of the chars (Hamilton, 1980). Also because of the wide range of heating rates associated with various coal utilization processes, it was decided to concentrate on the effects of the heating rate on the macropore structure of plastic coals.

II.B LABORATORY PYROLYSIS REACTORS

Several types of laboratory reactors have been used to study coal pyrolysis in the laboratory. The majority of them can be categorized as captive sample (Anthony et al., 1974), fluidized bed (Birch et al., 1960), entrained flow (Moseley et al., 1965), or free fall reactors (Moseley et al., 1967). Of these, all but the captive sample reactor can operate with a continuous feed system which more closely approximates actual operating conditions. Data analysis, however, can become quite complex for fluidized bed, entrained flow or free-fall reactors. The heating rates in
such reactors are largely unknown and can only be estimated. A more important limitation is that the heating rate achievable in such reactors is either fixed or can be varied only over a small range. Also, sample collection at intermediate conditions is very complicated involving the use of special water-cooled probes (Solomon, 1985).

Captive sample reactors on the other hand are relatively simple in design and overcome many of the shortfalls of other reactors. The most common type of captive sample reactor uses an electrically heated particle support (Anthony et al., 1974; Suuberg et al., 1978; Hamilton et al., 1979; Niksa et al., 1982 and Solomon et al., 1985). The particle support typically surrounds the coal sample to provide an isothermal environment. For small samples and small particle sizes, the heating rate of the coal particles may be assumed to be equal to the heating rate of the support material. This reactor configuration offers a very flexible method for effectively simulating a variety of operating conditions. Collecting samples at intermediate conditions during the heating period can be done by rapidly quenching the sample holder and sample. For example, Niksa (1982) developed a captive sample reactor which used a blast of liquid nitrogen aimed at the sample holder to rapidly quench the pyrolysing sample.
All but one of the previously mentioned reactors used a stainless steel screen as the particle support, a thermocouple in contact with the screen to track the temperature, and a high amperage power supply to heat the screen. The reactor described by Solomon (1985) used a tungsten screen for particle support to achieve higher heating rates and employed a Fourier-transform infrared (FT-IR) spectrometer for in situ analysis of the gas species and the temperature of the gas and solid. Screens are used as the particle support for several reasons: (1) they have a lower thermal mass than a solid strip and (2) volatiles can easily escape. Stainless steel is commonly used because of its high resistivity and high tolerance against temperature and corrosion.

Various schemes have been used to program and control the temperature of such reactors. Since all the previously mentioned captive sample reactors were used for kinetic studies of the pyrolysis process, a uniform heating rate was desirable. Anthony (1974) and Suelberg (1978) used storage batteries, power resistors, power relays and timers to deliver power in two cycles for independent control of the heating rate and final temperature. Niksa (1982) improved the temperature control by using an operational power supply with two independent cycles, one with constant current for
heating and another with constant voltage to maintain the temperature. Timers were still used to control the switching between various modes. The heating rates for these two schemes were not strictly linear and required extensive calibration to determine the proper settings for the timers. Nor would the timer calibration be able to account for any variability of resistance between screens or the effect of sample size. Hamilton (1979) used a sophisticated feedback controller to overcome these problems and to provide a linear heating rate over a wide range.

II.C A COMPUTERIZED REACTOR FOR RAPID PYROLYSIS

While incorporating several of the desirable features of the aforementioned reactors, the captive sample reactor designed and built for this study offers two significant improvements. A microcomputer-based control scheme is used to program the reactor time-temperature profile and the reactor's design allows it to operate as a high-temperature microscope hotstage where the pyrolysis process can be viewed directly. The microcomputer based controller was used to provide flexibility of operation. The hot stage mode of operation was used to obtain qualitative observations of the process and in the future it could be used with "cleaner" carbonaceous compounds to study the mesophase
region in greater detail to gain fundamental understanding about plastic coals (see Chapter VI). The reactor was able to provide a heating rate from 0.1°C/s (typical of coking ovens) to 1000°C/s (approaching pulverized coal gasifiers).

II.C.1 Apparatus

The reactor (Figure 1) was machined from 316 stainless steel measuring 3 inches in diameter and 2 inches in height. It is equipped with brass electrodes for the heating element connection, a set of gas inlet and outlet ports, a quartz viewing window and a water-cooled jacket. The vessel was jacketted for several reasons. First, by maintaining the large thermal mass of the reactor at a constant temperature, heat losses from the wire mesh to the surroundings were kept as constant as possible for a given wire-mesh temperature and an accurate process model could thus be developed. And secondly, by keeping the reactor vessel cool, the possibility of thermal damage to the microscope stage and objectives was eliminated and the reactor could be moved around under the microscope.

Gas inlet and outlet ports were fitted near the top of the vessel with the gas flow passing directly over the sample, sweeping away the volatiles to keep the quartz
Figure 1. PYROLYSIS HOTSTAGE REACTOR.
window free from condensables which would obscure the view. Even so, during heavy releases of volatiles the quartz window became smeared with heavy tars. To remedy this situation, the quartz window's center was offset from the reactor's centerline so as the window was rotated, a clean section was brought over the sample area thus allowing the sample to be continuously viewed. The quartz window was held firmly in place with a pair of spring clips while still allowing for it to be easily rotated.

The reactor dead volume was minimized by filling most of the empty cavity with a ceramic cement (Zircar Products, Inc., Florida, NY, ZIRCONIA CEMENT). The cement could be easily removed or its amount varied to accommodate different heating element/sample holder combinations.

The particle support is a single piece of 1/2 inch width 316 SS, 325 wire-mesh that is folded in half with the edges electrically welded to form an enclosure for the coal particles. The mesh is fastened between the two high amperage electrodes. A small hole is made on the top side of the mesh and a chromel-alumel (type K) thermocouple is inserted through it to track the temperature. When direct viewing of the pyrolysis process under the microscope was desired, the mesh was not folded and the coal sample was placed on the top of the mesh. While this method produced large tempera-
ture gradients within the particles, it was useful for qualitative observations (see Appendix A).

The thermocouple was made from stock 36 gauge thermocouple wire with glass braid insulation (Omega Engineering, Inc., Stamford, CT). A wire section was stripped of insulation at both ends and the thermocouple bead was made by arcwelding together the two wires at one end. A ceramic cement was then used to seal the ends and prevent the insulation from fraying. The thermocouple bead was then dipped in a concentrated HF bath to clean the tip of any carbon buildup formed during the arcwelding process. A new thermocouple was prepared for each pyrolysis run.

II.C.2 Interfacing the Reactor to the Microcomputer

Because of the many configurations in which the pyrolysis reactor could be set up, a flexible and versatile control and data collection system was required. This requirement was met by interfacing the reactor to a microcomputer and implementing a flexible software control scheme to program the reactor temperature and provide data logging capabilities.
An LSI-11 microcomputer system (Digital Equipment Corp.) available in our laboratory was used for implementing the digital control and data acquisition tasks. Although the LSI-11 CPU is vintage 1970 equipment and is considered obsolete by today's standards, it can offer a very cost-effective solution for reactor control provided that its limitations are recognized and that it is used for simple tasks. The microcomputer system used in our studies consisted of: (1) an LSI-11/2 CPU with floating point hardware; (2) 56 kilobytes of memory; (3) dual floppy disk drives (1.0 Mb total storage capacity); (4) dual TU58 cartridge tape drives (0.5 Mb total storage capacity); (5) three serial communications ports; (6) an 8-channel (0-10 volts) 12-bit A/D converter; and (7) a 4-channel (0-10 volts) 12-bit D/A converter. The microcomputer operates under the RT-11 real-time operating system.

A schematic showing the microcomputer interfacing is shown in Figure 2. The A/D and D/A channels are used to measure the reactor temperature and to regulate the reactor power supply respectively. Since a microcomputer-based control system was used, the nonlinearity of the thermocouples and the power supply could be easily accounted for. A combined feedforward/feedback algorithm was implemented to program and control the reactor temperature. The
Figure 2. Block diagram for pyrolysis reactor temperature control.
microcomputer was also used to log the time-temperature profile. When the reactor was being used as a microscope hot-stage, the microcomputer also transmitted the measured temperature to an alphanumeric inserter unit via an RS-232 line. The latter unit overlaid the temperature information and elapsed time for the experiment onto the video signal.

An interface box was constructed to amplify and condition the thermocouple signal before passing it on to the computer's A/D converter. The interface box was connected to the A/D convertor using shielded, grounded cables with twisted pair wires. Proper grounding of the equipment was essential.

The thermocouple signal is first amplified with a gain of approximately 10mV/°C to bring the signal within the dynamic range of the computer's A/D interface and passed through a low pass filter. The amplification is accomplished with a commercially available thermocouple amplification integrated circuit (AD595C, Analog Devices, Norwood, MA). The AD595C includes a cold junction compensation circuit to preclude the use of an external ice bath. A low pass filter follows the AD595C to filter any high frequency noise. A schematic of the temperature sensing circuit is shown in Figure 3. Although the AD595C provides a signal
Figure 3. Schematic for thermocouple signal amplifier and conditioner.
corresponding to roughly 10 mV/°C, the nonlinearity of the thermocouple must be accounted for when determining the exact temperature being measured. The computer's software easily handles this by constructing appropriate gain blocks.

The microcomputer reads a 12-bit value, $T_d$, from the A/D converter. The heated-grid temperature, $T$, can then be calculated from $T_d$ as follows. The output signal, $T_{ma}$, from the AD595C is given by

$$T_{ma} \text{ (mV)} = T_d \cdot (10000 \text{ mV})/4095$$

The AD595C circuit linearly amplifies and offsets the thermocouple signal, $T_m$, to trim the output, $T_{ma}$, to 250 mV for a thermocouple signal corresponding to 25 °C. Thus, the output voltage, $T_{ma}$, from the AD595C is related to the thermocouple signal, $T_m$, by

$$T_{ma} \text{ (mV)} = (T_m + 0.011mV) \cdot 247.3$$

and thus the thermocouple signal, $T_m$, is given by

$$T_m \text{ (mV)} = (T_{ma}/247.3) - 0.011mV$$

Finally, the temperature, $T$ (in °C), sensed by the thermocouple is calculated from a power series polynomial relating $T$ to the voltage potential, $T_m$, measured by the thermocouple
\[ T = a_0 + a_1 T_m + a_2 T_m^2 + a_3 T_m^3 + a_4 T_m^4 + a_5 T_m^5 + a_6 T_m^6 + a_7 T_m^7 + a_8 T_m^8 \]  
(4)

where \( a_0 \) through \( a_8 \) are the polynomial coefficients for a K type thermocouple (Omega Engineering Temperature Measurement Handbook).

Thus for a temperature range of 0-978°C with a type K thermocouple, an output voltage of 0-10 volts is produced which is the dynamic range of the A/D convertor used. By changing Equation (4) the software can be adjusted for various thermocouple types. Also the minimum error of ±1 LSB in the A/D conversion corresponds to a temperature tolerance of ±0.24°C.

A phase-fired heater controller was used to regulate the power supplied to the heating element. The schematic for the heater control circuit is shown in Figure 4. The main power supply (6 volts @ 20 amps AC) was regulated from 0-100% full power by varying a 0-10 volt control signal \( C \) set via the microcomputer's D/A converter. The value of the control signal \( C \) is computed via the digital control algorithm implemented on the microcomputer. With the rated power supply, uniform heating rates from 0.1°C to 1000°C per second were obtainable for final temperatures up to 900°C.
Figure 4. Schematic of SCR phase-fired power controller.
II.C.3 Digital Control Algorithm

The control algorithm used a combination of feedforward and feedback control. The feedback control block implemented a standard proportional-integral (PI) control law. The feedforward control block used a process model to calculate a control signal for the given setpoint and temperature ramp. Both signals were combined to provide the final control signal to the phase-fired power controller. A block diagram depicting the control scheme is shown in Figure 5. The control software allowed for either feedback only control, feedforward only control, or a combination feedforward/feedback control.

The process model for feedforward control was obtained by assuming that the reactor dynamics could be described by the following ordinary differential equation.

\[ a \frac{dT}{dt} = Q_{in} - Q_{out} \quad (5) \]

where \( T \) is the temperature of the heated grid (and sample), \( Q_{in} \) is the power input to the grid and \( Q_{out} \) is the rate of heat losses to the surroundings. Since the large thermal mass of the reactor block is kept at a constant temperature by circulating fluid through its jacket, \( Q_{out} \) will depend only on the grid temperature \( T \) and the flow rate and
Figure 5. Block diagram for temperature control algorithm.
properties of the purging gas. For a given gas flow rate, $Q_{\text{out}}$ can be determined as a function of $T$ by applying several constant power inputs, allowing the reactor to reach thermal equilibrium and recording the final grid temperatures. Experimental data from such step input tests and the final curve-fit for $Q_{\text{out}}$ are presented on Figure 6 for a nitrogen flowrate of 150 cc/min used in most pyrolysis experiments.

The other model parameter $a$ was first estimated from the heat capacity of the heating element as

$$a = m_g c_{ps}$$

(6)

where $m_g$ is the mass of the grid and $c_{ps}$ is its specific heat. Its value was then adjusted by fitting Equation (5) to the reactor response obtained from a step change of the power input. From Equation (5), the power input $Q_{\text{in}}$ required to achieve a given heating rate at any temperature setpoint can be directly calculated as

$$Q_{\text{in}} = Q_{\text{out}} + a \frac{dT}{dt}$$

(7)

By specifying a temperature program for the reactor, the temperature setpoint $T_{sp}$ and the desired heating rate $dT/dt$ are known at any point in time. The values of $Q_{\text{in}}$
Figure 6. Pyrolysis reactor steady-state energy loss as a function of reactor temperature.
required to implement the desired temperature program can then be computed from Equation (7). Finally, the value of the control signal $c$ required to produce the desired $Q_{in}$ is found from a nonlinear function relating the input, $C$, and output, $Q_{in}$, of the phase-fired heater control unit.

The developed software consists of four modules. The first handles the input of process parameters such as heating rate, final heat treatment temperature, data logging interval, etc. The second module handles clock interrupts and schedules the control algorithm to execute at specific time intervals. The third module is the control loop itself which obtains the temperature as described previously, applies a control algorithm and outputs a control signal via a D/A channel to the phase-fired controller. And lastly, the fourth module logs the time, temperature and control signal for the experiment. Through the program’s software we can not only control the reactor temperature but can also easily program the reactor to follow multiple ramp heating profiles.

The computation of the grid temperature $T$ from the discrete signal $T_d$ obtained from the A/D converter (Equations 1 through 4) and the computation of the control signal $c$ from the specified temperature program (Equation 7) can both be
very time consuming. In order to decrease the computation time required for each execution of the control algorithm, two lookup-tables (LUT) were employed. The first was used to quickly convert the A/D value to the corresponding temperature. Equations (1), (3), and (4) were used to preload a 4K word LUT with the temperature corresponding to each 12-bit A/D value. Since the accuracy of the circuit is taken to be ±0.24°C, the LUT was loaded with the integer value of the temperature multiplied by ten. This allowed the use of an integer format LUT as opposed to a floating point format LUT which would have taken twice the amount of memory. The cost is negligible as the error raises slightly to ±0.3°C.

The second LUT was used to determine the feedforward control signal. At the start of each run, the desired temperature profile with temperature ramp, holding times and final temperature values are used to compute the required feedforward control signal at each sampling interval during the experiment. The computed values were loaded into an LUT. During an actual run, the appropriate feedforward control value at each sampling interval was simply read from this LUT.
The use of look-up tables significantly reduced the computational times required for each execution of the control algorithm, thus allowing for the fastest sampling rate possible with the available CPU. The minimum allowable sampling time was limited by the CPU to 50 ms without support for the alphanumeric inserter and to 83 ms with support for the inserter. This corresponds to a sampling frequency of 20 and 12 Hz respectively. Even at these relatively low sampling rates the control algorithm provided control to within ±1°C with heating rates of 10°C/s or less.

For slow heating rates between 0.1 and 10°C/sec, feedback only control was found to be sufficient for maintaining the temperature to within ±1°C of the setpoint. However, for heating rates above 10°C/sec the feedback-only control scheme began to fail and near 100 °C/s errors of up to 75°C were common. To provide better control at heating rates higher than 10°C/s, a combined feedback/feedforward controller was necessary. With a temperature ramp of 100°C/s, the combination reduced the maximum error to ±10° with the average error being 3°. Figure 7 shows a typical time-temperature profile with feedback only control at a low heating rate of 1°C/s and Figure 8 shows a typical profile with combined feedback/feedforward control at a heating rate.
Figure 7. Pyrolysis reactor temperature profile.
Heating Rate: 1 C/s.
Figure 8. Pyrolysis reactor temperature profile.
Heating Rate: 100 C/s
Figure 9. Pyrolysis reactor temperature profile.

Heating Rate: 1000 C/s
Figure 10. Pyrolysis reactor temperature profile between 300 and 900 °C. Heating Rate: 1000 C/s
of 100°C. It can be seen from these figures that the achieved temperature profiles are essentially linear.

Figure 9 shows a typical time-temperature profile at 1000°C/s with feedforward only control. It can be seen here that at such a rapid heating rate the thermocouple lag is noticeable. The lag can be estimated from the plot to be approximately 0.3 seconds. However, if the curve is only examined between 300 and 900°C where the pyrolysis reactions occur, we see that the heating rate is almost linear (see also Figure 10). An examination of twenty runs with an intended ramp of 1000°C/s revealed an average rate of 1060°C/s with a standard deviation of 50°C. This amounts to only an average relative error of 4% while the maximum recorded relative error was 8%.

II.D PYROLYSIS REACTOR OPERATION

II.D.1 Calibration

The temperature sensing circuit was checked against the melting points of several compounds covering the temperature range of the reactor. The wire mesh sample holder was loaded with 5 mg of the sample and the temperature was ramped at a constant rate of 5°C/s. Examination of the
Figure 11. Calibration with potassium dichromate.
temperature and control signal profiles revealed the melting point of the compound. A typical example of this is shown in Figure 11 with \( \text{K}_2\text{Cr}_2\text{O}_7 \) as the sample with a melting point of 398°C. The melting point corresponds to the point at which the control signal suddenly peaks out and the corresponding portion of the temperature profile shows an oscillation about the setpoint. In this case the recorded melting point is 10°C lower than the actual melting point. After recording several such points with a variety of compounds, a correction factor was calculated covering the entire temperature range and the temperature LUT was adjusted accordingly.

II.D.2 Normal Pyrolysis Operation

When pyrolyzing coal samples, a 2 mg sample was carefully weighed and placed within the wire mesh sample holder. Although larger sample sizes have been used by previous investigators with similarly sized sample holders, it was discovered that with larger samples of our coal severe agglomeration occurred at the higher heating rates. By reducing the sample size to 2 mg, particle agglomeration was significantly reduced. The wire mesh was then firmly attached between the electrodes and the thermocouple inserted through the mesh into the sample cavity. A new thermocouple
was used for each run. A small amount of vacuum grease was applied to the o-ring seal for the quartz window and the window was lowered into place applying downward pressure on the thermocouple to hold it firmly in place. The reactor was purged with nitrogen at a flow rate of 150 ml/min to remove oxygen. During this time, the temperature profile and control parameters were specified and the control program was then started.

For a typical pyrolysis run, the temperature was first ramped to 120°C at 1°C/s and held constant for 10 min. This holding period allowed additional time for purging air from the reactor and for removing most of the moisture from the coal sample. Afterward the temperature was ramped at the specified rate to 900°C at which point the power was cut off and the reactor allowed to cool down by convection. The sample screen was removed and the devolatilized char particles collected. In order to acquire a large enough sample of char for embedding, the particles produced from ten identical pyrolysis runs were collected together.
II.D.3 Hot Stage Operation

When the reactor is used as a microscope hotstage, an unfolded wire mesh screen is attached between the electrodes. A thin layer of coal particles is then spread out in the middle of the screen. As before, the thermocouple is placed among the particles and the quartz window lowered into place. The reactor is then positioned onto the microscope stage for viewing of the pyrolysis process. A long working distance 4X objective (Nikon) is used. The long working distance helps to minimize the possibility of heat damage to the optics. Additionally, two air lines are attached to the microscope stage. One line is directed to blow horizontally across the top of the quartz window to minimize the possibility of heat damage to the objective lens and the second line is directed from beneath the stage to the electrical connections in the base of the reactor to minimize the possibility of heat damage to the microscope stage itself.

As mentioned before, when operating in the hot-stage mode, the control program also provides support for an alphanumeric inserter. The inserter and video microscopy system are described in greater detail in Chapter III. Essentially, the control program transmits the reactor
temperature to the inserter over a serial communication line and the inserter overlays it onto the video signal. A sample video frame with the temperature overlay is shown in Figure 12.
Figure 12. Single video frame of the pyrolysis process with the pyrolysis reactor used as a microscope hotstage.
CHAPTER III

MACROPORE ANALYSIS

Characterization of the pore structure for any porous solid undergoing reaction is essential for accurate modeling of the reaction process. This is not an easy task in the case of chars produced from the pyrolysis of plastic coals. As we recall from Chapter II, these chars exhibit a very nonhomogeneous pore structure with pore diameters ranging from a few angstroms to many microns. The macropores themselves can range in size from 1 μm to almost the size of the particle and the majority of these larger cavities are accessible only through smaller neck pores leading to an aperture-cavity type of arrangement.

The macropore structure of porous solids has traditionally been analyzed by mercury porosimetry. Mercury porosimetry involves simultaneous measurement of the capillary pressure and the volume of mercury that has penetrated the sample up to that pressure. The pore radius is calculated from
\[ r = \frac{-2\alpha\cos\theta}{P} \]  \hspace{1cm} (1)

where \( \theta \) is the contact angle between the mercury and the pore wall, \( \sigma \) is the surface tension and \( P \) is the capillary pressure. Application of mercury porosimetry to coal chars can produce very misleading results, especially if the chars involved are produced from plastic coals and contain many of the larger aperture-cavity type pores. When large cavities are accessible through narrow neck pores, they will fill with mercury only if the applied pressure is high enough to push the mercury through the small necks. An erroneously large volume will thus be assigned to pores having small radii. The size distribution calculated from Equation (1) will be incorrectly weighted toward the smaller neck pores and it may not even reveal the presence of the larger cavities. It becomes obvious that an alternative to porosimetry is required to accurately measure the macropore size distribution for such chars.

In a symposium on flow through porous media, Dullien and Batra (1970) reviewed various methods of macropore analysis which could be used as an alternative to mercury porosimetry. Among these were microscopic methods. A study by Dullien and Mehta (1969) noted that microscopic analysis
of porous media revealed the larger macropores much more readily than mercury porosimetry. These investigators employed stereological methods to interpret the observations made on two-dimensional microscopic sections of the porous solids studied.

III.A STEREOREOLOGICAL METHODS

Simply stated, "stereology" is a science for the investigation of three-dimensional parameters from the observation and analysis of two-dimensional measurements obtainable from sections and projections of a material (Wiebel, 1980). Its widespread use has been curtailed by the nature of the mathematics involved since it combines geometrical probability theory, integral geometry and statistics. Geometric probability justifies basic stereology procedures by showing that properties calculated from two-dimensional sections and projections are distributionally related to properties of the three dimensional structure (Nicholson, 1978). Statistical theory provides for the estimation of the precision of the analysis.

Stereological methods are highly statistical in nature and collecting a large data set of measurements can be very time consuming. In earlier days, these measurements often
involved viewing of microscopic fields and extracting measurements either directly through a ruled recticle or from photomicrographs. With the widespread use of video microscopy and high-speed, low-cost image analysis systems, however, the time required to perform such measurements can be drastically reduced and the entire structure analysis process may even be partially automated.

III.A.1 Application to Coal Chars

Though the main application of stereological methods has been by biologists and material scientists in the area of microscopic morphometry, these methods have been successfully applied to the analysis of porous media. To name a few, Nicholson and Merckx (1969) made reference to its use in the pore size analysis of uranium oxide fuel rods (see also Nicholson, 1978) and Mielenz et al. (1958) analyzed the porosity of concrete with such a method. Dullien et al. (1970) lists an extensive number of other references to its application to porous media.

Jones et al. (1985) used optical microscopy and digital image processing to analyze the macropore structure of coal chars but only median pore diameters and porosities were reported, without any mention of the size distribution.
It was mentioned that the three-dimensional diameters were calculated from the two-dimensional diameters by multiplication by a factor of $4/\pi$. This simple relationship holds true only if a uniform size distribution of spheres is assumed which is clearly not applicable to coal chars.

In order to develop a mathematical model, the pores must be modeled as some geometric object. After viewing polished sections of several of the chars, it was decided to assume that the macropores could be simply modeled as a collection of spheres with randomly distributed diameters embedded within the char matrix. Viewing the macropores as a collection of spheres appears to be reasonable if one realizes that the major mechanism for their formation is the presence and growth of gas bubbles within the coal melt as it is passing through the plastic region during pyrolysis. Because of the high viscosity of the coal melt and the small time scale involved, these gas bubbles are thought to remain stationary and grow in size. From both a hydrodynamic and thermodynamic standpoint, their shape would tend to be spherical. Thus, the pore radii may be assumed to be equal to the radii of equivalent spheres. The assumption of spherical pores is also used in the few pyrolysis models which have attempted to take into account the presence of
the gas bubbles during the pyrolysis process (Mills et al., 1975, 1976; Lewellen, 1975; and Oh et al., 1983).

The macropore structure of the chars is thus visualized as consisting of a population of non-overlapping spheres of unequal size. If this assembly of spheres is intersected with random planes, a two-dimensional distribution of circle sizes on the planes of intersection will result. According to the model presented in a later section, the size distribution of circles observed on the intersecting planes will be used to calculate the size distribution of the original three-dimensional assembly of spheres. A synthetic model was developed to test the application of the method to macropore size analysis in coal chars and to check the accuracy of calculated results.

The sectioning of the three-dimensional assembly of spheres by random planes can be accomplished experimentally by preparing polished sections of char particles. Several cross-sections of char particles are analyzed with a digital image processor to obtain the size distribution of the pore profiles. Again, the plane of polishing here is thought of as a random plane intersecting a population of three-dimensional pores. The size distribution of the three-dimensional pores can then be calculated using
stereological methods to relate pore profile distributions to the sphere distribution (Weibel, 1980). At the same time, the char porosity can be obtained from the porosity of the cross sections. Clearly, the observed porosity for a cross section will depend upon the plane of sectioning but by averaging these porosities over many particles, an estimate of the true mean porosity can be obtained. As a check, the porosity is also calculated from the three-dimensional pore size distribution.

III.B EXPERIMENTAL PROCEDURE

III.B.1 Sample Preparation

The first step of the macropore analysis procedure involves the preparation of polished sections of char particles. Pyrolyzed char particles were embedded in an epoxy resin block under vacuum. One side of the block was then ground and polished to reveal random cross-sections of the embedded char particles. These sections were then viewed under the microscope and analyzed using a digital image processing system.
III.B.1.1 Embedding of Char Particles -

Two classes of mounting compounds are available for specimen mounting: molding plastics and casting plastics. Since molding plastics are injected under high temperature and pressure into the sample mold, serious physical damage to the brittle char particles can occur during this process. Hence, casting plastics are more suitable for embedding coal chars. Of the casting plastics available, only epoxy resins physically adhere to the specimen itself. Since physical adhesion is a major factor in determining edge retention, an epoxy compound (EPO-KWICK, Buehler) was used to embed the char particles.

Reusable plastic cold mounting molds (SAMPL-KUP, Buehler) were first treated with a release agent (Buehler) to prevent the epoxy from binding to the surface of the mold itself. The char particles were then spread out in a thin layer along the bottom of the mold. A circular wire mesh was then placed on top of the particles. The screen kept the particles from being swept to the top of the mold when the epoxy was poured into the mold while, at the same time, it allowed the epoxy to flow down and surround the char particles. A schematic of the mold and the resin block showing the embedded char particles is given in Figure 13.
Figure 13. Char particles embedded within an epoxy block with a mold.
The embedding process is carried out under vacuum so that the epoxy can fill as many surface pores as possible, thus ensuring a tight binding between the epoxy and the char particles which is necessary for good edge retention (Samu-als, L.E., 1969). A vacuum dessicator was fitted with a motorized turntable and pouring cup to allow multiple samples to be embedded at the same time. A dual toggle hand controller was built with adjustable speed controls for the motors. After the molds were placed in the vacuum impregna-
tion unit, the epoxy compound was mixed and placed in a pouring cup within the unit. A vacuum of 100 mm Hg was pulled for 5 minutes which allowed the epoxy to de-gas. After the molds were filled with epoxy, the vacuum was released and the epoxy allowed to cure at room temperature and atmospheric pressure for eight hours.

III.B.1.2 Grinding and Polishing -

After removing the sample block from the mold, a belt sander was used to remove epoxy to just about the level of char particles and to bevel the edge of the block. The edge was beveled to prevent it from snagging on the grinding and polishing cloths thus ensuring a level polishing action.
A compact table top grinding/polishing unit was used to produce the polished sections (Buehler, Lake Bluff, IL; Model Minimet). The MINIMET is a low volume, semi-automated unit which employs a unique geometric action to combine the advantages of hand lapping and mechanical polishing. It is ideally suited for producing the polished sections because of its flexibility of operation and its capability of covering the entire spectrum from rough grinding to final polishing with a minimal of equipment interchange. Pressure sensitive adhesive grinding papers and polishing cloths are attached to glass platens which are then placed into interchangeable plastic bowls. Therefore, the whole process involves changing only the bowls. Predetermined parameters such as speed, load, and time are fully adjustable over a wide range of settings.

Grinding proceeded in stages from 320 to 400 to 600 grit abrasives. During the initial grinding stage with 320 grit, the sample was periodically examined with a stereo microscope to determine when the grinding had reached the level of the char particles. From that point, grinding continued with the 400 and 600 grit abrasives. In between grinding stages, the sample was immersed in an ultrasonic bath with a cleaning solution (ULTRAMET, Buehler) for 5 minutes. This removed residual abrasive material from the
prepared sample to prevent cross contamination when moving from a coarser to a finer abrasive.

A three stage polishing procedure was implemented using alumina oxide polishing compounds of 5 μm, 1μm, and 0.05 μm size (MICROPOLISH II, Beuhler). Separate glass platens and polishing bowls were used for each stage to prevent cross contamination of polishing compounds. A synthetic rayon polishing cloth (MICROCLOTH, Beuhler) was used for the first polishing step of 5 μm while a chemotextile cloth (TEXMET, Beuhler) was used for the second and third polishing stages. As with the grinding procedure, the samples were cleansed in an ultrasonic bath for 5 minutes in between stages. After the final polish and ultrasonic treatment, the sample was washed with isopropanol to provide the best possible surface for further microscopic examination.

III.B.2 Analysis System

Quantitative video microscopy has recently been recognized to be a powerful analytical tool. Its performance increases significantly when it is coupled with a digital image processor to increase processing speed and power. Such a system was used to analyze the char samples for
macroporosity and macropore size distributions. A block diagram of the analysis system is shown in Figure 14.

III.B.2.1 Video Microscopy System -

The microscopy was performed on a microscope (Nikon, Garden City, NJ) fitted with an epi-illumination attachment (Nikon) to provide the reflected light source. The light was passed through a Nikon-supplied diffusion filter and interference filter at 540 nm. This helped improve the contrast of the image.

A vidicon video camera (Hamamatsu, Waltham, MA; Model C1000-01) was fitted to the microscope. The camera control unit was equipped with gain and offset adjustment controls. The video signal was monitored on a display monitor (Videotek, Pottstown, PA; Model VM-8PRW) and waveform monitor (Videotek, Pottstown, PA; Model TSM-5A). The waveform monitor was useful for monitoring the video signal levels while adjusting the light source and the camera gain and offset levels. The video signal is then routed to a digital image processor (Perceptive Systems, Houston, TX; Model 327) for analysis of the images. The video signal may alternately be rerouted via switchers to either a 3/4-in video editing system (Sony, Park Ridge, NJ; Models VO-58000, 5850, RM-440) for making presentation quality video tapes or
Figure 14. Block diagram for video microscopy and digital image processing.
a photo module (Dunn Instruments, San Francisco, CA; Model 635) for making 35mm slides or prints or 8x10 prints.

When the pyrolysis reactor was used as a microscope hotstage, the light source was changed from the epi-illuminator to a fiber-optic ringlight (Hacker Instruments, Inc., Fairchild, NJ; Model Lucidia 150) that was fitted around the microscope objective. This provided brighter illumination and since the area being viewed was not flat, oblique lighting was required instead of normal reflected lighting. Also in this mode of operation, the temperature of the reactor is superimposed onto the video signal through use of the CYPHER time code generator. The CYPHER is capable of superimposing three adjustable windows onto the video signal. The position and contents of the windows are controllable through a RS-232 serial interface. The microcomputer used for the reactor control outputs the temperature to the CYPHER during each control loop for superimposition onto the video signal. The three windows are used to display an identification string, the current temperature and elapsed time onto the video signal. Thus when reviewing video tapes of the pyrolysis process, the exact temperature is known for each video frame.
III.B.2.2 Digital Image Processor -

The digital image processor (Perceptive Systems Inc, PSICOM 327) consists of a microcomputer system equipped with special hardware that perform a large variety of image processing tasks at high computational rates.

As shown in Figure 15, the digital image processor's microcomputer system has the following components: LSI-11/73 CPU with floating point hardware and memory management; 1 megabyte of memory; a Winchester disk with 160 megabytes of storage; a dual-sided floppy disk drive (1 Mb total capacity); 8 serial communication ports; and, a 3 button trackball for interactive graphics input.

The image processing hardware associated with it consists of

- a 4 channel 8-bit video digitizer for acquiring images with resolution of 480x512 pixels;

- three 512x512x8 bit frame buffers for fast storage and manipulation of digitized images;
o a pipeline ALU for real-time image manipulation;

and

o a three channel video display with 16 adjustable
look-up tables (LUT).

The contents of the three frame buffers can be displayed
separately or as the red, green and blue channels of a color
or pseudo color image.

One of the main advantages of the PSICOM 327 is that it
is not a turnkey system. Instead, it is a powerful
microcomputer system using DEC's RT11-v5.1 single-user
operating system as an environment for software development.
The image processing hardware can be accessed using FORTRAN
callable subroutines for easy image manipulation and pro-
cessing. Both FORTRAN and MACRO-11 compilers were available
for program development. FORTRAN was the main language used
and only critical CPU-intensive routines were written in
MACRO-11.

The PSICOM 327 was supplied with a menu driven software
package to provide for: (1) system calibration; (2) image
digitization and storage; (3) image recall and editing;
(4) image processing, including arithmetic operations,
Figure 15. Block diagram of digital image processor hardware.
logical operations, geometric transformations and grayscale transformations; (5) object measurement; and (6) database analysis of object measurements. However, it was found that moving through the menus could be very cumbersome when having to process a large number of images in a very similar manner. Because of this, several customized programs were developed that are specifically tailored for the char particle analysis. Two main programs were developed to optimize this procedure. The first was for digitizing and storing images and the second was for the actual image processing which consisted of object identification and measurement extraction.

III.B.3 Image Analysis Procedure

The actual pore analysis algorithm depends upon obtaining a statistical representation of the char cross section. Since a large number of samples is required, the analysis procedure was automated as much as possible by fully utilizing the capabilities of the programmable digital image processor. The image processor was used to digitize an image, threshold it to create a binary image, label and store the image on disk. Sizes of pore cross-sections were then extracted from a series of images and the results were stored in a database.
The analysis process can be divided into two main steps. The first step involves collecting and processing images of char particle cross-sections to transform them to a binary image that can be scanned for pores. This step requires operator interaction to select the char particles under the microscope, to start the digitization and to (possibly) edit particle or pore boundaries. The second step requires no operator intervention. The collection of binary images is sequentially scanned for pores and the results stored in a database for further analysis.

III. B. 3. 1 Image Collection -

To collect images, the prepared polished section is placed under the microscope and viewed with reflected light. The light intensity and video levels are adjusted at this stage. A program specifically developed for this purpose facilitates the rapid collection of digitized images from char particle cross-sections. This program provides for:

1. digitization of the image;

2. image segmentation to distinguish the char matrix from the pores;
3. particle isolation, and;

4. labelling and saving the image.

Given the large number of video components in our system, there exist several possible sources for signal noise that can degrade the image quality. This is a common problem with video systems. The simplest way to improve the signal-to-noise ratio (SNR) is through signal averaging. With frame averaging the SNR improvement is proportional to $\sqrt{2N-1}$, where N is the number of frames averaged. When digitizing images with the PSICOM, two 8 bit frame buffers can be stacked to look like a 16 bit frame buffer to the digitizer. Combining this with the ALU allows for automatic realtime image summation of up to 256 images before arithmetic overflow is likely to occur. After summation, the ALU is used to divide the 16 bit image by the total number of frames summed to provide the final 8 bit image with an improved SNR. For our purposes, 64 images are summed to provide the graylevel image when the program receives the digitization command.

The digitized image consists of three main components: the epoxy matrix, the char matrix and the pores. For object
identification it is only necessary to distinguish the char matrix so it is desirable to convert the graylevel image to a binary image showing the char matrix. An additional advantage of this is that the binary images need only one-eighth the disk storage space as a 256 graylevel image. When viewed under the microscope, the char matrix has a higher reflectance than the pores or the surrounding epoxy. Therefore, the image can be thresholded to produce a binary image in which the char matrix shows up as white with everything else (pores or epoxy) being black.

Since the epoxy background is relatively constant, a global threshold technique is sufficient to segment the image (Castleman, 1979). A global threshold applies the same threshold value to all the pixels (picture elements) within the image. When applying a threshold to the image, all the pixels at or above the threshold value are defined as being char and are reset to a value of 255 (pure white), while all pixels below the threshold value are assigned to be pores or exterior space and reset to a value of 0 (pure black). A binary image is thus formed.

The graylevel histogram of the original image is used to determine the threshold value. Figure 16 shows a graylevel image resulting from averaging 64 frames. Figure
Figure 16. Gray-level image obtained by averaging 64 frames.
Figure 17. Gray-level histogram.
Figure 18. Binary image obtained by global thresholding.
17 shows the graylevel histogram corresponding to Figure 16. The histogram is typical in that it shows three very distinct peaks. The first peak corresponds to all the pixels associated with pores, the second peak to all pixels associated with the epoxy matrix, and the final peak to all pixels associated with the char matrix. The minimum between the second and third peaks is used to determine the global threshold value for image segmentation. Figure 18 shows the results of applying a global threshold value of 145 to Figure 16. The global thresholding is performed with two passes through the pipeline ALU thus requiring only 1/15 of a second. The graylevel image, binary image, and graylevel histogram are simultaneously displayed through each of the PSICOM's three output channels.

After the image is segmented, the system's trackball or keyboard is used to define a rectangular window around the particle of interest to isolate it from neighboring particles. After the window is selected, all pixels exterior to the window are erased. A paintbrush routine using the trackball is then implemented to erase any portion of neighboring particles that are still showing inside the selected window and to fix any boundaries that were broken during the global thresholding. The paintbrush size and
color (black or white) are interactively adjustable and a 2X hardware zoom is also available.

The binary images are labelled with a six character alphanumeric name. Once specified, the first three characters remain the same for all images saved until the characters are respecified. The last three characters represent a sequence number which is incremented after each image is stored. The starting value of this number can also be specified. Since the images are in binary form, they are stored in compressed format with each bit of every stored byte representing a single image pixel. In this way, 512x512 binary images are stored using only 32 Kbytes of disk space.

III.B.3.2 Object Identification and Measurement -

The second program developed for the PSICOM was to provide automated object identification and measurement extraction. Once a sizable number of particle cross sections were digitized and saved, a list of these images and the magnification factor was made available to this program. Each image in the list was loaded from disk storage into one of the PSICOM's frame buffers. Then an object identification algorithm was applied to the image to identify all the
objects (pores) whose area (measured in number of pixels) is greater than a preset value. Once the pores have been identified, their equivalent diameter is calculated, and the values for both the area and equivalent diameter are converted to real units and stored in a database.

The object search and identification algorithm utilizes a line-by-line technique known as line segment encoding (Castleman, 1979). Once a binary image is loaded into a frame buffer, the image is scanned vertically line-by-line. On each line, object segments are located and tracked. When proceeding on to the next line, comparisons are made to see whether segments are attached to segments on the previous line and if so, then the segments are assigned to the same object.

In addition, a circularity factor defined by the formula below is calculated for each pore cross-section.

\[
\text{CIRCULARITY FACTOR} = \frac{\text{PERIMETER}^2}{4 \cdot \pi \cdot \text{AREA}}
\] (2)

The digitization procedure leads to artificially jagged object boundaries introducing errors in the perimeter measurement. To reduce these errors, two intermediate perimeters are calculated. The first perimeter is calculated by assuming that the pore is defined by the edge pore pixels. The
second perimeter is calculated by assuming that the edge char pixels define the pore. The pore perimeter is then set as the root-mean-square value of the two intermediate perimeters. A sample listing of the database from the analysis of Figure 18 is shown in Table 1.

Upon examination of the circularity factors in Table 1, it is evident for very small objects that there is a large difference between the two calculated perimeters. This is due to pixelization errors become significant for small objects. For this reason, an area equivalent diameter was calculated for each object instead of a perimeter equivalent diameter.

Once the database of object measurements for a given char sample was completed on the PSICOM, it was uploaded to a VAX 11/750 minicomputer (DEC) for further processing. It is here that the three-dimensional macropore size distribution is actually computed. The VAX is used for this step because of the ease of programming with large arrays under VAX/VMS as compared to RT-11 and to make use of the extensive software libraries available on the VAX that include numerical, graphics, and plotting packages.
Table 1. Sample listing of object measurement database.

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The database can be uploaded via floppy disk interchange or serial communications lines. Customized communication software was developed to allow a variety of hookup modes. The RT-11 v5.1 operating system has a virtual terminal emulator but its file transfer support is extremely slow and without flow control. Therefore, another virtual terminal program was developed that supported faster and more reliable file transfer capabilities. Additionally, a virtual TU58 emulator was developed for the VAX that allowed for ASCII or binary file transfer with RT-11 monitor commands (Sandmann, 1986).

III.C CALCULATION OF THE 3-D PORE SIZE DISTRIBUTION

The stereological model used to obtain the three-dimensional pore size distributions is now presented. Consider a population of spheres whose radius $r$ is randomly distributed and let $N(r)$ be the corresponding probability density function. Thus, the number of spheres per unit volume with radii between $r$ and $r+dr$ (or in the interval $r±1/2r$) is given by $N(r)dr$. If the population of spheres is intersected with a plane of random orientation, the sphere cross-sections will yield circles with randomly distributed radius $\rho$ having a probability density function $n(\rho)$. The total number of circles per unit area of the intersecting plane with radii between $\rho$ and $\rho+d\rho$ is thus equal to $n(\rho)d\rho$. 
The problem is now to compute $N(r)dr$ from a given distribution $n(\rho)d\rho$.

As early as 1925, Wicksell derived the fundamental probability density function relating the profile size distribution to the sphere size distribution. He showed that the two were distributionally related by,

$$n(\rho)d\rho = \int_{\rho}^{r_{\text{max}}} \frac{2N(r)\rho drd\rho}{\sqrt{r^2 - \rho^2}}$$  \hspace{1cm} (3)

Thus the problem is to unfold the three-dimensional size distribution, $N(r)dr$, from the measurable profile distribution, $n(\rho)d\rho$. If the profile size distribution were known exactly in an explicit mathematical form, Equation (3) could be solved analytically. In practice however, this is more often the exception instead of the rule and some numerical scheme must be used to evaluate Equation (3).

The simplest and most often used approach is based on the so-called finite difference methods (Cruz-Orive, 1983). These methods are based upon various integration rules to discretize the problem. Wiebel (1980) reviewed the two most popular methods proposed by Saltykov (1958) and Wicksell (1925) and noted their limitations in estimating the tails
of the distribution. The limitations stem from the choice of simple rectangular rules for their integration schemes.

A similar approach is used here, but a more accurate trapezoidal integration rule is employed instead. We first discretize the problem by allowing \( \Delta \rho \rightarrow \Delta \rho \) and \( \Delta r \rightarrow \Delta r \) with \( \Delta \rho = \Delta r \). Therefore,

\[
\rho_i = i \cdot \Delta \rho \quad \text{and} \quad r_i = i \cdot \Delta r
\]

with \( i = 1, 2, \ldots, m \)

The profile density function is discretized as

\[
n_i(\rho_i) \Delta \rho = \int_{\rho_{i-1}}^{\rho_i} n(\rho) \, d\rho
\]

Equation (3) can now be written as

\[
n_i(\rho_i) \Delta \rho = \int_{\rho_{i-1}}^{\rho_i} \int_{r_{i-1}}^{r_m} \frac{2N(r) \rho \, dr \, d\rho}{\sqrt{r^2 - \rho^2}}
\]

The integration with respect to \( \rho \) is exact so

\[
n_i(\rho_i) \Delta \rho = \int_{r_{i-1}}^{r_m} 2N(r) \, dr \left\{ \left[ \frac{r^2 - \rho_i^2}{2} \right]^{1/2} - \left[ \frac{r^2 - \rho_{i-1}^2}{2} \right]^{1/2} \right\}
\]
\[ = \int_{r_{i-1}}^{r_m} F(r) \, dr \]  

(8)

By discretizing Equation (8) we obtain

\[ n_i(\rho_i) \Delta \rho = \sum_{j=i}^{m} \int_{r_{j-1}}^{r_j} F(r) \, dr \]  

(9)

At this point we apply the trapazoidal integration rule to get

\[ n_i(\rho_i) \Delta \rho = \sum_{j=i}^{m} \frac{1}{2} \Delta r \left[ F(r_{j-1}) + F(r_j) \right] \]  

(10)

\[ = \sum_{j=i}^{m} \Delta r \left\{ N(r_j) \left\{ \left[ r_j^2 - \rho_i^2 \right]^{1/2} - \left[ r_{j-1}^2 - \rho_i^2 \right]^{1/2} \right\} + \right. \]

\[ \left. N(r_j) \left\{ \left[ r_{j-1}^2 - \rho_i^2 \right]^{1/2} - \left[ r_j^2 - \rho_i^2 \right]^{1/2} \right\} \right\} \]  

(11)

Substituting Equation (4) into Equation (11) gives

\[ n_i(\rho_i) \Delta \rho = \sum_{j=i}^{m} \Delta r \left\{ N(r_j) \left\{ \left[ j^2 - (i-1)^2 \right]^{1/2} - \left[ j^2 - i^2 \right]^{1/2} \right\} + \right. \]

\[ \left. N(r_j) \left\{ \left[ (j-1)^2 - (i-1)^2 \right]^{1/2} - \left[ (j-1)^2 - i^2 \right]^{1/2} \right\} \right\} \]  

(12)
\[ = 2\Delta r^2 \sum_{j=i}^{m-1} N(r_j) \left\{ \left[ j^2 - (i-1)^2 \right]^{1/2} - \left[ j^2 - i^2 \right]^{1/2} \right\} \]

\[ + N(r_m) \left\{ \left[ m^2 - (i-1)^2 \right]^{1/2} - \left[ m^2 - i^2 \right]^{1/2} \right\} \quad (13) \]

\[ = \sum_{j=i}^m k_{ij} N(r_j) \quad (14) \]

where

\[ k_{ij} = \begin{cases} 
2\Delta r^2 \left\{ \left[ j^2 - (i-1)^2 \right]^{1/2} - \left[ j^2 - i^2 \right]^{1/2} \right\} & \text{for } i < j < m \\
\Delta r^2 \left\{ \left[ j^2 - (i-1)^2 \right]^{1/2} - \left[ j^2 - i^2 \right]^{1/2} \right\} & \text{for } j = m 
\end{cases} \]

This then represents a linear transformation of the circle distribution to the sphere distribution. The matrix \( K \) is upper triangular with the elements \( k_{ij} \) defined from Equation (15) and the system of linear equations may be solved using a variety of software packages such as LINPACK.

The database of pore profile measurements taken with the image processor is sorted into appropriate histogram classes to produce the discrete distribution function \( n(\rho) \Delta \rho \). Equation (14) is solved for \( N(r_j) \) and the desired quantity, \( N_j(r_j) \Delta r \) is calculated as
\[ N_j(r_j) \Delta r = \int_{r_j}^{r_{j-1}} N(r) \, dr \]
\[ = \frac{1}{2} \Delta r \left[ N(r_j) + N(r_{j-1}) \right] \] (15)

for \( j = 1, 2, \ldots, m \)

When speaking of porous solids from a reaction engineering standpoint, the pore volume distribution is more often the distribution reported rather than the pore size distribution (Smith, 1981). The cumulative pore volume function is given by

\[ CV(r) = \int_{0}^{r} \frac{4}{3} \pi r^3 N(r) \, dr \] (16)

The discrete distribution is calculated from the previous results as

\[ CV_1(r_i) = \frac{2}{3} \pi \Delta r \sum_{j=1}^{i} \left[ r_{i-1}^3 N(r_{i-1}) + r_i^3 N(r_i) \right] \] (17)
III.C.1 TESTING OF THE STERELOGICAL METHOD FOR PORE ANALYSIS

Dullien and coworkers (1969) used a computer simulation to critically test a stereological method which was very similar to the method used in this study. The sphere size distribution was calculated from the distribution of profile measurements. Only the numerical integration scheme was different. He found that a relatively small sample of about 5000 measurements produced results with less than a 10% relative error. A sample size of approximately 15000 measurements was required to decrease the error to less than 5%.

To minimize the error due to scatter, the profile data was twice smoothed with a seven point averaging algorithm. While this produced good results with the Gaussian type distribution he used, it would severely dampen the sharp peak of a strongly skewed distribution such as is known to exist for the pore size distribution in coal-derived chars. Anderssen and Jakeman (1975) used Lagrange polynomials to smooth the data with very good results and Taylor (1983) made reference to using splines as a possible alternative.

A computer simulation similar to the one used by Dullien et al. (1969) was used to test the effectiveness of using B-splines to smooth the profile data. A distribution
that was weighted towards the smaller sizes was used as a model. The distribution was of the form

$$n(r) = a \cdot e^{-r/\beta}$$  \hspace{1cm} (18)

In order to implement the simulation, certain parameters had to be arbitrarily chosen. The parameter $\beta$ was chosen to 0.05. A collection of 500 cubes of unit volume was selected to represent char particles. With a chosen porosity of 35%, the parameter $a$ was adjusted until the target porosity was achieved. The spheres were then randomly thrown into each of the cubes and a plane of sectioning was randomly chosen. The circle profiles generated from the random sectioning were saved in a database for further processing. For the given distribution, porosity and number of cubes, 3382 circle profiles were generated.

The purpose of this exercise was not to repeat the work done be Dullien but to see if B-splines could be used to smooth the profile data. Figures 19 through 21 show the effect of smoothing the profile data. Two smoothing schemes were compared. A two pass, 5-point averaging scheme similar to that used by Dullien was compared to curve fitting the profile data with B-splines. Three comparison's were made with a different number of profiles for each one;
approximately 3000, 2000 and 1000 profiles. From the plots it is clear that B-spline smoothing gave the best results and was less sensitive to the number of profiles measured. Thus it's evident that smoothing of the profile data with a spline curve effectively minimizes the error due to scatter.

From these tests and the work by Dullien we see that approximately 2000 to 3000 profile measurements are required to unfold the 3-D distribution to within roughly a 10% error. With the B-spline smoothing the method is less sensitive to the number of profile measurements than without smoothing. For the char particles in this study, analysis of 50 polished sections produced anywhere from 2000 to 7000 pore profiles.
Figure 19. Effect of smoothing profile data.

- Actual
- Calculated
- 3382 Profiles
- No Smoothing
- 18% Error
- 3382 Profiles
- 5 Pt Averaging
- 18% Error
- 3382 Profiles
- Spline Smoothing
- 9% Error

Pore Radius - arbitrary units
Figure 20. Effect of smoothing profile data.
Figure 21. Effect of smoothing profile data.
CHAPTER IV

RESULTS OF MACROPOROUS ANALYSIS ON COAL CHARS

The pore size analysis method described in the previous chapter was used to characterize the macropore structure of chars derived from the pyrolysis of several parent coals under a variety of conditions. An Illinois #6 coal and a Texas lignite were used in our pyrolysis studies. Several other chars produced under different pyrolysis conditions and coal pretreatments (Ballal, 1985; Sandmann, 1986) were also analyzed.

Pore volume distributions are usually reported in the reaction engineering literature (Smith, 1981). For the subsequent discussion, the computed pore size distributions were converted to cumulative pore volume distributions as mentioned in Chapter III. The pore volume distributions were then calculated by differentiating the cumulative pore volume vs radius function. A continuous pore volume distribution is obtained from this differentiation. This is advantageous because now the macropore volume distributions can be compared from sample to sample without regard for the
histogram bin size $\Delta r$ used for unfolding the three-dimensional pore size distribution.

It should be noted that the pore volume distribution curves presented in this chapter all fall off to zero for a pore size of 1 $\mu$m. This is an artifact of the analysis procedure since we are limited by optical microscopy as to the minimum pore size which can be detected. Hence, the large number of pores smaller than 1 $\mu$m and their associated pore volume are not detected.

IV.A COMPARISON TO MERCURY POROSIMETRY ANALYSIS

To compare the stereological macropore analysis procedure to mercury porosimetry results, three different char samples were analyzed by each method and the results compared. Two of the char samples were plastic coals, Illinois #6 and Pittsburgh #8. The third char sample was a nonplastic coal, Texas Lignite. All three samples were composed of 50-60 mesh (250-300 $\mu$m) particles that had been pyrolyzed in an annular fluidized bed reactor at $4^\circ$C/min (Moudgalya and Zygourakis, 1987; Ballal, 1985).

Binary images obtained from polished sections for each char sample are shown in Figures 22 through 24. The
corresponding cumulative pore volume distribution curves obtained from mercury porosimetry analysis are shown in Figure 25 and those obtained from the stereological analysis are shown in Figure 26.

The distribution from mercury porosimetry analysis, Figure 25, show a maximum pore radius of about 88 μm detected for all char samples. It is well known, however, that the initial penetration volume is associated with interparticle voids in the char sample and not with large pores in the particle interiors. Polished section images for the same chars confirm this statement. This is particularly evident in the case of the lignite char. Its polished sections display a large number of smaller pores, but no pores even approach a radius of 88 μm.

The initial penetration volume detected during porosimetry measurements and associated with interparticle voids complicates a comparison of char macroporosities measured by the two methods. In the case of the Illinois #6 char, this volume is approximately equal to 1 cc/g. For the Pittsburgh and lignite chars, this initial volume is equal to 0.82 cc/g and 0.69 cc/g respectively. When the initial penetration volumes are ignored, the maximum pore radius detected by mercury porosimetry would be 2.33 μm, 0.42 μm and 0.77 μm
for the Illinois #6, Pittsburgh #8 and Lignite chars respectively. A comparison of these values to those obtained from the polished sections immediately shows the well-known limitations of mercury porosimetry. Most of the large pores seen in the polished sections for the two plastic coals are of the aperture-cavity type and, as discussed in Chapter III, mercury penetration cannot detect the large pores. Some of the large cavities that were not of the aperture-cavity type may fill at a lower capillary pressure but would be confused with the interparticle voids. It is thus evident that mercury porosimetry cannot be used to accurately describe the macropore distribution in coal-derived chars.

The results from the stereological analysis of the same chars, Figure 26, quantify what is immediately obvious from the images of polished sections. Note that the maximum radii calculated for the two plastic chars are different and the maximum radius for the Illinois #6 char is larger than the largest interparticle void detected by porosimetry. In conclusion, the stereological method is able to detect the larger macropores in the char samples giving an accurate characterization of their macropore structure.
We do see, however, that the mercury porosimetry method covers a much larger range of pore sizes than is possible with optical microscopy and the stereological method. The size of the smallest pores detected in our studies was limited by the initial particle size, since the maximum magnification used was that which would allow the entire cross-section of a particle to be within the field of view. So with smaller particles it would be conceivable to increase the magnification and detect smaller pores, up to the limitations of optical microscopy.
Figure 22. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 23. Pittsburgh #8 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 24. Texas Lignite char cross sections

Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 25. Mercury Porosimetry Analysis.
Particle Size: 50 - 60 mesh
Heating Rate: 4 C/min
Figure 26. Stereological Pore Analysis
Particle Size: 50 - 60 mesh
Heating Rate: 4 C/min
IV.B EFFECT OF PYROLYSIS HEATING RATE

The pyrolysis reactor described in Chapter II was used to pyrolyze 50-60 mesh (250-300 μm) Illinois #6 coal particles at five different heating rates from 0.1°C/s to 1000°C/s. In addition, 50-60 mesh particles of the Texas lignite coal were pyrolyzed at three heating rates covering the same range. All the pyrolysis runs were performed in a nitrogen atmosphere and the final heat-treatment temperature was 900°C.

Increased heating rates caused dramatic differences in the macropore structure of the chars produced from the plastic Illinois #6 coal. Figures 27 through 31 present representative cross-sections of char particles produced at the various heating rates. Low heating rates (0.1 °C/s) produced chars with a few scattered large cavities with thick walls and several smaller cavities. When the heating rate increased to 1 °C/s, the formation of several thin-walled cavities was observed that led to highly cellular internal structure for the corresponding particles. 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.

The pore volume distributions presented in Figures 33 and 34 quantify the previously stated observations. For the char produced at a heating rate of 0.1°C/s, most of the pore volume is distributed between the 2-110 µm range, with another large fraction assigned to pores within a very narrow range around 130 µm. This second peak is clearly separated from the first distribution. As the heating rate is increased to 1°C/s, the distribution of larger cavities widens and the smaller pores are grouped more toward the low end of the plot. The pore volume distribution is almost uniform with a heating rate of 10°C/s. Finally, heating rates of 100 and 1000°C/s resulted in chars with a group of large primary pores and a group of smaller secondary vesicles.

In contrast to the Illinois #6 chars, the cross-sections of lignite char particles show almost no visible change as the heating rate is increased. Figures 35 through 37 give representative images of the polished char sections taken for each sample. The corresponding pore volume distribution curves presented in Figures 38 and 39 also show no significant changes from an increase in heating
rate. One should note, however, the distinct bimodal nature of the pore volume distribution curves.

Tables 2 and 3 summarize the global properties of the eight char samples that were measured by stereological analysis. Increasing heating rate cause an increase in the porosity and the maximum pore radius for the Illinois #6 chars but have a very small effect on the Texas lignite chars. The increase in porosity with increased heating rate is not linear but tends to level off at the higher heating rates. This is in agreement with earlier work by Hamilton (1980, 1981).
Table 2. Global parameters for Illinois #6 char at various heating rates.

<table>
<thead>
<tr>
<th>Heating Rate °C/s</th>
<th>Porosity</th>
<th>Surface Area 2 cm³/cm³</th>
<th>Maximum Radius μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>33 %</td>
<td>450</td>
<td>133</td>
</tr>
<tr>
<td>1.0</td>
<td>55</td>
<td>626</td>
<td>157</td>
</tr>
<tr>
<td>10</td>
<td>69</td>
<td>695</td>
<td>152</td>
</tr>
<tr>
<td>100</td>
<td>77</td>
<td>605</td>
<td>173</td>
</tr>
<tr>
<td>1000</td>
<td>82</td>
<td>649</td>
<td>187</td>
</tr>
</tbody>
</table>

Particle Size: 50-60 mesh

Table 3. Global parameters for Texas Lignite char at various heating rates.

<table>
<thead>
<tr>
<th>Heating Rate °C/s</th>
<th>Porosity</th>
<th>Surface Area 2 cm³/cm³</th>
<th>Maximum Radius μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>15 %</td>
<td>826</td>
<td>28</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>826</td>
<td>24</td>
</tr>
<tr>
<td>1000</td>
<td>19</td>
<td>959</td>
<td>25</td>
</tr>
</tbody>
</table>

Particle Size: 50-60 mesh
Figure 27. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 0.1 C/s
Figure 28. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 1 C/s
Figure 29. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 10 C/s
Figure 30. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 100 C/s
Figure 31. Illinois #6 char cross sections
Particle Size:  50-60 mesh
Heating Rate:  1000 C/s
Figure 32. Macropore cumulative pore volume distribution for Illinois #6 chars pyrolyzed at various heating rates.
Figure 33. Pore volume distribution for Illinois #6 char.
Figure 34. Pore volume distribution for Illinois #6 char.
Figure 35. Texas Lignite char cross sections
Particle Size: 50-60 mesh
Heating Rate: 0.1 C/s
Figure 36. Texas Lignite char cross sections

Particle Size: 50-60 mesh
Heating Rate: 10 C/s
Figure 37. Texas Lignite char cross sections

Particle Size: 50-60 mesh
Heating Rate: 1000 C/s
Figure 38. Macropore cumulative pore volume distribution for Texas Lignite chars pyrolyzed at various heating rates.
Figure 39. Pore volume distribution for Lignite char.
IV.C EFFECT OF PARTICLE SIZE

The difficulties of elucidating the effects of particle size on the pyrolysis process were noted in Chapter II. A preliminary study was carried out to determine whether changes in particle size had a major effect on the macropore structure of chars derived from our plastic Illinois #6 coal. Two additional size fractions of this coal were pyrolyzed at a heating rate of 10°C/s. One size fraction was 25-28 mesh (589-710 μm) and the other was 100-120 mesh (125-149 μm).

Table 4 summarizes the measurements for the macropore properties. The macroporosity of the particles was not affected by their size while the maximum pore radius decreased substantially with decreasing particle size as expected. The specific macropore surface area for the 100-120 mesh sample was much higher than that of the other larger particle samples and this is attributed to the large number of smaller pores.

Examination of the polished sections and of the pore volume distribution curves, Figures 40 through 43, reveals a drastically different pore structure for the smallest char particles (100-120 mesh). A large fraction of the pore
volume for these particles is associated with large pores approximately 50 \( \mu \text{m} \) in radius. The pore volume distribution for the intermediate particles (50-60 mesh) is more uniform. A distinct shift toward smaller pores is observed, however; in the case of the largest particles studied here (25-28 mesh).

Table 4. Global parameters for Illinois #6 char for various particle sizes.

<table>
<thead>
<tr>
<th>Particle Size, mesh</th>
<th>Porosity</th>
<th>Surface Area ( \frac{2}{3} ) cm(^2/cm)</th>
<th>Maximum Radius ( \mu \text{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 - 28</td>
<td>69 %</td>
<td>638</td>
<td>284</td>
</tr>
<tr>
<td>50 - 60</td>
<td>69</td>
<td>695</td>
<td>152</td>
</tr>
<tr>
<td>100 - 120</td>
<td>71</td>
<td>1440</td>
<td>51</td>
</tr>
</tbody>
</table>

Heating Rate: 10\(^o\)C/s
Figure 40. Illinois #6 char cross sections

Particle Size: 25-28 mesh

Heating Rate: 10 C/s
Figure 41. Illinois #6 char cross sections
Particle Size: 100-120 mesh
Heating Rate: 10 C/s
Figure 42. Macropore cumulative pore volume distribution for Illinois #6 chars of various size pyrolyzed at 10 C/s.
Figure 43. Pore volume distribution for Illinois #6 char.
IV.D EFFECT OF ASH

It is well known that the inorganic material (ash) present in coals and devolatilized chars can have a catalytic effect on the gasification reactions. Much less is known, though, about the effect of ash or added catalysts on the pyrolysis process. Hirsch et al (1982) found that chars from coking coals impregnated with potassium carbonate exhibited less swelling and agglomeration than those produced from untreated coals. Pretreatment of parent coals with alkaline solutions is also used to minimize particle agglomeration in fluidized bed reactors.

Six char samples available from parallel investigations in our laboratory were used for a preliminary investigation of the effects of ash on the macropore structure of devolatilized chars. Two char samples were prepared by demineralizing (DEM) the parent coals (lignite and Illinois #6) and then pyrolyzing it at low heating rates in a fluidized bed to produce chars with very low ash content (Sandmann and Zygourakis, 1987). Two other samples were prepared by pyrolyzing the raw lignite and Illinois coals first and then demineralizing the produced chars (ibid.) The last two char samples (lignite and Illinois) were non-demineralized (Ballal and Zygourakis, 1985).
A striking difference was observed between the behavior of the Illinois #6 samples and that of the Texas lignite samples. We see from Tables 5 and 6 and Figures 47, 48, 52 and 53 that the porosity of the Illinois char decreased with demineralization while it increased for the Lignite char. The same trend is noticed with the maximum pore radius detected.

From Figure 48, it appears that the decrease in the porosity of the ash free Illinois chars is due to the decrease in the size of the largest pores. The small scale used in Figure 47 exaggerates the differences in the porosities but in actuality they are still within about 10% of each other. The pore volume distribution curves in Figure 48 are also very similar except for the decrease in the maximum pore size. Thus the effect of ash on the pyrolysis of plastic coals are inconclusive. Certainly if any effects are present they are swamped out by the much more drastic effects of heating rate and particle size.

Since the pyrolysis process has limited effect on the macropore structure of nonplastic coals, it follows that demineralization should lead to an increase in porosity for the lignite chars. This increase in porosity is caused by the physical removal of ash particles from the coal/char
matrix. If the ash particles were in the order of 20 to 40 μm in size, then their removal would account for the increase in the pore volume within this size range as shown in Figure 53.
Table 5. Global parameters for Illinois #6 char with various ash conditions.

<table>
<thead>
<tr>
<th>Ash Condition</th>
<th>Porosity</th>
<th>$2^2/\text{cm}^3$</th>
<th>$3^3/\text{cm}^3$</th>
<th>Maximum Radius $\mu\text{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>21 %</td>
<td>448</td>
<td></td>
<td>110</td>
</tr>
<tr>
<td>DEM, pyrolyzed</td>
<td>17</td>
<td>292</td>
<td></td>
<td>91</td>
</tr>
<tr>
<td>pyrolyzed, DEM</td>
<td>20</td>
<td>372</td>
<td></td>
<td>96</td>
</tr>
</tbody>
</table>

Particle Size: 50-60 mesh  
Heating Rate: 4 $^\circ\text{C/min}$

Table 6. Global parameters for Texas Lignite char with various ash conditions.

<table>
<thead>
<tr>
<th>Ash Condition</th>
<th>Porosity</th>
<th>$2^2/\text{cm}^3$</th>
<th>$3^3/\text{cm}^3$</th>
<th>Maximum Radius $\mu\text{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal</td>
<td>10 %</td>
<td>673</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>DEM, pyrolyzed</td>
<td>13</td>
<td>710</td>
<td></td>
<td>46</td>
</tr>
<tr>
<td>pyrolyzed, DEM</td>
<td>15</td>
<td>965</td>
<td></td>
<td>32</td>
</tr>
</tbody>
</table>

Particle Size: 50-60 mesh  
Heating Rate: 4 $^\circ\text{C/min}$
Figure 44. Illinois #6 char cross sections
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 45. Illinois #6 char cross sections
DEM, Pyrolyzed
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 46. Illinois #6 char cross sections
Pyrolyzed, DEM
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 47. Macropore cumulative pore volume. distribution for Illinois #6 chars showing effect of ash.
Figure 48. Pore volume distribution for Illinois #6 char.
Figure 49. Texas Lignite char cross sections

Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 50. Texas Lignite char cross sections
DEM, Pyrolyzed
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 51. Texas Lignite char cross sections
Pyrolyzed, DEM
Particle Size: 50-60 mesh
Heating Rate: 4 C/min
Figure 52. Macropore cumulative pore volume distribution for Texas Lignite chars effect of ash.
Figure 53. Pore volume distribution for Lignite char.
CHAPTER V

EFFECT OF MACROPORE STRUCTURE ON GLOBAL GASIFICATION RATES UNDER STRONG DIFFUSIONAL LIMITATIONS

As mentioned in the Introduction, the ultimate objective of our studies was to determine how the macropore structure of chars affects the true gasification rates of char particles under the operating conditions encountered in commercial processes. Having presented a novel analytical method for accurate characterization of the macropore structure, we now turn our attention to the gasification process.

The development of models providing accurate predictions of gasification rates is a challenging problem. Since the introduction of adjustable parameters limits the range of applicability of such models, one must impose the requirement that all model parameters be directly obtainable from measurable properties of the unreacted chars. In the absence of intraparticle diffusional limitations, the gasification rate can be expressed in the following simplified form
\[ \frac{dx}{dt} = A(x) \cdot S_g(x) \cdot f(T, c_i) \]  

(1)

where \( R \) is the gasification rate \([s^{-1}]\), \( x \) is the solid reactant conversion, \( A(x) \cdot S_g(x) \) is the active pore surface area \([m^2/g \text{ of solid reactant}]\), \( S_g(x) \) is the total pore surface area \([m^2/g]\) and \( f(T, c_i) \) is the expression yielding the intrinsic reaction rate \([(g \text{ of solid reactant})/m^2]\) that depends only on the gaseous reactant concentrations \( c_i \) and temperature \( T \). The total surface area \( S_g \) is a strong function of conversion. The concentration of active sites per unit surface area is often assumed to be constant, but this may not be true for some reacting systems (Sandmann and Zygourakis, 1987). Finally, solid additives or impurities may catalyze or hinder the reaction under study and their effects must also be considered.

Our studies will concentrate on determining the evolution of total surface area \( S_g \) with conversion. Two competing mechanisms determine the temporal evolution of surface area \( S_g \) in the absence of intraparticle diffusional limitations. The first of these is pore growth. As heterogeneous reactions occur on the pore walls, solid reactants will be consumed to form gaseous products. This will result in an increase in the pore size and, hence, in the available
surface area. Secondly, combination of adjacent pores will occur as pores grow due to reaction and the walls separating them are consumed. Pore combination will lead to a decrease in the available surface area and reactivity. Pore growth dominates during the initial stage of the gasification process, but as the conversion and porosity increase pore combination becomes dominant. Thus, the available surface area may pass through a maximum as the reaction proceeds.

The situation becomes even more complex when gasification occurs in the regime of strong intraparticle diffusional limitations. Heterogeneous reactions will now occur only on a small fraction of the total pore surface area \( S_g \), that is only on the surface that is "close" to the particle exterior. Pore exposure becomes important in this case. Initially, pores in the particle interior may be inaccessible to the reactants because of the diffusional limitations. As the reaction proceeds, pores near the particle exterior will grow and will eventually combine (or coalesce) with internal pores. Now, the previously unexposed surface area associated with internal pores will become accessible to the reactants. Increased pore accessibility will thus lead to an increase in the surface area available for reaction and, consequently, to an increase in the observed reaction rate.
Clearly, a knowledge of how the available surface area evolves with the extent of reaction is essential for the development of accurate models for the gasification process.

V.A AVAILABLE MODELS

Heterogeneous char reaction models can generally be classified as macroscopic or microscopic (Smoot and Smith, 1985). The majority of existing gasification models follows a macroscopic approach. According to the macroscopic approach, the evolution of the actual pore structure is not rigorously modeled but is taken into account through the use of an effectiveness factor. This effectiveness factor is a measure of the degree of utilization of the total surface area during gasification. Effectiveness factors depend strongly upon the effective diffusivities of the gaseous reactants in the porous solid and these diffusivities are usually assumed to be constant throughout the particle. The classical shrinking core model is included in this group.

It is well known, however, that macroscopic models fail to accurately account for situations in which the available surface area changes dramatically during the reaction process.
Microscopic models, on the other hand, attempt to look at the reaction process in individual pores and then relate this to the overall particle by an appropriate statistical model. Perlmutter and coworkers (1980, 1981, 1985) and Gavalas (1980) each developed random pore models with two adjustable parameters obtainable from experimental data. These models gave very good results for several chars but failed with chars containing a wide pore size distribution such as those derived from plastic coals. Zygorakis and coworkers (1982) considered a char particle characterized by two populations of pores: large spherical macropores and smaller cylindrical micropores. That model, however, contained several adjustable parameters which had to be adjusted to fit the experimental data. A different approach was used by Ballal and Zygorakis (1987) to develop a random pore model that could treat porous solids with complex pore size distributions and various pore shapes. The latter model required no adjustable parameters as all its parameters were directly obtainable from physical measurements.

All of the aforementioned models, however, fail to take into account such factors as initially inaccessible pores, diffusional limitations or particle fragmentation. To overcome these difficulties, Sandmann and Zygorakis (1986a,b) followed a discrete modeling approach. The discrete models
use a computational grid consisting of a large number of discrete cells to model the porous solid. Regions corresponding to pore voids or solid reactant are defined by setting the cells to appropriate values and these regions are grown or shrunk according to simple rules simulating gas-solid reactions. The evolution of structural properties as a function of conversion is easily obtainable by examining the grid at intermediate conversions. The grids may also be displayed pictorially to aid in visualizing the reaction process. Details of the model will not be given here but are available elsewhere (Sandmann and Zygourakis, 1986a,b). These studies established that discrete models were extremely useful for studying the gasification process in the presence of strong diffusional limitations and reported results demonstrated the importance of the macropore structure on the observable reaction rate.

V.B NOVEL DISCRETE MODELS

The main assumptions for simulating char gasification reactions under strong diffusional limitations are: (a) only the macropores take part in the reaction process, and (b) only the surface area on the irregular exterior of char particles participates in the reaction.
The original discrete models (ibid.) considered only regions defined by overlapping regular geometrical entities (circles or spheres) of uniform size or having a given distribution of sizes. For example, two-dimensional simulations modeled the pore cross-sections as circles, grew the pores by increasing the circle diameters by a fixed amount at each time step and then determined which cells had to be changed (from char to pore) to reflect the new pore dimension. That required the use of recursive programming to simulate the pore exposure process.

However, it is rather difficult to approximate the highly irregular pore cross-sections observed directly under the microscope (see Chapter IV) by a collection of overlapping regular entities (e.g., circles). Thus, generalized versions of the discrete models were developed and used here to study the effects of the different macropore structures reported in Chapter IV on the observed gasification rates under strong diffusional limitations.

According to the new approach, the initial computational grids are obtained directly from the digitized images of actual particle cross-sections viewed under the microscope. This is the most attractive feature of the new
approach and it allows us to easily simulate very complex pore structures.

Digital image processing techniques are directly applicable to the discrete gasification model since digital images are in fact discrete models of real images. Specifically, object search, object identification, and erosion techniques can be applied to treat the reaction of complex pore structures while maintaining reasonable computational time. Instead of modeling the pores as overlapping regular geometric shapes and growing the pores according to that shape, erosion techniques essentially scan an image and erode away all edge pixels regardless of the complexity of the edge boundary.

The char cross sections are digitized during the macro-pore analysis procedure described in Chapter III. They consist of a 512x480 grid with a 5/4 pixel (picture element) aspect ratio. These images are first uploaded to a VAX-11/750 minicomputer where the discrete simulations are run. Each image is first magnified to fit the simulation grid size (i.e. 1024x1024) using nearest neighbor interpolation. The pixel aspect ratio is also taken into account so that the final discrete cells have a square aspect ratio. The magnification procedure results in some pixelization and
thus a boundary smoothing algorithm (Castleman, 1981) is used to smooth the edges.

To enhance computational efficiency and reduce memory requirements, the bitmaps employed by Sandmann (1986) were no longer used to keep track of the discrete cells. Instead, a line segment encoding technique is utilized in which only the endpoints of each char segment along a given line are tracked. This method is also convenient because the object search algorithm uses a similar line segment encoding scheme in which the object segments are tracked (Castleman, 1979). The pore segments are easily computed from the char segment information. Thus the object search routine can quickly identify pores or char fragments to investigate char fragmentation during gasification.

At each time step, the computational grid is scanned lined by line for pore segments and the pores are identified. Once the pores have been identified, an erosion algorithm is used to erode away a single layer of cells from the exterior of the char particle (or the exterior of all particle fragments). The erosion algorithm examines the 3x3 neighborhood around each cell to determine whether or not it is on an edge boundary and should be eroded away. The algorithm merges the char and pore segments together
temporarily so that only edge cells that are available to the exterior are identified and tagged for erosion. The number of cells eroded away is easily summed during the process so the conversion is immediately known. The process can be repeated until a specified conversion has been achieved. Particle fragmentation can also be easily investigated with this model by calling the object search routine and searching for char segments instead of pore segments.

The presence of ash particles within the char matrix can also be taken into account. The segment encoding is expanded to track both char and ash segments. During the pore search routine, the char and ash segments are merged to enable the calculation of the pore segments. This is also done during the erosion process so that only the char elements are eroded away.

V.C RESULTS AND DISCUSSION

Gasification of the chars analysed in Chapter III were simulated under conditions of strong diffusional limitations to investigate the effect of the macropore structure on observable reaction rates. Our discrete simulations employed 1024x1024 grids. Digitized images of 50 char particle
cross-sections were used as initial simulation grids and predicted gasification rates from these 50 runs were averaged. Figure 54 shows the calculated reaction rate for a single particle and for an average of 50 particles. The sudden jump in the reaction rate for the single particle is attributed to the pore exposure phenomenon.

Care must be exercised in drawing rigid conclusions from the simulations performed here. The simulations were carried out on a two-dimensional grid assuming that over a given number of simulations the results will average out to reflect the actual three-dimensional behavior of the chars. There was a large degree of scatter among the individual particles for each sample but the averaged results show some definite trends.

Figures 55 and 56 show the effect of pyrolysis heating rate on the reaction rates for Illinois #6 and Lignite chars respectively. The curves were normalized with respect to the lowest initial rate among the given set of curves. For the Illinois #6 chars, increased heating rates produce a sharper maximum in the reaction rate curve. However, there is little difference in the reaction rate profiles for the char produced with heating rates above 10°C/s. In contrast, the reaction rate profiles for the lignite chars are not
significantly altered as the pyrolysis heating rate is increased. This reflects the similarity of the macropore structure of the lignite chars as noted in Chapter IV. The maximum in the rate curve for the lignite char pyrolyzed at 1000°C/s probably reflects the increased porosity, and hence increased the chance of the pore exposure phenomenon, of that char sample compared to the other two. Figures 57 through 59 show sample reaction sequences as obtained from the simulations for three different chars.

Figure 60 compares the reaction rates obtained from Illinois #6 chars produced by pyrolyzing particles of varying size but at the same heating rates. Each curve was normalized with respect to its initial rate to emphasize the shapes of the curves in relation to one another. The shape of the curves is similar but the height of the maximum observed in the rate curves is seen to increase as the particle size is increased. Recall from the previous chapter that an increase in particle size was accompanied by an increase in secondary vesicle formation. With an increase of secondary vesicle formation, the char structure becomes more cellular with thin walls. This would logically seem to increase the probability for pore exposure as the reaction sequence proceeds. This would then account for the differences among the rate curves in Figure 60.
The simulation was modified to account for the difference in ash content between the demineralized chars and regular chars mentioned in Chapter IV. The ash content of the chars was known from previous studies (Ballal, 1985) so particles of ash were randomly added to the simulation grid for chars which contained ash. Two sets of simulations were run with a different size ash particle specified for each one. Figures 61 and 62 reflect the results for the Illinois #6 and Texas lignite chars. Figures 63 and 64 show sample reaction sequences for an Illinois #6 char particle with different ash particle sizes. As expected, the rate curves for the ash containing particles are lower as the ash blocks some of the surface area. The size of the ash particles seemed to have little effect on the reaction rate except at the very beginning of the reaction sequence.
Figure 54. Reaction rate curves for a single particle and for an average of 50 particles for Ill #6 char pyrolyzed at 0.1 C/s to 900 C.
Figure 55. Reaction rate curves of 50 averaged simulations for Illinois #6 char pyrolyzed at various heating rates.
Figure 56. Reaction rate curves of 50 averaged simulations for Texas Lignite char pyrolyzed at various heating rates.
Figure 57. Macropore reaction sequence in the diffusion controlled regime for Illinois #6 char pyrolyzed at 0.1 C/s to 900 C.
Figure 58. Macropore reaction sequence in the diffusion controlled regime for Illinois #6 char pyrolyzed at 1000 C/s to 900 C.
Figure 59. Macropore reaction sequence in the diffusion controlled regime for Texas Lignite char pyrolyzed at 1000 C/s to 900 C.
Figure 60. Reaction rate curves for averaged simulations for Illinois #6 char of varying particle diameter.
Figure 61. Effect of ash on gasification rates for Illinois #6 char.
Figure 62. Effect of ash on gasification rates for Texas Lignite char.
<table>
<thead>
<tr>
<th>X</th>
<th>X</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0%</td>
<td>20.3%</td>
</tr>
<tr>
<td>42.0%</td>
<td>61.7%</td>
</tr>
<tr>
<td>80.3%</td>
<td>99.0%</td>
</tr>
</tbody>
</table>

Figure 63. Macropore reaction sequence in the diffusion controlled regime for Illinois #6 char with ash
<table>
<thead>
<tr>
<th>X = 0.0%</th>
<th>X = 20.4%</th>
</tr>
</thead>
<tbody>
<tr>
<td>X = 40.7%</td>
<td>X = 60.8%</td>
</tr>
<tr>
<td>X = 80.9%</td>
<td>X = 99.0%</td>
</tr>
</tbody>
</table>

Figure 64. Macropore reaction sequence in the diffusion controlled regime for Illinois #6 char with ash.
CHAPTER VI

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

VI.A CONCLUSIONS

The results reported in Chapter V show that the macro-pore structure of coal-derived chars strongly affects the observable gasification rates when the reaction proceeds with strong intraparticle diffusional limitations. This reaction regime is typical for the operating conditions encountered in most commercial combustors. The devolatilized chars contain a number of pores that are not initially accessible to the gaseous reactants but become exposed at higher char conversions. Depending upon the pore distribution within the char particle, the available surface area can pass through a maximum as the reaction proceeds. This will cause the observable reaction rate to also pass through a maximum. Chars which had a large number of secondary pores produced a larger maximum in the rate curve than chars with mainly primary cavities.
The presented rate predictions demonstrate that the discrete models are superior to shrinking core models traditionally used to treat gas-solid reacting systems with strong diffusional limitations. Shrinking core models cannot account for the "rough" external surface of char particles nor for the opening of interior cavities due to burn-through. Discrete simulations for single cross-sections bear striking qualitative similarities to experimental data obtained by gasifying single coal particles in a fluidized bed (Sundback and colleagues, 1984). These experimental measurements revealed that combustion rates increased initially in a "stepwise" fashion with periodic jumps and distinct maxima were observed for many particles. This behavior was attributed to particle fragmentation and agrees qualitatively with predictions from our discrete models.

The large differences in predicted gasification rates for the various chars investigated here strongly indicate that a good macropore characterization is necessary for accurate predictions of gasification behavior in the regime of strong intraparticle diffusional limitations. The novel stereological method developed here for macropore size analysis appears to meet these requirements.
By examining polished sections of coal-derived chars, it has been shown that traditional indirect methods of macropore size analysis (like mercury porosimetry) will give an inaccurate picture of the char's macropore structure. Mercury penetration cannot distinguish between the larger pores seen in the polished sections and the intraparticle voids. This results in a pore volume distribution which is significantly weighted toward the smaller pores. The error is particularly evident in the case of plastic coals where their macropore structure contains a large number of larger cavities. The analytical method developed here for macro-pore size analysis overcomes most of the shortcomings of the indirect mercury porosimetry technique. Direct measurements of pore cross-sections revealed in polished sections of char particles are utilized for the new method and this method can accurately characterize the macropore structure of the chars for pore radii greater than 1 μm. The new approach was made possible through the use of a programmable digital image processor with customized software which optimized the data collection and analysis procedures.

The usefulness and applicability of the method was demonstrated by characterizing the macropore structure of several chars. The new method was able to reveal the subtle differences in the char structures such as an increase in
the number of larger pores under certain pyrolysis conditions and the progressive appearance of bimodal pore size distributions resulting from the formation of secondary pores in the walls of larger primary cavities. With the pore size analysis method developed here, the effects of the pyrolysis conditions on the macropore structure of chars were quantified. This constitutes a major contribution in this area since all previous studies by other investigators reported only qualitative results that could not be used for modeling purposes.

The flexibility of the discrete models pioneered by Sandmann and Zygourakis was demonstrated here. Image processing algorithms utilizing object identification and boundary erosion techniques were easily adapted for the discrete simulations and they allowed us to treat the reaction of complex pore structures. Indeed, actual images of char particle cross-sections were used to describe the initial char structure for the simulation. This approach can now be used to validate future pyrolysis models which would describe the temporal evolution of pores during this stage.
VI.B SUGGESTIONS FOR FUTURE WORK

Since the importance of the macropore structure to high temperature gasification has been demonstrated, further work should be conducted in two main areas: (a) high-temperature gasification and (b) pore evolution during the pyrolysis process.

Most gasification studies in the past have been concerned with extracting intrinsic rate data for the gasification reaction. Because of this, studies have been carried out at lower temperatures to ensure that the reaction is not diffusion-limited. Hence, very little experimental data exist for higher temperatures where the reaction is diffusion-limited. Experiments in this area should be conducted to validate the results of the discrete model. Intermediate samples should be collected during the run and their char structure analyzed to validate and further refine the pore evolution model. The pyrolysis reactor used in this study could be used for these experiments if suitable modifications were made to track the extent of reaction.

Since the pore structure of coal-derived chars is determined during the pyrolysis stage, modeling pore evolution during this stage is essential. Pore evolution
has not been one of the primary concerns when modeling the pyrolysis of coals but in light of this study it should be seriously considered. Much work has been done on volatiles transport in nonplastic coals which can be directly applied to modeling the pore evolution process in nonplastic coals. However, very little work has been done on the modeling of plastic coals with its complex morphological transitions and bubble formation. It has been shown that plastic coals exhibit the largest variation of pore structure so it is more important that pore evolution be modeled for plastic coals. The discrete model used for modeling the char gasification process could possibly be applied to modeling the pore evolution for plastic coals.

The pyrolysis reactor should be modified by the addition of a rapid quenching system such as a liquid nitrogen blast directed at the particle support. With such an addition it would be possible to effectively halt the pyrolysis process at intermediate time intervals. Subsequent analysis of the chars would reveal how the pore structure is evolving during the pyrolysis process.

To improve and speed up the stereological pore analysis procedure, two changes are recommended. To improve the analysis procedure an inverted microscope should be used.
This would produce sharper images and allow higher magnifications to be used. Secondly, the image analysis procedure could be sped up by automating the microscope and incorporating its control into the analysis software. The automation should include motorized stage control and focusing. As it is now, the microscope is separated from the computer terminal by several feet and the constant movement from the terminal to the microscope, to locate char cross sections and focus the optics, and back to the terminal leads to rapid operator fatigue and eyestrain.

The discrete model used for the gasification simulations should be extended to three dimensions. The primary obstacle is the extensive computer memory requirements necessary to simulate large grids in three dimensions. However, with the falling prices of computer memory, this should soon no longer be an obstacle. With a three-dimensional simulation model of the gasification process, the simulation grid can be processed to reveal particle fragmentation results. Particle fragmentation poses a serious design problem for fluidized bed reactors and modeling of this behavior would be very important.
REFERENCES


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APPENDIX A

ESTIMATION OF TEMPERATURE GRADIENTS WITHIN COAL PARTICLES WHILE HEATING UPON AN OPEN WIRE MESH

The heated wire mesh pyrolysis reactor described in Chapter II can be operated in a mode such that the reactor is used as a microscope hotstage. The purpose of this is the desire to directly view the pyrolysis process while it occurs. To facilitate the viewing, the coal particles are spread out in a single layer upon an open wire mesh through which an electrical current is passed to provide the heat generation. In such a case the particles are heated only from the bottom with the remaining surfaces in contact with the surrounding gas. In such a configuration, a temperature gradient will exist within the coal particles and it is desirable to quantify the magnitude of the gradient. If the gradients are very large then only gross qualitative correlations can be drawn between what is observed from the pyrolysis process and a normal process where the coal particles are subjected to an isothermal environment.
Figure 65. Geometry of the problem.
A.A GOVERNING EQUATIONS

To simplify the modeling, the coal particle is represented as a cylindrical pellet having a diameter equal to its height. Figure 65 shows the spatial orientation of the problem. The governing heat transfer equation when the wire mesh instantaneously heated and held at a constant temperature is given by

\[
\rho c_p \frac{\partial T}{\partial t} = k \left[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right]
\] (A1)

for \( t=0 \)  \[ T = T_\infty \] for all \( z \) and \( r \)

for \( t>0 \)  \[ T = T_f \] \( z = 0 \)

\[ -k \frac{\partial T}{\partial z} \bigg|_H = h(T-T_\infty) \] \( z = H \)

\[ \frac{\partial T}{\partial r} \bigg|_0 = 0 \] \( r = 0 \)

\[ -k \frac{\partial T}{\partial r} \bigg|_R = h(T-T_\infty) \] \( r = R \)

The above equations can be put in dimensionless form by
defining the following dimensionless quantities

\[ \Theta = \frac{T-T_\infty}{T_f-T_\infty} \quad \tau = \frac{ta}{R^2}, \quad a = \frac{k}{\rho c_p} \]

\[ u = \frac{r}{R} \quad \text{for all } u \text{ and } v \]

\[ v = \frac{z}{H} = \frac{z}{2R} \]

\[ \lambda = \frac{k}{hR} \]

so the governing equation becomes

\[ \frac{\partial \Theta}{\partial \tau} = \frac{1}{\rho u} \left( r \frac{\partial \Theta}{\partial u} \right) + \frac{1}{4} \frac{\partial^2 \Theta}{\partial v^2} \quad (A2) \]

for \( r=0 \) \quad \Theta = 0

for \( r>0 \) \quad \Theta = 1

\[ v = 0 \]

\[ \left. -\frac{1}{2} \frac{\lambda \partial \Theta}{\partial v} \right|_1 = \Theta \]

\[ \left. \frac{\partial \Theta}{\partial u} \right|_0 = 0 \]

\[ \left. -\lambda \frac{\partial \Theta}{\partial u} \right|_1 = \Theta \]

\[ \left. u = 0 \right|_1 \]
First we investigate the simplest of cases, that of steady-state. Here the temperature gradients should be minimized compared to a time dependent temperature ramp of the heat source. The equation to be solved is

\[
\frac{1}{u \partial u} \left( \frac{\partial \Theta}{\partial u} \right) + \frac{1}{4} \frac{\partial^2 \Theta}{\partial v^2} = 0
\]  
(A3)

\[\Theta = 1\]

\[v = 0\]

\[-\frac{1}{2 \lambda} \frac{\partial \Theta}{\partial v} \bigg|_1 = \Theta\]

\[v = 1\]

\[\frac{\partial \Theta}{\partial u} \bigg|_0 = 0\]

\[u = 0\]

\[-\lambda \frac{\partial \Theta}{\partial u} \bigg|_1 = \Theta\]

\[u = 1\]

Equation (A3) is solved using collocation on finite elements with bicubic hermite polynomials being the trial functions. The temperature profile was estimated at 500°C and 900°C.
A.B PARAMETER ESTIMATION

In Equation (A3) the parameter \( \lambda \) must first be calculated and then to calculate the actual temperature, \( T_\infty \) must be known. \( T_\infty \) was taken to be the steady state temperature of the nitrogen atmosphere within the reactor. This was experimentally determined by measuring the temperature at the outlet port. For a wire mesh temperature of 500°C, \( T_\infty \) was measured to be 75°C and for a mesh temperature of 900°C, \( T_\infty \) was measured to be 180°C. The \( \text{N}_2 \) properties were taken at these temperatures were taken from Welty, et. al (1976). The thermal conductivity, \( k \), for coal char could not be found in the literature so it was taken to be the same as for granular coke. This should not be a bad approximation since coke is a pyrolyzed carbon often produced from coal by pyrolysis at low heating rates. The value for \( k \) was taken to be 3 BTU/hr*ft*°F or 5 W/m*°C (Bennett and Myers, 1974). Since 50-60 mesh (250-300 \( \mu \text{m} \)) particles were the main size used in the reactor, the particle radius, \( R \), was taken as 125 \( \mu \text{m} \).

The convective heat transfer coefficient, \( h \), was estimated from Nussalt number correlations. For cylinders in a crossflow at low Re the correlation used is (Welty, et. al., 1976)
\[
\text{Nu} = \frac{hD}{k} = 0.43 + 0.48 \cdot \text{Re}^{1/2}
\]

For a wire mesh temperature of 900°C, \( \lambda \) is estimated by

\[D = 2R = 125 \ \mu \text{m}\]

\(\text{N}_2\) flow rate = 150 ml/min

flow channel cross sectional area = 2.77 cm²

so, \( V = 9 \times 10^{-3} \) m/s

\(\text{N}_2\) properties,

\[v = 3.2 \times 10^{-5} \ \text{m}^2/\text{s}\]

\[k = 3.6 \times 10^{-2} \ \text{W/°C.m}^2\]

\[\text{Re} = \frac{V \cdot D}{v} = 3.5 \times 10^{-2}\]

\[\text{Nu} = 0.52\]

therefore \( \lambda = 1.5 \times 10^2\)
Figures 66 and 67 show the calculated steady-state particle temperature profiles at 500 and 900°C respectively. Even with a 100% error in $\lambda$, the maximum temperature gradient was still $>100$°C at 500°C and $>200$°C at 900°C. Thus the large temperature gradients within the particles when the reactor is operated as a microscope hotstage prevent any quantitative conclusions to be drawn from viewing the pyrolysis process.
Figure 66. Single particle steady-state temperature profile with wire mesh at 900 C.
Figure 67. Single particle steady-state temperature profile with wire mesh at 500 C.