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Fundamental mechanisms of coal pyrolysis and char combustion

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Rice University, 1992
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FUNDAMENTAL MECHANISMS OF COAL PYROLYSIS AND CHAR COMBUSTION

by

ANDREAS N. MATZAKOS

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

DOCTOR OF PHILOSOPHY

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ABSTRACT

Coal pyrolysis and combustion have been systematically investigated at high temperatures where external and intraparticle transfer limitations become important. A thermogravimetric reactor equipped with in-situ video imaging capabilities provided the reaction rate measurements while its video microscopy system simultaneously allowed observation of the pyrolyzing or combusting coal particles.

Video microscopy permitted direct observation of several transient phenomena occurring during combustion (particle ignition, macropore opening, particle fragmentation) or pyrolysis (particle swelling and bubbling) and these phenomena have been correlated with the combustion or devolatilization rate measurements. Particle ignition causes a sharp increase in the char combustion rates. The probability of particle ignition increases with increasing particle size, increasing porosity, increasing oxygen concentration and decreasing gas flow rate. Macropore opening also enhances char reactivity. During pyrolysis, the most vigorous bubbling of the particles occurred when the devolatilization rate was at its maximum.

Pyrolysis conditions also affect char ignition behavior. Increasing pyrolysis heating rates result in chars with more open macropore structure and higher reactivity in the diffusion-limited regime. However, heating rates do not affect reactivity in the kinetic control regime. Chars pyrolyzed in 5% oxygen are more swollen and more porous than chars produced in pure nitrogen and are also more reactive in the diffusion-limited regime.
Finally, increasing soak times and heat treatment temperatures deteriorate char reactivity in all regimes.

A cellular automaton algorithm was developed to simulate combustion of chars with complex macropore structures in the diffusion-limited regime. This model accounts for diffusional limitations by assuming a finite penetration length of gas inside the porous solid and by treating the closed pores as inaccessible to the reactants. Computational grids were generated to model the structure of chars prepared at three different heating rates. Simulation results suggest that char reactivity depends strongly on macroporosity and macropore specific surface area. In agreement with our experimental reactivity measurements, the simulations show significant reactivity differences of the studied chars, even under isothermal conditions. The simulations do not detect significant particle fragmentation at conversions as high as 81%. Small fragments were produced though, at all conversions and their number reached a maximum at about 95% conversion.
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and Prometheus, ..., stole the mechanical arts of Hephaestus and Athene, and fire with them, and gave them to man. Thus man had the wisdom necessary to the support of life, but political wisdom he had not;

Plato: Protagoras

“... ὁ Προμηθέας ... κλέπτει Ἡφαίστου καὶ Ἀθηνᾶς τὴν ἐντεχνὸν σοφίαν σὺν πυρὶ ... καὶ οὕτω δὴ δωρεῖται ἄνθρωπῳ. Τὴν μὲν όδον περὶ τὸν βίον σοφίαν ἄνθρωπος ταύτῃ ἔσχεν, τὴν δὲ πολιτικὴν οὐκ ἔχειν ... ”

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CHAPTER 1

INTRODUCTION

1.1. General

Coal is one of the most abundant energy sources on earth. Its mining started some 2000 years ago, and at the beginning of the 20th century coal provided the 95% of the world's energy needs. Today, coal accounts for 31% of the world's energy production compared to 43% for oil and 22% for natural gas (Industrial Coal Handbook, 1985). Although oil has become the major energy source, it has proven reserves for only 29 years according to 1980 standards. Even with the ultimately recoverable resources, oil reserves are only expected to be two or three times larger (World Energy Outlook, 1982).

Proven coal reserves, on the other hand, are sufficiently large to meet the energy demand for at least the next 250 years. The more even geographic distribution of coal reserves on earth is another major advantage. Every large geographic region has sufficient coal reserves for many years.

Although coal is used extensively in industrial applications for energy generation and chemical synthesis, it has some drawbacks:

i) Coal is a solid and that complicates its utilization. Storage, transportation and conversion are harder for a solid than for a fluid. Therefore, it is more convenient to gasify or liquefy coal and use its derivatives as fuels or feedstock for organic reactions.
ii) The high sulfur content of coal is responsible for the formation of sulfur dioxide during combustion. This is an atmospheric pollutant responsible for the acid rain.  

iii) Like all other fossil fuels (e.g. oil), coal combustion produces carbon dioxide. These emissions may be responsible for the global warming attributed to the greenhouse effect.

These problems must be overcome before coal can become a major and environmentally acceptable energy source. The most promising coal utilization processes listed below attempt to solve the first two problems by converting high-sulfur coal into gaseous products, low-sulfur liquids and low-sulfur solid fuels.

(A) **Direct coal utilization:** Fine particles of coal are fed to reactors operating at high temperatures, pressures and oxygen concentrations (Shell coal gasification process) (McCullough, Roberts et al. 1982; Volkel, Eckstein et al. 1980). Direct coal utilization achieves high heat generation rates and yields mostly gaseous products (carbon monoxide, hydrogen, methane etc.) that are later used as feedstock for organic synthesis pathways.

(B) **Mild coal gasification:** Coal is processed at mild conditions (temperatures below 750 °C and pressures below 50 psig) to produce a collection of valuable co-products: liquid fuels, solid fuel (char), gaseous products and electricity (Khan and Kovach 1989).

We can distinguish two major stages in both of these coal utilization processes.

1) **Pyrolysis** occurs when coal is first heated to temperatures higher than 350 °C. Both the chemical and the pore structure of coal change significantly during this stage, as the volatile constituents of coal are released in the form of gases and tars.
Pyrolysis also yields solid products (chars) that have higher carbon to hydrogen ratio and higher porosity than the parent coals.

2) **Gasification** usually refers to the reaction of the solid products of pyrolysis (chars) with oxygen, carbon dioxide or steam. **Combustion** is the term we use for the gasification of coal chars with oxygen. The heterogeneous gasification reactions are carried out in a wide range of temperatures (300-2500 °C) and consume the carbon in the char matrix leaving behind the ash that consists of all the inorganic impurities present in the parent coal.

Under the severe conditions of direct coal utilization, the pyrolysis stage lasts for very short periods of time and it is immediately followed (or even accompanied) by the gasification reactions. The final products of such processes are gases and ash.

Mild gasification, on the other hand, yields large amounts of gas and liquid products. The low severity conditions of mild gasification favor the pyrolysis reactions and result in low conversions for the gasification reactions. Chars produced via mild gasification processes must be reacted in a separate stage to recover its energy content.

Carbon dioxide production is a disadvantage shared by all fossil fuels (coal, oil and natural gas). Until alternative energy sources are developed, we can only attempt to lower the production rates of carbon dioxide by designing and operating more efficient fuel combustion processes.

### 1.2. Scope and significance

The main objective of our studies is to **improve the efficiency of coal gasification (or combustion) processes**. In order to achieve this goal, however, we must first elucidate the fundamental mechanisms of pyrolysis and combustion.
The fundamental combustion mechanisms will determine the coal particle burning
times in industrial reactors. By knowing the particle burning times, we can determine the
optimal reactor configuration for a given coal feed rate and energy output.

Since pyrolysis conditions affect char reactivity, it is reasonable to inquire about the
optimal heat treatment of coal that will give the maximum reactivity. Highly reactive
chars will allow the use of smaller reactors operating at lower combustion temperatures.
We can thus lower the operating cost of coal combustors.

It is also important to know the relation between the pyrolysis and gasification
processes, since coal is devolatilized and gasified simultaneously in the same reactor. The
reactor temperature and configuration will determine the rates of devolatilization and
combustion.

Another phenomenon that can be both useful and undesirable is particle
fragmentation. Although fragmentation decreases particle burning times, it also
produces fine ash and coal fragments that may escape in the exhaust system as fly-ash, a
condition that is environmentally unacceptable. Previous investigators found that
fragmentation is more prevalent at higher combustion temperatures where smaller fly-ash
particles form (Ericson, Ludlow et al. 1990).

The reactor temperature has also important environmental implications. For instance,
larger amounts of nitrogen oxides (NOₓ) are produced when fuels burn at high
temperatures. If we could operate a reactor at lower temperatures, this might lead to
significant decreases of NOₓ emissions. Sulfur emission into the atmosphere in form of
dioxide or trioxide is also a harmful effect that needs to be suppressed. An experimental
study with synthetic coal found that high combustion temperatures cause a decrease in the
formation of sodium sulfates in favor of sodium silicates. Thus, more sulfur is swept
through the reactor without reacting (Ericson, Ludlow et al. 1990). Hydrocarbon emission
is responsible for the thermochemical effect that produces smog. It is obviously better not
to let the volatiles and tar produced from coal pyrolysis be released in the atmosphere. A process that guarantees the reaction of volatiles in the gas phase can eliminate such a danger.

The direct coal utilization process ensures high reaction rates, and the use of fine particles minimizes any undesirable diffusional limitations. However, the use of high combustion temperatures and pressures involves several drawbacks:

i) High capital investment.

ii) High heat losses to the surroundings.

iii) High operational costs to start and shut down the combustor.

iv) High energy requirements for grinding the coal particles to very small sizes.

v) Safety problems involving the danger of leaks under high pressures and reactor runaway. The need of an accurate and sophisticated process control system is apparent.

vi) Higher pollutant emissions in the form of fly-ash, nitrogen oxides and sulfur dioxide.

These pollutants are preferentially formed at higher temperatures as stated earlier.

In contrast, capital investment and operating costs of mild gasification processes are considerably lower. The environmental impact is also less pronounced. Mild gasification can produce sulfur-free liquids and low-sulfur solid fuels with high intrinsic reactivity as expected from the use of lower heat treatment temperature. The chars also may have higher particle size since at the low combustion temperatures diffusional limitations are less significant. Finally, fewer and larger fly-ash particles are formed at lower temperatures, thus alleviating the problem of downstream fine particle collection.

However, in the mild gasification conditions the reaction rates are low and the residence times need to be longer (up to several minutes). This implies that one must have larger reactors and should carefully choose the appropriate heat treatment conditions that will produce the most reactive chars.
1.3. Pyrolysis

Complex morphological transformations accompany the chemical reactions occurring during the pyrolysis of coals. Loosely bound H₂O and CO₂ are evolved when coal is heated at temperatures below 350 °C. Above 350 °C, primary (rapid) devolatilization occurs to produce low molecular weight gases, liquids, and semisolid tars due to the thermal rupture of chemical bonds. If the heating rate is constant, then the devolatilization rate passes through a maximum. This maximum is shifted toward higher temperatures when the heating rate increases. The primary devolatilization is essentially complete at 550 °C. Secondary devolatilization occurs in the range 600-800 °C producing mainly H₂ and CH₄ (Gorbaty, Larsen et al. 1982).

Some coal particles soften when heated in an inert atmosphere to 350-450 °C. This is attributed to thermoplasticity; coals with this property are called plastic. Brown and Waters (1966) suggested that low molecular weight, hydrogen-rich compounds (called bitumens) serve as the initiators of plastic behavior. These materials, which may begin to melt at 200°C, solvate the coal micelles as they become thermally loosened. Most important, however, they serve as mobile hydrogen donors that stabilize the free radicals that are produced thermally before general coal plasticity begins (Neavel, 1976). As the temperature increases, general mobility of the micelles begins, pyrolytic bond rupture becomes significant, additional low molecular weight bitumen forms, and free radicals can contact donor hydrogen in thermobitumen molecules.

Thermal decomposition yields volatile material that forms bubbles in the particle interior before escaping to the surrounding gas phase. The viscous plastic mass tends to retain the gases which cause pressure build-up and swelling in the particle. Interestingly, the expansion alternates with contraction during the plasticity stage (Matsunaga, Nishiyama
et al. 1978). Expansion is believed to occur through the formation of a bubble film containing evolving gas and the contraction through the rupture of the film. The plasticity region, however, occurs in a specific temperature range (between 400-600 °C for Illinois #6). Beyond a threshold the formation of free radicals exceeds the capacity of the coal to cap them by hydrogen-donor reactions; the free radicals combine or attack available large molecules, increasing the cross-linking and leading to the resolidification of the coal.

Non-plastic coals neither soften and nor undergo drastic structural changes during pyrolysis. Bituminous and subbituminous coals are generally considered to be plastic, while low rank coals (like lignites) and very high rank coals (like anthracites) belong to the non-plastic category.

Coal preoxidation has been found to deteriorate its plasticity. This can be explained by the depletion of the hydrogen-donor compounds that would otherwise stabilize the free radicals formed during pyrolysis. Another explanation involves the initiation of cross-linking reactions (Gorbaty, Larsen et al. 1982). The same influence of oxygen in plasticity should be expected if the pyrolysis is carried out in an oxygen containing atmosphere.

The structural transformations occurring during the plasticity stage are responsible for the pore structure of the resulting chars. Structural studies on char particles have revealed the existence of large internal vesicles interconnected via smaller neck pores and open to the exterior. The size of the vesicles and their connectivity depends strongly on the pyrolysis heating rate. When the heating rate is slow (0.1 °C/s) the rate of volatile release is slow enough to give sufficient time for the gases to diffuse through the pores and escape without any internal pressure build-up. However, as the heating rate increases the gas generation rate is faster than the rate of gas diffusion through the pores. Pressure build-up occurs due to gas accumulation which results in particle expansion. Therefore, particles pyrolyzed at high heating rates develop higher porosities and macropore sizes than ones pyrolyzed at
lower rates. This conclusion has been deduced by direct measurements of digitized particle cross-sections (Zygourakis 1988; Zygourakis and Glass 1988).

Macroscopic measurements have revealed that the charred particles increase in diameter by a factor of 1.1 to 3 (Matsunaga, Nishiyama et al. 1978). In addition, the particle shape changes dramatically during the pyrolysis stage. Finally, for non-plastic coals primary particle fragmentation has been observed (Stubington and Linjewile 1989). Fragmentation is defined as the breaking up of a single particle into two or more pieces of roughly similar size. It should not be confused with the process of attrition, which produces a large number of very fine particles but leaves the original particle almost at its original size. Two types of fragmentation may be defined: (a) \textit{primary fragmentation}, occurring during devolatilization. It can be attributed to the inability of non-plastic coals to deform and relieve internal thermal and mechanical stresses created by the fast release of volatiles. (b) \textit{secondary fragmentation}, occurring during combustion of the char by burn-out of carbon bridges connecting parts of the particle. Primary fragmentation decreases the devolatilization times since heat and mass transfer resistances between the particle and the ambient gas are suppressed (Dakic, Van der Honing et al. 1989; Stubington and Linjewile 1989).

Further study of the macropore structure of those particles with the method of cross-sectioning has revealed an interesting internal cellular macropore structure. There is a significant dependence of the particle porosity, macropore specific surface area and macropore size on the pyrolysis heating rates. Specifically, low heating rates produce chars with few scattered cavities having thick walls and almost the same particle size and shape as the parent coal. However, higher heating rates lead to chars with larger cenospheres having thinner walls and significantly higher porosity (Gay, Littlejohn et al. 1983; Glass 1987; Hamilton 1980; Zygourakis and Sandmann 1988). Moreover, the macropore specific surface area and the final particle size are increasing functions of the heating rate.
(Zygourakis 1989b). This gives evidence that the chars treated with higher heating rates have a larger and more open macropore network more accessible to the diffusion of gaseous reactants during the gasification stage.

Furthermore, high heating rates increase the total volatile and tar yields as confirmed experimentally (Gibbins-Matham and Kandiyoti 1988; Gibbins-Matham and Kandiyoti 1989; Matzakos and Zygourakis 1990) and predicted theoretically (Fletcher, Kerstein et al. 1989). The liquid product distribution and average molecular weight are also affected in a complex way by the pyrolysis heating rate (Khan, Serio et al. 1989). Low pressures also enhance the total product yield (Gibbins-Matham and Kandiyoti 1988).

Other pyrolysis conditions like heat treatment temperature and soak time have more influence on the chemical and micropore structure of chars. Specifically, previous investigators have observed that higher heat treatment temperatures and longer soaking times lead to chars with low micropore specific surface areas and reactivities (Serio, Solomon et al. 1989). The lower reactivity of those chars during combustion in the kinetic control regime confirms this argument (Matzakos and Zygourakis 1990). The possible explanation is that extended exposure of the chars at higher temperatures leads to an increase in their molecular order due to the enhanced annealing of their organic and mineral components and their microporosity. In other words, there is destruction of active sites via the process of sintering.

Therefore, the understanding of the chemical and structural transformations of coal during pyrolysis is very important. First, we need to know the type (gas-liquid-solid) and distribution of the pyrolysis products in order to determine their value as fuels or chemical feedstock. Moreover, we need to know the pore structure and reactivity of produced chars because this will affect the combustor efficiency.
1.4. Combustion

Combustion (gasification with oxygen) involves a complex process of heat and mass transfer inside the char particle and through its boundary layer. This process is coupled with heterogeneous reactions occurring on the solid surface and usually with an homogeneous oxidation of carbon monoxide to carbon dioxide in the gas phase.

\[ 2C(s) + O_2 \rightarrow 2\ CO \quad \text{exothermic} \quad (R1) \]
\[ C(s) + CO_2 \rightarrow 2\ CO \quad \text{endothermic} \quad (R2) \]
\[ 2CO + O_2 \rightarrow 2\ CO_2 \quad \text{exothermic} \quad (R3) \]

The gaseous reactants must diffuse through the boundary layer surrounding the particle and within its pore structure until they access some available reactive sites. The reaction of the gas with the solid matrix will produce gases that must diffuse back through the pore network and the boundary layer to reach the ambient gas phase. As carbon molecules are gasified, new pores open up, older pores grow and generally new surface area becomes available to the reactants. Thus, the reaction rate increases with conversion. As pores continue to grow, neighboring pores start to coalesce and the surface area decreases. This is a reason we observe a maximum in the total reaction rate vs. conversion curves in the range of 20-40% conversion.

Therefore, the heterogeneous reaction has a complex transient behavior. Reaction rates do not remain constant during coal conversion. The intraparticle diffusional
resistances may also change dramatically during the reaction because the pore structure changes.

The rate of reaction $r$ can be written as:

$$ r = \frac{dx}{dt} = \eta(T,x) \ A(x) \ S(x) \ f(T,c_i) \quad (1.1) $$

where:

- $x$ is the conversion
- $S(x)$ is the internal pore surface area available for reaction
- $A(x)$ is the concentration of active sites per unit surface area
- $f(T,c_i)$ represents the intrinsic reaction kinetics
- $\eta(T,x)$ is the effectiveness factor for diffusional limitations

Determining the initial pore structure and predicting its temporal evolution during gasification is a very hard task. This is due to our limited ability to fully characterize the pore structure of coal. There are several techniques for the determination of the pore structure of coal (Gorbaty, Larsen et al. 1982).

(a) Gas adsorption techniques are the most popular for measuring the porosity and the specific surface area of coal. This is done by means of measuring the amount of gases adsorbed by the samples as a function of temperature and adsorbate pressure. Typical gases used are $N_2$, $CH_4$, $CO$, $CO_2$, $H_2O$, $O_2$, $Xe$ etc. The BET or Dubinin-Polanyi equations are used to calculate the specific surface area. The methods are good only for small size pores, in the size range of the gas molecules. Very often, however, the
measurements give conflicting values of the specific surface areas according to which adsorbate is used.

(b) Heats of wetting techniques measure the specific surface area of coal by the heat released during the wetting of coal with liquids. The chemical interaction of the sample with the solvent casts strong doubts on the reliability of the method.

(c) Mercury porosimetry techniques are used to determine the porosity and the pore size distribution of coal. They measure the volume of mercury penetrating the pores as a function of pressure (up to about 1100 atm). However, they have serious drawbacks due to the fact that they are measuring mostly the size of openings or constrictions between pores rather than the actual pore sizes themselves.

(d) Small angle X-ray scattering is a promising technique having the advantage of avoiding chemical interaction with the sample. It is still under development and it has not yet been proven to give results that are reliable and consistent with those obtained by other methods.

(e) Digital image processing techniques can be used for determining the coal macropore structure. Digitized images of particle cross-sections under the microscope can be obtained and later processed to give measurements of macroporosity, macropore size distribution and macropore surface area (Zygourakis and Glass 1988).

The surface area evolution during gasification $S(x)$ has been obtained by gas adsorption techniques (Adams, Glasson et al. 1989; Dudek, Longwell et al. 1989). A reliable estimate can also be obtained by the reaction rate versus conversion patterns in the kinetic control regime (if we assume $A(x)$ is constant) (Ballal and Zygourakis 1987a; Sandmann and Zygourakis 1986). This method can only provide normalized values of the surface area with respect to the initial surface area. Previous investigators found that there is different concentration of active sites for each coal (e.g. $A(x)$ is different for each coal).
For example, two coals that have the same total surface area (as measured by gas adsorption) may have widely different gasification rates (Radovic, Steczko et al. 1983). Some other investigators showed a correlation of coal reactivity with its surface area (Ehrburger, Louys et al. 1989) and porosity (De Koranyi 1989) for the same coal during conversion. In other words they claim that $A(x)$ is a constant for a given coal.

Modeling of the surface area evolution has been attempted by several investigators. The techniques range are usually analytical probabilistic models (Ballal and Zygourakis 1987b; Bhatia 1987; Bhatia and Perlmutter 1980; Bhatia and Perlmutter 1981; Gavalas 1980; Zygourakis, Arri et al. 1982) and discrete models (Sandmann and Zygourakis 1987; Zygourakis 1989a; Zygourakis and Sandmann 1988). Their main feature of the former ones is the modeling of the pore structure as a network of overlapping geometric void entities placed inside the solid in three different orientations. In discrete models, the simulation grids are obtained in the two dimensions by the superposition of circles (simulating spheres or cylinders of unimodal or bimodal distributions) or more realistically by digitized images of particle cross sections. The agreement of the model predictions with experimental results is quite satisfactory, although it has a drawback. The models predict the evolution of the total surface area during conversion and not the actual reactive surface area that is responsible for the reaction. Their assumption is that $A(x)$ does not change with conversion. Although this is true in many cases (De Koranyi 1989; Ehrburger, Louys et al. 1989), nevertheless the need for experimental and theoretical estimate of the reactive surface area is important for determining intrinsic reaction rates. Experimental measurements of the RSA have confirmed its strong correlation with the reactivity (Lizzio, Jiang et al. 1990). In this work, the reactive surface area (RSA) is defined as the concentration of carbon atoms on which the carbon-oxygen C(O) surface intermediate forms and decomposes to give gaseous products. A temperature-programmed desorption
technique and a transient kinetics technique were developed to determine the values of RSA.

Combustion of coal in fluidized bed reactors has revealed another interesting phenomenon. This is the fragmentation of the reacting particles (Chirone, Salatino et al. 1989; Sundback, Beer et al. 1984). This is the secondary fragmentation compared to the primary fragmentation observed in the devolatilization stage. The reaction of the solid matrix causes the destruction of the bridges connecting its pieces together. Fragments are released when there are no bonds connecting them with the rest of the particle. Attrition also causes abrasion of fines that are not strongly bonded to the particle. The ash content determines strongly the degree of fragmentation of a coal particle. If the particle does not feel the considerable stresses of a fluidized bed, but it is stably located on a plane, then after complete combustion the ash skeleton may remain intact. Even for a fluidized bed combustion, high ash coals (47.3%) did not exhibit any fragmentation or shrinkage (Durao and Ferrao 1990). At the other end, low ash coals are expected to exhibit strong fragmentation due to the low connectedness of the ash molecules in the solid matrix. Fragmentation enhances significantly the gasification rates (Sundback, Beer et al. 1984). This is explained by the fact that more surface area is exposed to the reactants and concentration or temperature gradients if previously present are relieved.

Gasification at elevated temperatures gives rise to significant external and intraparticle diffusional resistances. Concentration gradients are created and reaction does not occur uniformly throughout the particle. Intraparticle diffusion depends strongly on the pore structure of the char. Since the micropores account for most of the surface area, their accessibility to reactants is essential for the determination of the reaction rate. The macropores operate as the main arteries of gas transport and account for most of the porosity of the particle. Under diffusional limitations, we expect low utilization of the surface area associated with the micropores and the transitional pores. Reaction in these
small pores should occur only in a small region in the vicinity of the intersection with a larger macropore. As the surface of the macropores recedes due to chemical reaction, new micropore and transitional pore area is exposed. Thus, it becomes reasonable to assume (Gavalas 1980) that the smaller pores make a constant contribution to the reaction rate when the rate is expressed per unit area of the macropores.

The diffusional resistances are very hard to estimate and model. This is caused by the limited ability to characterize fully the pore structure of coal, as mentioned earlier. A few attempts to model the coupled reaction-diffusion problem in coal are based on assumptions about the diffusion process. Sotirchos & Amundson neglect the diffusion in the micropores and account only the diffusion in the macropores (Sotirchos and Amundson 1984a; Sotirchos and Amundson 1984b; Sotirchos, Srinivas et al. 1984). They lump the macropore diffusional resistance in to a parameter representing the average macropore size. However, there was no way to model the transient behavior of this parameter according to the time evolving properties of the porous solid. Later work from Sotirchos and Burganos (1986) tackled the problem by incorporating a pore structure evolution model in their analysis (Sotirchos and Burganos 1986). This way they correlated the structural properties of the solid as a function of local conversion. The dependence of the diffusional resistance on the local and temporal value of the pore size was assessed. The results obtained show that the intraparticle diffusion and its dependence on conversion are among the most important parameters of coal combustion.

When the reaction rate is very fast (at high temperatures), heat conduction and convection are not adequately fast to dissipate the excessive amounts of heat released during the exothermic reaction of coal. Heat conduction inside the particle depends on the effective conductivity. This is found as a weighted average of the solid and gas conductivities. The weighting factors depend on the square of the volume fraction of each phase in the particle. This means that at the higher levels of conversion, when most of the
solid has been consumed, the effective conductivity will be very low. Therefore intraparticle temperature gradients will be more pronounced. External heat and mass transfer resistances are determined by the external heat and mass transfer coefficients. Their nature is fluid mechanical and they depend on the flow rate and pattern around the particle. It is expected that these coefficients will increase with increasing flow rate around the particle, provided that the other conditions remain constant.

Finally, an interesting and most important phenomenon observed during coal combustion is particle ignition. This transient phenomenon occurs in coal particles during high rates of heat production. When the rates of heat conduction and convection are not fast enough to dissipate the heat released, the particle moves to an "ignited state" where its temperature is much higher than the ambient. This phenomenon is characterized by a luminous flame engulfing the particle, a sharp increase of the reaction rate, a rapid change in product concentration and large amounts of heat released. Several experimental observations of coal ignition have been made. They refer to both coal and char particles. In the case of coal particles, the stages of pyrolysis and gasification were performed simultaneously. Investigators have classified the ignition of coal in two categories. When the rate of particle heating is greater than the rate of volatile release, then ignition takes place on the particle surface. This mechanism is called heterogeneous ignition. When the release of volatiles is faster than the rate of heating of the particle surface then the volatiles evolve first and they ignite on the gaseous phase around the particle. This mechanism is called homogeneous ignition (Essenhigh, Misra et al. 1989; Gomez and Vastola 1985). It is obvious that precharred particles ignite through the heterogeneous mechanism, since all (or at least most) volatiles have already been removed.

The ignition phenomenon has been modeled in several ways. Thermal explosion theory (TET) has been used to tackle the problem (Essenhigh, Misra et al. 1989). However, the most specific and detailed model of coal ignition was made by Sotirchos and
Amundson (Sotirchos and Amundson 1984a; Sotirchos and Amundson 1984b; Sotirchos, Srinivas et al. 1984) who developed a comprehensive model to simulate the reaction, mass and heat transfer in the particle and in the surrounding boundary layer. Although their model makes the questionable assumption that diffusional resistances appear only in the macropores, it allows a qualitative parametric analysis of the diffusional resistances through a lumped parameter attributed to the average macropore size.

The model by Sotirchos and Amundson predicts that there is a region of ambient temperatures where the pseudo-steady state initial solution of the system has three steady states. One is stable with oxygen penetrating and reacting with the entire particle; the temperature is only slightly higher than ambient. The second is non-stable with oxygen reacting on the particle surface with little penetration; the temperature is moderately higher than ambient. The third is a stable solution in which CO₂ reacts with the particle to produce CO that burns in a sheath surrounding the particle. The temperature in the third solution is considerably higher than the ambient (around 500 °C higher). There is a threshold of ambient temperatures above which only the third solution is possible. This is called the ignition temperature. Above this temperature only the ignited state is possible.

The model predicts that the ignition temperature is lower for larger particles something also confirmed experimentally (Chen, Fan et al. 1984). Parametric analysis of the dependence of the ignition temperature on the diffusional resistance of the particles gave a very interesting result. Ignition temperatures decrease with decreasing diffusional resistances. This may mean that the more open the macropore network, the more possible it is for the char to ignite. Furthermore, it is expected that after ignition the reaction rate reaches a level which is the same for all diffusional resistances (probably because of low penetration of the solid or external transport control). Another experimental observation is that ignition is initiated in localized reactive spots on the particle surface and then propagates all over the entire surface (Levendis, Sahu et al. 1989). These spots may be
attributed to localized macro- and transitional pores that serve as feeders to the micropores and enhance reactivity. Furthermore, high oxygen pressures seem to accelerate ignition propagation and decrease the ignition temperature (Tognotti, Malotti et al. 1985). Solomon et al. (1990) have observed a primary and a more intense secondary ignition of particles injected into a hot gas stream. The second ignition showed a spiral or oscillatory path (Solomon, Chien et al. 1990). Finally, the ignition of coal particles can be induced by external excitation (spark) and may lead to a flame propagation phenomenon from one particle to the other (Gieras, Klemens et al. 1988).

1.5. Objectives-Techniques-Achievements

It is apparent that coal combustion is a very complicated process. Our goal is to understand the reaction mechanism. This will enable us to quantify the temporal reaction rate behavior and to calculate the burning time for given particles. The knowledge of the burning time is essential for sizing the particles and establishing the operating conditions of the combustor. The problem is mainly one of economics. It has to do with the efficient burning of coal under the minimum cost conditions.

Experimental findings have provided strong evidence that pyrolysis conditions significantly affect the development of pore structure in the char particles. Moreover, pore structure determines char reactivity. Therefore, it is justifiable that pyrolysis conditions will also affect char reactivity. The micropore structure affects the reactivity in the kinetic control regime. Therefore, by measuring the reactivity of various chars in the kinetic control regime it is possible to determine the effects of the pyrolysis conditions on the micropore structure. The macropore structure influences the reactivity of chars in the diffusion limited regime because the utilization of micropores is lower in this regime. Therefore, by measuring char reactivity in the diffusion limited regime, it is possible to
determine the effects of the pyrolysis conditions on the macropore structure. This way, we may be able to find the correlation between the heat treatment of coal during pyrolysis and its reactivity during combustion. If we find a relation between heat treatment and reactivity then we will be able to control the combustion behavior of coal by using the appropriate heat treatment.

This work will attempt to answer the following important issues:

i) Do particle swelling and bubbling have a direct correlation with the macropore structure of coal?

ii) How do pyrolysis conditions (like heating rate, heat treatment temperature, soak time and presence of oxygen) affect the pore structure and reactivity of chars?

iii) How does the particle size influence the pyrolytic and reactive properties of coal?

iv) What are the boundaries between the kinetic control and the diffusion limited regimes? For this reason activation energies, preexponential rate factors and effectiveness factors for the apparent reaction rates were obtained.

v) What is the importance of phenomena like particle ignition, particle fragmentation, macropore opening and macropore coalescence on the gasification rates?

vi) What is the mechanism of ignition and flame propagation?

vii) How can the macropore structure can affect reactivity in the diffusion limited regime (modeling work)?

The experimental techniques used to achieve these objectives are:

a) **Thermogravimetry**, for obtaining the devolatilization and gasification rates through the loss of the weight.

b) **In situ video microscopy**, for obtaining qualitative observation on the macroscopic structural transformations of the sample during the actual experiment. Phenomena like
swelling, ignition and fragmentation are easily detectable with this technique and directly correlated with the simultaneous measurements of reaction rates.

c) **Digital image processing** of char cross-sections for obtaining macropore structural information developed during pyrolysis.

d) **Computer simulations** that model the pore structure of chars and can implement gas solid reaction rules.

Figure 1 summarizes the objectives of this work and the techniques used to tackle each objective.

**OBJECTIVES & TECHNIQUES**

![Diagram of objectives and techniques](image)

**Figure 1.1:** Objectives and techniques of this work.

The results obtained from the application of these techniques are very interesting and can be summarized below:
1) Pyrolysis conditions are very essential in the development of char pore structure. Consequently, the reactivity is directly or indirectly affected. In specific, heating rates and presence of little oxygen affect the reactivity only at high temperatures (thus the macropore structure), while heat treatment temperatures and soak times affect the reactivity at both low and high temperatures (thus the micropore structure and the concentration of active sites).

2) Particle ignitions are occurring at high temperatures and are responsible for significant reactivity enhancements. They are detectable by bright flames engulfing the particles, by rapid change in the color and the roughness of the particle surface and finally by sharp peaks in the reactivity curves.

3) The diffusional limitations begin at the same temperature range with the heat transfer limitations (at least for the 250-800 mm particle size range investigated). As a result, the reactivity drop due to diffusion is partially or fully screened by the reactivity enhancement due to particle overheating.

4) The particle size determines the ignition temperature. Although the larger particles are generally more heat transfer limited and therefore are igniting easier there is another factor determining ignitability and this is specific surface area. Small particles (250-300 mm) develop higher surface areas during pyrolysis and therefore are more reactive.

5) A discrete model was developed to simulate the heterogeneous reaction of a porous solid with known macropore structure. This structure could be generated in a 3-dimensional cellular grid using direct measurements of the physical properties of the solid. The process of gas diffusion in the solid was implemented by assuming a finite penetration thickness within the solid with non-uniform gas concentration. Reactivity versus conversion curves could be obtained for various pore structures (obtained by using different pyrolysis conditions) and various extends of diffusional limitations. The effect of
macropore structure, ash content and diffusional limitations on the reactivity patterns is investigated.
CHAPTER 2

EXPERIMENTAL EQUIPMENT AND PROCEDURES

2.1. TGA Reactor with in-situ Video Imaging Capabilities (TGA/VIM)

To meet our research objectives, we needed an experimental apparatus with the following capabilities.

1) We should be able to perform sequential pyrolysis and gasification experiments, so that we can investigate the influence of pyrolysis conditions on char reactivity.

2) The experimental apparatus should allow us to observe and record for post-processing the structural transformations that the particles undergo during pyrolysis. It should also detect and monitor the occurrence of transient combustion phenomena like particle ignition, fragmentation and macropore opening.

3) The reactor should have a high-power furnace and an accurate temperature control algorithm that we can achieve high heating rates or isothermal conditions with small temperature errors.

We modified a Perkin-Elmer TGS-2 thermogravimetric reactor to meet these requirements. This reactor was already interfaced to a PDP-11/23+ microcomputer that performed temperature control and the data acquisition tasks (Figure 2.1). Our main additions to the original setup were the following.
Figure 2.1: Schematic showing the TGA reactor and the flow control system interfaced to the computer.
a) We attached to the reactor an optical microscope equipped with a video camera connected to a video tape recorder and monitors. This setup allowed for direct viewing and tape recording of pyrolyzing and reacting particles.

b) We replaced the reactor furnace with an improved version that allowed us to achieve heating rates as high as 50 °C/s with excellent reproducibility. The computer control algorithm was also improved.

c) We installed a gas-feed system using computer-interfaced mass flow controllers. This allowed us to automate the entire experimental procedure.

Our thermogravimetric reactor with in-situ video microscopy imaging (TGA/VMI) can provide real time reaction rates while simultaneously allowing for direct visualization of the structural changes that coal particles undergo during pyrolysis or combustion. Since it can also achieve heating rates as high as 50 °C/s, we can expose our coal to a wider range of pyrolysis conditions that are closer to the conditions encountered in practical applications. Finally, our data collection algorithm can detect reaction rate changes occurring within a few tenths of a second.

A different microscope hot-stage reactor (Glass and Zygourakis, 1988) was also used in our experiments (see Figure 2.2 for a schematic diagram). This hot-stage was placed under a monocular zoom microscope with higher magnification than the one provided by the TGA/VMI microscope. The simpler operation of the hot-stage reactor allowed us to (a) quickly obtain many video sequences from pyrolysis and gasification experiments and (b) produce large numbers of char particles for pore structure studies through digital image analysis. Unlike the TGA/VMI setup, however, the hot-stage reactor can not provide reactivity measurements. The hot-stage reactor was interfaced to the same computer with the TGA/VMI reactor and utilized the same mass flow controllers. The obtained video images were videotaped and later digitized in a VAXstation-II/GPX computer (Digital Equipment Corp.).
Figure 2.2: Schematic showing the video microscopy system for the hot stage reactor.
2.1.1. Reactors

The thermogravimetric reactor (TGS-2, Perkin-Elmer) is interfaced to a microcomputer control system (PDP 11/23+, Digital Equipment Corp.) that controls the reactor temperature and the gas flow and performs the data acquisition tasks (Fig. 2.1). Three mass flow controllers (MFC) are used to obtain the desired mixture of nitrogen, oxygen and carbon dioxide fed to the reactor. The MFC set points are set by the computer that is interfaced to the MFC readout and control unit.

The coal sample is placed in a Pt pan and suspended from the weighing mechanism with a Pt wire. The balance accuracy is 0.1% and the sensitivity 0.1 μg. The weight signal is read and stored by the computer at regular time intervals.

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

The gas enters the reactor from two inlets. One passes through the weighing mechanism on top of the reactor and is always purged with nitrogen. The second is at the side of the furnace tube and contains either nitrogen or nitrogen/oxygen mixture. The feed rates in the reactor are in the range of 240-360 st.cc/min and the velocity of the gas stream inside the tube in the range of 0.8-1.2 cm/s. The location of the sample is almost 3.3 cm lower than the intersection of the two streams. This implies that the streams need 2.8-4.2 seconds to reach the sample. Therefore, adequate gas mixing is expected before the two streams, moving downwards, react with the sample.
Figure 2.3: Schematic showing the TGA reactor with the side window which allows direct observation of the sample.
A glass side arm was attached to the furnace tube with a tilted flat optical window at its top (Fig. 2.3). At the same time, the furnace element was lowered by about an inch. This eliminates any image obstruction from other objects in the furnace. Thus, pyrolyzing or reacting particles are directly visible through the window. The angle of incidence of the image beam and the window surface is close to 90°, thus preventing any diffraction and distortion of the image.

The imaging of the coal sample is provided by a high-magnification, extra-long working distance microscope placed on the top left side of the reactor facing downwards into the furnace. The highest magnification possible with this microscope allows us to image an area as small as 2.8 x 2.1 mm. This gives a pixel size of 4.3 μm for our 640x480 pixel digital image acquisition board. Illumination of the sample pan is provided by a bifurcated fiber optic bundle connected to a light source providing 50,000 ft. candles of light.

A color video camera with 760x485 lines resolution is attached to the microscope. The signal from a video timer is superimposed on the image from the camera, so that elapsed time for each experiment is shown on the TV monitor and recorded on a S-VHS video tape recorder (400 lines of resolution). The video tape recorder has a video signal sensor that can start recording a sequence whenever a video signal is supplied by the camera. This way, by remotely activating the video camera we can record only the important stages of the experiment and ignore the rest. Images obtained from videotaping can be later digitized in our VAXstation computer. Digital image processing techniques are used to provide image enhancement and image analysis (Fig. 2.2).

The hot stage reactor is using a Ni-Cr ribbon as heating element. A transformer of 6.7 VDC is supplying the power of about 200 W to the furnace reaching a current of up to 30 Amp. Under this configuration, the reactor can reach a maximum heating rate of 10 °C/s and a final temperature of 700 °C which is sufficient for our purpose. The sample is placed
in a platinum pan (same as the one in the TGA) and is located on a piece of zirconia felt. The latter is used to insulate electrically the sample pan and the thermocouple. The thermocouple is a chromel-alumel type K thermocouple isolated and with inconel sheath to resist chemical corrosion. It is placed such that it is touching both the side of the pan and the protective felt. It is covering the range 0-1000 °C.

2.1.2. Microcomputer Hardware

The requirements for an accurate and versatile control and data acquisition system were met by interfacing the reactor to a microcomputer. A digital control algorithm was implemented to program the reactor temperature and to automate the operations needed during the pyrolysis-gasification sequence. The micro-computer system used in our studies consisted of: i) a LSI 11/23+ CPU (Digital Equipment Corp.) with floating point hardware; ii) 256 kbyte memory; iii) 10 Mbyte hard disk storage capability; iv) dual floppy disk drives (1.0 Mbyte total storage capacity); v) four serial communications ports; vi) eight-channel (0-10 V) 12-bit A/D converter; and vii) eight-channel (0-10 V) 12-bit D/A converter. The computer operated under the RT-11 V5.1 real time operating system.

2.1.3. Temperature measurement

The temperature signal is being conditioned, amplified, and linearized by an isolated thermocouple module manufactured by Analog Devices (model 3B47). The gain is 10 mV/°C which brings the output signal into the dynamic range of 0-10 V for a 0-1000 °C temperature range. The temperature accuracy is ±1.0 °C including the combined effects of repeatability, hysteresis and linearity. The response time to a step change is equal to 0.2 secs for 90% of the span. The variations in ambient temperature are very small and they
don’t affect the output signal significantly (0.0025% of reading for every °C variation). Zero and span adjustments are also available for further calibration. The microcomputer A/D board reads the output voltage and converts it to an integer value between 0 and 4095 (for a 12-bit converter). Thus, the resolution of the A/D converter is 0.24 °C.

2.1.4. Heater control

A phase-fired heater controller circuit is used to regulate the power supplied to the heating element (Glass and Zygourakis 1988). The power supply (110 VAC @10 A) is regulated between 0-100% full power by varying the (0-10 VDC) input signal coming from the computer’s D/A converter. The value of this input signal is determined by the digital control scheme implemented on the computer. With the available power of 950 Watts, heating rates up to 100 °C/s are obtainable for final temperatures up to 950 °C. However, the maximum acceptable heating rates we can achieve with the available hardware and software cannot exceed 50 °C/s. A faster computer would be necessary to implement higher rates without significant temperature errors.

2.1.5. Mass flow controllers-Remotely activated devices

The control of the three mass flow controllers is performed by their readout/control unit. Three D/A channels and 3 TTL signals are interfaced to the control unit. They determine the set points and the remote activation of the MFCs respectively. This configuration allows the control of the total flow rate and composition of the gas mixture. For example, it allows the switching from pure nitrogen during pyrolysis, to an oxygen/nitrogen mixture for the onset of combustion.
Several other devices need to be activated and deactivated during an experiment. For instance, the reactor is equipped with a cooling fan that needs to be activated whenever fast cooling is desired (i.e. after the end of pyrolysis) or temperature overshoot occurs. The fan is connected to an 110 VAC outlet that is in series with a solid state relay. The computer assigns a value to a TTL signal to trigger the relay and then the fan starts. The same configuration is used to remotely control the operation of other AC powered devices like: the video camera and the solenoid valve that allows the premixing of nitrogen and oxygen before entering the reactor. Finally, a TTL logical signal is directly connected to the remote port of the video timer to trigger its START function. This way, there is synchronization of the computer and the video displayed time.

2.2. Computer control

2.2.1. Digital control algorithm

The digital control algorithm is a combination of a predictive technique (based on a convolution model) and a standard proportional–integral (PI) feedback control. The control program is an upgraded version of the control program written previously by Sandmann (Sandmann 1986). The model of the system is obtained experimentally and it is used to implement the desired temperature program. To compensate for the inaccuracies of the model and the temperature dependence of the process parameters, a feedback part is used, based on the deviations of the present temperature from the set point.
2.2.2. Process model

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

\[
G(z) = \sum_{i=0}^{\infty} h_i z^{-i}
\]

where \( h_i \) are the discrete model coefficients.

If we apply an impulse of power (actually a pulse of very short length) which has a Z-transform of unity and measure the temperature changes at regular time intervals we can obtain the discrete model coefficients \( h_i \) experimentally (Seborg, Edgar et al. 1989). These coefficients are normalized so that their sum equals unity. Three different sets of model coefficients are obtained for three temperature ranges (25-400 °C, 400-710 °C, 710-950 °C) by performing pulse tests in the center of each range. This is necessary, because furnace dynamics are non-linear due to radiation and therefore the process model changes with temperature. The temperature dependence of the heat losses \( Q_{out}(T) \) is assessed by supplying known power inputs to the furnace and measuring the steady state temperature. This function is interpolated with a fourth order polynomial. Furthermore, we can measure the furnace heat capacity \( a(T) \) by increasing the power stepwise by the known amount. The heat capacity is calculated as the ratio of the excess power (input power minus heat losses) over the temperature derivative.

At each control loop the process model is used in the following manner. First, we calculate the setpoint \( n \) intervals ahead of time (termed as prediction horizon). Then, we
calculate the power input needed for achieving that setpoint. This power is found as the sum of the heat losses and the ramp power.

\[ Q_{\text{sum}}^i = Q_{\text{out}}(T) + \alpha(T) \left| \frac{dT}{dt} \right|_{t=i} \]  

(2.2)

where: \( Q_{\text{sum}}^i \) is the power input prediction at time \( i \)

\( T \) is the temperature at time \( i \)

\( Q_{\text{out}}(T) \) the heat losses

\( \alpha(T) \) is the furnace heat capacity and

\( (dT/dt)_{t=i} \) the slope of the curve connecting the future set point with the present temperature \( T \).

After finding \( Q_{\text{sum}}^i \) we apply the convolution theorem to all previous power inputs to ascertain that their total sum together with the present input will all be equal to the desired power.

\[ Q_{\text{sum}}^i = Q_{\text{in}}^i h_1(T) + \sum_{j=2}^{t_s} Q_{\text{in}}^{i+j-1} h_j(T) \]  

(2.3)

where: \( t_s \) is the model horizon or the time needed to achieve steady state

\( h_i(T) \) the model coefficients (from eq.1) and

\( Q_{\text{in}}^i \) the present input necessary to achieve the set point after \( n \) time intervals.

The previous equation (3) is used to calculate \( Q_{\text{in}}^i \).

The feedback part of the controller is proportional and integral (PI). The deviation from the present set point is used to correct for the model inaccuracies. There are two kinds of prediction errors however. One is relative to the heat losses and the other to the heat
capacity. Therefore, integral accumulation during a ramping stage may be meaningless when we move to a steady state. Thus, two integrals are stored: a steady state integral stored while in steady state accounting for the error in the calculation of heat losses and a ramp integral stored while in ramping state accounting for error in heat capacity predictions. The algorithm does not accumulate integral at the corners when transition between states occurs. Both integrals are used, however, at all three regimes.

The control algorithm is repeated every 0.5 seconds. Shorter time is not indicated since instabilities due to thermocouple and system lags are exhibited. Furthermore, the computer used is not fast enough to perform shorter control loops. However, temperature and weight measurements can be performed meanwhile with frequency up to 12 times per sec. Data logging can be performed with the same frequency.

2.2.3. Performance of control algorithm

The controller's performance is very important since we want to achieve good reproducibility between experiments and also steady linear heating rates or stable steady state temperatures. This controller is very good at fulfilling these requirements. The error is at most 0.2 °C at steady state conditions (as much as the resolution of the A/D board) far from the corners. During ramps of 0.1-1.0 °C/s the $L_1$ norm of the error (which is the average absolute error) is at the order of 0.3 °C except for small deviations at the corners. During ramps of 10 °C/s the $L_1$ norm of the error is at the order of 1 °C.

At the corners the maximum error observed for a 10 °C/s ramp is 3-5 °C (for 1-3 secs). For 30 °C/s rate the maximum error is 13 °C at the corners, but it is smoothed out very fast (within a few seconds). The norm of the error at this case is about 4.7 °C.

Figure 2.4 shows a ramp of 20 °C/s. As we see, the control is very good especially for the control period of 0.5 secs that the algorithm uses.
Table 1:

Norms of temperature error during a typical ramp
(from 200 to 700 °C) until steady state is achieved

<table>
<thead>
<tr>
<th>Heating Rate °C/s</th>
<th>Ramping state</th>
<th>Transient to Steady State</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L₁ (°C)</td>
<td>L₁ (°C)</td>
</tr>
<tr>
<td>1</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>10</td>
<td>1.1</td>
<td>0.6</td>
</tr>
<tr>
<td>20</td>
<td>2.0</td>
<td>1.3</td>
</tr>
<tr>
<td>30</td>
<td>4.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

---

Figure 2.4: A typical temperature ramp showing the performance of the control algorithm. The temperature plotted is the actual. Notice the error magnitude on the right axis.
From process dynamics theory we expect that for a 20 °C/s ramp, a feedback controller would have a minimum error of 10 °C (lag of the controller 0.5 sec). But our predictive technique suppresses the error to a lower value than 10 °C (maximum 7.3 °C).

Note also that overshooting is avoided at the end of the temperature ramp. As shown in Figure 2.4, the overshooting is only 2 °C (error -2 °C) and lasts one second.

2.3. Experimental procedures

2.3.1. Sample preparation

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

For each run, the reactor was loaded with less than 1 mg of coal (that is, 30-40 coal particles for the 50-60 fraction, 8 particles for the 28-32 mesh fraction and 2-3 particles for the 20-24 mesh fraction). The particles are placed in the pan in a configuration that keeps them far from eachother. This way we can prevent particle agglomeration during pyrolysis. This is not entirely feasible with the 30-40 particles needed to achieve weight close to 1 mg which is appropriate for accurate, noise-free weight measurements. This number complicates the creation of a monolayer of particles on the pan surface. Although we put diligent effort to place them one far from the other, the swelling during pyrolysis forces
some particles to coalesce and stick together. We consider that this is not a problem for rate measurements in the kinetic control regime. It could create additional diffusional resistances though, for the particles of interest in the diffusion-limited regime.

The weighing mechanism is constantly purged with nitrogen to prevent intrusion of air in it. The microscope is focused on the sample and the illumination is adjusted to get the best image quality. The VTR is set in the video sensor mode. Each time the camera gives an output signal the VTR starts recording. The video timer is zeroed and put in the stand-by mode that awaits for a remote signal to start time counting.

2.3.2. Experimental protocol

A typical experiment performed is including the following stages (Figure 2.5):

a) The sample is held at 150 °C in nitrogen (or 5% oxygen in nitrogen) flow for a few minutes in order to remove any moisture present. Then it is ramped to 200 °C which is the starting point of pyrolysis.

b) The pyrolysis ramp starts in a constant rate (0.1 to 20 °C/s). Videotaping and time counting start. The ramp lasts until the final heat treatment temperature (HTT) is reached (500 to 900 °C). Then the temperature is held constant for a period equal to the desired soak time (0 or 3 minutes).

c) After the end of the pyrolysis videotaping stops. The reactor is cooled fast to 250 °C. Then the desired oxygen/nitrogen mixture is fed (33% usually) and is allowed enough time to achieve a steady state concentration in the reactor.

d) Videotaping starts and the temperature is ramped fast to the desired combustion temperature (400-600 °C). There, it is kept constant long enough to burn the coal at a level of 90-100 %.
Figure 2.5: Temperature program and weight vs. time measurements for a typical run (Pyrolysis heating rate: 1.0 °C/s; Combustion temperature: 550 °C).

e) Finally, it is ramped to 650 °C and the sample is burned-out for 5 minutes to measure its ash content.

During a typical loop of the control program (repeated every 0.5 secs) the following tasks are performed. The weight and temperature measurements are obtained and stored along with the time in a computer file. The power input for the future set point temperature
is calculated and the appropriate D/A signal is given to the controller. Several conditions are also checked during the experiment. These are tests like if it is time to feed oxygen or if the combustion rate has achieved a level of almost complete conversion and coal burn-off needs to follow. Also, the time instants when the VTR needs to start videotaping are determined. Sometimes when fast data collection is needed the program can read the A/D channels in a frequency up to 12 times per second. After the end of the experiment the furnace is cooled to room temperature, the mass flow controllers are turned off and the videotaping stops. This set-up is very convenient because it virtually eliminates any operator intervention and allows for other important tasks to be handled during the course of an experiment. Table 2 gives the range of the conditions used for pyrolysis and gasification.

<table>
<thead>
<tr>
<th>Table 2:</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXPERIMENTAL CONDITIONS</td>
</tr>
</tbody>
</table>

**Pyrolysis Stage**

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

**Combustion Stage**

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

After the end of the experiment, the data file is transferred to the VAXstation computer and processed with a custom made software. We have carefully analyzed our procedure for obtaining the reaction rates. Usually, our data acquisition system will collect about 300 data points during the pyrolysis stage of each run and 300-3,000 data points during the combustion stage (depending on the reaction temperature). The collected weight vs. time data are interpolated in the least-squares sense (L^2 norm) using B-splines and this polynomial approximation is then differentiated to obtain the observed reaction rate per unit mass of initial or unreacted solid. These are calculated according to Equations (1),(2).

\begin{equation}
    r_o(t) = \frac{dx}{dt} = -\frac{1}{m_o} \frac{dm(t)}{dt}
\end{equation}

\begin{equation}
    r_m(t) = \frac{1}{1-x} \frac{dx}{dt} = -\frac{1}{m(t)} \frac{dm(t)}{dt}
\end{equation}

where: 
- \( x \) is the conversion of the solid
- \( m_o \) is the initial mass of the solid in ash-free basis
- \( m(t) \) is the mass of the unreacted solid at time \( t \)

The first rate \( r_o \) gives absolute values of the reaction rate and as mentioned in the literature it exhibits a maximum at 20-40% conversion (for this coal reacting with oxygen). The second rate \( r_m \) gives specific values of the reaction rate per mass of remaining solid. Experimental observations show that it follows a monotonic increase in the conversion range of 0-90%. From now on we will follow the convention of plotting \( r_m \) in our figures as most investigators do.
In our numerical differentiation procedure, it is essential to determine the appropriate order of polynomials and the number of breakpoints to use for the interpolation of the raw weight data. If high order polynomials are used, the reactivity curves will be smoothed out and fine details will be lost. Also, the curves will be very noisy if a large number of breakpoints are used. Our choice of polynomials was dictated by the form of our data that indicated the reaction rate is continuous in time but not necessarily smooth (i.e. it has a discontinuous first derivative). Such behavior has also been observed by Sundback et al. (1984) who attributed it to particle fragmentation. Our earlier studies (Zygourakis 1989a; Zygourakis and Sandmann 1988) indicate that these jumps may also be caused by the opening of large internal pores during combustion in the diffusion-limited regime (high temperatures). Therefore, we decided to use C-1 quadratics for the interpolation instead of the more often used C-2 cubic splines. This assumes that the reaction rate is a linear function of time at each interval and can exhibit sharp maxima and minima which would be smoothed out with a cubic spline. The number of intervals is in most cases larger than 30 and our software allows for dynamic placement of the breakpoints in regions with rapidly changing sample weight, a feature that improves our ability to resolve fine details of the reactivity curve. Since we always have more than 20 data points in each subinterval, any noise disturbances cannot significantly influence our results. Standard plotting software allows direct visualization of the reaction patterns as a function of conversion or time.
CHAPTER 3

EFFECT OF PYROLYSIS ON MACROPOROUS STRUCTURE

3.1. Coal Plasticity and Swelling

The experiments both on the TGA/VMI and the microscope hot-stage reactor were performed with Illinois #6 particles of size 28-32 mesh. An analysis of the video-taped histories of these experiments showed that the coal particles swell considerably and that the swelling increases with increasing heating rates. We also observed vigorous bubbling during this stage, as the particles expanded and contracted in rapid succession.

Figures 3.1, 3.2 and 3.3 illustrate the dramatic shape and size changes of coal particles observed within a few seconds. The images of Figure 3.1 present the temporal evolution of specific particles during a pyrolysis run with a 10 °C/s heating rate. For this run, the platinum pan of the TGA/VMI reactor was covered with a platinum wire mesh to prevent the particles from agglomerating. The elapsed time is shown on the bottom left part of the screen. Time zero corresponds to the beginning of the heating ramp at 200 °C.

The images of Figure 3.2 are blow-ups from the corresponding images of Figure 3.1 showing in more detail the transformations of two specific particles. One particle starts with a triangular shape (Figure 3.2A), swells and becomes elongated (Fig. 3.2C). After a few contractions and expansions, it ends up with a rounded shape (Fig. 3.2F). Rapid particle expansions and contractions occurred within time intervals as short as 1.5 s. Figure 3.3 shows the images of Figure 3.2 enhanced with an artificial illumination technique. The digitally enhanced images clearly show bubbling effects on the particle surface.

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Figure 3.1: Sequence of images showing eight particles pyrolyzing in the hot-stage reactor at various temperatures. Heating rate is 10 °C/s. The grid separates the particles to prevent agglomeration.
Figure 3.2: Sequence of images showing two pyrolyzing particles at various temperatures. Note the large variations of both the shape and the size of the lower particle. This is the detail of the image sequence on Fig. 3.1.
Figure 3.3: Processed images showing the three-dimensional contours of the outside surface of pyrolyzing particles. Note growing bubbles on the surface of the lower particle at images for $T=537\,\,^\circ C$ and $T=552\,\,^\circ C$
The mechanism of expansion and contraction is as follows. Bubble formation inside the particle induces an internal pressure build-up that forces the particle to expand. The surface tension of the bubble film increases and when it exceeds a limit value the film breaks releasing to the particle exterior the volatile gases contained in the bubble. The particle contracts again until new bubbles start forming in the particle interior and the internal pressure starts building up again.

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

3.2. Devolatilization rates

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

Figure 3.4 shows the weight loss rates for several runs at two different heating rates. The results for each heating rate show very good reproducibility and the maximum pyrolysis rate is observed in a narrow temperature range. A comparison of the results for 0.1 and 10 °C/s, but, shows a significant shift of the range of maximum devolatilization rates toward higher temperatures as the heating rate increases (see Figure 3.4 and Table 3).
Figure 3.4: Experimental devolatilization rates for several pyrolysis runs performed at two different heating rates

Figure 3.5: Weight loss curves obtained for three different heating rates (HTT=900 °C)
Figure 3.5 compares the weight loss curves obtained for three different pyrolysis heating rates: 0.1, 1.0 and 10 °C/s. The important result here is that the amount of released volatiles increases slightly with increasing heating rates (Figure 3.5 and Table 3). This observation agrees with the theoretical predictions (Fletcher, Kerstein et al. 1989) of the chemical percolation devolatilization (CPD) model and the experimental observations of Gibbins-Matham and Kandiyoti (1987).

Table 3:

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

<table>
<thead>
<tr>
<th>Pyrolysis Heating Rate (°C/s)</th>
<th>0.1</th>
<th>1.0</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature Range for Maximum Weight Loss Rate (°C)</td>
<td>410-425</td>
<td>460-480</td>
<td>510-545</td>
</tr>
<tr>
<td>Average Weight Loss (%)</td>
<td>36.5</td>
<td>42.4</td>
<td>46.2</td>
</tr>
</tbody>
</table>

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

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

3.3. Effect of oxygen on plasticity

The video images obtained from pyrolysis experiments in the presence of oxygen provided us with some interesting observations. Particles pyrolyzed in oxidating atmospheres do not "bubble" as vigorously as in inert atmospheres. The particles seem less plastic. Surface eruptions and bubble escape that cause particle contraction are less frequent. The particles spend more time expanding without surface eruption. Bubble breaking occurs in a more violent manner due to the accumulated pressure of the volatiles inside the particle. This can be seen by observing the particles "bouncing" from one place to another due to the momentum of the released gases.

In addition, the long residence time of the bubbles in the particle interior increases the probability that they will coalesce with each other and form one large cenosphere. When the char particles resolidify, they are frozen in an "expanded" state where their average size is larger than the average size of char particles produced in nitrogen. This observation is confirmed by our digital image processing measurements (Boissiere 1991).
Visual observation of particles pyrolyzed with and without oxygen suggest that the former ones are more spherical than the latter. This is another phenomenon attributed to the reduced plasticity of the former chars. The surface tension is higher for them and therefore they prefer the spherical shape that has lower energy and surface area.

During pyrolysis in oxidative atmospheres, holes may open at the surface of the particles and liquid material from the particle interior can be seen flowing out through these holes. Shortly afterward, this liquid material solidifies forming a small "bump" protruding from the smooth surface of the particle. These formations tend to react first during combustion, thus opening up the particle interior to reactants. Video histories of combustion experiments have revealed that particle ignitions usually occurred whenever one of these formations was disappearing. Microscopical observations of cross sectioned particles pyrolyzed to an HTT of 500 °C with oxygen showed that the majority of them are impervious to the resin suggesting that their macropores are initially less accessible to gaseous reactants. These “bump” formations have very thin walls, and when they react, they collapse rapidly exposing the particle interior that resembles a cenosphere.

Our observations agree with experimental findings showing that preoxidation hinders coal plasticity. By the same token, we can expect that the presence of oxygen during pyrolysis may hinder coal plasticity.

We should finally emphasize that all the previously mentioned results are not due to partial reaction of the coal matrix with oxygen during pyrolysis. Our experimental results show that chars produced in either inert or oxygen atmospheres exhibited similar devolatilization patterns and intrinsic reactivities. More detailed explanations will be given in subsequent section.
3.4. Macropore structure measurements

Some preliminary measurements of the macropore structure of devolatilized chars were performed by another investigator in our group (Boissiere 1991). The coal particle size and origin used for these measurements were identical with the ones we used (Illinois #6 from the Argonne collection, 28-32 mesh). These measurements show that the char particles have very open cellular macropore structures similar to those quantified via digital image analysis in earlier studies with the same parent coal (Zygourakis 1988). As we expected, the heating rate strongly affected the swelling (and therefore the macroporosity) of the char particles.

The results obtained by Boissiere (Boissiere 1991) provide information on the particle and macropore size distribution of pyrolyzed chars. He analyzed char particles produced in inert (N₂) and oxidative (5% O₂ and 95% N₂) atmospheres at 500 or 700 °C HTT, with various heating rates. His measurements of average particle size are given in Table 4 below.

The initial average particle radius before pyrolysis was 0.349 mm with standard deviation 0.03923 mm. The number of particles examined is sufficient to secure that the error is less than 10% with a 95% confidence level.

These measurements with the results reported by Zygourakis (1988) lead to the following conclusions:

1. The final particle size, the average macropore size, the macropore specific surface area and the macroporosity of a char particle increase as the pyrolysis heating rate increases.
2. The macroporosity does not depend on the initial particle size (Zygourakis, 1988).
3. The macropore specific surface area decreases as the initial particle size increases.
Table 4:
Average Radii of Particles
Produced under Different Pyrolysis Conditions (mm)

<table>
<thead>
<tr>
<th>Heating Rate (°C/s)</th>
<th>HTT = 500 °C</th>
<th>HTT = 700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nitrogen Only</td>
<td>5% Oxygen 95% Nitrogen</td>
</tr>
<tr>
<td>0.1</td>
<td>0.316</td>
<td>N/A</td>
</tr>
<tr>
<td>1.0</td>
<td>0.335</td>
<td>0.331</td>
</tr>
<tr>
<td>10</td>
<td>0.387</td>
<td>0.443</td>
</tr>
</tbody>
</table>

4. The heat treatment temperature (500 or 700 °C) does not influence the particle swelling at the low heating rates (0.1 and 1.0 °C/s). However, the chars treated with 10 °C/s have lower swelling when they are ramped to 500 °C. This is because the particles do not reach their maximum devolatilization rate that occurs at around 520 °C under these conditions (see Table 3).

5. The presence of oxygen does not influence the final particle size at the low heating rates (0.1 and 1 °C/s). At 10 °C/s, however, the bubbling is more vigorous and the final particle size is larger for the chars that were pyrolyzed in the presence of oxygen.
6. The presence of oxygen significantly influences the final macroporosity of the chars pyrolyzed at 10 °C/s.

3.5. Effects of pore structure on reactivity

The pore structure of a solid is a major factor in determining its reactivity and the intraparticle transport processes.

1. The micro pore surface area is the dominant factor for determining the intrinsic reactivity of a solid. Since it is usually much larger than the macropore surface area, the micropore surface area determines the reaction rates in the kinetic control regime.

2. The average micro- and macropore size and length are the factors determining the extent of diffusional limitations. In the case of intermediate diffusional limitations, the concentration gradients develop mainly in the micropores, while the macropores are large enough not to have any concentration gradients. In the case of strong diffusional limitations though, concentration gradients develop also in the macropores. Thus, the average macropore size and length become also important in the determination of reaction rates.

3. As discussed earlier (Gavalas 1980), in the case of strong diffusional limitations the smaller pores make a constant contribution to the reaction rate when the rate is expressed per unit area of the macropores. Or otherwise, the gas concentration profile emanates from the macropore surface and penetrates the solid to a finite constant depth. Thus, the macropore surface area affects the reaction rates significantly.

4. The average macroporosity also controls the effective thermal conductivity of a porous solid even in a minor way. The effective thermal conductivity is calculated with the following formula:
\[ k_{\text{eff}} = (1 - \varepsilon_M)^2 k_m + \varepsilon_M^2 k \]  

(3.1)

where: \( k_{\text{eff}} \) is the effective thermal conductivity
\( \varepsilon_M \) is the macroporosity of the solid
\( k_m, k \) are the thermal conductivities of the microporous solid and the gas mixture respectively.

The gas thermal conductivity \( k \) is much lower than the solid \( k_m \) so whenever the macroporosity increases the effective thermal conductivity decreases drastically.

All the above conclusions prepare us to expect the following:

i) Char particles prepared at high pyrolysis heating rates have a more efficient gas transport to their interior. The combined increase of macropore size and specific surface area will lead to an increased apparent reactivity of those chars in the diffusion limited regime. These chars will have lower gas concentration gradients in their macropores and thus higher effectiveness factors. Besides, they will probably have fewer pores trapped inside the solid and thus increased macropore accessibility.

ii) For the same reasons, increased reactivity is also expected for chars that were treated at high heating rates and in the presence of oxygen.

iii) Finally, intraparticle temperature gradients are more easily attainable in chars with higher porosity and thus, with lower effective thermal conductivity. Thus, the chars will react with higher reaction rates than those expected at the given ambient temperature. This may lead to effectiveness factors larger than one.

All the above conclusions will be examined experimentally in the following chapters to test the validity of our assumptions. For this purpose, we will perform experiments in a whole range of pyrolysis conditions and combustion temperatures. The reaction rate measurements at low combustion temperatures that belong to the kinetic control regime will
provide us information about char intrinsic reactivity associated with the **micropore structure**. The same measurements of apparent reactivity at high temperatures that belong to the **diffusion limited regime**, will provide information on the **macropore structure** of chars. With this methodology, we will explore the effect of pyrolysis conditions on both the intrinsic reactivity and the macropore structure. Both of them are important in the determination of reaction rates at high temperatures. So we need to decide how to optimize pyrolysis conditions, in order to produce chars with high intrinsic reactivity, high macropore surface area and low macropore diffusional limitations.
CHAPTER 4

FUNDAMENTAL MECHANISMS OF COAL COMBUSTION

4.1. Reactivity patterns

As we described earlier, our analysis will focus on combustion both on the kinetic control and the diffusion-limited regimes. The quantities that interest us, are the intrinsic reactivity and the macropore structure. Our main concern is to find how combustion occurs and how these two quantities affect observable rates.

The temporal evolution of reactivity can provide the initial information on the mechanism of combustion. The reaction rate vs. conversion curve at 450 °C (kinetic control regime) is shown in Figure 4.1a. As we see, char reactivity (as measured by \( r_m(t) \)) increases continuously with conversion. This reaction pattern agrees with theoretical models for gasification in the kinetic control regime where the active surface area associated with the micropores is easily accessible to the reactants (Ballal 1985; Zygourakis and Sandmann 1988). These and similar models predict that the intrinsic reaction rate will follow an increasing pattern due to the increasing accessibility and specific surface area of the enlarging micropores.

The experimental reactivity curve at 550 °C (diffusion limited regime), however, reveals a different behavior. Figure 4.1b shows that the reaction rate increases sharply and in a rather "discontinuous" fashion in the early stages of gasification with sharp maxima spanning a conversion range of approximately 10%. After one (or more) such maxima, the reaction rate settles at a fairly constant plateau for the remainder of the reaction.
Figure 4.1: Reactivity patterns for the kinetic control and the diffusion-limited regimes.
We carried out a systematic analysis to make sure that these sharp maxima were not artifacts due to measurement errors or to the interpolation of the numerical data. Indeed, we concluded that the sudden and sharp drop of the sample weight cannot be due to errors in weight measurements or failures of our controller to maintain constant sample temperature (Figure 4.2). Note that the curve in Figure 4.2 is the same with the one in 4.1b.

The video microscopy apparatus provided the first piece of conclusive evidence that helped us determine the cause of the observed "spikes" in the reactivity curves. Visual observation revealed that some particles ignited, usually during the very early stages of gasification at the higher temperatures (e.g. 550 °C). The time of the ignition as shown on the video monitor coincided with the time that the reaction rate increased sharply. A digital image sequence of combusting particles is shown in Figure 4.4, as obtained from the video microscopy apparatus. Note that this figure corresponds to the same sample that was presented in Figures 3.1-3.3. We note that in the middle image one of the particles emits light, showing that it moves to a new steady state with higher temperature. We can also see the ash skeleton remaining after complete combustion of the carbon. From this image and several other ones we can conclude that there is not significant fragmentation.

Additional confirmation that the spikes observed in the reaction rates are due to particle ignitions is provided by the controller power signal (see Figure 4.3). If the reaction rate is high, the controller cuts down the power it provides to the furnace to counterbalance the heat released by the reaction. Note that the reaction rate maxima correspond to the maxima of the power control signal.

Ignited particles were rapidly consumed but not always entirely. This can be deduced by the fact that sometimes, even after the disappearance of the flame the particle continued shrinking and deforming. The width of the spikes corresponds to about 10% total conversion and, thus, each spike should be attributable to the ignition of one of the 8 particles loaded in our reactor for each run.
Figure 4.2: Measurements of weight and temperature vs. time and computed reaction rate.

Figure 4.3: Correlation between controller feedback power and particle reaction rate.
Figure 4.4: Video image sequence of eight reacting particles before, during and after combustion. Note the ignition at the center image and the ash content at the bottom one.
After the extinction, the reaction rate remains almost constant for a wide range of conversion. This behavior is in (at least qualitative) agreement with the gasification models that assume that the macropore structure is the major rate-determining factor in the regime of diffusional limitations (high temperatures). While at first only the outer macropores are available for reaction, closed macropores open up as the reaction front reaches them and the observed reaction rate remains relatively constant (Zygourakis 1989a).

4.2. Observations on the ignition mechanism

The images of particle ignitions gave us some new insights into the ignition mechanism. The hot stage reactor provided us with video sequences of particles under high magnification where one particle of 500-595 μm diameter is occupying the entire screen. We reacted the particles with oxygen concentrations as high as 100% to observe violent ignitions. We watched the videotapes in slow motion (as low as 10 times slower than real time speed) to observe the mechanism through which the ignitions occurred. Our conclusions are given below:

i) One type of particle ignition, which we will call from now on global ignition, involves the generation of an orange or yellow flame engulfing the entire particle. The particle surface changes from shiny-black to rough-grey with many cavities and fissures. The light emission is strong and is easily distinguishable from the background. Gas is released rapidly carrying away small fragments and sometimes providing momentum for the particle to move.

ii) Ignition starts from a localized area on the particle surface and it propagates rapidly over the entire surface (within 30-100 msec)
iii) The duration of the flame is between 1-3 secs reaching a maximum emission intensity and yellow color at an intermediate time.

iv) At high temperatures or oxygen concentrations the ignition starts at very low conversions and ends after the almost complete conversion of the particle. The flame shrinks towards the center of the particle which was probably excluded from the reaction at the early stages of ignition, due to complete consumption of oxygen on the surface (diffusional limitations).

v) At moderate temperatures or oxygen concentrations the particle ignites at intermediate conversions. The extinction also leaves some of the particle unreacted. The particle continues to react on the unignited state with lower reaction rate. This observation agrees with the predictions of Sotirchos and Amundson of the transient combustion behavior of a char particle. A possible explanation is what they propose. When the particle reacts at low conversions it may have low micropore surface area and therefore lie in the unignited branch of the solution locus. As the conversion proceeds the micropores grow providing more surface area and higher reaction rates. The particle obtains a new solution locus displaced to lower temperatures. Therefore its new ignition temperature may decrease and become even smaller than the ambient. Ignition is the consequence of this new surface area. Later on, though, as the micropores coalesce and the micropore specific surface area drops, the ignition temperature also moves to higher temperatures and may exceed the ambient. Extinction is the result of this decreased surface area.

vi) In several cases we observed multiple ignitions in the same particle. They are mostly occurrences of another type of ignition. This type is a localized, short ignition lasting only a few tenths of the second (30-300 msec). The flame is less bright and is visible only when the background illumination is low. The flame color is more orange, an indication of lower ignition temperatures than those prevailing during
global ignitions (yellow is emitted by hotter objects). The local ignitions are much harder to detect with the weight measurements since their effect on the total reaction rate is small. Furthermore, our data acquisition computer is only able to collect 1-4 weight measurements during a short ignition (our data collection is performed every 87 msec). With so few weight measurements, it is impossible to detect a maximum in the reaction rate. These arguments strongly support the use of a video imaging device if every ignition is to be detected. The multiple ignitions have rarely been mentioned in the literature (Solomon, Chien et al. 1990). No models have been devised to explain them either. A possible explanation is that the structural inhomogeneity of the char particles exposes different fractions of the surface area as the conversion increases. Probably, large macropores that are initially inaccessible to the gas, open-up inducing sudden enhancements in the reaction rate.

vi) Finally, at high oxygen concentrations the flame obtains a size larger than the outline of the particle suggesting that gas phase ignition occurs. It involves the oxidation of CO to CO$_2$ in a sheath surrounding the particle. We should note that when the particle ignites it may exceed the heat treatment temperature and therefore further devolatilization can occur. However, we know that the major devolatilization happens at temperatures of less than 600 °C. Thus, only a small amount of additional volatiles is released during ignition. This should not influence significantly the gas phase ignition.

vii) Induced ignition can occur in one particle if a neighboring one is in the ignited state. The violent emission of hot gas and small particle fines from an ignited particle to the surroundings can spark an ignition to the unignited ones. This was observed in high oxygen concentrations were chain ignitions were observed.
Figure 4.5 shows the reaction rate measurements from a combustion experiment. The reaction rate pattern exhibits three spikes (local maxima). A careful analysis of the video sequence for this run clearly showed that the first two rate spikes (at -2 and 2 secs) were attributed to ignition of one particle each time. This confirms our hypothesis concerning the connection between particle ignitions and local maxima in the reactivity curve. A third maximum in the reactivity pattern was observed at time 10 seconds but it did not correspond to light emission. However, at this instant a particle shrunk rapidly leaving back a sponge-like structure composed of its ash skeleton. This maximum was observed at higher conversions when very little mass of solid is left. If we plot the reaction rate per unit mass of initial solid ($r_0$) the maximum is less prominent.

The correspondence between ignitions and reactivity maxima is not as simple. If many particles ignite at the same time or if the ignitions are short and localized, the reaction rate curve may not show any sharp spikes. This is demonstrated in Figure 4.6 that shows a very smooth reaction rate pattern. Although we would expect no ignition to occur during that time, the video sequence showed that there were 4 ignitions in the -5 to 0 sec period. Three of the ignitions occurred in the same particle: first a global ignition and, later, two localized ones. The fourth ignition was also a global one and occurred at time zero. The effect of this ignition on the reaction rate was probably masked, however, by the two localized ignitions occurring exactly before and after the global one.

Similar observations were made for the Blind Canyon coal. There were 12 localized ignitions and a few global ones but only two were detected. In another run, about 14 ignitions occurred but only one was detected thermogravimetrically.

Our conclusion is that although some ignitions can be detected by the thermogravimetric method, the majority cannot. That is why a video microscopy system is necessary to detect all particle ignitions.
Figure 4.5: Reaction rate measurements during combustion of Illinois #6 char at 600 °C (HTT: 700 °C; Soak time: 3min; Heating rate 20 °C/s).
Figure 4.6: Reaction rate measurements during combustion of Illinois #6 char at 600 °C (HTT: 700 °C; Soak time: 3 min; Heating rate 10 °C/s).
4.3. Effect of flow rate on particle ignitions

Heat dissipation from the particle is limited when reaction takes place at elevated temperatures. Thus, the heat transfer coefficient determines partially the extent of heat removal and therefore the magnitude of intraparticle temperature gradients. It is expected that a higher gas flow rate will increase the heat transfer coefficient and also prevent intraparticle temperature gradients and ignition.

This hypothesis is confirmed by the results of Figures 4.7-4.8. Under a flow rate of 240 sccm the particles ignite at 550 °C. When the flow rate is increased to 360 sccm, however, particle ignitions are less prominent (if ever existent) since no peaks are observed. At any rate, since we observe higher reaction rates this means that the intraparticle temperature gradients are higher. This observation was made in several experiments and suggests that the particles at the flow rate of 240 sccm are more external heat transfer limited.

![Combustion at 550 C HTT 700 C, soak 3 min Heat. rate 1 C/s](image)

Figure 4.7: Effect of gas flow rate on ignition phenomena during combustion at 550 °C (Heating rate is 1 °C/s).
Combustion at 550 °C  
HTT 700 °C, soak 3 min  
Heating rate 10 °C/s

![Graph showing reaction rate vs conversion for different gas flow rates.

Figure 4.8: Effect of gas flow rate on ignition phenomena during combustion at 550 °C
(Heating rate is 10 °C/s).
CHAPTER 5

EFFECT OF PYROLYSIS ON REACTIVITY

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

The first investigation of the effect of pyrolysis conditions on reactivity focuses on the heat treatment temperature (HTT). It is an important parameter of reactor design and as described in Chapter 3 it also influences the swelling of the particles (Table 4). Our experiments involved the pyrolysis of coal at several HTT's and the measurement of their reactivity at both the kinetic control and diffusion-limited regimes. Figure 5.1 shows the reaction rate patterns at 450 and 550 °C, for char samples prepared at the heating rate of 1 °C/s and four different heat treatment temperatures (HTT): 500, 700, 800 and 900 °C. Soak time at the HTT for all these samples was 3 minutes.

The experimental gasification data at 450 °C show the expected char reactivity pattern (as described in Chapter 4). Besides, chars produced at higher HTT (e.g. 800 and 900 °C) are less reactive than chars produced at higher HTT (500 and 700 °C). Since this decline in reactivity is observed in the kinetic control regime (where macropore structure has no effect), this suggests necessarily a decline in the intrinsic reactivity.

These observations of declining reactivity with increasing HTT are in agreement with earlier studies on char combustion (see, for example, Serio et al, 1989).
Figure 5.1: The effect of heat treatment temperature on reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at 450 and 550 °C (Heating rate 1 °C/s, soak time 3 min).
These observations indicate an increase in the molecular order of chars produced at high HTT due to enhanced annealing of the organic and mineral components and the microporosity of the chars. In other words, the high treatment temperatures cause a sintering of active carbon sites and consequently deterioration of the intrinsic reactivity. This observation strongly supports the principles of mild gasification (as described in the Introduction).

The experimental gasification data at 550 °C show the char reactivity pattern that we found to correspond to ignitions (Chapter 4). The decline in reactivity with increase of HTT is still observable. This is expected, since intrinsic reactivity affects observable reaction rates in the entire temperature range (except for the case of strong external mass transfer limitations, which are excluded here). Another important observation is that chars produced at lower HTT's have higher likelihood of ignition. For example, the chars treated at 700 and 800 °C exhibit ignitions (as observed by the peaks in the reactivity curves), while the chars treated at 900 °C do not ignite. This gives an indication, consistent with theoretical predictions, that increased reactivity results to lower ignition temperatures.

Finally, the effect of HTT on macropore structure can not be deduced from these measurements since it is screened by the change in intrinsic reactivity.

5.2. Effect of soak time on char reactivity

The effect of soak time (e.g. the time that the coal sample is kept at the heat treatment temperature) on reactivity is studied in the entire range of HTT's. Figure 5.2a shows the effect of soak time at the HTT of 800 °C. Longer soak times decrease the intrinsic reactivity of the chars as measured by the reaction rate at 450 °C.
Figure 5.2: The effect of soak time on reactivity vs. conversion patterns for Illinois #6 chars gasified with oxygen at 450 and 550 °C (Heat treatment temperature: 800 °C; Heating rate: 0.1 °C/s).
The sample that was kept instantaneously at 800 °C was by about 40% more reactive than the sample that was kept for 3 minutes.

Our results at the combustion temperature of 550 °C, also strongly indicate that the shorter soak times (0 mins) rendered the chars much more likely to ignite. This is shown in Figure 5.2b. One of the two runs containing chars with zero soak time exhibited ignition phenomena. This is again consistent with the argument that increased reactivity results to lower ignition temperatures.

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

5.3. Effect of heating rate on char reactivity

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

Figures 5.3 through 5.8 demonstrate the relative reactivity of chars prepared at heating rates from 0.1 °C/s to 20 °C/s. At low combustion temperatures (400 to 450 °C) that belong to the kinetic control regime we observe the all the chars have quite similar reactivities and burn-off times (times required to achieve a specific conversion level).
Combustion at 400 °C
Heat treatment at 700 °C
Soak 3 minutes

Figure 5.3: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 400 °C (HTT: 700 °C; soak time: 3 minutes).
Figure 5.4: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 420 °C (HTT: 700 °C; soak time: 3 minutes).
Figure 5.5: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 450 °C (HTT: 700 °C; soak time: 3 minutes).
Figure 5.6: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 500 °C (HTT: 700 °C; soak time: 3 minutes).
Combustion at 550 °C
Heating treatment at 700 °C
Soak for 3 min

Figure 5.7: The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 550 °C (HTT: 700 °C; soak time: 3 minutes).
The effect of heating rate on the reaction rates and burn-off times of Illinois #6 chars (28-32 mesh) gasified with 33% oxygen at 600 °C (HTT: 700 °C; soak time: 3 minutes).
The reactivity patterns are also quite similar. This is a conclusive evidence that: (i) the micropore surface area of chars is not affected by pyrolysis heating rates and (ii) the chemical nature and concentration of the reactive sites is not altered by the different heating rates.

On the other side, as the combustion temperature increases we observe a progressive divergence of the reactivities starting from the combustion temperature of 550 °C. The chars produced at 1 and 10 °C/s are more reactive although they exhibit reactivity patterns without sharp maxima. Finally, at the combustion temperature of 600 °C the chars exhibit the reactivity patterns that are clearly attributable to ignition (Figure 5.8). When the particles ignite, the reactivity curve exhibits several maxima, one for each ignition. It is clear that the chars pyrolyzed at higher heating rates are igniting more frequently. This results to a significantly higher reaction rate. Therefore, we can state that increasing pyrolysis heating rates produce chars with higher observable reaction rates in the diffusion-limited regime and with lower ignition temperatures. Since the heating rates did not affect reaction rates at the kinetic control regime we can certainly assume that the intrinsic reactivity was not affected. The reason the caused the difference in reactivities at the diffusion-limited regime must be the macropore structure. It seems that the chars prepared at higher heating rates have a more open macropore structure that allows for higher reaction rates at high temperatures. The exact explanation will be given in the following section.

5.4. Effect of pyrolysis on combustion

The results presented in the two previous Chapters need interpretation. The explanation of the effect of pyrolysis on reactivity will allow us to determine the optimal pyrolysis treatment to produce the most reactive chars.
Our experimental results agree in principle with the theoretical predictions mentioned earlier (Sotirchos and Amundson 1984; Sotirchos, Srinivas et al. 1984). Sotirchos and Amundson predicted that when the ambient temperature exceeds a threshold value then ignition occurs. The ignition temperature is lower when Knudsen diffusion in the macropores is less dominant. That is, when the average macropore size of the particle is higher then the diffusional limitations are lower and the ignition temperature is also lower.

This approach can be used to explain the difference in reactivity at high temperatures of the chars treated at various heating rates. The differences we observe can be attributed to the following factors:

(a) The use of low heat treatment temperatures and short soak times during the pyrolysis stage lead to the production of chars with high intrinsic reactivity. These conditions produce chars with higher reactivity at all temperature regimes. They also cause lowering of char ignition temperature. Thus, chars may exhibit observable reaction rates as much as 10 times larger than in the case of no ignition. In other words, chars produced at milder combustion conditions are more reactive.

(b) The structural changes occurring during the pyrolysis stage due to particle softening and swelling can lead to chars that have a highly cellular pore structure when the heating rate is relatively high. As mentioned earlier, the average macropore size, particle size, porosity and macropore specific surface area are all monotonically increasing with the pyrolysis heating rate. Therefore, a more open and more accessible macropore network would significantly decrease the diffusional limitations in the macropores and also increase the available macropore surface for reaction. The decrease of intraparticle diffusional limitations makes the internal surface more accessible to the gaseous reactants. Thus, their concentration is higher inside the particle and consequently the reaction rate is enhanced.
(c) The ignition temperature will be lower for chars with lower macropore diffusional limitations (or else treated at higher heating rates). This is apparent in Figure 5.8a where only 1, 10 and 20 °C/s treated chars have significant ignition phenomena. On the other hand, the ignition temperature for the 0.1 and 0.3 °C/s chars is higher than 600 °C and that is why they don't ignite. The increased temperature of the ignited particles induces a much higher reaction rate that is detectable by a sharp peak in the reactivity curves.

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

5.5. Kinetic measurements

The reactivity measurements in a whole range of combustion temperatures can be used to determine kinetic parameters of coal combustion. These can be activation energy, preexponential rate factor and effectiveness factor.

There is an easy way to determine the activation energy. If we know the reaction rate at a specific conversion $x$ and the temperature we can make an Arrhenius plot. The curve should be a straight line in the kinetic control regime and its slope can help calculate the activation energy. A problem with using the instantaneous reaction rate is that it has more
variation, since the rate curves exhibit small peaks probably attributed to structural
inhomogeneities. On the other side, if we use average reaction rates up to a specific
conversion, these will be statistically more significant. The average reaction rate can be
obtained as following:
\[
\bar{r}_{x_0} = - \frac{1}{t_0} \int_0^{t_0} \frac{1}{m_0} \frac{dm}{dt} \, dt = \frac{1}{t_0} \frac{m_0 - m_{t_0}}{m_0} = \frac{x_0}{t_0}
\] (5.1)
where: \( x_0 \) is the reference conversion
\( t_0 \) is the time to achieve this conversion \( x_0 \)
\( m_0 \) is the initial mass of the solid in ash-free basis
\( m_{t_0} \) is the unreacted mass at conversion \( x_0 \)

Therefore it is only sufficient to know the burn-off time at a specific conversion to
determine the average reaction rate from the onset of reaction up to this conversion. In
Figure 5.9 we see an Arrhenius plot of the average reaction rate with reference conversions
10\%, 25\% and 50\%. The combustion temperatures used are 400, 420, 430 and 450 °C.
The curves are very well fitted by a straight line. The correlation coefficients were 0.9991,
0.9998 and 0.9973. This linearity confirms our claims that this temperature range belongs
to the kinetic control regime. The slope of the three curves was very similar giving the
following values of the activation energy: 32.6, 32.6 and 31.4 Kcal/mol. Since the average
rate is more reliable at the early stages of reaction where the error is smaller and the
reactivity patterns more similar it is reasonable to accept the two identical values of 32.6
Kcal/mol as activation energy.
Figure 5.9: Arrhenius plot for the kinetic control regime 400-450 C for Illinois #6 chars (HTT: 700 C; soak time: 3 minutes).

Figure 5.10: Arrhenius plot for the entire temperature range (400-600 C) for Illinois #6 chars (HTT: 700 C; soak time: 3 min). Reference conversion is 10%.
Figure 5.11: Arrhenius plot for the entire temperature range (400-600 °C) for Illinois #6 chars (HTT: 700 °C; soak time: 3 min). Reference conversion is 25%.

Figure 5.12: Arrhenius plot for the entire temperature range (400-600 °C) for Illinois #6 chars (HTT: 700 °C; soak time: 3 min). Reference conversion is 50%.
The preexponential factors are different for each reference conversion. This is expected since the reaction rate changes with conversion. Their values are $1.742 \times 10^8$, $2.536 \times 10^8$, $1.440 \times 10^8$ min\(^{-1}\) for reference conversions 10\%, 25\% and 50\% respectively. Actually, this preexponential factor includes the intrinsic reaction kinetics (kinetic constant and order of reaction), the concentration of active sites and the specific surface area. Since none of these quantities is easily measurable, we cannot draw any further conclusion from the value of the preexponential factor.

In Figures 5.13 through 5.15 we see the effectiveness factors as a function of combustion temperature for chars treated with three different heating rates. They were calculated as the ratio of the observed rate over the expected rate (according to the kinetic parameters obtained earlier).

The three different figures are made for three different reference conversions (10\%, 25\% and 50\%). We can clearly see that the chars treated with 10 °C/s have effectiveness factors larger than unity at 500 °C (1.2-1.3). This is due to the external temperature gradients. Although the reactivity patterns at 500 °C did not exhibit any sharp peaks, the results suggest that the particles were reacting at temperatures larger than the ambient. The visual observations did not suggest any ignition phenomena either. Thus, the particles react in a regime of moderate temperature gradients (first steady state). From the figures we can see also that the chars treated at lower heating rates are more diffusionaly limited since they have lower effectiveness factors.

Another observation is that the effectiveness factor at high temperatures (600 °C) increases as the conversion increases, while this does not happen at lower temperatures (500 °C). The reason of the increase of the effectiveness factor with conversion is the enlargement of the macropores that decreases their diffusional resistances and increases their accessibility. In other words, the progressive growth of the macropores reveals more surface area to the gaseous reactants that was previously closed and inaccessible.
Figure 5.13: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 C; soak time: 3 minutes). Reference conversion 10%.

Figure 5.14: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 C; soak time: 3 minutes; Reference conversion 25%).
Figure 5.15: Effectiveness factor as a function of temperature for three different Illinois #6 chars (HTT: 700 C; soak time: 3 minutes; Reference conversion 50%).

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

5.6. Statistical significance of our results

We should note that not all the particles in the same sample behave the same. Their slightly different pore structures, ash content and particle size produce a slightly different
behavior for each one under the same conditions. For example, not all particles treated at 20 °C/s ignite as seen in Figure 5.8a. Only two of them ignited and the others did not show any light emission. This is caused by the fact that ignition is a runaway phenomenon that is caused by whether the ambient temperature exceeds or not the ignition temperature. Therefore, the particles in the batch that have ignition temperature slightly lower than 600 °C will ignite, while the others will not (even though their ignition temperature may be 605 °C). But even then, the non-ignited particles still contribute to a reaction rate that is larger than that of the chars treated with lower heating rates. In other words, even in the non-ignited portions of the experiment the total reactivity is larger for the chars treated with higher heating rates. Besides, the repetition of the combustion experiment showed that consistently there is a small number of particles igniting every time. In the overall, burn-off times for different runs were very similar due to the averaging of the rates of the eight particles in each run. This is showing that there is statistical significance in our results even with three performed runs because the number of particles examined then is 24. The statistical analysis of the burn-off times was performed with the usual t-test. The standard deviation of the experimental measurements was found and the error margin was calculated using the t-coefficient from the T distribution. Our calculations showed that the error achieved in three runs is about 25-30 % with 95% level of confidence.
CHAPTER 6

EFFECT OF PARTICLE SIZE ON REACTIVITY

6.1. Effect of size on intrinsic reactivity

In this Chapter we investigate the effect of initial particle size on the reactivity patterns. Our analysis included reactivity experiments with particles in the range 250-841 μm. Three size fractions were used: 20-25 mesh (707-841 μm), 28-32 mesh (500-595 μm) and 50-60 mesh (250-300 μm). We reacted those particles in both the kinetic control regime and the diffusion limited regime to determine the effect of particle size on the reactivity or burn-off times. In all cases, we used the 28-32 mesh fraction as point of reference for reactivity measurements since most of our experiments were performed with this particle size. Unfortunately, the direct comparison between the smallest (50-60 mesh) and the largest (20-25 mesh) sizes is not possible with our experiments. This is because the pyrolysis conditions that we used for these two sizes were different.

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

Combustion at 550 °C
HTT 700 °C, soak 3 min
Heat. rate 10 °C/s

Figure 6.1: Reaction rate measurements for Illinois #6 chars of two different sizes (28-32 mesh and 20-25 mesh) at combustion temperatures of: a) 450 °C and b) 550 °C (HTT: 700 °C; Soak time: 3 min; Heating rate: 10 °C/s).
The same comparison was made between the smallest particles (50-60 mesh) and the intermediate size particles (28-32 mesh). Figure 6.2a shows the average burn-off times as a function of the heating rate for three reference conversions of 25%, 50% and 75% at the combustion temperature of 420 °C. As we can see, there is no significant deviation of average burn-off times among different heating rates or particle sizes (as far as the kinetic control regime is concerned).

6.2. Effect on ignition temperature

At the combustion temperature of 550 °C the 20-25 mesh particles exhibit a dramatic difference from the 28-32 mesh. The larger particles are reacting at rates that are twice or three times as high as the rates of the 28-32 mesh particles (Figure 6.1b). This is counter-intuitive, since we would expect that the larger particles would react slower in the presence of diffusional limitations. The phenomenon is solely attributed to thermal effects. The rate enhancement is due to the ignition of one of the two large particles that were loaded in the sample pan (the ignition covers the range of 0-50%). This ignition occurred in repeated experimental runs and it is not a pure coincidence. After the ignition though, the other large particle reacted with a rate lower than the rate of the smaller particles. Here is where the diffusional limitations determine the reaction rate.

The above observations are in agreement with experimental and theoretical results like the ones presented by Sotirchos and Amundson. They predicted that the ignition temperature decreases with increasing particle size (the large particles have lower external surface to volume ratio). It seems that one of the 20-25 mesh particles had ignition temperature lower than 550 °C, while all the 28-32 mesh particles had ignition temperature higher than 550 °C.
Figure 6.2: Effect of size and heating rate on burn-off times of Illinois #6 chars at 420 °C. Dashed line: 28-32 mesh; solid line: 50-60 mesh. (HTT = 500 °C; Soak time = 3 min)
6.3. Effect of size on macropore structure

The effect of particle size on the development of macropore structure during pyrolysis was discussed earlier in Chapter 3. We have mentioned that the smaller particles have higher macropore specific surface areas although they have the same macroporosity with the larger ones (Zygourakis and Glass 1988). Their diffusional resistances will be lower than the resistances of the larger particles at the same temperature (the Thiele modulus is proportional to the particle size).

This part of our analysis involved the comparison of the reference particle size of 28-32 mesh with the 50-60 mesh size which is 2 times smaller (500-595 μm with 250-300 μm).

The devolatilization patterns are identical for all particle sizes as mentioned previously. Therefore, they should not affect the development of macropore structure. The resistance to diffusion of the volatile gas, though, is larger for the larger particles. Therefore we could expect that the larger particles will have higher pressure build-up and consequently higher swelling index. This is consistent with the macroscopic measurements obtained by Boissiere and Zygourakis & Glass for both sizes. Indeed, the larger fraction has a slightly higher swelling index. For instance the ratio of sizes between 10 °C/s and 1 °C/s treated chars at 700 °C was 1.25 for the 28-32 mesh fraction (see Table 4) while the same ratio for the 50-60 mesh (treated at 1000 °C) was 1.14. This observation suggests that the larger particles have a stronger dependence of their macropore structure on the heating rate than the smaller ones. This will be shown in the next paragraphs.
6.4. Reactivity dependence on heating rate-The role of particle size

The effect of heating rate on reactivity is examined for the 20-25 and 50-60 mesh sizes. Figures 6.3a,b show the reaction rates and burn-off times of large particles in the diffusion limited regime (550 °C) for the large fraction of 20-25 mesh. As we see, the same conclusion can be drawn on how the heating rate influences reactivity as in Chapter 5. For the large particles we see again that the increasing heating rates make the particles more reactive. The additional observation we can do is that the difference of reactivities between 0.1 and 10 °C/s is larger for the larger particles. In other words, if we compare the ratio of reactivities between the 0.10 and 10 °C/s we will notice that this ratio is larger for the large particles. The difference of ratios can be attributed to the following three reasons:

i) Lowering of the ignition temperature for the large particles and thus higher external temperature gradients.

ii) Increase of the diffusional resistances in the large particles makes the macropore structure more important. Thus, variations in the macropore structure will be become more important for the reactivity of the large particles.

iii) Particle swelling index is larger for the large particles (see previous section). Thus, the larger particles will be more affected by the heating rates.

The effect of the heating rate on reactivity was further investigated for the smaller particles of 50-60 mesh. There the differences are more subtle. First, in Figure 6.4a we see the ratio of burn-off times at 500 °C for different heating rates, using the 20 °C/s treated chars as reference. We see a difference of a factor of 1.5-2 in burn-off times between the 0.1 °C/s and 20 °C/s chars.

Our conclusion is that the heating rate does not affect macropore structure and reactivity as much in the smaller particles as it does in the large ones.
Figure 6.3: Effect of heating rate on reactivity and burn-off times of Illinois #6 chars of size 20-25 mesh at 550 °C (HTT: 700 °C; Soak time: 3 min).
Figure 6.4: Effect of heating rate on reactivity and burn-off times of Illinois #6 chars of size 50-60 mesh at 500 °C. Small: 50-60 mesh; Large: 28-32 mesh. (HTT: 500 °C; Soak time: 3 min).
By comparing also the burn-off times of the small and the large particles at 500 °C we get the following Figure 6.4b. We see that the burn-off times of the 28-32 mesh and the 50-60 mesh fractions are almost the same, except for the chars treated at 10 °C/s. The difference is close to the error margin, however it is systematic in all three reference conversions.

The difference can be attributed to the ignition behavior of the chars at this temperature. As we see in Figure 6.5a, all three runs performed with 50-60 mesh particles at 500 °C exhibited ignition phenomena. On the other side, in Figure 6.5b we see that the 28-32 mesh particles do not show any ignitions in either of the two runs! This deviation may be created by a difference in the macropore specific surface areas or the macropore resistance to diffusion. This can be a reason of decrease in the ignition temperature. As seen in Table 4 of Chapter 3, the 1 °C/s and 10 °C/s treated chars have similar particle sizes. This suggests that they have similar macropore structures and they do not ignite. This may not be the case for the smaller particles of 50-60 mesh. It may be that the transition from 1 to 10 °C/s at this size is more important.

It is interesting to mention that the chars produced at the heating rate of 20 °C/s exhibit similar reactivities for both sizes. However, the reaction patterns suggest that the smaller particles exhibit ignition phenomena (in two of the three runs) while the larger ones did not (at none of the two runs). This fact though, does not exclude the possibility that the large particles are reacting at temperatures larger than the ambient. Temperature gradients were found to appear at the chars treated at 700 °C when reacted at 500 °C (see section 5.2). One way to investigate the internal thermal gradients is to find the effectiveness factors. By knowing the burn-off times at 420 °C and calculating the activation energy for the 500 °C treated chars (close to 32.6 kcal/mol as for the 700 °C treated chars) we can calculate the expected burn-off times at 500 °C. The ratio of the expected over the observed times is the inverse of the effectiveness factors (note that we refer to an average effectiveness factor.
over a range of conversion). Figure 6.6 shows the effectiveness factors of chars for two sizes and three heating rates during combustion at 500 °C. The dependence of effectiveness factor on conversion shows two different patterns. One is increasing, as it is expected since the opening of the macropores facilitates the diffusion of gases. The second is decreasing and is contrary to the previous argument. It can be due though, to the moderate temperature gradients or ignition of the particles at the early stages of the reaction (low conversion). Later, the thermal gradients are eliminated because of the decrease of reactive surface area and the drop of the reactivity.

Thus, the shape of the curves might suggest which mechanism is dominant:

1) Increasing effectiveness factors imply diffusion control
2) Decreasing effectiveness factors imply external heat transfer control

Figure 6.6 indicates also that, indeed, the 20 °C/s chars of 28-32 mesh size have also temperature gradients since their effectiveness factor decreases with conversion. Therefore, we can justify their increased reactivity, even in the absence of visible ignitions.

It is interesting also to compare the effectiveness factors of chars of 28-32 mesh when treated at HTT of 500 °C or 700 °C. By looking at Figures 5.13-5.15 and 6.6 we realize that the 700 °C treated chars have higher effectiveness factors. This suggests that they have a more open macropore network and also they have higher temperature gradients. This agrees with the structural measurements presented in Table 4. The chars treated at 700 °C have higher average particle size and possibly higher macropore size.
Figure 6.5: Effect of particle size on the ignition behavior of Illinois #6 chars at 500 °C (HTT: 500 °C; Soak time: 3 min; Heating rate: 10 °C/s).
Figure 6.6: Effectiveness factors of Illinois #6 chars at 500 °C, as a function of particle size and heating rate (HTT: 500 °C; Soak time: 3 min; large: 28-32 mesh; small: 50-60 mesh).

As a conclusion, we believe that the difference in reactivities and heat transport behavior among different particle sizes is important but also complicated. Experimental findings have demonstrated that the ash and sulfur content and the specific surface area of coals vary with the particle size (for sizes less than 1 mm) (Palmer, 1990). This variation although not very significant may complicate our analysis. More detailed investigation is needed through the measurements of surface area and macropore size for different size fractions.
CHAPTER 7

PYROLYSIS IN THE PRESENCE OF OXYGEN - IMPLICATIONS ON REACTIVITY

The effect of the presence of oxygen during pyrolysis on char macropore structure and reactivity is a very important issue. Since most industrial applications perform the stages of pyrolysis and gasification simultaneously, it is necessary to explore the role of oxygen during pyrolysis.

The macroscopic observations and macropore structure measurements of the chars pyrolyzed in oxygen were presented in Chapter 3. Here we present the reactivity measurements and try to correlate them with those of the macropore structure.

We pyrolyzed coal particles of the 28-32 mesh size fraction in a pyrolytic atmosphere of 95% nitrogen and 5% oxygen or pure nitrogen. The particles were later combusted with a 33% oxygen/67% nitrogen mixture. Their reactivity was measured first in the kinetic control regime (420 and 450 °C). Figures 7.1 and 7.2 are illustrating the reaction rate and burn-off times of these chars as a function of conversion. As we see, the effect of pyrolysis heating rate on the reactivity at 420 °C and 450 °C is again confirmed to be minimal. Besides, the chars pyrolyzed in inert and reactive atmospheres have the same levels of reactivity and burn-off times.
Figure 7.1: Effect of heating rate and oxygen during pyrolysis on the reactivity and burn-off times of Illinois #6 chars of size 28-32 mesh at 420 °C (HTT: 500 °C; Soak time: 3 min).
Figure 7.2: Effect of heating rate and oxygen during pyrolysis on the reactivity and burn-off times of Illinois #6 chars of size 28-32 mesh at 450 °C (HTT: 500 °C; Soak time: 3 min).
From these results we can draw the following conclusions:

(1) Pyrolysis heating rates have minimal influence on reactivity patterns and burn-off times when the chars are reacted in the kinetic control regime (same as in earlier sections).

(2) The presence of oxygen during pyrolysis does not influence the reactivity when the char is reacted at 420 and 450 ºC.

These results strongly indicate that all chars produced in these runs had similar values of reactive surface areas and concentration of active sites. Moreover, the reactive surface areas of all these chars followed similar temporal evolution patterns during combustion in the kinetic control regime. This also suggests that the micropore structure has not been altered by the reaction with oxygen during pyrolysis.

The reactivity of chars at 500 ºC is shown in Figures 7.3 and 7.4. We see that chars produced under different pyrolysis atmospheres exhibit different reactivity patterns when reacted with 33% O₂ at 500 ºC. Figure 7.3 shows smooth reactivity patterns for the chars produced in an inert (nitrogen) pyrolysis atmosphere. Furthermore, the reactivity does not change as we go from 1 ºC/s to 10 ºC/s treated chars. This is compatible with the similar sizes of both chars as seen in Table 4 of Chapter 3 and explained in the previous Chapter. The reactivity changes slightly when moving from 10 to 20 ºC/s treated chars. The 20 ºC/s treated chars were the only ones that showed signs of temperature gradients (Figure 6.7).

As seen in Figure 7.4, the particles pyrolyzed in a reactive atmosphere (5% oxygen) and high heating rates (10 or 20 ºC/s) exhibit reactivity patterns with sharp maxima caused by particle ignitions. Our video sequences verified the occurrence of those ignitions, although the bright flames we observed in earlier experiments were not present. In their place, we observed a sudden and rapid consumption of the particle exterior resulting in
changes of surface roughness and color, as the carbon was quickly gasified leaving behind it an ash structure. Chars produced at lower heating rates (1 °C/s), on the other hand, did not exhibit ignitions.

The reason we did not observe bright flames during these particle ignitions, may be due to the fact that this series of experiments was performed at 500 °C. This temperature is 100 °C lower than the one we used (600 °C) when we observed bright flames during particle ignition. When we combust chars at 600 °C, the ignited particles can easily reach the temperature levels where they can emit radiation in the visible range (around 650 to 700 °C for most black objects). On the other hand, particles reacting at 500 °C ambient temperature must develop temperature gradients of more than 150 °C before they can emit visible radiation. Using the previously calculated value of 32.6 kcal/mol for the apparent activation energy, we estimate that the particle temperature must rise from 500 °C to 595 °C in order to observe a 10-fold increase in reaction rate due to thermal ignition. If we want to account for diffusional limitations in the micropores, then the temperature increase caused by particle ignition must be larger. Assuming the asymptotic value of E/2 for strong diffusional limitations in the micropores, the ignition must raise the particle temperature from 500 to 710 °C in order to observe a 10-fold increase in reaction rates. Even in this extreme case, we are still at the lower end of the temperature range where ignited particles should emit visible light.
Figure 7.3: Effect of heating rate on the reactivity and burn-off times of Illinois #6 chars of size 28-32 mesh at 500 °C (HTT: 500 °C; Soak time: 3 min; Gas: Nitrogen).
Figure 7.4: Effect of heating rate on the reactivity and burn-off times of Illinois #6 chars of size 28-32 mesh at 500 °C (HTT: 500 °C; Soak time: 3 min; Gas: 5% O₂/95% N₂).
Figures 7.4, 7.5 and 7.6 help us draw the following conclusions:

(1) The presence of oxygen during pyrolysis is not influencing the reactivity of chars in the diffusion limited regime if they are treated at low heating rates of 1 \(^\circ\)C/s (Figure 7.5a).

(2) The presence of oxygen during pyrolysis is increasing the reactivity of chars in the diffusion limited regime, if they are treated with high heating rates of 10 and 20 \(^\circ\)C/s (Figure 7.5b).

(3) The increase in reactivity obtained by adding 5% oxygen to the pyrolysis atmosphere is larger by about a factor of 2 than the increase obtained when we raise the pyrolysis heating rate from 10 to 20 \(^\circ\)C/s (Figure 7.4b).

(4) The effectiveness factors of the chars prepared in oxygen atmosphere is larger than unity for the heating rates of 10 to 20 \(^\circ\)C/s (Figure 7.6). This shows clearly extraparticle temperature gradients. Char treated at 20 \(^\circ\)C/s reach effectiveness factors of 3, e.g. they react 3 times as fast as if they were isothermal and without diffusional limitations! This result is very important because it shows the benefit of using oxygen in pyrolysis.

We did not react these char samples at temperatures higher than 500 \(^\circ\)C, since we did not want to exceed the pyrolysis heat treatment temperature of 500 \(^\circ\)C, above which new pyrolysis reactions would be initiated.

The video images obtained from pyrolysis experiments in the presence of oxygen and the structural measurements gave strong indications on why the chars produced under these conditions are more reactive in the diffusion limited regime. Particles pyrolyzing in reactive atmospheres result in an average size which is by 10-15% larger than the one of the particles produced in nitrogen atmospheres.
Figure 7.5: Effect of heating rates and oxygen on the burn-off times of Illinois #6 chars of size 28-32 mesh at 500 °C (HTT: 500 °C; Soak time: 3 min).
Figure 7.6: Effectiveness factors of Illinois #6 chars of size 28-32 mesh at 500 °C as a function of heating rate (HTT: 500 °C; Soak time: 3 min; Gas: 5% O₂/95% N₂).

This observation was presented in Chapter 3. It is evident that the chars treated with oxygen have a higher macropore size, macroporosity and macropore specific surface area. For all the reasons mentioned earlier in Chapter 5 they will react faster than the chars produced in nitrogen.

We should emphasize that all the previously mentioned results are not due to partial reaction of the char with oxygen during the pyrolysis stage as proven in earlier Chapters.
CHAPTER 8

A CELLULAR AUTOMATON MODEL FOR SIMULATING REACTION OF POROUS SOLIDS IN THE DIFFUSION-LIMITED REGIME

8.1. Model Development

8.1.1. General description

We developed a discrete model to simulate the reaction of coal or other solids with complex pore structure in the diffusion-limited regime. Coal is a reactive solid with a complex micro- and macropore structure. The macropore structure has an important effect on reactivity during reaction in the diffusion limited regime. This model accounts for the effect of this structure on char reactivity during gasification. Since the pyrolysis heating rates and atmosphere affect significantly the macropore structure of chars, it is necessary to know how chars produced at different pyrolysis conditions react in the diffusion-limited regime.

The model can handle different extents of diffusional limitations by using different penetration lengths of the gas into the solid. Moreover, it models diffusional limitations by considering the closed pores as inactive. It also considers the presence of ash inerts in the solid, in the form of inorganic minerals and it investigates their role in the availability of reactive surface area. Finally, we analyze the fragmentation phenomena by measuring the number and size distribution of fragments at each reaction step.
8.1.2. **Cell states**

Simulations are carried out in two- and three-dimensional cellular arrays (or lattices) consisting of square or cubic cells respectively. In three-dimensional arrays, each cell represents a small volume element containing either microporous solid reactant, inert solid (ash) or gaseous reactants. We can thus distinguish the type of a cell $c_i$ by assigning to it a unique integer number or state $s_i$ corresponding to reacting solid, inert solid or gas.

![Diagram showing solid and gas cells](image)

**Figure 8.1:** Part of a three-dimensional simulation grid showing solid reactant and open pore cells. The different shadings of solid cells may indicate different conversions.
To model heterogeneous gas/solid reactions, the state of solid cells must be changed to reflect the conversion of the solid to gaseous products. In our simulations, the cell states are updated at equally spaced time instants $t^1, t^2, ..., t^r, t^{r+1}, ...$ (where $t^r = t^{r-1} + \Delta t$) as follows: If at time $t^r$ a solid reactant cell is adjacent to one or more gas cells, then part of the reactant in the solid cell will be gasified at the next time level $t^{r+1} = t^r + \Delta t$.

Since our discrete model allows for partially reacted solid cells, the state $s_i$ of a solid cell must be related to its conversion $x_i$, where $x_i$ ranges from 0.0 (for unreacted cells) to 1.0 (for completely gasified cells). Thus, the state of a cell containing solid reactant can take the following integer values.
1) A cell containing **unreacted solid** is assigned a state value

\[ s_i = 16 \]

2) The state \( s_j \) of a cell containing **partially reacted solid** is an integer given by the following equation

\[ s_j = 16 + 223 \times x_j \quad (8.1) \]

where \( x_j \) is the conversion of this cell. Since \( 0 < x_j < 1 \), the states of partially reacted cells take integer values ranging from 17 to 238.

3) A **completely reacted solid cell** (or, equivalently, a cell occupied by gaseous reactants) is assigned a state value

\[ s_k = 239 \]

To account for closed porosity, that is for pores that are not initially accessible to the gaseous reactants, the model distinguishes two types of gas cells:

i) Cells that belong to **open pores** (i.e. pores connected to the particle exterior). These cells contain reactant gases and are assigned a state value of 239.

ii) Cells that belong to **closed pores** (i.e. pores inaccessible to the gaseous reactants). All cells belonging to closed pores are assigned a state value equal to 15 and they remain at this state until the closed pores open due to the chemical reaction. When a cluster of closed pore cells gets exposed to a reacting gas cell, the state of the cluster cells is reset from 15 to 239.

Finally, the model accounts for the presence of inert solid (ash) regions by assigning to the corresponding clusters of cells a state value of 14. These cells remain this inert state throughout the gasification process.
In summary, our discrete model distinguishes the following types of cells.

i) **Open pore cells** \((s = 239)\).

ii) **Partially reacted solid cells** \((17 \leq s \leq 238)\)

iii) **Unreacted solid cells** (\(s = 16\)).

iv) **Closed pore cells** \((s = 15)\).

iv) **Solid inert or ash cells** \((s = 14)\).

8.1.3. **Initial Simulation Grids**

The initial simulation grids model the **macropore structure** of porous chars studied in our laboratory. For two-dimensional simulations, the initial computation grids are directly obtained from digital images of actual particle cross sections. Realistic grids for three-dimensional simulations are generated using measurable structural quantities like macroporosity, macropore specific surface area and macropore size distribution.

We generate the initial three-dimensional grids by randomly distributing overlapping spheres in a cubic lattice. Stereological measurements provide the size distribution of the spherical macropores that is characterized by the following probability density functions:

\[
\begin{align*}
n(r) \, dr &= \text{number fraction of spherical pores with diameters in the range } [r, r+dr]. \\
v(r) \, dr &= \text{volume fraction of spherical pores with diameters in the range } [r, r+dr].
\end{align*}
\]

Macropores larger than 100 \(\mu\text{m}\) in diameter must be treated very carefully. Although a char particle may contain only a few of these large pores, they account for as much of 60% of the total macroporosity. These large pores must be distributed in such a way as to avoid
significant overlapping that will lead to the creation of even larger pores. This is accomplished by the following procedure.

1) We determine the appropriate number of large pores (>100 microns) needed to achieve the fraction of macroporosity attributed to this class of pores. This selection is done by randomly choosing values from the number average cumulative distribution of pore volume.

2) We sort the large pores in order of decreasing size and position them on the grid one at a time starting with the largest one.

3) After the position of each pore is randomly selected, we check to make sure that the pore does not touch the particle exterior and does not overlap with other previously positioned pores by more than 5%. If this is not true, a new position for this pore is selected. After 20 unsuccessful attempts to position a pore, the overlapping tolerance level is increased by 10% and the procedure is repeated. In most cases, 20-40 iterations are sufficient and the pores preserve their integrity with maximum 25% overlapping.

We follow a similar procedure to randomly distribute on the grid the small pores (diameter < 100 microns). Pore sizes are now chosen in random to ensure that the pores positioned on the grid follow the measured size distribution. **We start with 10% tolerance and continue searching for a location for the pores. The tolerance increases by 10% after every 20 unsuccessful steps.** This procedure is repeated until we reach the desired level of total macroporosity.

Finally, the ash inclusions are distributed on the grid as spheres of uniform size until the desired ash content is achieved. Ash cells can only replace solid reactant cells and not gas cells. The same iterative procedure as before is used for positioning the ash inclusions with initial overlapping tolerance of 20%.
8.1.4. Assignment of closed pores

After distributing the pores and ash inclusions, the initial computational grid is analyzed to identify the open and closed pores.

1) All pores are initially considered to be closed.

2) We first identify the pores that are directly open to the exterior. For these pores, the distance from their center to the grid boundaries is smaller than the pore radius. The cells of all these pores are set to a state equal to 239.

3) We then find the pores that intersect with the open pores identified in the previous step. A pore with radius $R_i$ and center coordinates $(x_i, y_i, z_i)$ will be open if there exists an open pore with radius $R_0$ and center coordinates $(x_0, y_0, z_0)$ such that

$$\sqrt{(x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2} \leq R_i + R_0$$

(8.2)

4) Step (4) is repeated until the accessibility of all pores is determined. All pores that are not connected to open pores remain identified as closed pores for our simulations.

8.1.5. Gas-solid reaction rules

The rules of our cellular automaton are chosen so that the simulations model heterogeneous reaction occurring at the gas-solid interface.

The open pore cells preserve their state throughout the reaction and serve only in defining the solid-gas interface. They have uniform gas concentration that is equal to the bulk concentration of the gaseous reactant. Macropore diffusional resistances are thus considered to be negligible (at least compared to the micropore diffusional resistances).
The ash cells preserve their state throughout the reaction and do not participate in it. Their only effect is to block surface area of the solid-gas interface.

Solid reactant cells exposed to one or more cells containing gaseous reactants will undergo a heterogeneous reaction. Our earlier discrete models assumed that reaction occurred only at the solid-gas interface. Thus, these models assume very strong diffusional limitations in the micropores emanating from the macropores.

In the regime of intermediate diffusional limitations in the micropores, the gas reactant penetrates the microporous solid phase forming a reaction zone. This zone has a constant depth below the macropore surface area and the gas concentration drops to zero beyond this layer (Figure 8.3).

The thickness of this reaction zone and the gas concentration profile may be estimated from the analytical solution of the diffusion-reaction problem in a reactive porous sphere or a porous solid with one spherical macropore. The mass balance equations for this problem are (Froment and Bischoff 1979):

\[
\frac{\partial (\varepsilon_s C_A)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( D_e r^2 \frac{\partial C_A}{\partial r} \right) - \rho_s r_A \tag{8.3}
\]

\[
\frac{\partial C_s}{\partial t} = - \rho_s r_s \tag{8.4}
\]

where: \( \varepsilon_s \) is the porosity of the solid;
\( C_A \) is the gas concentration;
\( C_s \) is the solid concentration;
\( D_e \) is the effective diffusivity in the solid;
\( r_A \) and \( r_s \) are the gas and solid reaction rates; and
\( \rho_s \) is the density of the solid
Figure 8.3: An open macropore in a microporous solid reactant and the reaction zone around it.

The solution of the above equation can be obtained by making the pseudo-steady state approximation. We also assume first order reaction with respect to the gas and zero w.r.t. the solid.

\[ r_a \rho_s = \alpha r_s \rho_s = \alpha k' c_{s0} c_{as} \]  \hspace{1cm} (8.5)

where:  
- \( a \) is the number of moles of A reacting with one mole of S
- \( k' \) is the rate constant in the kinetic expression
The effective diffusivity is also assumed constant and independent of porosity.

Under those assumptions the solution depends on the domain geometry and therefore on the boundary conditions. For a porous sphere the boundary conditions are:

\[
\frac{\partial c_s}{\partial r} = 0 \quad @ \quad r=0 \quad \& \quad c_{as} = c_{as0} \quad @ \quad r=R
\]  

(8.6)

and the solution to the problem is given by:

\[
\frac{c_{as}}{c_a} = \frac{1}{\xi} \frac{\sinh(\phi \xi)}{\sinh \phi} \\
\frac{c_{s}}{c_{s0}} = 1 - \frac{\Theta}{\xi} \frac{\sinh(\phi \xi)}{\sinh \phi}
\]

(8.7ab)

with:

\[
\xi = \frac{r}{R}, \quad \Theta = \alpha k' c_{as0} t \\
\phi = R \sqrt{\frac{\alpha k' c_{s0}}{D_e}}
\]

(8.8ab)

where: \(c_{as0}\) and \(c_{s0}\) are the initial gas and solid concentrations

\(x\) is the dimensionless distance

\(\theta\) is the dimensionless time (at \(\theta=1\) the solid starts shrinking)

For a porous solid with one spherical macropore the boundary conditions are:

\[
\frac{\partial c_s}{\partial r} = 0 \quad @ \quad r=+\infty \quad \& \quad c_{as} = c_{as0} \quad @ \quad r=R
\]  

(8.9)

and the solution to the problem is given by:
\[
\frac{c_{as}}{c_{a}} = \frac{1}{\xi} \exp[-\phi(\xi-1)] \\
\frac{c_{s}}{c_{so}} = 1 - \frac{\Theta}{\xi} \exp[-\phi(\xi-1)]
\] (8.10ab)

The reaction-diffusion process is performed in two stages. The first stage lasts until the solid concentration takes zero value at the surface of the particle. The second stage involves the shrinkage of the porous sphere or the growth of the spherical pore.

Both of the solutions above are describing the first stage. The gas concentration is time independent at this stage because the effective diffusivity is assumed constant. This means that until the interface starts receding (\(\Theta=1\)) the reaction rate is constant. When \(\Theta=1\) the solid conversion profile has reached its final shape. We can observe from (8.10) that for \(\Theta=1\) the gas concentration and solid conversion profiles are equal:

\[
\frac{c_{as}}{c_{a}} = 1 - \frac{c_{s}}{c_{so}} = x_s
\] (8.11)

where: \(x_s\) is the solid conversion

This implies that if we know the solid conversion at each cell at \(\Theta=1\), we can also determine the gas concentration at that cell!

In both cases and for high values of the Thiele modulus the gas concentration drops to virtually zero very close to the interface. In our approach, we assume the penetration length \(L\) is equal to the distance from the interface that the gas concentration drops to 1% of the bulk. For the above two cases the ratio of this length \(L\) to the radius of the sphere \(R\) takes the following values depending on the Thiele modulus:
Table 5:
Values of the dimensionless penetration length (L/R) for various extends of diffusional limitations.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>porous sphere</td>
<td>complete penetration</td>
<td>0.537</td>
<td>0.244</td>
<td>0.118</td>
</tr>
<tr>
<td>spherical pore</td>
<td>0.803</td>
<td>0.425</td>
<td>0.220</td>
<td>0.112</td>
</tr>
</tbody>
</table>

The gas concentration profile within the penetration layer is shown in Figure 8.4. It is obvious that it has exactly the same shape for both geometries.

One observation we can make from this Table 5 is that there is a quasi inverse linear relation between the penetration ratio and the Thiele modulus. This can be seen in Figure 8.5 where L/R is plotted as function of 1/\(\phi\). The relation is almost linear. The correlation coefficient is 0.9996. This means that for high values of \(\phi\) we have:

\[
\frac{L}{R} = \frac{K}{\phi} = \frac{K'}{R} \Rightarrow L \approx K'
\]  

(8.12)

This means that the penetration thickness is constant and independent of the value of R. The penetration length is almost constant at high values of \(\phi\). Actually, we can prove that for the slab geometry the penetration thickness is exactly constant and is dependent only on the kinetic constant and the diffusivity. This enables us to find the gas and solid concentration profiles during the second stage. In principle, the solution of the second stage is determined by using the above equations for a new value of R and \(\theta=1\).
Figure 8.4: Comparison of calculated and approximated solid concentration profiles within the penetration layer.

Figure 8.5: Quasi inverse linear relation of the penetration ratio with the Thiele modulus.
However, since the penetration thickness is constant the profiles are going to be exactly the same as the profiles established at the end of the first stage.

The model is taking advantage of this conclusion. The solid and gas concentration profiles at $\theta=1$ are determined by using the following procedure. By assuming a penetration length ($L$) we can find how many cells deep is the reaction layer. Then, we determine the distance of each solid cell from the closest interface. This is a direct way to know the gas concentration at each cell as a function of the distance from the interface. After this is done then the solid pixels are reacted according to the gas concentration on their location. This lasts until the solid conversion on the interface reaches unity (end of first stage). The second stage begins. The solid conversion profile, as already established from the first stage, can be used at the second stage to form the solid conversion profile at the moving reaction layer. The reaction rate of each cell during the second stage is determined by the gas concentration at this cell, or equivalently, by the solid conversion of the same cell.

The model for simplicity uses a solid concentration profile made up of two piecewise linear functions that approximate very closely the analytical solution given in Figure 8.4. In order to achieve this profile we use a simple and very realistic rule. We divide the range of solid conversions in two regimes:

A) If the solid conversion (or porosity) is higher than or equal to a threshold value (here is $s=32$) then we are in the regime of complete gas penetration. The gas concentration at this cell is equal to the bulk. The reaction rate takes its maximum value. The solid concentration profile is a steep straight line;

B) In the other regime, the solid conversion is non-zero but lower than the threshold. This suggests that this cell is further away from the solid-gas interface. Thus, the gas concentration at this cell is only a fraction of the bulk (here 26 times smaller than the
maximum value). The reaction rate is lower than the maximum. The profile in this layer is a straight line with very small slope.

The first linear region is near the interface and has half the width of the second region that is further inside the solid. It has a slope 26 times larger the slope of the second region. This value makes the linear terms have very small difference from the actual profile. Actually, the integral of the real curve is 0.208 whereas the integral of the two approximating linear terms is 0.202.

The following rule determines the reaction of solid cells:

1) If the cell has already some non-zero conversion then this means that it is already accessible by the gas front. Therefore, it reacts according to which regime it belongs.

2) If the solid cell has zero conversion then we need to decide if the gas front has reached it. Then, a search of the neighborhood of the solid cell is performed. The neighborhood is defined by all cells contained in a sphere with center the current cell and with radius n cells. If we find in this neighborhood at least one cell with non-zero conversion, this means that the gas front was within n cells distance in the previous time step. Therefore, the front will propagate and react with the current pixel at this time step.

The definition of a spherical neighborhood is not easy when we are using cubic lattices. Discretization errors come into play and the neighborhood can only be approximated by a polygon in two dimensions or a polyhedron in three dimensions. The smaller the radius of the neighborhood the larger the discretization errors are. This is the reason we chose a 9x9x9 neighborhood (n=4). In 2-D the 9x9 neighborhood is producing
a dodecagon with 61 cell area and 24 cell perimeter. Its performance was tested by starting with a pore of size one pixel. The growth of the pore resulted in the dodecagon shape. The inscribed circle to that 12-gon would be our exact solution and the ratio of the polygon area to that of the circle is about 1.02. As we see the polygonal approximation is rather accurate for a 9x9 neighborhood. However, hardware limitations in the computer do not allow us to use grids with very high resolution. A neighborhood with radius 4 is very large and for solids with thin walls it might erode a large fraction of them in one step only. Thus, we chose to use the 5x5x5 neighborhood (n=2). Its use in two dimensions is resulting in the formation of an octagon.

The boundary points for the 9x9x9 neighborhood are generated by applying this simple rule:

\[ 13 \leq (x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2 \leq 18 \]  
\[ (8.13a) \]

or

\[ 3.61 \leq \sqrt{(x_i - x_0)^2 + (y_i - y_0)^2 + (z_i - z_0)^2} \leq 4.24 \]  
\[ (8.13b) \]

where: \((x_0, y_0, z_0)\) are the coordinates of the current cell and \((x_i, y_i, z_i)\) are the coordinates of the neighboring cells

Similar bounds are used for the 5x5x5 neighborhood (3 and 5 or 1.73 and 2.24). The number of volume cells of the 9x9x9 neighborhood is 341 and the boundary cells that satisfy the above equation is 162 (the numbers for the 5x5x5 neighborhood are 57 and 38 respectively). The volume of a sphere of diameter 9 (as much as this neighborhood) is 382 (or 66 for the 5x5x5). The growth of a sphere of initial radius 9 cells was performed and the ratio of the volume of the resulting polyhedron over the expected sphere was calculated. The ratio converged to the value around 1.05 for both neighborhoods. The 5x5x5
neighborhood though, gave a higher ratio of polygon surface area over that of a sphere (1.06). This value is acceptable, compared to the accuracy we expect from the simulations.

Reasons of optimization can lead us in using only the boundary points of the neighborhood in our search (instead of the entire volume points). This is possible except for the following case. The boundary points might "miss" the adjacent pore if the pore is entrapped within the neighborhood. But in order for this to happen the pore should be of n-1 cells diameter or less. In our approach, whenever we use grids that simulate pores with diameters smaller than n we expand the 3-D neighborhood to all the volume points. Otherwise, it is computationally efficient to use only the boundary points.

8.1.6 Opening of closed pores

The closed pores are inert since they are impenetrable by the gas. Therefore, they can not change the state of their surrounding solid cells.

When a closed pore cell becomes adjacent to an open pore cell (something that will happen as the gas-solid reaction proceeds), however, the entire closed pore associated with this cell is automatically converted to an open pore. We assume that the time the gas front needs to penetrate this macropore completely is very small, compared to the time needed for the reaction of the solid.

The way to determine if a closed pore becomes open is the following. Every time a solid cell becomes gas, due to complete reaction, the surrounding 6 cells connected with the 6 faces of the cell are checked. Any neighboring cell that is belonging to a closed pore is identified. Then the closed pores that possess those points are identified and are automatically set to the open pore state. As soon as a pore is opened, then all the closed pores that are connected to it are also opened. This procedure is repeated until all pores are filled and then the test is not performed anymore.
8.1.7 Measurement of number and mass of fragments

The model contains an algorithm that is able to locate and measure the number and mass of fragments resulting from the disintegration of the reacting solid. This information is very important in designing reactors where the fragmentation shortens the combustion times and produces fly-ash. In this model, fragmentation influences reactivity only in the extent that it increases the available surface area. Its influence on the macropore diffusional limitations is not accounted for in the model since these are neglected. The number and mass of the fragments is providing information on the amount of fly-ash produced during combustion. Of course, we cannot account for the fragmentation that occurs when the particle collapses under the high stresses of the flowing gas stream. The only time fragmentation occurs in this model is when the solid loses the connectivity of its parts. This is in agreement with the configuration of our reactor where the sample is fixed and not subject to high stresses. The migration of the ash particles as the solid matrix deforms and shrinks is not also possible in the model. This migration may increase the connectivity of the particle, although it is doubtful whether the ash particles have strong attraction with the solid matrix to hold it together. Thus, there may be only a slight possibility that a real particle will keep its integrity up to higher conversions than those predicted in the model. In general, the fragmentation information in the three dimensions is much more reliable than the one obtained from cross sections of the solid in the two dimensions because in the sections the connectivity of the parts can not be accounted for.

We use the following rules to determine the number and mass of the fragments:

i) We store two 3D grids in our procedure. The first one is the grid we mentioned earlier, representing the spatial distribution of solid conversion. The second one is
used to store the fragment number to which every solid cell belongs. This way we cannot confuse different fragments.

ii) We scan the first grid, one cell at a time in one direction. Whenever we find a cell that represents solid and does not yet have a fragment number in the second grid we consider we found a new fragment. We increment the current fragment number (n) by one (initially n=0).

iii) We start searching all the solid cells in the first grid, that do not have fragment number in the second grid but they lie in the neighborhood of cells which posses this fragment number n. Since they are neighbors with such cells, they are connected to them and they belong to the same fragment. Thus, they obtain the fragment number n of their neighbors.

iv) We continue the step (iii) until no new cells can be found to obtain the current fragment number. Then we repeat step (ii) by moving one cell ahead.

v) The procedure ends when step (ii) has examined all the solid cells of the first grid.

It is apparent that this procedure can find as many as 256 fragments, a limitation imposed by the 8-bit storage of each cell in the second grid. However, in our simulations we never reached a number of fragments greater than two hundred. Thus, it is not an essential limitation.

8.2. Model validation and results

8.2.1. Comparison with other models-Test runs

This cellular automaton is tested by comparing its results with predictions from analytical models available in the literature. These models have no provision for gas penetration in the solid, so the model is tested for the case of zero penetration. The results
of the simulations are in very good agreement with available theoretical results (Ballal and Zygourakis 1987b). In Figure 8.6 we see the reaction rate pattern for a solid grid in 2-D that is formed by the superposition of 100 circles of radius 64 times smaller than the size of the grid. The model results are tested for several random grids with good reproducibility. The simulation results are falling very close to the analytical prediction and their average seems to coincide with it.

Figure 8.6: Comparison of model predictions with simulation results for a two dimensional cellular automaton grid.
Figure 8.7: Two dimensional cellular automata computational grids at 0% solid conversion (left column) and 50% conversion (right column).
8.2.2. Reaction of coal-chars in diffusional limitations

As stated earlier, the model may use the macropore structural properties of coal particles to generate the simulation grid. The simulations will consider three different pore structures as produced from three different pyrolysis heating rates of 0.1, 1.0 and 10 °C/s in nitrogen. The grid that models chars prepared at 10 °C/s in 5% oxygen was very hard to generate. At the porosity of 85%, pore overlapping is inevitable. The grid does not preserve its agreement with the desired pore size distribution. For this reason we limited our modeling efforts to porosities as high as 70%. The independent variables we use are the macroporosity and the macropore size distribution. We are also using the average major and average minor axis of the particle projection under the microscope. The third dimension is not possible to measure, therefore it is assumed equal to the minor axis. The following Table 6 summarizes the main structural properties of the four different simulation grids. In our approach, we noticed that the macropore size distributions of the 0.1 and 1 °C/s chars are quite similar (Figure 8.8). That is why we used the same histogram approximation for both grids. This is also a convenient way to investigate the direct effect of porosity on reactivity without the influence of the pore size distribution. The 10 °C/s chars had a different macropore size distribution as we can see in Figure 8.8. It seems that the larger pores (>100 microns) occupy a larger percent of the macroporosity in the 10 °C/s chars than in the 0.1 and 1 °C/s chars.

We see from Table 6 that for all chars the macroporosity associated with pores smaller than 100 microns is almost the same for all cases. It is the larger pores that contribute to the increased porosity when we increase the heating rate or we add oxygen. Thus, the increased swelling is mostly attributed to large pores.
Table 6:
Structural Properties of Simulation Grids

<table>
<thead>
<tr>
<th>Heating rate (°C/s)</th>
<th>Total porosity</th>
<th>Porosity &lt;100 mm</th>
<th>Porosity &gt;100 mm</th>
<th>Dimensions (mm)</th>
<th>Grid size (voxels)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.35</td>
<td>0.17</td>
<td>0.18</td>
<td>540.540.540</td>
<td>256.256.256</td>
</tr>
<tr>
<td>1.0</td>
<td>0.50</td>
<td>0.24</td>
<td>0.26</td>
<td>760.540.540</td>
<td>360.256.256</td>
</tr>
<tr>
<td>10</td>
<td>0.70</td>
<td>0.24</td>
<td>0.46</td>
<td>996.658.658</td>
<td>472.312.312</td>
</tr>
<tr>
<td>10 (5%O₂)</td>
<td>0.85</td>
<td>0.21</td>
<td>0.64</td>
<td>1076.658.658</td>
<td>510.312.312</td>
</tr>
</tbody>
</table>

Figure 8.8: Cumulative macropore size distribution of chars prepared in various pyrolysis conditions (HTT: 700 °C).
The large pores may have a smaller contribution to the macropore specific surface area but they enhance the accessibility of the internal core of the solid by the gas. Thus, more large pores means higher pore accessibility. In order to prove this point, we reacted grids belonging to the three configurations with and without the accounting of closed porosity.

In Figures 8.9-8.11 we see the evolution of the pore structure as the reaction proceeds. Each figure shows three digital images (left to right) of the solid particle that were obtained at three different conversions. Each image contains five cross sections of the solid at: \( z = 0, \ L/D/4, \ L/D/2, \ 3/4 \ L/D \) and \( L/D \) (as we move from the bottom to the top). Figure 8.9 shows the temporal evolution of a solid grid modeling the chars treated at 0.1 \(^\circ\)C/s (35% porosity) and has no ash in it. A blow-up of Figure 8.9 is shown in Figure 8.10. Figure 8.11 models the pore structure of a char particle produced at 1 \(^\circ\)C/s (50% porosity) and with 25% ash content (in total solid mass).

Our simulation results are presented in Figures 8.12-8.14. In Figure 8.12 we see the reaction rates for the first 3 computational grids with the treatment of the closed porosity. The gas penetration thickness is 12.6 \( \mu \)m. It seems that the deviation is quite significant. The grids with the highest porosities exhibit the highest reaction rates. The ratio of reactivities for the three grids is about: 1:1.8:2.7. This means that the 10 \(^\circ\)C/s treated chars are almost 3 times more reactive than the 0.1 \(^\circ\)C/s treated chars. This is in qualitative agreement with our experimental results presented in previous Chapters. The increasing pyrolysis heating rates (or the use of oxygen) produce more reactive chars in the diffusion-limited regime. We should note that the model does not even account for temperature gradients that might develop within the particles and could make these differences more acute.
Figure 8.9: Three images (left to right) showing the configuration of a grid with 35% initial porosity and no ash at: 0, 25 and 79% conversion. Each image is made up of five cross-sections of the grid at the planes z=0, L/4, L/2, 3L/4 & L (penetration thickness: 25.2 μm; magenta: closed pores; green: partially reacted solid).
Figure 8.10: Blow-up of center image in Figure 8.9 (at 25% conversion). Note the green contours created by the partially reacted solid around the pores. Shades of green represent different conversions.
Figure 8.11: Three images (left to right) showing the configuration of a grid with 50% initial porosity and 25% ash at 0, 53 and 90% conversion. Each image is made up of five grid cross-sections at the planes z=0, L/4, L/2, 3L/4 & L (penetration thickness: 12.6 μm; orange: ash inerts; magenta: closed pores).
Figure 8.12: Reaction rate and burn-off time calculations for three different grids (penetration thickness is 12.6 μm).
Figure 8.13: Fraction of total pores that are open during reaction. Note that at high conversions all pores are open.

Figure 8.14: Variations in reactivity among different grids with and without the accounting of the closed porosity.
As we can see in Figure 8.13, the percentage of pores that are open to the exterior is monotonically increasing with the increasing porosity, at all conversions. This means that the \textit{macropore accessibility} is a major factor contributing to the deviations in reactivity among different grids. Figure 8.14 gives the reaction rates for the first two grids \textit{without} the treatment of the closed porosity. In other words, we assume that all pores are accessible to the gaseous reactants and, thus, reactive. It seems that the reactivities of the grids deviate less without the accounting of the closed porosity. This implies that \textit{higher reactivity is not only due to higher pore accessibility but also to higher specific surface area}.

The influence of the penetration length on reactivities and burn-off times is also investigated. We run the simulations with twice the penetration length of 25.2 \textmu m to find out how much the effectiveness factors would increase. Figure 8.15 shows the reactivities and burn-off times of the three grids. We expect, of course, the reactivity to be almost double than in the case of 12.6 \textmu m penetration. This however, may not be true if the walls of the solid are so thin that the reaction layer emanating from one macropore overlaps with the layer emanating from a adjacent macropore.

Figure 8.16a gives the effectiveness factors of the simulation grids for two different penetration lengths. We can observe first that \textit{the grid modeling the 0.1 °C/s chars with 25.2 \textmu m penetration has less reactivity than that of 1 °C/s chars with 12.6 \textmu m penetration!}

Figure 8.16b shows that the ratio of the effectiveness factors between the two different penetration lengths. The ratio for the 0.1 °C/s chars is initially two. This shows that the pore walls are thicker than 50 \textmu m, so the reaction layers don't overlap. As the reaction front proceeds, at higher conversions, the ratio becomes less than two, showing thinning of the walls. At very high conversions, the ratio approaches unity meaning the the penetration thickness is not important anymore.
Figure 8.15: Reaction rate and burn-off time calculations for three different grids (penetration thickness is 25.2 μm).
Figure 8.16: Calculations of the effectiveness factors of the three different grids and two penetration lengths (12.6 and 25.2 μm). The ratio of the effectiveness factors for the two different lengths is given on the bottom.
For the grids of 1 and 10 °C/s the ratio of effectiveness factors is less than two even at the start. This means that these grids have thinner walls (or higher macropore specific surface area for a given solid mass). This is one of the reasons that they have also higher effectiveness factors.

We have also investigated the presence of ash inerts in the grid. Figure 8.17 shows the reaction rate patterns for two simulation grids modeling the 1 °C/s chars and with 12.6 μm penetration. The first one contains no ash while the second contains 25% ash in total solid basis. The ash particles have a radius of 10.5 μm. As we can see, the reactivities are almost identical. There is a small initial reactivity enhancement for the grid with the ash. This might be artificial and due to the fact that the ash clusters are buried inside the solid and don't block a lot of the initial surface area on the gas-solid interface. Our conclusion is that the ash inerts did not affect reactivity, at least in the modeling approach we used. Migration of ash on the surface or catalytic activity around the ash clusters might give different results.

Figure 8.17: Reaction rate patterns of the grid representing 1 C/s treated chars without and with 25% ash content (penetration of 12.6 μm).
The fragmentation behavior of a simulation grid for chars prepared with 1 °C/s heating rate, was tested with the algorithm mentioned earlier. We assumed zero penetration and no ash. At each level of conversion the number and volume of fragments was measured. These data were used to calculate the histograms of the fragment number and volume size distributions. The histograms are shown in the following Figures 8.18,8.19.

Our main observation from the number size distribution is that the first time we have two large fragments is at conversion 93%! The conversion at the previous step was 81.04% where most of the mass was included in only one large fragment. Thus, significant fragmentation occurs at very high conversions (above 81%). This result confirms our experimental results that showed no significant fragmentation phenomena until high conversions. The video images presented in Chapter 4 confirm that the particles did not collapse and may only have fragmented to few large pieces.

The production of small fragments much smaller than the particle itself (called attrition), is present from the early stages of the reaction. The creation of the grid itself produced 3 fines of mass 1, 1 and 3 cells respectively, with no significance in the following results though (they will disappear after the first step). The fines produced exhibit a maximum number at the 93-98% conversion range and start disappearing just above 98%. These fines are three to five orders of magnitude smaller than the main fragment. Thus, it would be impossible for us to detect them all with our video microscopy apparatus.
Figure 8.18: Histograms of the fragment number and volume size distributions of the simulation grid at 0.00% (n=4), 59.82% (n=31) and 93.00% (n=108) conversion (from top to bottom).
Figure 8.19: Histograms of the fragment number and volume size distributions of the simulation grid at 98.08% (n=109), 99.65% (n=49) and 99.99% (n=16) conversion (from top to bottom).
CHAPTER 9

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

9.1. Conclusions

This work has presented some important results that provide new insights on the fundamental mechanisms of coal pyrolysis and combustion. We have demonstrated that the combination of thermogravimetry and video-microscopy is a valuable tool for measuring the temporary evolution of reactivity and at the same time monitoring the macroscopic transformations occurring in the solid. Light emission patterns, surface color and roughness, particle expansion, contraction and final size, particle integrity and ash content are all easily detectable visually by the use of the video microscopic apparatus. These macroscopic transformations coincide with some specific changes in the reactivity patterns. For example, particle ignition is observed in our video-microscopy apparatus as a light emission from the particle surface and a change in the final color and roughness of the particle. It is also accompanied by a sudden reaction rate increase, as observed by a sharp peak in the temporal reactivity curves. Also, devolatilization during pyrolysis is accompanied by a continuous particle expansion and contraction resulting in a porous swollen char particle after the end of this stage. This phenomenon coincides with the maximum in the devolatilization rates. Presence of oxygen in pyrolysis deteriorates coal plasticity and results in less frequent particle expansion and contraction. The char particles prepared in oxygen are larger and more porous than the ones prepared in pure nitrogen. Macropore opening is also detected and in many cases it has been followed by sudden
reactivity enhancements even leading to subsequent ignition. Finally, particle fragmentation is generally not very usual in the experiments with the Illinois #6 coal, probably due to its high ash content (≈25% in total char mass).

All the above observations have demonstrated the importance of heat and mass transport processes on the observed reactivity of chars. Knudsen diffusion, as well as heat conduction and convection are very important processes controlling the reaction rates. Diffusional limitations compete with particle overheating. The former are causing a reaction rate decrease while the latter are causing a reaction rate enhancement. As a result, we may observe effectiveness factors that may sometimes exceed unity, while some other times are less than unity.

The phenomenon of coal ignition was more extensively investigated because of its great importance. The flame initiation and propagation are very fast and start from the particle surface moving gradually inwards. The duration of ignition is in the order of a few seconds thus making combustion a very fast and efficient process. The reoccurrence of ignition is an interesting phenomenon not fully understood yet. Forced ignition happens to many particles when they lie in the vicinity of ignited ones. The experimental results also reconfirm findings that increasing particle size or oxygen concentration facilitate ignition.

The most important contribution of this work may be the establishment of a strong correlation between pyrolysis treatment and reactivity in the diffusion-limited regime. This correlation is initially confirmed experimentally by direct measurements of reactivity. But it can be also explained by means of the pore structure. Detailed measurements of pore structure of chars produced under a variety of pyrolysis conditions gives evidence about how the pore structure develops. Theoretical predictions estimate the role of the macropore structure in the combustion process. Both approaches (experimental and semi-theoretical) agree qualitatively. This allows us to establish also a strong and fundamental correlation between macropore structure and reactivity at high temperatures. Moreover, we have
obtained the information on how to choose the pyrolytic conditions in order to produce more reactive chars. The most influential condition for the macropore structure is the heating rate. The higher the heating rate is, the larger the particle swelling. The micropore structure is affected by the heat treatment temperature and the soak time. Higher heat treatment temperatures and longer soak times alter the micropore structure by decreasing the concentration of active sites.

The effect of initial particle size on reactivity was found to be significant. It is known that both mass and heat transfer limitations decrease with decreasing particle size. In addition, the particle size influences the macropore structure created during pyrolysis. In general, we found that larger particles swell more during pyrolysis and they are more sensitive to the pyrolysis heating rates. They also have lower ignition temperature. The ignition of the smaller particles however, is facilitated by their lower diffusional limitations and their increased macropore specific surface area. Thus, at the small sizes of 250-300 microns the particles showed more ignition phenomena than the larger 500-597 micron particles. It seems that the correlation between particle size and ignition temperature is more complicated than what the previous investigators have reported. This is because pyrolysis changes the initial particle size, the macropore size and the macropore surface area. Thus, the comparison of different initial particle sizes is not as simple.

The presence of oxygen during pyrolysis has given very important conclusions. Its influence on coal plasticity alters the swelling behavior. The particle surface eruption is more difficult in a less plastic coal. Thus, bubbles are trapped inside the particle resulting in a higher swelling and porosity. This is resulting in the increased reactivity of the oxygen treated chars in the diffusion limited regime as compared to the reactivity of nitrogen treated chars. The ignitions of the former chars at the low temperatures of 500 C have resulted to effectiveness factors approaching 3. Thus, the chars at 3 times more reactive than we would normally expect.
Finally, the creation of a three-dimensional cellular automaton algorithm has allowed us to correlate the evolution of reactivity of a porous isothermal solid reacting in the diffusion-limited regime with its macropore structure. The model investigates the importance of available surface area and open porosity in the reactivity. It models closely the macropore structure of chars prepared under the previously mentioned pyrolysis conditions. The results of the model confirm the increasing reactivity trends for the chars prepared at increasing heating rates. This is due to the increasing specific surface areas as well as the ascending accessibility of the pores to the reactants. The model is using the experimentally found macroporosity and macropore size distribution as parameters to generate the grid. The resulting macropore specific surface area has a reasonable agreement with the one measured by stereological methods. The model points out the importance of diffusional limitations on the reactivity patterns. The diffusional limitations seem to have less importance in chars treated at high heating rates. This is because thinner walls form at these chars, thus these walls are more penetrable by the gas, increasing the effectiveness factor. The model also investigates the effect ash inerts in the available surface area. This was found to be minimal, although systematically the ash inerts decrease slightly the specific surface area.

9.2. Implications of this study

The results presented in this work can be used to optimize the efficiency of combustion processes. Although we realize that a very detailed combustor analysis and design was not the purpose of this study, there are some simple facts from this work that designers can use to improve coal combustors.
The usual strategy followed in industrial processes is to combust very fine coal particles at high temperatures and pressures. This way high reaction rates are achieved and undesirable diffusional limitations are avoided. However, the use of high combustion temperatures and pressures involves several drawbacks:

i) High capital investment.
ii) High heat losses to the surroundings.
iii) High operational costs to start and shut down the combustor.
iv) High energy requirements for grinding the coal particles to very small sizes.
v) Safety problems involving the danger of leaks under high pressures and reactor runaway. The need of a more accurate and sophisticated process control system is urgent.
vi) Higher pollutant emissions in the form of nitrogen oxides and sulfur dioxide. These pollutants are preferentially formed at higher temperatures.

The alternative of the "high-severity" conditions is the use of mild gasification. Mild gasification is the processing of coal at mild conditions (temperatures below 750 °C and pressures below 50 psig) to produce a collection of valuable co-products: liquid fuels, solid fuel (char), gaseous products and electricity. The capital investment and operating costs of such processes are considerably lower. The environmental impact is also significant. The chars produced from mild gasification are sulfur-free. The liquid fuels have low sulfur content. The solid fuels produced have higher specific reactivity as expected from the use of lower heat treatment temperature. The chars also may have higher particle size since at the low combustion temperatures diffusional limitations are less significant. Finally, fewer and larger fly-ash particles are formed at lower temperatures, thus alleviating the burden of collecting them downstream.
However, in the mild gasification conditions the reaction rates are low and the residence times need to be longer (up to several minutes). This implies that we must have larger reactors to ensure the same production rates. However, the mechanism of ignition can be used to alleviate this disadvantage. Ignition can be initiated to char particles to increase their reaction rates. Our claim is that higher size particles can be used at these low combustion temperatures. This way we can achieve lower ignition temperatures. In fact, modeling efforts have concluded that there is a range of ambient temperatures where the larger particles react faster than their corresponding smaller fractions (Sotirchos and Amundson 1984; Sotirchos and Amundson 1984; Sotirchos, Srinivas et al. 1984). This happens because the larger particles burn in the ignited state.

The choice of pyrolysis heating rate and atmosphere is also crucial in upgrading reactor efficiency. Our goal is to design a devolatilization reactor that heats particles in a few seconds to the final heat treatment temperature (always lower than 750 °C) and in the presence of low oxygen concentration (probably an entrained flow reactor). This way we can obtain a macropore structure that is very open and with the lowest diffusional limitations. This will be an additional advantage of lowering the ignition temperature. Thus, we may use a combustor that operates at low temperatures but it includes particles that react locally at much higher temperatures due to their ignitions. Their heat will be dissipated to the ambient gas but due to the high gas flow rates, the temperature may be kept low, just as high as needed for producing steam and subsequently electricity.

The outline is that by selecting the pyrolysis conditions and by triggering the ignition mechanism we may be able to make the combustion stage more efficient in terms of energy utilization, emission control and heat production rates.
9.3. Recommendations for future work

The mechanism of pyrolysis and its influence on macropore structure is a very interesting but also a complicated one. The role of coal origin, rank, volatile content and additives on coal swelling behavior must be investigated in a variety of coals. It is known that only bituminous and subbituminous coal are plastic. However, there must be some organic additives (solvents or plasticizers) or preprocessing (like hydrogenation) that can render these coals plastic. The results of this work could thus be extended to these coals.

More detailed time resolved measurements of particle expansion and contraction can be made. These can be correlated with the final particle porosity and size. The production of higher quality images is essential in their digitization and segmentation and in the definition of the particle outline. For this purpose, the sample illumination system must be redesigned to prevent any shadowing effects.

The effect of oxygen in plasticity and swelling index needs more investigation. It is unknown what is the optimum concentration of oxygen in pyrolysis that would induce the highest swelling. Probably, too low oxygen does not decrease the plasticity sufficiently. But on the other side, too much oxygen could eliminate any plasticity and subsequently any swelling. Thus, there must be an optimum concentration of oxygen at which the swelling index takes its maximum value. Using the same rational, we can suppose that pyrolysis of non-plastic coals could be performed in the presence of hydrogen to induce plasticity.

The pure effect of diffusion on reactivity without the interference of thermal gradients can be obtained if we react the chars at lower oxygen concentrations. The extent of diffusional limitations does not depend on gas concentration if the order of reaction is one (the order of char-oxygen reaction is close to one). On the other hand, the rate of heat release and ignition temperature depend greatly on the oxygen concentration.
The role of heating rate on reactivity should be explored at even higher rates to investigate if the dependence is monotonic or if there is leveling-off above a value of heating rates. Some few elementary observations showed that the reactivity of the 20 and 30 °C/s treated chars is almost similar. Some people would also argue that the structure of chars produced at heating rates of 100 or 1000 °C/s is dissimilar to that of chars treated at 10 °C/s (number of pores and wall thickness change).

The effect of initial particle size on reactivity at high temperatures is not very clear. Here we run across the competition of diffusional limitations, limiting the reactivity the large particles and ignition favoring the reactivity of large particles. Besides, the development of macropore specific surface area during pyrolysis favors the small particles. More investigation should be conducted in this area with extended macropore structure measurements in a range of particle sizes. More detailed experimental reactivity measurements are needed to cover a wider range of particle sizes. The use of the cellular automaton algorithm can also be helpful in predicting the effect of macropore structure on reactivity for all these particle sizes.

The cellular automaton algorithm can be extended to include thermal effects created by the heat generation in the grid. A temperature grid can be used to keep track of the development of local hot spots. A heat conduction algorithm can be devised by applying a finite difference scheme in the temperature grid. The only problem with this approach is memory availability, CPU capacity and algorithm convergence by the choice of a sufficiently low time step. Finally, the implicit dependence of micropore specific surface area (or intrinsic reactivity) on local conversion can also be included in the model, although it will complicate the development of the gas concentration profiles.

Finally, the laboratory instrumentation necessary for the above experimental approach must be an improved version of the one used in this study. Initially, the computer control and acquisition system must be replaced with one that offers higher CPU speeds and more
elaborate software capabilities. This way the furnace can run at higher heating rates (up to about 100 °C/s) if an accurate computer control is achieved with the faster computer. More data points will be collected per second and thus more resolution in reaction rate measurement will be feasible. The digital image processing and analysis should be performed in the same computer to avoid transferring the files to different computers. More sensitive cameras would be able to detect the short ignitions on the particles that are not distinguishable from the background. The use of an accurate optical pyrometer is necessary to measure the actual temperature of an ignited particle. This way we would be able to correlate reactivity and temperature and thus calculate the unknown effectiveness factor with reference to the solid temperature rather than the ambient. The optical window of our reactor allows the use of a pyrometer in place of the microscope. In a better set-up, both the camera and the pyrometer can be used if we use the fact that the microscope creates two image beams for stereo vision. One beam can go to the camera and the other one can be sent to the pyrometer. However, it is unknown what the influence of the microscope optics will be in the readout of the pyrometer.
REFERENCES


