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IGNITION OF COAL AND CHAR PARTICLES:
EFFECTS OF PORE STRUCTURE AND PROCESS CONDITIONS

by

DOSITE SAMUEL PERKINS, II

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IN PARTIAL FULFILLMENT OF THE
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May, 1998
ABSTRACT

IGNITION OF COAL AND CHAR PARTICLES: EFFECTS OF PORE STRUCTURE AND PROCESS CONDITIONS

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DOSITE SAMUEL PERKINS, II

This study reports the results from experimental and theoretical studies aimed at elucidating the effects of particle pore structure and process conditions on the ignition of coal and char particles.

A novel reactor combining thermogravimetric analysis and video microscopy imaging (TGA/VMI) was used for our combustion studies. By allowing simultaneous observation of light emissions from igniting particles and measurement of sample reactivity from weight-loss data, the TGA/VMI reactor was very effective in detecting and characterizing particle ignitions.

Investigations of ignition mechanism showed that the ignition of char particles typically occurs heterogeneously, while coal particles may ignite heterogeneously, homogeneously, or by a combination of both mechanisms. Homogeneous ignitions were favored by high oxygen concentrations and close particle interactions. Other transient phenomena such as multiple ignitions of a single particle were also observed.

A second hot stage reactor was also used for our studies to achieve heating rates as high as 1000 °C/sec. We found that chars prepared at
higher pyrolysis heating rates ignited more frequently and exhibited higher reactivity when combusted at temperatures leading to diffusional limitations. Due to inherent differences in the two reactors, chars prepared in the hot stage at the same conditions as those prepared in the TGA/VMI exhibited lower ignition and reactivity behavior. Despite these differences, chars prepared at the highest heating rates in the hot stage reactor clearly exhibited higher reactivity and ignited more frequently.

Mathematical modeling efforts focused on the coupled transient mass and energy balances governing the diffusion-reaction problem in char combustion. Changes in particle size and pore structure with conversion were described using experimental data obtained in our laboratory. Combustion kinetics were also measured experimentally. Theoretical predictions agreed very well with experimentally observed trends. Important char structural properties which favored ignitions were larger particle radii, more open macropore structures, and larger macropore surface areas. Process conditions which increased particle ignitions were high pyrolysis heating rates, high combustion temperatures and increased oxygen concentrations during combustion.
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CHAPTER 1

INTRODUCTION

1.1 General

Coal is the most abundant natural solid fuel accounting for about 75% of the world's fossil fuel reserves (Bartok and Sarofim 1991). Utilization of this chemically rich compound, formed from the decomposition of plant materials through years of exposure to high temperatures and pressure, varies from the generation of electric power to the production of feedstock chemicals.

Throughout the 20th century, oil and gas have overtaken coal as the primary source of fuel for heating and transportation uses. However, the supplies of recoverable oil and gas resources are quite limited compared to the tremendous reserves of coal present throughout the world. In addition, coal is often a desirable alternative for countries who must rely on imported oil and gas. The decline in coal utilization is generally attributed to the difficulty of consuming coal in a clean and efficient manner. To improve the efficiency and environmental impact of coal consumption, an understanding of the fundamental physical and chemical processes in coal combustion is necessary.

1.2 Coal Utilization

The three major coal utilization technologies are direct combustion for power generation, gasification, and liquefaction. Among these, the first
is clearly the most widespread. Coal is estimated to account for 55% of the electric power generated in the United States (Hong 1996).

1.2.1 Coal combustion

The most common type of reactor utilizing coal for energy production is the pulverized fuel combustor. In this furnace, fine particles of coal, typically less than 0.1 mm in size, are blown through a flame where they burn at approximately 1500 °C. As the particles burn, they radiate heat to tubes forming the walls of the combustion chamber containing water and steam. The steam is either used as process steam or is sent through a turbine for power generation (Merrick 1984).

In some cases, maintaining ignition of the fuel can be a problem in these furnaces, thus preheating of the combustion air is required (Meyers 1981). Bituminous coals are most commonly used in pulverized fuel combustors, though coals of all ranks are used (Meyers 1981). As the coal particles are combusted, the minerals present yield ash, some of which become entrained in the combustion gases. Ash may also contact and fuse to the steam tubes, causing fouling and loss of heat transfer efficiency. Consideration must therefore be given to the ash content of the coal. The ash fusion temperature, the temperature at which the ash begins to melt (Meyers 1981), is an important property.

Another common reactor type in coal combustion is the fluidized bed combustor (FBC). One major advantage of combusting coal in a fluidized bed is that control over environmental pollutants is much more effective. Fossil fuel combustion is a major source of atmospheric pollutants, introducing large quantities of CO, CO₂, SOₓ, NOₓ, and particulate matter into the atmosphere. These pollutants contribute to problems such as acid
rain, global warming, and photochemical smog. In fluidized bed combustion, coal particles are fluidized along with inert particles. These particles can be chemical sorbents for compounds such as sulfur. This type of pollution control is often more efficient than the gas "scrubbing" techniques employed in typical pulverized fuel combustors (Cooper and Ellingson 1984).

Another important advantage of the fluidized bed combustor is an increase in heat transfer capability. Placing tubes within the fluidizing bed allows for direct contact and can also allow more compact combustor designs (Cooper and Ellingson 1984). In all cases of coal combustion, interactions among particles are obviously of great importance. Though single particle experiments are useful in providing information on dilute coal combustion conditions, experimental studies involving particle interactions are essential for practical knowledge of coal combustion.

1.2.2 Coal gasification

The rich molecular nature of coal has brought about interest in utilizing it as a source of feedstock chemicals for the chemical industry. Many different processes have been developed for the recovery of gaseous products from coal gasification. Currently, very few of the proposed liquefaction or gasification processes are considered economically viable in the United States. However, studies continue due to the uncertain nature of fossil fuel reserves.

One important coal gasification process is the production of a synthetic natural gas. In this process, the major objective is to increase the yield of methane to produce a gas with high heating value (970-1000 BTU/scf), capable of replacing natural gas (Meyers 1981). One approach
commonly used is hydrogasification, in which hydrogen is used as the primary reactant with coal to enhance cracking of the primary tars produced during the devolatilization stage (Merrick 1984).

Synthesis gas is another important product of coal gasification. Synthesis gas consists primarily of CO and H₂, and is also commonly produced via hydrogasification of coal. Synthesis gas is used as a chemical feedstock to produce methanol, as well as a variety of long chain alcohols. Processes aimed at producing liquid products from coal-derived gases are called indirect liquefaction. The production of methanol can be used in conjunction with the methanol to gasoline (MTG) process developed by Mobil in the 1970's to produce gasoline from coal through indirect liquefaction.

1.2.3 Coal liquefaction

Coal is much less suitable for production of liquid products, particularly when compared to crude oil, for a number of reasons. Firstly coal has a much lower hydrogen content than crude, making the conversion to liquid fuels difficult. Additional problems are the presence of minerals in coal, and its complex and highly crosslinked molecular structure.

For these reasons, coal liquefaction processes often focus on the hydrogen rich tars produced during coal pyrolysis. Refinement of these tars can lead to various liquid compounds such as benzene and naphthalene. Pyrolyzing the tars the presence of hydrogen (hydropyrolysis) can increase the yield of liquids, which typically does not exceed 35% based on the organics present in the coal (Cooper and Ellingson 1984).

Direct liquefaction is another common method which involves the consumption of coal in the presence of a hydrogen donor solvent.
However, catalysts and extreme conditions of temperature and pressure are required to hydrogenate the organic components for significant liquid production.

1.3.1 Chemical composition, rank

Coal has a heterogeneous and highly complex molecular structure. Its two major components are inorganic crystalline minerals and organic carbonaceous macerals. The plant material from which coal is formed consists of highly oxygenated multiple ring organic compounds. The process by which this material is converted to coal, called coalification, causes a gradual elimination of this oxygen. This leads to compounds which are progressively richer in carbon. The primary organic constituents of coal are highly condensed aromatic compounds with molecular weights approaching polymeric values. Crosslinking of these various multiple ring aromatics is often achieved through ether or methylene bridges (Gorbaty, et al. 1982). Coals also contain a large amount of low molecular weight volatile compounds which are rich in hydrogen.

Coal is generally classified by rank, which is a measure of the carbon content of the coal. The conditions under which the coal was formed determine the degree of coalification and, thus, the rank of the coal. The highest rank of coal is anthracite, which contains anywhere from 90-97% carbon on a dry mineral matter free basis (dmmf). Anthracite is followed by bituminous (85-90%), sub-bituminous (75-85%), and finally lignite (50-60%)(Meyers 1981). Bituminous coals are further classified by their volatile content into high, medium, and low-volatile bituminous coals.

While classification of coal by rank may be useful in describing coal samples, its tremendous complexity and heterogeneous nature make it
difficult to compare any two individual samples. Coal is often described as a polymeric compound. Yet, the macromolecules forming the coal lamellae do not consist of repeating monomeric units. In fact, coal samples taken from the same seam may differ significantly in aromaticity, molecular weight, mineral matter content, and so on.

1.3.2 Plasticity

When coal is heated in an inert or reactive atmosphere, thermal rupturing of the various bonds generally occurs first, liberating the volatile molecules. The result of this process, called devolatilization or pyrolysis, is a char particle which is richer in carbon content than the parent coal.

During the devolatilization process, certain coals go through a transient plastic state where they behave like highly viscous fluids. As the volatiles are released, they form bubbles that grow in an expanding fluid structure, until they break through the particle surface allowing the volatiles to escape. Once the volatiles escape, the particle contracts and expands again when more volatiles are liberated. This sequence of rapid expansion and contraction of the particle continues until the devolatilization is complete, and the particle returns to a solid state. Coals which exhibit this behavior are called plastic, or caking coals. If multiple particles are in contact with one another during pyrolysis, they will agglomerate and form a cake.

The chemical transformations which occur during plasticity are quite interesting. Rupturing of the ether and methylene bridges results in a great increase in mobility of the resulting lower molecular weight components. The ends of these compounds are typically free radicals which are quite reactive, yet are stabilized by the presence of hydrogen-containing
compounds. As the hydrogen-rich volatiles are removed, the free radicals are no longer stable and eventually recombine. These polymerization reactions result in a decrease in mobility due to the increased molecular weight (Gorbaty, et al. 1982). Thus the particle loses its plasticity and becomes solid again.

The presence of oxygen during pyrolysis has been shown to inhibit the plastic behavior of caking coals. Low-rank coals such as lignite do not exhibit plastic behavior, perhaps due to their high oxygen content (Gorbaty, et al. 1982). The degree of swelling or plasticity is also greatly affected by the heating rate employed during pyrolysis. Higher heating rates leads to more rapid thermal rupturing of bonds and, thus, a greater rate of volatile release. This in turn leads to greater pressure build up within the expanding particle.

1.3.3 Pore structure

The imperfect packing and crosslinking of various macromolecules present in coal results in a very fine microporous structure. Larger voids may be formed where differing solid constituents come in contact. In general, these internal pores are interconnected. As coal rank increases, so does the crosslinking of various aromatic rings and, thus, micropores become the dominant pore feature (Meyers 1981).

The pore structure of devolatilized char particles may be quite different from the parent coal. In the case of plastic coals, the expansion and contraction of the particle associated with plasticity leads to the formation of large internal cavities, termed "cenospheres" by Sinnat et al. (Sinnat, et al. 1927). The micropore structure of the parent coal may be retained to some extent. With the development of these large cenospheres
(that are also called macropores), however, char particles have a highly bimodal pore distribution. The macropores account for nearly all the porosity of the particle, while most of the internal surface area is associated with the micropores.

Several investigators have shown that the conditions of pyrolysis, particularly heating rate, are instrumental in determining the features of the macropore structure of char particles (Boissiere 1993, Sinnat, et al. 1927, Zygourakis 1993). Earlier work in our laboratory (Boissiere 1993, Glass 1987, Zygourakis 1993) quantified the macroscopic features of the internal char structure by applying digital image analysis techniques to images taken from polished cross sections of pyrolyzed char particles. Several experiments conducted with chars prepared from Illinois #6 coals established that higher pyrolysis heating rates led to chars with larger particle sizes, more open macropore structures and higher specific macropore surface areas.

1.3.4 Intrinsic and specific reactivity

Nearly all practical uses of coal involve the chemical reaction of coal or char with a reactive gas such as oxygen. Thus, the intrinsic reactivity of the sample towards oxygen or any other reactive gas is of great importance to coal utilization. The list of reactions which may occur when coal is combusted with oxygen is quite expansive. Only a few of the many possible reactions will be presented here. Heterogeneous reactions involving the carbon surfaces include:

\[
C(s) + \frac{1}{2}O_2 \rightarrow CO \quad \text{exothermic} \quad (1.1)
\]
\[
C(s) + O_2 \rightarrow CO_2 \quad \text{exothermic} \quad (1.2)
\]
\[ C(s) + CO_2 \rightarrow 2CO \quad \text{endothermic} \quad (1.3) \]

Homogeneous (gas phase) reactions include:

\[ 2CO + O_2 \rightarrow 2CO_2 \quad \text{exothermic} \quad (1.4) \]
\[ \text{volatiles} + O_2 \rightarrow CO + CO_2 + H_2O \quad \text{exothermic} \quad (1.5) \]

Heterogeneous reactions of oxygen with coal or char surfaces naturally require the following steps to occur: (1) adsorption, or chemisorption of oxygen on the surface, (2) reaction of the surface complex, (3) desorption or removal of the reaction products. Chemisorption of oxygen on a carbon surface preferentially occurs at the grain edges and imperfection sites within the graphite-like crystalline domains. In addition, inorganic material present often catalyzes heterogeneous reactions. Locations within the pore structure of coal or char which contain one of these reactive moieties are called active sites. The surface area occupied by these sites is consequently designated as active surface area (ASA).

Not all active sites are of appropriate reactivity to participate in heterogeneous reactions. Some form surface complexes that are too stable to undergo further reaction or desorption (Lizzio, et al. 1990). Others may not be reactive enough to allow the surface reactions to occur. Furthermore, a certain portion of active sites may be inaccessible to oxygen due to diffusional limitations. The portion of the active surface area which is capable of completing heterogeneous reactions is sometimes referred to as the reactive surface area (RSA).
Depending on the internal pore structure, operating conditions, and extent of reaction, not all of the internal surface area of the particle may be accessible to oxygen. As the reaction proceeds, the reacting solid is consumed and pores begin to enlarge, increasing the surface area and the accessibility to oxygen. Eventually, the walls separating the pores are consumed and the pores coalesce, decreasing the total surface area. Thus, the measured, or specific reactivity of the sample may exhibit a maximum at intermediate conversions, while the intrinsic reactivity should remain constant. Measurement of the intrinsic reactivity of a coal or char sample requires a measurement of the reactive surface area at various conversions.

Since reactive surface area measurements may be difficult, it is reasonable to suggest that there is a direct correlation between the total surface area and the number of active sites present within a particle. Thus, many investigators measure only the total surface area (TSA) and make assumptions about the relation between the active (or reactive) surface area and the total surface area in reporting intrinsic reactivities.

Intrinsic reactivity data of a coal or char sample is certainly important in the study of coal utilization. However, it is perhaps more important to understand the effects of operating conditions which ultimately determine the specific reactivity which is observed. Operating conditions will determine what fraction of a sample's active sites are available for reaction. Furthermore, thermal effects such as particle ignitions may raise the particle temperature leading to greatly increased specific reaction rates.

At high combustion temperatures, where diffusional limitations are rate limiting, the macropore surface area of char particles become of much greater importance. This is because the larger macropores act as major
arteries, supplying oxygen to the interior of the particle. At higher combustion temperatures, however, oxygen is consumed before accessing all of the smaller pores. Thus the macropores are essential in allowing oxygen to reach the micropores. Matzakos (Matzakos 1991), and Ismail (Ismail 1994) have shown that in this regime of diffusional limitations, the conditions of pyrolysis greatly affect the specific reactivity of chars prepared from plastic Illinois #6 coals.

1.4 Particle Ignitions

The heterogeneous reactions of carbon with oxygen are very exothermic. When these reactions proceed at high rates, a large amount of heat is rapidly generated inside a coal or char particle as the carbon is consumed. If the rates of heat removal from the particle are not fast enough to dissipate the heat generated, particle ignition will occur. Ignition phenomena were first studied by Semenov (Semenov 1928), whose thermal explosion theory (TET) described heterogeneous ignitions (i.e. ignitions caused by heat generated from heterogeneous chemical reactions) and demonstrated the existence of multiple steady states. Many attempts at modeling coal and char particle ignitions are based on this theory of ignition. When the temperature of an ignited particle is high enough, it will radiate bright emissions of light, thus allowing for visual detection of ignition.

Ignitions may also occur through a homogeneous mechanism. Homogeneous ignitions result from heat generated by reactions occurring in the gas surrounding a coal particle. These gas phase reactions usually involve the combustion of volatiles, which burn producing a bright flame with very high temperatures.
1.4.1 Ignition detection

The detection of particle ignitions is very important for coal and char combustion studies, since ignitions are instrumental in determining the combustion properties of the fuel. For example, the fuel reactivity determines the size and operating conditions of the reactor necessary to achieve complete conversion. In most cases, particle ignition is a desirable occurrence. However, the high temperatures associated with ignitions may lead to an increased production of NO\textsubscript{x}, which is formed primarily at high temperatures.

In most practical reactors, particle interactions play a key role in determining the combustion behavior of the fuel. For this reason, many investigators have studied combustion in laboratory setups that approximate the conditions encountered in actual combustors. A common type of laboratory reactor is the drop tube or entrained flow reactor. Multiple particles are dropped through or entrained in a heated region in the presence of a reactive gas. Sample ignitions are detected with photomultipliers which record various ignition flashes (Gupta, et al. 1990, Wall, et al. 1988). With many particles present, however, ignition flashes occur so often that individual particle ignitions are impossible to detect. Thus hindering the detection of secondary ignitions.

To avoid the experimental difficulties of large sample sizes, many investigators study the combustion of single coal or char particles. This approach allows for detailed measurements such as color pyrometry, in which the particle temperature can be monitored. Utilizing this technique, Levendis et al. (Levendis, et al. 1989) observed that the ignition of char particles originated from localized "hot spots" on the particle surface.
before spreading across the entire particle. Gomez and coworkers (Gomez and Vastola 1985) studied ignitions by combining luminosity measurements with simultaneous analysis of the carbon monoxide and carbon dioxide produced when a single coal particle ignited and burned. Since total luminosity measurements cannot distinguish between volatile matter ignition (homogeneous mechanism) and surface reaction (heterogeneous mechanism), the product gas was analyzed to determine the mechanism of ignition.

In contrast to total luminosity measurements, video microscopy is effective in tracking the fate of individual coal particles during pyrolysis and combustion experiments with multi-particle samples. Video microscopy techniques detect ignitions by directly observing light emissions from individual particles and are also useful for investigating ignition mechanism.

Yang and Tsai (Yang and Tsai 1990) utilized video techniques to visualize the ignition of coal particles with diameters ranging from 6 to 15 mm. They concluded that particles ignite by both mechanisms and noted the appearance of luminous flames in the area surrounding the particle as well as on the particle surface. For experiments where ignitions result in easily observable emissions of light, video microscopy can be very effective for detection and mechanism identification. However, when used alone this technique may be inadequate for detecting ignitions where light emissions are faint.

To directly detect the combustion of volatiles in the region surrounding a coal particle, Huang and coworkers (Huang, et al. 1988) combined luminosity measurements with measurements of temperature profiles around coal particles. This approach can provide useful
information about the ignition mechanism by differentiating between volatile burning around the particle and reactions occurring at the surface or in the particle interior.

Tognotti et al. (Tognotti, et al. 1985) utilized thermogravimetric measurements to detect the ignition of coal particles. Their technique involved comparison of weight loss vs. temperature curves obtained by combusting coal in inert and reactive atmospheres. The ignition temperature was determined as the temperature at which these two curves deviated. Thus, the thermogravimetric technique provided information about the onset of combustion rather than ignition, only identifying ignition in cases where it was the first combustion event. Our studies have shown, however, that in many cases significant conversion is achieved before the particles ignite. This thermogravimetric ignition detection was also not effective for multiple particle experiments since it did not provide information about which or how many particles ignited.

Some recent studies have utilized the electrodynamic balance to study the combustion behavior of single levitated char particles (Cozzani, et al. 1995, Wong, et al. 1995). In these experiments, single char particles were suspended in an electric field while heated by laser irradiation. Pyrometry measurements provided particle temperatures and video imaging provided images of the reacting particle. This method has proven itself very useful in studying heterogeneous reactions. However, the loss of particle charge upon ignition or at high temperatures may cause the particle to drop out of view in the apparatus, making observation of ignition phenomena difficult in these instances.

From this discussion, it is apparent that experiments designed to study particle ignitions fall into one of two categories:
(1) Multiple particle experiments which allow particle interactions but provide little or no detail about individual particle ignitions.

(2) Single particle experiments which do not allow particle interactions but provide great detail about individual particles.

The need is thus apparent for an experimental approach to efficiently detect individual particle ignitions in a multiple particle experiment, while preserving the effects of particle interactions.

### 1.4.2 Ignition modeling

Ismail (Ismail 1994) conducted a theoretical study of char particle ignitions by extending Semenov's thermal explosion theory (Semenov 1928). The model accounted for diffusional limitations in both macropores and micropores of a single char particle reacting with oxygen. The solid energy balance and oxygen mass balance considered by Ismail took the form:

\[
a_x h(T_s - T_f) = (-\Delta H_k) V_p \eta Ae^{-\left(\frac{E}{RT_s}\right)} C_S
\]

(1.6)

\[
a_x k_g (C_f - C_s) = V_p \eta Ae^{-\left(\frac{E}{RT_s}\right)} C_S
\]

(1.7)

where \(a_x\) and \(V_p\) are the external area and volume of the char particle. \(C_s\) is the oxygen concentration within the solid particle. \(C_f\) and \(T_f\) are the oxygen concentration and temperature of the gas surrounding the particle. \(T_s\) is the solid temperature, and \(\eta\) is the particle effectiveness factor representing the extent of diffusion limitations. The mass and heat transfer coefficients are
denoted by $k_g$ and $h$ respectively. $(-\Delta H_r)$ is the exothermic heat of reaction, $A$ and $E$ are the pre-exponential factor and activation energy. $R$ is the universal gas constant.

Figure 1.1 presents the steady state solution structure of this model. Plotting the particle versus ambient temperature yields a sigmoidal shaped curve. For a certain range of ambient temperatures, the particle temperature may be in one of three possible states (see Fig 1.1). This range of ambient temperatures is called the multiplicity region. At point 1, the particle temperature is approximately equal to the ambient temperature, indicating an unignited state. At point 3, the particle temperature greatly exceeds the ambient temperature, and the particle reacts in an ignited state. Point 2 represents an intermediate unstable steady state.

The minimum ambient temperature required for ignition while heating a particle is represented by the vertical line $T_i$, which is tangent to the right edge of the multiplicity region. For ambient temperatures exceeding $T_i$, only the ignited state exists. At lower ambient temperatures, the particle temperature tends to move away from the intermediate steady state towards the unignited state. Similarly the ambient extinction temperature for a previously ignited particle is represented by the line $T_e$. 
Figure 1.1 Particle temperature versus ambient temperature for a reacting char particle.

Modeling studies can be very useful in identifying the effects of particle properties and operating conditions on particle ignitions. The model of Ismail agrees with most other studies in predicting that ignition temperatures vary inversely with oxygen concentration regardless of ignition mechanism. In addition, it is widely predicted that larger particles ignite at lower ambient temperatures (Karcz, et al. 1980, Sweeney and

More detailed models of Sotirchos and Amundson (1984a, 1984b, 1984c, 1984d) have shown that inclusion of intraparticle thermal gradients significantly affects the solution structure by expanding the multiplicity region and shifting it to lower ambient temperatures. Increasing diffusional limitations were found to have the opposite effect, shrinking the multiplicity region and shifting it to higher ambient temperatures. Sotirchos and Amundson found that larger particles ignite at lower ambient temperatures. However, smaller particles reacting in the ignited steady state attain higher particle temperatures than larger particles.

A steady state model is useful in describing the solution structure of the particle versus ambient temperature. However, steady state models cannot determine which state the particle will react in when multiple steady states are present. In addition, the model must be solved at a range of conversions, since the solid properties change as conversion progresses.

The dynamic models of Sotirchos and Amundson quantified the changes in the steady state solution structure with conversion. In particular, they showed that the solution structure depends strongly on the evolution pattern of internal surface area with conversion. Two surface area evolution patterns were considered. One pattern exhibited a maximum at intermediate conversions, while the other decreased monotonically with conversion from its initial value. Comparing the transient particle ignition behavior to the initial solution structure, they showed that particles reacting at ambient temperatures existing in the multiplicity region initially, may go from an unignited state to an ignited state at later conversion depending on the evolution pattern of surface area with conversion.
Therefore, regardless of the initial pseudo steady state solution structure, a transient model is necessary for accurate predictions of particle ignition phenomena which depend strongly on the evolution of pore structure and other properties with conversion as in the case of char particle combustion. The pattern of evolution will be dependent on many factors, most notably the presence of diffusional limitations. By assuming that no concentration gradients existed in the micropores of the char, Sotirchos and Amundson uncoupled the pore evolution from the diffusion and reaction problem. However, this assumption may be quite incorrect at conditions where particle ignitions occur. The pattern of surface area evolution was a model parameter, taken from the experimental estimations of other investigators.

Sotirchos and Amundson clearly showed that the evolution pattern of internal surface area is very important in char combustion. Many different approaches to modeling the evolution of pore structure have been attempted. The random pore models of Bhatia and Perlmutter (Bhatia and Perlmutter 1980, Bhatia and Perlmutter 1981) as well as Gavalas (Gavalas 1980) are widely used to describe the evolution of internal pore structure in both the kinetic and diffusion control regime. Other discrete (Sandmann and Zygourakis 1987) and probabilistic models (Ballal and Zygourakis 1987, Zygourakis, et al. 1982) of pore evolution have been developed to describe the evolution of pore structure in both regimes.

Currently, much more is known about the internal pore structure of char particles due to the studies of Boissiere and Zygourakis (Boissiere 1993, Zygourakis 1993). This information can now be incorporated into transient ignition models to better account for the internal structure of char particles. In addition, experimental or theoretical estimations of the
evolution of internal surface area with conversion in the diffusion limited regime can be used as inputs to transient models.

1.5 OBJECTIVES OF THIS STUDY

The primary goal of this research was to obtain a fundamental understanding of the effects of various process conditions on the specific reactivity and ignition behavior of coal and char particles. Information about this behavior is of importance for the efficient design and operation of industrial coal fired power plants and utility boilers.

1.5.1 Detecting particle ignitions

Despite the large number of experimental studies of coal and char particle ignition in combustion reactors, the need is still apparent for an approach in which individual ignitions can be detected among particles reacting in a multi-particle experiment.

The technique we will describe here relies on the capabilities of the TGA/VMI reactor, developed by Matzakos (Matzakos 1991), which combines reactivity measurements with video microscopy imaging. The TGA/VMI reactor allowed the study of particle interactions in a multiple particle experiment, while still providing information about individual particle ignitions, thus combining the qualities of single and multiple particle experiments. Characterization of ignitions included determination of ignition mechanism (heterogeneous or homogeneous), and the dependence of mechanism on operating conditions. Transient phenomena such as multiple ignitions of a single particle were also detected.
1.5.2 Role of process conditions in determining ignition and reactivity of coal and char particles

The influence of the pyrolysis process on the internal pore structure of char particles merits an investigation of the effects of pyrolysis on the combustion behavior of char. In order to study these effects, it was necessary to conduct sequential pyrolysis and combustion experiments. Pyrolysis experiments were performed, usually in the absence of oxygen to ensure no heterogeneous reactions, producing a char sample which was then combusted in a sequential experiment without removing it from the reactor.

Previous studies on the effects of pyrolysis conditions have revealed that the heating rate, heat treatment temperature, soak time, and oxygen composition significantly affect char reactivity. The current study focused on better quantifying the effects of the most important of these parameters, pyrolysis heating rate, on char reactivity in both the kinetic and diffusional control regimes of combustion. Furthermore, we will report on previously unavailable reactivity and ignition data for chars prepared in the hot stage reactor at heating rates as high as 500 °C/sec. We also studied the effects of various combustion conditions such as oxygen composition, combustion temperature, and particle size.

Coal combustion experiments in which pyrolysis and combustion occurred simultaneously were also conducted. The effects of combustion conditions such as heating rate, oxygen concentration, and combustion temperature were quantified. Additionally, the effects of these and other parameters on the ignition mechanism of coal particles were investigated.

Combination of digital image processing with the video microscopy capabilities of the TGA/VMI allowed for observation and quantification of
changes in char properties with conversion such as particle radius. Observation of combustion phenomena was useful in the development of a char ignition model.

1.5.3 Transient char ignition model

As discussed previously, theoretical studies of coal or char particle ignitions are most effectively achieved by transient models. Earlier models have shown the importance of particle pore structure on ignition behavior. We now have a much more accurate description of the internal structure of char particles. Thus, we can utilize this information to solve the transient equations describing the ignition of char particles.

We will describe the dependence of char reactivity and ignition behavior on process conditions and internal pore structure. Parameters studied include combustion temperature, oxygen concentration, particle radius, macropore surface area, porosity, micropore radius, ash content, and ambient velocity.

Experimental results and observations were essential in the development of the model. Values for all important model parameters were obtained by experimental measurements made in our laboratory. Evaluation of the combustion kinetics and evolution of internal surface area with conversion were achieved experimentally and incorporated into the model. Internal char surface areas were obtained from chars prepared previously in our laboratory and analyzed with digital image processing. Experimental data on the change in char particle radius with conversion were also used as model inputs.
CHAPTER 2

EXPERIMENTAL EQUIPMENT AND PROCEDURES

2.1 TGA/VMI Reactor System

The primary reactor used in this study is a custom modified thermogravimetric analyzer (Perkin-Elmer, TGS-2). Modifications were made to the furnace tube (see Figure 2.1) by Matzakos (Matzakos 1991), allowing the reactor to be used in conjunction with a video microscopy imaging system. The video microscopy system (Figure 2.2) includes an optical microscope with an extra-long working distance objective (JENA, Model 121). A color video camera (Javelin, Chromachip II) with 760x485 lines of resolution, is attached to the microscope. Illumination of the sample is provided by a split fiber optic light source (Dolan-Jenner, Fiber Lite). The video signal from the camera is sent through a video timer (FOR-A, UTG-33) which inserts the elapsed time and experiment number on the image before the signal is sent to a S-VHS video recorder (Panasonic, AG-7300).

The TGA/VMI provides sample weight measurements with a micro balance having a sensitivity of 0.1 μg and 0.1 % accuracy. Coal samples were placed in a platinum sample pan which is suspended in a cylindrical ceramic furnace wrapped with a wire heating element (FeCrAl). A phase fired heater controller provides a voltage through the wire which heats the furnace area. The TGA/VMI is capable of achieving heating rates as high
Figure 2.1  Detailed view of TGA/VMI furnace tube and sample image of platinum pan with six 28-32 mesh particles.
Figure 2.2  Summary of components in the video microscopy system.
as 20 °C/sec and a maximum final temperature of 1150 °C. A fan is utilized to cool the reactor furnace as quickly as possible when necessary.

2.2 Hot Stage Reactor System

The custom built hot stage reactor shown in figure 2.3 (Glass 1987) was designed to achieve heating rates as high as 1000 °C/sec, thus approaching the rates observed in industrial reactors. The heating element of the hot stage, a stainless steel mesh, also serves as the sample holder. The coal particles were placed either on top of the mesh or between a folded piece of mesh which is attached to two brass electrodes. A similar phase fired heater controller to the one used in the TGA/VMI provides a voltage across the electrodes. The hot stage is also equipped with its own microscope stage and utilizes the same video microscopy system described earlier. The hot stage is capable of higher magnifications than the TGA/VMI reactor. The primary use of the hot stage was for rapid pyrolysis experiments rather than combustion since it can not monitor sample weight.

The width of the mesh heating element determines its electrical resistance and, thus, its ability to generate heat. For heating rates above 100 °C/sec, the folded mesh width used was approximately 0.6 cm. Observations of the glowing mesh during heating suggested the presence of temperature gradients within the mesh. Portions of the mesh adjacent to the electrodes and near the center of the folded edge appeared to be cold spots since these areas did not glow as bright as the rest of the mesh. Because of the presence of cold spots, the position of the particles and thermocouple was chosen so as to avoid these regions. Despite these precautions, it is still possible that the particle and thermocouple temperatures were different for
Figure 2.3  Schematic of hot stage reactor.
any given run. This is the primary difference between the hot stage and TGA/VMI reactors. The TGA/VMI provides for more uniform heating of the sample particles.

2.3 Mass Flow Control, Temperature Measurement

For both reactors, two mass flow controllers were used to provide the appropriate flowrates of oxygen and nitrogen during pyrolysis and combustion. In each reactor, flow restriction was used at the reactor outlet so that the reactor pressure was slightly higher than atmospheric. This ensured that atmospheric oxygen did not enter the reactor. Temperature measurements for both reactors were made with Chromel-alumel thermocouples (type K). The signals from the thermocouples are isolated and linearized for a temperature range of 0-1000 °C by signal conditioning modules (Analog Devices, 3B47). The modules have a gain of 10 mV/°C so that 0-10 Volts DC corresponds to the temperature range 0-1000°C.

2.4 Data Acquisition and Control

It was first necessary to change the control of the reactor systems from a PDP-11 computer to a much faster Macintosh Quadra 900. Interfacing the equipment with the Quadra was achieved through the use of two data acquisition boards (NB-MIO-16L, NB-AO6, National Instruments). Figure 2.4 shows an overview of the various components in the TGA/VMI reactor system and their signals. Operation of the reactor systems required computer control of the signals listed in Table 2.1.
Figure 2.4  Various components of the TGA/VMI reactor system.
Table 2.1 Summary of experimental components and their control signals.

<table>
<thead>
<tr>
<th>Component</th>
<th>Inputs</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA/VMI</td>
<td>Heater Voltage</td>
<td>Weight, Temperature</td>
</tr>
<tr>
<td>HOT stage</td>
<td>Heater Voltage</td>
<td>Temperature</td>
</tr>
<tr>
<td>MFC's</td>
<td>Flow Setpoints</td>
<td>Flowrates</td>
</tr>
<tr>
<td>VCR</td>
<td>Record/Pause/Stop</td>
<td>-</td>
</tr>
<tr>
<td>Camera</td>
<td>Power ON/OFF</td>
<td>-</td>
</tr>
<tr>
<td>Fan</td>
<td>Power ON/OFF</td>
<td>-</td>
</tr>
<tr>
<td>Video timer</td>
<td>Start/Stop</td>
<td>-</td>
</tr>
</tbody>
</table>

The first 3 component signals are analog inputs and outputs and the last four components have digital, TTL (on/off) signals.

With the new control computer, data acquisition and control algorithms were performed 5 to 10 times faster. Increasing the rate at which weight measurements were taken vastly improved the accuracy of the reactivity data, which depends on the derivative of the sample weight versus time. The increased speed of algorithm execution also improved the control of the reactors, particularly at high heating rates.

Temperature control was achieved through a modified PID-velocity algorithm running at speeds ranging from 1 to 20 Hz depending on the temperature program. The control algorithm includes separate control parameters for the ramp and steady state portions of the temperature program. Separate time steps can be chosen for data acquisition versus control for the same experiment. This was accomplished by establishing separate algorithm loops for weight sampling versus temperature sampling.
and control. This was necessary to reduce the size of the data file containing the time, reactor temperature, sample weight, and temperature error. For slow heating rates, temperature control was easy enough so that large time steps could be used. However, time steps for the acquisition of weight samples still needed to be small to obtain the most accurate reactivity data.

In addition, setpoint modification was used to prevent overshoot of the final combustion or pyrolysis temperature at heating rates above 1.0 °C/sec. Figure 2.5 shows how the setpoints were modified for a pyrolysis experiment conducted at a heating rate of 10 °C/sec with a final temperature of 700 °C. For higher heating rates, setpoints had to be modified at lower temperatures in order to avoid overshoot.

2.5.1 Sequential pyrolysis and combustion experiments

In order to isolate the effects of pyrolysis conditions on the combustion of char particles, sequential pyrolysis and combustion experiments were conducted. The pyrolysis stage was conducted in either reactor. For heating rates larger than 20 °C/sec, the pyrolysis was conducted in the hot stage reactor and the resulting char was transferred to the TGA/VMI for combustion. The following outlines the steps involved in a sequential pyrolysis and combustion run in the TGA/VMI.

1) The sample area is purged with 240 sccm N₂. A constant flow of nitrogen is used at all times, particularly when the reactor is unsealed, to ensure that atmospheric oxygen does not enter the reactor at any time.
Figure 2.5  Example of setpoint modification for a pyrolysis run conducted at a heating rate of 10°C/sec to a final temperature of 700 °C.
2) Coal samples are loaded into the TGA/VMI reactor and spaced evenly to avoid contact during pyrolysis.

3) After loading the coal, nitrogen is allowed to flow for an additional 10 minutes.

4) The sample is heated to 200 °C and held there for 2.5 minutes to remove any moisture present.

5) The sample is then heated at the specified pyrolysis heating rate (0.1-20.0 °C/sec), until the temperature reaches the heat treatment temperature (HTT), generally 700 °C in this study, or some value just below the HTT to avoid overshoot. When the temperature reaches the HTT it is kept there for a soak time of either 0 or 3 minutes. A 3 minute soak time was most commonly used for this study.

6) After cooling the devolatilized char as quickly as possible to 200 °C using the reactor fan, a reactive mixture of oxygen and nitrogen is introduced and the system is allowed to equilibrate for 10 minutes.

7) The char is heated at a rate of 20 °C/sec to the final combustion temperature and held there until the weight change is negligible.

8) The temperature is then raised to 800 °C, to burn off any remaining carbon. When the weight no longer changes, the reactor temperature is brought back to the original combustion temperature and the weight is recorded to determine the ash content of the sample.

Initiation of the video timer and VCR recording was performed automatically by the control program. For each experiment the VCR was cued at the appropriate time to begin taping depending on the portion of the experiment which was of interest. For combustion experiments aimed
at studying particle ignitions, the fiber optic lighting was turned off to enhance observation of light emissions. During both pyrolysis and combustion, the sample weight, reactor temperature, time, and temperature error were continuously written to a data file at a chosen rate for later analysis. Choice of the data file writing rate depends on the duration of the experiment. For longer experiments, data was written to the file once or twice per second. For most experiments, data was written 10 times per second.

2.5.2 Rapid pyrolysis experiments

For experiments in which pyrolysis was conducted in the hot stage reactor, indentations were made in the mesh of the hot stage where the coal particles were placed. This was done to keep the particles from moving towards each other and agglomerating during pyrolysis. The mesh was also folded over so that both the samples and the thermocouple were surrounded by the mesh heating element. This was necessary to avoid the large thermal gradients which exist in the hot stage reactor as estimated by Glass (Glass 1987). Following pyrolysis in the hot stage, the devolatilized char was cooled to about 40 °C and transferred to a tared TGA/VMI reactor for combustion.

For a heating element having a width of 0.6 cm, only three 28-32 mesh sized particles fit in the reactor and thus multiple pyrolysis runs were conducted to obtain five char particles for combustion in the TGA/VMI. For 100 °C/sec and lower, the mesh was large enough to accommodate five 28-32 mesh coal particles. It should also be noted that the control parameters used in the temperature control, particularly the gain, had to be
changed as the mesh width was changed since the mesh characteristics determine its response to a particular control signal.

As heating rates approach and exceed 100 °C/sec, consideration must be given to the lag in temperature between the thermocouple and reactor. This is an additional reason why the heating rate was reduced before reaching the final temperature. The hot stage controller was tuned to achieve reproducible heating rates of up to 500 °C/sec. Figure 2.6 shows several runs conducted in the hot stage at 500 °C/sec. The control was quite reproducible considering that in the ramp portion of the temperature program, the algorithm could only be performed about 50 times.

Post analysis of the temperature versus time curves shows, however, that the actual heating rate was not constant at 500 °C/sec. Figure 2.7 shows that the heating rate varies, exhibiting a maximum at around 1000 °C/sec. Oscillations in the actual heating rate seen in figure 2.7 are a direct result of the PID control. We must keep in mind that when referring to heating rates of 500 °C/sec, the maximum heating rate of the reactor reaches approximately 1000 °C/sec. For future discussions, we will only refer to the nominal heating rate, 500 °C/sec in the case of figure 2.7.

### 2.5.3 Direct coal combustion experiments

In industrial coal combustion, pyrolysis and combustion processes are not conducted in sequential experiments. However, zones of differing oxygen concentration do exist in most industrial combustors. Near the reactor entrance where coal samples are loaded, the oxygen concentration is close to zero. In this zone, pyrolysis certainly predominates over combustion. A zone of higher oxygen concentration generally exists beyond the pyrolysis zone. In this zone, combustion predominates.
Figure 2.6  Temperature control for repeated pyrolysis runs conducted at 500 °C/sec.
Figure 2.7  Actual heating rate for 500 °C/sec temperature program.
Conducting sequential pyrolysis and combustion experiments is a good approximation to these reactor zones. However, we have also chosen to conduct direct combustion experiments in which coal particles are heated in a reactive gas mixture. Even for these types of experiments, pyrolysis of individual coal particles generally occurs first. However, at any given time different particles may be pyrolyzing at the same time that others are combusting.

Either reactor may be used for coal combustion experiments, but to obtain reactivity data they must be conducted in the TGA/VMI reactor. For more detailed observations of combusting coal particles, the hot stage reactor with its higher magnification may be used. The procedure for direct coal combustion experiments is the same as the pyrolysis stage of the sequential experiments except that a reactive mixture of oxygen and nitrogen is used.

2.6.1 Reactivity measurements

Sample reactivity was determined from the weight versus time data through the following calculation:

\[ R_o = \frac{dx}{dt} = -\frac{1}{m_o} \left( \frac{dm}{dt} \right) \]

where x is the conversion of the solid, m_o is the initial ash free solid weight, and m is the mass of unreacted sample at any time t. Calculating the reactivity of the sample depended on the way in which the weight versus time curve was fit. To achieve a proper fit, the number of curve fit points and the type of curve fit was modified. For samples which did not exhibit
ignition, and had low reactivity, a smooth curve fit was used. For samples which ignited, however, sharp changes in weight required a large number of curve fit points and were generally fit with cubic spline interpolates. From this curve fit information, the weight data was regenerated in a new data column. The fitted data was then point-wise differentiated and divided by the initial ash free weight to calculate reactivity.

In an attempt to better quantify the reactivity data of samples reacting under a wide range of conditions, average reactivities were calculated from combustion experiments. Reactivity data was averaged over a specified conversion range for each sample. Also, averages for several samples were computed for multiple experiments conducted at each set of conditions. With this data we quantified the differences in reactivity observed experimentally.

2.6.2 Digital image processing

Digital images with a resolution of 640x480 8-bit pixels were acquired from the video tapes of experiments using a Macintosh computer (Quadra 900) equipped with a frame grabber (Data Translation, Quick Capture). Analysis of digital images obtained allowed for quantification of visual data such as light intensity and particle size.

By acquiring a sequence of images at fixed time intervals, we were able to obtain time-resolved light intensity traces for individual particles or the entire pan. Experiments designed to study particle ignitions were typically conducted in the absence of fiber optic lighting. Before turning off the lights, images were acquired to determine the precise location of each particle in the pan. This allowed us to define regions of interest (ROI) such that each ROI included only one particle. For each ROI, we monitored
the maximum light intensity for each subsequent image in order to detect light emissions.

Figure 2.8 shows a digitized image from an experiment in which 4 particles were placed in the pan. ROI's C and D are centered on particles which cannot be seen because they are not emitting light. ROI's A and B, however, are centered on particles which are in ignited states. Char particles rarely moved during combustion experiments. However, if particle movement occurred, the intensity of the entire pan was monitored. All steps of the image analysis procedure developed to obtain light intensity traces were performed using NIH Image, a public-domain image processing software available by anonymous ftp from zippy.nimh.nih.gov. Figure 2.9 illustrates an example of a light intensity trace for an experiment in which all five particles present in the TGA/VMI reactor ignited.

In the past, data on particle ignitions consisted only of descriptions of those individual occurrences. We have better quantified data on particle ignitions by recording the number or percentage of particles in the sample which ignited when combusted at each particular set of conditions (again a number which represents data from multiple experiments). Determination of the number of particle ignitions was made through the combination of reactivity and video microscopy data.

2.7 Coal Samples

Most of the experiments discussed here were carried out with Illinois #6 coal, provided as part of the Argonne Premium Coal Sample Program (Vorres 1990). Illinois #6 is a high volatile bituminous coal having a high
Figure 2.8  Digitized frame from combustion experiment showing regions of interest (ROI) being monitored for light emissions.
Figure 2.9  Light intensity trace from a char combustion experiment illustrating the ability to monitor light intensities of individual particles during a multiple particle experiment.
ash content of 15%. Some experiments were also conducted on Pocahontas #3 coal, which is a low volatile bituminous coal with only 5% ash content.

Three coal particle sizes were used: 50-60 mesh (250-300 μm), 28-32 mesh (500-600 μm), and 20-24 mesh (710-840 μm). For each run, we placed several coal particles in the sample pan of the TGA/VMI reactor. To achieve a fairly uniform total sample weight as close to 1 mg as possible we placed 10-20 particles of the 50-60 mesh size, 4-6 particles of the 28-32 mesh size, and 2-3 particles of the 20-24 mesh size. For hot stage experiments, the number of particles used varied depending on whether chars were being prepared for combustion in the TGA/VMI.
CHAPTER 3

DETECTION AND CHARACTERIZATION OF PARTICLE IGNITIONS

3.1 Overview

The detection of particle ignitions is essential in studying coal combustion for many reasons. Firstly, particle ignitions are instrumental in determining the combustion behavior of coal and char particles. Secondly, particle ignitions lead to the highest reactive state of a particle, and are thus a good measure of reactivity. Furthermore, ignition detection is important since meaningful kinetic data can only be obtained in cases where particle ignitions do not occur.

Our approach to ignition detection involves the combination of thermogravimetric measurements and video microscopy. As noted in the introduction, the problems of detecting ignitions in multi-particle samples have led many investigators to conduct single particle experiments (Cozzani, et al. 1995, Gomez and Vastola 1985, Huang, et al. 1988, Levendis, et al. 1989). This prevents the study of particle interactions which are of importance in industrial coal utilization processes. However, the TGA/VMI reactor along with digital image processing combines the qualities of single and multiple particle experiments by allowing for efficient detection of individual particle ignitions during a multiple particle experiment.

3.2.1 Heterogeneous ignition
The video imaging capabilities of the TGA/VMI apparatus were very useful in identifying the ignition mechanism of coal and char particles. Our studies show that char particles appear to always ignite heterogeneously, with bright ignition regions that never exceed the boundary of the particle. Figure 3.1 shows a typical ignition sequence for char particles. The char used for this run was prepared from 28-32 mesh Illinois #6 coal particles pyrolyzed at 5 °C/s to a final heat treatment temperature of 700 °C. In Frame B, the left particle has ignited and its entire surface is glowing. Ignition of the other particle starts from a "hot-spot" localized in the leftmost part of the particle (Frame B) and propagates over the entire surface (Frames C and D). The glowing zone, however, never exceeds the particle boundary. By Frame D, the ignition of the left particle appears quenched. But, large holes appear on the surface of the right particle (seen as dark spots) indicating the opening to the exterior of large internal cavities (macropores) that have formed during pyrolysis (Zygourakis 1993).

3.2.2 Homogeneous ignition

Figure 3.2 shows a typical sequence of digital images obtained during combustion of a pair of 28-32 mesh Illinois #6 coal particles. The particle in the upper part of the image appears to ignite heterogeneously at first with a flame originating from a "hot-spot" on its surface (Frames A and B). This particle is then engulfed by a flame that appears to extend slightly beyond the original particle boundary in a few places (Frame C), indicating the presence of a small volatile combustion front close to the particle surface. The next frame (Frame D) shows that volatiles emitted from the bottom particle have clearly ignited with a large luminous flame
Figure 3.1  Sequence of digital images from a char combustion experiment illustrating heterogeneous ignition. Conditions: 28-32 mesh Illinois #6 particles, pyrolysis heating rate: 5 °C/sec, HTT: 700 °C, combustion temp.: 700 °C, 50% O$_2$. Elapsed time in seconds of respective frames A-F: 0.0, 1.0, 1.1, 1.9, 2.2, 2.5.
Figure 3.2  Sequence of digital images from a coal combustion experiment illustrating homogeneous ignition. Conditions: 28-32 mesh Illinois #6 particles, combustion heating rate: 5 °C/sec, combustion temp.: 750 °C, 50% O$_2$. Elapsed time in seconds of respective frames A-F: 0.0, 0.1, 0.2, 0.3, 0.4, 0.5.
emanating from the particle surface. This flame seems to ignite volatiles released by the other particle and a second flame emanating from the top particle now joins the original flame (Frame E). Both particles continue to glow in the last frame (Frame F) indicating that heterogeneous reactions continue to take place on the particle surfaces (and, most likely, throughout the particle interior) after the volatile flames have been extinguished.

Although Figure 3.2 clearly indicates a homogeneous ignition mechanism, we have also observed ignitions in which only the surface of the coal particles becomes illuminated and the bright ignition regions never exceed the particle boundaries. This transition to a predominantly heterogeneous ignition mechanism occurs when we lower the oxygen concentration in the gas flowing through the TGA/VMI reactor. Ignitions of the type shown in Figure 3.2 have never been observed with char particles. This observation is consistent with the accepted mechanism of heterogeneous ignitions since chars produced with our experimental protocols contain insignificant amounts of volatiles.

These observations agree with literature results reporting that coal particles ignite with a combination of homogeneous and heterogeneous mechanisms, depending on the flow velocities of reactant gases (Huang, et al. 1988, Yang and Tsai 1990). We must note, however, that the image sequence of Figure 3.2 also shows interactions among neighboring particles with one particle triggering the homogeneous ignition of another one. Such interactions must be important in actual combustors, but will remain undetected in experiments that use a single coal particle. Our studies have revealed that occurrence of this homogeneous mechanism is aided by high oxygen concentrations, high combustion temperatures, and most notably the presence of multiple particles during combustion. The presence of
multiple particles is perhaps the most crucial of these factors because it increases the chances of having volatile matter present in the gas surrounding an igniting particle.

3.3 Detection of Char Particle Ignitions

Before discussing the effectiveness of our approach to ignition detection, we will consider the two possible types of heterogeneous char particle ignitions. Ignitions characterized by high particle temperatures are accompanied by bright emissions of light. When this occurs, the ignition is easily observed by video microscopy regardless of the intensity of the light source which illuminates the reacting char sample. We will refer to such ignitions as type I ignitions. When, on the other hand, the particle temperature is not significantly elevated during a heterogeneous ignition, the intensity of light emission from the particle is low. Such ignitions may be difficult to detect with video microscopy, particularly when the fiber optic lighting of the sample is on. Ignitions associated with faint light emissions will be referred to as type II ignitions.

3.3.1 Detection of isolated ignitions

Figure 3.3a shows the reactivity plot obtained for a type I ignition when only one of the particles in the char sample ignited. A peak in reactivity is observed and corresponds to ignition of one of the five particles present in the reactor as shown by the accompanying light intensity trace (Figure 3.3b). This isolated ignition is, thus, detected by both reactivity and video microscopy measurements.

High particle temperatures associated with the ignition lead to sharp increases in reactivity. Once the ignition is extinguished, the particle
Figure 3.3  Reactivity pattern [A] and accompanying light intensity trace [B] obtained for a char combustion run during which 1 out of the 5 char particles ignited. Conditions: 28-32 mesh Illinois #6, pyrolysis heating rate: 10 °C/sec, HTT: 700 °C, combustion Temp.: 550 °C, 33% O₂.
temperature drops quickly. The result of this drop in temperature is a sharp decrease in reactivity. These sharp changes in reactivity associated with ignition lead to the observed spikes in the reactivity measurements. The presence of these peaks in the reactivity measurements thus provide another means of detecting particle ignitions. In the ideal case, those ignitions which are undetected by video microscopy will be detectable with reactivity measurements.

3.3.2 Detection of multiple ignitions

When multiple ignitions occur in the reacting char sample, however, we may not be able to distinguish the individual ignitions using only reactivity data. Figure 3.4a presents the reactivity plot for an experiment in which video microscopy shows that 4 out of the 5 char particles in the sample ignited. Despite the fact that 4 ignitions occurred, only 3 peaks are observed in reactivity. The light intensity trace of Figure 3.4b shows that the final peak is a result of 2 individual ignitions. When ignitions occur close together in time, reactivity peaks may overlap and video microscopy becomes the only means of determining which particles ignited and when the ignitions occurred.

3.3.3 Detection of faint ignitions

Video microscopy has been proven to be very powerful in ignition detection, however, used alone it may not be sufficient to detect all particle ignitions of type II associated with faint light emissions. Typical ignition experiments are carried out with the external illumination source turned off to enhance the sensitivity of our video microscopy system to light emissions. Even in the absence of external illumination, however, some
Figure 3.4  Reactivity pattern [A] and accompanying light intensity trace [B] obtained for a char combustion run during which 4 out of the 5 char particles ignited. Conditions: 28-32 mesh Illinois #6 particles, pyrolysis heating rate: 1.0 °C/sec, HTT: 700 °C, combustion Temp.: 550 °C, 33% O₂.
type II ignitions may not be visible. Fortunately, however, peaks in reactivity plots obtained through weight measurements may help us detect these ignitions.

Figure 3.5 is an example of this case and illustrates the sensitivity of the weight measurements. Figure 3.5 shows reactivity plots from 2 experiments, both conducted at a combustion temperature of 550 °C and in the absence of fiber optic lighting. In one experiment, no ignitions were observed. In the other, light emission from one of the 11 particles present in the sample was barely visible on video tape and would have undoubtedly been invisible if the fiber optic lighting was used. The image analysis procedure used to obtain an intensity trace for this particle was not able to distinguish the light emission from the signal noise. Despite the relatively small fraction of ignited particles, Figure 3.5 shows a sharp peak in reactivity that clearly distinguishes this reactivity pattern from the one obtained from the non-ignited sample. This example shows that reactivity data can help to effectively detect particle ignitions of type II, which are difficult to detect with microscopy.

As illustrated in Figure 3.5, isolated type II ignitions are detected through reactivity data. However, when multiple type II ignitions occur, detection becomes more difficult. If the ignitions occur close together in time, reactivity data may not be able to distinguish individual ignitions. Furthermore, if external illumination is too bright to observe the ignitions, or if the ignitions are simply too faint, video microscopy may also be unable to detect the ignitions.

One possible example of this occurrence is presented in Figure 3.6. The light intensity trace given in Figure 3.6b represents the maximum observed light intensity for the entire sample pan. Comparison with the
Figure 3.5 Reactivity patterns for 2 char combustion runs. During one, a faint ignition was observed for 1 out of the 11 particles in the sample. Conditions for both: 50-60 mesh Illinois #6 particles, pyrolysis heating rate: 10 °C/sec, HTT: 700 °C, combustion temp.: 550 °C, 21% O₂.
Figure 3.6 Reactivity pattern [A] and accompanying light intensity trace [B] showing secondary peak which may not be due to ignition. Conditions: 28-32 mesh Illinois #6 particles, pyrolysis heating rate: 10 °C/sec, HTT: 625 °C, combustion temp.: 550 °C, 33% O₂.
reactivity plot shows that the first peak in reactivity is a result of particle ignition (one ignition in this case). The second peak in reactivity has two possible explanations. It may be due to one or several type II ignitions that were undetectable by microscopy. The peak may also be a result of the opening of the internal pore structure of the particle through heterogeneous reaction (Sundback, et al. 1984). As the reaction proceeds, the opening of previously inaccessible porosity can lead to a sharp increase in the surface area available to reactants and, thus, to a sudden jump in particle reactivity.

3.3.4 Detection of secondary ignitions

Our setup also enabled us to observe that some char particles ignited multiple times in the same combustion sequence. These secondary ignitions commonly occurred at harsh conditions of high combustion temperatures and oxygen concentrations. Secondary ignitions produced a separate reactivity peak provided that the ignitions occurred sufficiently later in time than the primary ignitions. An example of the detection of secondary ignitions with our setup is presented in Figures 3.7a and 3.7b. In this experiment, 5 char particles were combusted in the TGA/VMI at 700 °C in 50% oxygen. The first peak in reactivity shown in Figure 3.7a, corresponds to the ignition of 4 of the 5 particles in the reactor within a span of about 3 seconds. Six seconds after the first group of ignitions, 3 of the previously ignited 4 particles ignited again and the new group of ignitions produced a second distinct peak. The light intensity traces of Figure 3.7b demonstrate the ability of video microscopy to distinguish between the primary and secondary ignitions. In this case, the secondary ignitions were delayed enough to produce a separate reactivity peak. In
Figure 3.7  Reactivity pattern [A] and accompanying light intensity trace [B] showing primary and secondary peaks, illustrating the detection of secondary ignitions. Conditions: 28-32 mesh Illinois #6 particles, pyrolysis heating rate: 10 °C/sec, HTT: 700 °C, combustion temp.: 700 °C, 50% O₂.
many cases, however, the secondary ignitions occur very soon after the primary ignitions and video microscopy is the only means of detection.

3.3.5 Ignition detection at high combustion temperatures

Up to this point, we have focused on the effectiveness of ignition detection at a combustion temperature of 550 °C. When the combustion temperature is raised, ignitions become more frequent and overlapping of individual ignitions is more likely. Figure 3.8a presents a typical reactivity curve for a combustion run conducted at 750 °C. The accompanying light intensity trace (figure 3.8b) shows that all 5 particles in the sample ignited. The shape of the reactivity curves is much smoother than those at 550 °C, it does not exhibit the same sharp ignition peaks. When reactivity is plotted versus conversion as in figure 3.9, the curves at 750 °C bear more of a resemblance to those obtained at 450 °C, a temperature at which ignitions do not occur.

The reason the reactivity curves at 750 °C look more similar to 450 °C curves than 550 °C is not because particle ignitions do not occur. Particle ignitions are, in fact, much more common at 750 °C. When multiple particles in the sample ignite however, individual ignition peaks blend together, as discussed earlier.

Because of this behavior, ignition detection at higher combustion temperatures will rely more heavily on observation of ignitions with video microscopy than on reactivity data. Furthermore, the detection of faint particle ignitions (type II) will be much more difficult since reactivity data is not as available to complement video microscopy.
Figure 3.8 Reactivity pattern [A] and accompanying light intensity trace [B] for char combustion run in which all five sample particles ignite. Conditions: 28-32 mesh Illinois #6 particles, pyrolysis heating rate: 500 °C/sec, HTT: 700 °C, combustion temp.: 750 °C, 33% O₂.
Figure 3.9  Comparison of reactivity plots for char combustion experiments at 450 and 750 °C. For both runs 28-32 mesh Illinois #6 char particles, HTT 700 °C. For 750 °C run: pyrolysis heating rate: 10.0 °C/sec, 33% O₂. For 450 °C run: 0.1 °C/sec, 21% O₂.
3.4 Detection of Coal Particle Ignitions

Most of the issues discussed for char ignition detection also apply to the detection of coal particle ignitions. However, studies on the combustion of coal particles have revealed that at heating rates equal to or above 10 °C/sec, the devolatilization rates are large enough to produce peaks in $R_0$ quite similar to ignition peaks. Figure 3.10 shows the reactivities measured for a series of coal combustion experiments conducted at heating rates between 0.1 and 20 °C/sec. The two highest heating rates each reveal two reactivity peaks, one at a low conversion and another at a higher conversion. Without the aid of video microscopy, these might be interpreted as particle ignitions. However, comparison of the reactivity plots versus time and the video tapes clearly shows that the first reactivity peaks which are observed at lower conversions correspond to the devolatilization of the coal particle. Devolatilization is visible due to the plastic behavior of the Illinois #6 coal, which rapidly swells and contracts while devolatilizing. High heating rates result in increased devolatilization rates and give rise to the primary peaks observed in Figure 3.10. Similar peaks are observed when pyrolyzing coal particles in pure N$_2$ (see figure 3.11).

Video tapes from these coal combustion experiments revealed that the secondary peaks observed for 10 and 20 °C/sec heating rates (see figure 3.10) were overlapping peaks from multiple particle ignitions. Again, video microscopy is necessary in this case to provide information about individual particle ignitions. No ignitions were observed at a heating rate of 0.1 °C/sec. This is confirmed by the flat reactivity curve.

The video tape for the 1 °C/sec experiment revealed that several very faint ignitions occurred in one of the four particles. The faint emission of
Figure 3.10 Series of coal combustion experiments showing the presence of a devolatilization peak as well as a blended ignition peak for higher heating rates. Conditions: 28-32 mesh Illinois #6 particles, combustion temp.: 700 °C, 21% O₂.
Figure 3.11  Series of coal pyrolysis experiments illustrating the peak in devolatilization rate occurring in pure N2. Conditions: 28-32 mesh Illinois #6 particles, HTT: 700 °C.
light by these ignitions is in agreement with the relatively low reactivity of this sample. Since these experiments were conducted without external illumination, it was possible to detect the faint ignitions. If image analysis had not detected any ignitions for this experiment, the reactivity data would still provide evidence of the occurrence of ignitions. However, the reactivity data would only have served to indicate that ignitions had occurred, without providing specific information about the ignition of individual particles.

The devolatilization peaks of Figures 3.10 and 3.11 occur regardless of whether the particles ignite or not, provided that the heating rate is 10 °C/sec or higher. We should note, however, that the ambient temperatures at which these first peaks occur (about 600 °C for 10 and 20 °C/sec heating rates when combusted at 700 °C) do suggest that heterogeneous reactions may contribute to the weight loss associated with this peak. However, we cannot be certain that the particle temperatures were equal to the ambient at these peaks since pyrolysis is an endothermic process.
CHAPTER 4

EFFECTS OF PYROLYSIS HEATING RATE ON CHAR IGNITION AND REACTIVITY

4.1 Overview

The previous studies of Matzakos (Matzakos 1991) and Ismail (Ismail 1994) have investigated the dependence of char reactivity on the conditions of pyrolysis. In particular, the conditions found to increase char reactivity were high pyrolysis heating rates, low heat treatment temperatures, and short soak times. Of these effects, pyrolysis heating rate is, perhaps, the most interesting. One objective of the current study is to better quantify the effects of pyrolysis heating rate on char ignition and reactivity behavior. This is possible, in part, due to improvements in the accuracy of the reactivity data measurements.

Matzakos and Ismail focused on pyrolysis heating rates equal to or below 20 °C/sec, corresponding to the limitations of the TGA/VMI. In the present work, we have been able to study the reactivity of chars prepared at heating rates approaching industrially observed rates (approximately 1000 °C/sec), utilizing the hot stage as a rapid pyrolysis reactor.

4.2 Steady State Ignition Model

As discussed previously, the pyrolysis heating rate has a major influence on the resulting internal pore structure of a char particle. As mentioned in chapter 1, Boissiere (Boissiere 1993) and Zygourakis (Zygourakis 1993) studied char particle cross sections to determine the
effects of pyrolysis on char particle size, macroporosity, and macropore surface area. Chars were prepared by pyrolyzing the parent coals in the hot stage reactor. However, a different heating element was used in the hot stage. Instead of placing a wire mesh heating element between the electrodes, a metal ribbon was used. A platinum sample pan from the TGA/VMI was placed on the heating element. In this setup, heating of the sample occurred primarily by conduction through the pan. Ismail's heterogeneous steady state ignition model introduced in section 1.4.2, was used to elucidate the effects of these char structural properties on ignition.

4.2.1 Parametric results

Although steady state models are unable to describe the evolution of char properties with conversion, they are capable of describing trends in the effects of model parameters. For example, Ismail's model predicted that char particle ignitions were favored by increasing particle radii and macropore surface area. Increasing particle size favors ignition as a result of the trade off between heat generation through reaction and heat removal by heat transfer to the surroundings. Heat transfer is dependent on the external surface area of the particle while heat generation occurs in the interior volume of the particle. Larger particles have a lower surface area to volume ratio thus resulting in greater amounts of heat accumulation favoring ignition. We will delay the discussion of the effects of macropore structure until section 4.3.4.

4.2.2 Confirmation of model predictions

Ismail utilized the structural data of Boissiere and Zygourakis to relate experimental pyrolysis conditions to model parameters in order to
compare the model with experimental results. Since vast improvements have been made in the detection of particle ignitions and the accuracy of reactivity data, additional experiments were conducted to test Ismail's model. In these experiments, the heating rates studied were 0.1, 1.0, and 10.0 °C/sec since these are the only values studied by Boissiere. Illinois #6 char particles from both 28-32 and 50-60 mesh sizes were prepared at these three heating rates. All combustion runs were conducted at 550 °C and the oxygen concentration was either 21 or 33%. The ignition detection procedure outlined in chapter 3 was utilized to determine how many particle ignitions occurred at each set of conditions.

Figure 4.1 summarizes the comparison between Ismail's model and the experimental results. Each cell in figure 4.1 corresponds to a unique set of values for pyrolysis heating rate, oxygen concentration, and char particle size. The upper entry in each cell indicates the number of particle ignitions detected for repeated combustion experiments at 550 °C. The lower entry states whether Ismail's model predicts the possibility of ignition for those particular conditions. Because of the limitations of a steady state model discussed in chapter 1, we will focus on the predicted trends.

From figure 4.1, we see that both the model and experimental results agree quite well concerning the trends in char particle ignitions with pyrolysis heating rate. In general both agree that particle ignitions were favored by larger particles, higher oxygen concentrations, and higher heating rates. However, the experimental results show that ignitions were most common at 1.0 °C/sec. This was not predicted by Ismail's model.
Figure 4.1  Comparison of Ismail's steady state ignition model with experimental results on the effects of particle size, pyrolysis heating rate, and oxygen concentration on the ignition of Illinois #6 char particles when combusted at 550 °C. HTT: 700 °C.
4.3 Char Ignition and Reactivity Studies

The ignition detection technique discussed in chapter 3 was very useful in analyzing the effects of pyrolysis heating rate on char ignition behavior. We recorded the number of particles which ignited during repeated experiments at each set of conditions to compare the behavior at different heating rates and combustion conditions. Furthermore, average reactivities were calculated for repeated experiments as outlined in chapter 2. This data combined with the particle ignition data was very useful in identifying the effects of pyrolysis heating rate on the combustion behavior of char particles. In the following sections, we have divided the results corresponding to the conditions of combustion. Results at combustion temperatures existing in the kinetic control regime are discussed first, followed by results in the transition and diffusion limited regime.

4.3.1 Kinetic control regime

Previous studies have indicated that char particles prepared from 28-32 mesh Illinois #6 coal react in the regime of kinetic control at temperatures below 450 °C. To determine the effect of pyrolysis heating rate on char ignition and reactivity in the kinetic control regime, chars have been prepared at various heating rates between 0.1 and 500 °C/sec and combusted at 450 °C in 21% oxygen.

Figure 4.2 shows the reactivity plots obtained when chars prepared at the various heating rates were combusted in 21% oxygen at 450 °C. The reactivity is plotted versus conversion, and for most runs it exhibits a maximum at an intermediate conversion of about 30%. This maximum is a result of the competition between pore enlargement and coalescence. As pores are consumed by reaction, their surface area increases and new active
sites are exposed. Eventually however the pores begin to coalesce, resulting in a decrease in available surface area until the particles are completely consumed (Ballal and Zygourakis 1987, Bhatia and Perlmutter 1980, Bhatia and Perlmutter 1981, Gavalas 1980)

We can see from Figure 4.2 that the effects of pyrolysis heating rate on char reactivity are minimal in this regime. To quantify the reactivity of each sample, an average reactivity was determined by computing an average of the values at uniform conversion points in a range spanning 0 to 95% conversion. These are presented in Figure 4.3, which verifies that little difference in reactivity is observed for chars prepared at the various heating rates. At this low combustion temperature of 450 °C, no particle ignitions were detected in any of the sample particles.

4.3.2 Transition regime

As the combustion temperature is raised to 550 °C, diffusional limitations begin to appear in Illinois #6 char particles. Verification of this assertion is made by using kinetic data to predict the effectiveness factor at this temperature. The extent of diffusional limitations, expressed by the effectiveness factor \( \eta \), can be calculated by dividing the observed reactivity by the value predicted by kinetic data obtained under kinetic control conditions:

\[
\eta = \frac{R_{obs}}{Ae^{\left(-\frac{E}{RT}\right)y}}
\]  

(4.1)
Figure 4.2 Reactivity plots for 28-32 mesh Illinois #6 chars prepared at heating rates of 0.1, 1.0, 10.0, 20.0, 100 and 500 °C/sec and combusted at 450 °C in 21% O₂. HTT: 700 °C.
Figure 4.3  Average reactivities calculated from the reactivity plots of figure 4.3.
where A and E are the pre-exponential factor and activation energy. T is the combustion temperature and \( y \) is the mole fraction of oxygen. We will discuss how we obtained values for the kinetic parameters in section 4.4.

One complication of this analysis is that at 550 °C, char particles begin to exhibit ignition due to the increased reaction rates and associated heat generation. Particle ignitions lead to greatly increased reaction rates over the predicted reaction rates since the particle temperature is no longer 550 °C. Nonetheless, effectiveness factors for char samples combusting at 550 °C which do not ignite are found to be considerably below 1.0, which is the limit of kinetic control.

Figures 4.4 through 4.9 present the reactivity versus conversion plots for chars prepared at each of the chosen pyrolysis heating rates between 0.1 and 500 °C/sec and combusted at 550 °C in 33% oxygen. A minimum of 3 experiments for each heating rate were conducted. As shown in the previous chapter, the various observed peaks in the reactivity curves are directly attributable to particle ignitions. The width of the ignition peaks is an indication of how many particles ignited. However, the exact number of particle ignitions also relied on microscopy measurements as discussed in chapter 3.

Because of the irregular nature of the peaks, it is difficult to present multiple reactivity curves on one plot. Thus, only two of the reactivity curves obtained for each heating rate are given here for the sake of clarity.

Average reactivities for these various experiments were calculated by the previously described procedure and are summarized in figure 4.10a. The average reactivity for each experiment represents the average value of the multiple experiments conducted at each heating rate. Also given in figure 4.10a are the standard deviations of the average reactivities. The
Figure 4.4 Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 0.1 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.5 Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 1.0 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.6  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 10.0 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.7 Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 20.0 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.8  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 100 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.9  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 500 °C/sec and combusted at 550 °C in 33% O₂. HTT: 700 °C.
Figure 4.10  Summary of average reactivity data [A] and particle ignitions [B] for chars prepared at heating rates between 0.1 and 500 °C/sec and combusted at 550 °C in 33% O₂.
ignition detection procedure described in chapter 3 was used to determine the number of particle ignitions which occurred in all experiments. Figure 4.10b shows the percentage of sample particles which ignited at each set of conditions.

Perhaps the most striking feature of the average reactivity data is the magnitude of the standard deviations. These large variations in reactivity result from particle ignitions. At 550 °C and 33% oxygen, the conditions are favorable for particle ignitions to occur. However, they do not occur in all cases. Because igniting char particles react at temperatures which greatly exceed 550 °C, the difference in reactivity for samples in which many ignitions occur versus those where very few or no ignitions occur is tremendous.

Differing ignition behavior among the various chars prepared at the same pyrolysis conditions may be due to many factors, but is generally attributable to the heterogeneous nature of coal. Although all the particles were prepared by the same pyrolysis procedure, this does not automatically ensure that they have the same size, catalytic mineral content, internal surface area, etc.

Comparison of the average reactivity data with the ignition data in figures 4.10a and 4.10b shows the same observed trends in reactivity and ignition as the heating rate is varied. From this we can conclude that particle ignitions are instrumental in determining the reactivity of char samples at this temperature. Despite the large variation in the data, the trends show that chars prepared at higher heating rates ignite more commonly and exhibit higher reactivity. Among the heating rates below 20 °C/sec, however, there is a peak in both reactivity and ignition for chars prepared at 1.0 °C/sec.
For heating rates between 0.1 and 20 °C/sec, the TGA/VMI reactor was used for char preparation. The hot stage was used as a rapid pyrolysis reactor for preparation of the chars at 100 and 500 °C/sec. Because of the inherent differences in the two reactors, it was essential to compare the combustion behavior of chars prepared in the hot stage and TGA/VMI reactors at the same pyrolysis conditions. Because of the heating rate limitations of the TGA/VMI, this was only possible by preparing chars in the hot stage at the lower heating rates for combustion in the TGA/VMI.

To compare the reactivity of chars prepared in different reactors, we chose to study the combustion of chars prepared in the hot stage at 0.1 and 20 °C/sec, the highest and lowest rates employed in the TGA/VMI. Figure 4.11a presents the average reactivity data for these experiments. For this combustion temperature of 550 °C, large differences are observed in the reactivity of chars prepared under the same conditions in different reactors. We see from the data that chars prepared in the hot stage exhibit considerably lower reactivity for both heating rates. Again the standard deviations in average reactivity are fairly high at this combustion temperature due to particle ignitions.

Particle ignitions, shown in figure 4.11b, were also less common in the chars prepared in the hot stage, as expected from the reactivity data. No chars prepared at 0.1 °C/sec in the hot stage exhibited ignition when combusted at 550 °C. Thus the standard deviation in average reactivity for these runs is much lower.

The implications of these results are quite important. While the previous results have shown that chars prepared at 100 and 500 °C/sec exhibit the highest reactivity, the actual difference in reactivity may be much greater because of inherent differences in the two reactors.
Figure 4.11  Summary of average reactivity data [A] and particle ignitions [B] for experiments to study the differences in chars prepared in the TGA/VMII and hot stage reactors. Chars were prepared in both reactors at 0.1 and 20.0 °C/sec, and combusted at 550 °C in 33% O₂. HTT: 700 °C.
The fact that differences are observed in the reactivity of chars prepared in each reactor is not surprising because of the design of the reactors. Perhaps the most important aspect of the design is the means by which the samples are heated. As discussed in chapter 2, the TGA/VMI provides for more uniform heating of the sample and thermocouple, which occurs mainly through radiation from the furnace heating element. On the other hand, samples in the hot stage are heated by conduction and radiation since they are in direct contact with the heating element. Since the thermocouple and sample particles must be placed in various portions of the mesh, it is difficult to ensure that they are at the same temperature.

It is well known that increasing pyrolysis temperatures lead to chars with lower reactivities. Very high pyrolysis temperatures may lead to a deactivation or sintering of active sites on the carbon surface. The lower reactivity exhibited by hot stage chars is evidence that perhaps the sample particles were subjected to higher temperatures than those measured by the thermocouple.

4.3.3 Diffusion Limited Regime

To study the combustion behavior of char particles in the regime of diffusional limitations, we have conducted experiments at a combustion temperature of 750°C and oxygen concentration of 33%. At this combustion temperature, particle ignitions are much more prevalent than at 550 °C. The widespread occurrence of particle ignitions prevents the estimation of effectiveness factors at 750 °C, since the particles react at temperatures much higher than 750 °C.

To determine the effects of pyrolysis heating rate on char ignition and reactivity behavior in this regime, we have undertaken the same
analysis as in the previous discussions. Figures 4.12 through 4.17 present the reactivity curves obtained for each heating rate studied. The smoother curves obtained at 750 °C allow us to present more of the repeated runs to on each individual plot.

Average reactivity data for these combustion experiments is shown in figure 4.18a. The magnitude of the reactivities at this temperature is now much higher. In figure 4.18b we also see that particle ignitions are much more frequent. Now that ignitions occur more commonly, we see much smaller magnitudes of the standard deviations than those obtained at 550 °C. The reactivity data of figure 4.18a clearly shows an increase in reactivity with increased pyrolysis heating rate. The largest increase is observed for chars prepared in the hot stage at higher heating rates, despite the differences between the two reactors discussed earlier.

Among heating rates lower than 20 °C/sec, the char reactivity data shows little deviation. Despite the small magnitude of the standard deviations in average reactivity, there is still overlap in the reactivity data for chars prepared at these heating rates. The small differences in reactivity are somewhat surprising considering the differences in particle ignitions presented in figure 4.18b. One possible explanation for this behavior is the presence of undetected faint particle ignitions. As discussed in chapter 3, detection of faint ignitions (type II) are more difficult at higher combustion temperatures where reactivity curves are smooth.

It should also be noted that the particle ignition data does not provide any information or distinguish between faint and strong particle ignitions. This could also be an important factor leading to the different trends in reactivity and ignition data. Furthermore, the data does not reflect cases where multiple ignitions occurred within a single particle. These secondary
Figure 4.12 Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 0.1 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.13  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 1.0 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.14  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 10.0 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.15  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 20.0 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.16  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 100 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.17  Reactivity plots for 28-32 mesh Illinois #6 char particles prepared at 500 °C/sec and combusted at 750 °C in 33% O₂. HTT: 700 °C.
Figure 4.18  Summary of average reactivity data [A] and particle ignitions [B] for chars prepared at heating rates between 0.1 and 500 °C/sec and combusted at 750 °C in 33% O₂.
ignitions, which are more common at harsher combustion conditions, often lead to greatly increased average reaction rates.

4.3.4 Reactivity mechanism

From the previous results, we have seen that 28-32 mesh sized Illinois #6 chars prepared at higher heating rates ignite more commonly and exhibit higher reactivity when combusted in the diffusion limited regime. Differences in reactivity were not observed when chars were combusted at low combustion temperatures corresponding to the kinetic control regime.

To describe the experimentally observed effects of pyrolysis heating rate on char ignition reactivity, we must consider the effects of pyrolysis heating rate on char structure. For 28-32 mesh Illinois #6 chars, Boissiere's structural data for heating rates between 0.1 and 10.0 °C/sec is presented in table 4.1. Figure 4.19 also presents examples of the cross sections of char particles obtained by Boissiere for pyrolysis heating rates of 0.1 and 10.0 °C/sec.

Table 4.1 Structural Data for 28-32 mesh Illinois #6 chars.
(Boissiere 1993)

<table>
<thead>
<tr>
<th>Heating Rate (°C/sec)</th>
<th>Radius (mm)</th>
<th>Macroporosity</th>
<th>Macropore SA (cm²/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.317</td>
<td>0.592 ± 0.030</td>
<td>865 ± 73</td>
</tr>
<tr>
<td>1.0</td>
<td>0.325</td>
<td>0.595 ± 0.025</td>
<td>1244 ± 98</td>
</tr>
<tr>
<td>10.0</td>
<td>0.407</td>
<td>0.648 ± 0.025</td>
<td>1040 ± 85</td>
</tr>
</tbody>
</table>
Figure 4.19  Cross sections of char particles prepared by Boissiere. Pyrolysis heating rates 0.1 and 10.0 °C/sec.
The data of table 4.1 indicates that increasing pyrolysis heating rates leads to larger char particles. Since larger char particles favor ignitions, as discussed in section 4.2.1, this should lead to more particle ignitions and higher reactivity. However, the data of table 4.1 also shows a peak in macropore surface area at a pyrolysis heating rate of 1.0 °C/sec. We must now consider the effects of macropore surface area.

Consider two char particles prepared at 0.1 and 10.0 °C/sec having similar cross sections to those in figure 4.19. The char prepared at 10.0 °C/sec will thus have a much higher macropore surface area. If these two chars are combusted at 450 °C, the reaction rates are fairly slow, allowing oxygen to fully penetrate both the larger macropores and micropores of the chars internal surface before it is consumed as indicated in Figure 4.20. Since the micropores of a char account for nearly all the internal surface area, and pyrolysis heating rate has little effect on the microporous surface area, these chars are expected to have similar reactivities at this temperature existing in the kinetic control regime.

When the same two chars are combusted at 750 °C, the rate of oxygen reaction is much faster, and oxygen may be completely consumed before penetrating the micropores of the char as indicated in Figure 4.21. In this case of diffusion limitation, only the portion of the chars micropores which are near the mouth of a macropore are utilized. Now, the char with larger macropores have an advantage in reactivity since more of its micropores are accessible along the perimeter of the larger macropores. Thus, we expect that at conditions giving rise to diffusional limitations, chars with higher macropore surface areas will exhibit higher reactivity. Furthermore, these higher rates of internal reaction may also
Figure 4.20  Illustration of the utilization of the internal surface area of two structurally different chars when combusted in the kinetic control regime.

Figure 4.21  Illustration of the utilization of the internal surface area of two structurally different chars when combusted in the diffusion limited regime.
lead to greater heat generation by the exothermic reactions, and increase the likelihood of particle ignition.

Since higher macropore surface areas lead to more reactive chars when combusted at high temperatures, the data of table 4.1 lends support to the experimentally observed peaks in ignition and reactivity for 1.0 °C/sec chars in figure 4.10. This difference is most dramatic at 550 °C where the conditions are borderline in favoring particle ignitions. However, as the combustion temperature is raised to 750 °C, particle ignitions become inevitable, and the differences in reactivity observed in figure 4.18 are much smaller.

Unfortunately, no structural data is available for similar chars prepared at heating rates exceeding 10 °C/sec. The measurements reported by Zygourakis (Zygourakis 1993) do include heating rates up to 1000 °C/sec, but were obtained for smaller mesh sizes and different coal types. This high heating rate data does show, however, larger particle sizes and much higher macropore surface areas for chars prepared at rates approaching 1000 °C/sec. It is expected that large increases in macropore surface area for high heating rates are responsible for the much higher experimentally observed reactivities in figures 4.10 and 4.19.

4.4 Kinetic Data

The reactivity of a char particle is in general a function of the following variables:

\[
R = \frac{dx}{dt} = f(T_s, C_s) \cdot RSA(x) \cdot \eta(T_s, C_s)
\]  

(4.1)
where \( f(C_s, T_s) \) represents the intrinsic reactivity of the char, RSA is the reactive surface area which is dependent on conversion, \( \eta \) is the effectiveness factor or extent of diffusion limitations, and \( T_s \) is the solid temperature.

The regime of kinetic control is the most appropriate range in which to attempt to measure intrinsic reactivity, since diffusional limitations should be minimal. As mentioned in the opening chapter, intrinsic reactivity should be independent of solid conversion. However, it is obvious from the reactivity plots of section 4.3 that our reactivity is a strong function of conversion. This is due to the dependence of internal surface area, or reactive surface area, on conversion. Since this relationship cannot be measured directly in the present study, we can only report on observed, or specific reactivity.

While knowledge of intrinsic reactivity is important, the actual observed reactivity of a char particle at given set of conditions will in general be quite different from the intrinsic value. Observed reactivity will be highly dependent on the other terms found in equation (4.1), particularly diffusional limitations. These terms are ultimately determined by combustor process conditions. Thus, we have focused our efforts on determining the effects of pore structure and process conditions which ultimately determine the observed or specific reactivity.

To determine the kinetic parameters for Illinois #6 chars we have chosen the following rate expression to fit our reactivity data:

\[
R_o = k y^n
\]  
(4.2)
where \( R_0 \) is the conventional reaction rate (min\(^{-1}\)), \( y \) is the mole fraction of oxygen, \( k \) is the reaction rate constant, and \( n \) is the order of reaction. Previous studies in our laboratory have determined that the reaction order for Illinois char combustion is 1.0 (Ismail 1994, Matzakos 1991). This value will therefore be assumed here. The reaction rate constant will be described by the Arrhenius form:

\[
k = A \cdot e^{\left( \frac{-E}{RT} \right)}
\]  

(4.3)

where \( A \) is the pre-exponential factor (min\(^{-1}\)), and \( E \) is the activation energy of the reaction (kcal/mol). \( R \) is the gas constant, and \( T \) is the temperature in Kelvin.

Since the observed reactivity is a strong function of conversion, we must normalize the reactivity data with respect to a reference conversion (10% in this case). This kinetic data therefore does not take into account the variation of reactivity with conversion. A total of 7 separate char combustion experiments were conducted at temperatures ranging from 400°C to 450 °C, to obtain reactivity data. The oxygen mole fraction for the various experiments was either 0.21 or 0.33.

The reaction rate constant was calculated for each experiment based on the chosen rate expression. These values of \( k \) are plotted in Figure 4.22 on a log scale versus the inverse of temperature. Plotting the data in this way produces a straight line having a slope of \( -E/R \) and a \( y \) intercept of \( A \). This analysis yields an activation energy of 28.3 kcal/mole and a pre-exponential factor of \( 4.45 \times 10^6 \) min\(^{-1}\). Choosing a reference conversion of
Figure 4.22 Arrhenius plot of reaction rate constant versus (1/Temperature) at 10% reference conversion for 28-32 mesh Illinois #6 chars prepared at various heating rates and combusted at temperatures between 400 and 450 °C. HTT: 700 °C.
25% yields an activation energy of 25.6 kcal/mol and pre-exponential factor of $5.31 \times 10^7\ \text{min}^{-1}$.

4.5 Normalized Reactivity Measurements

Among the terms which determine the reactivity of a char particle in equation (4.1), the reactive surface area term is the strongest function of conversion. Therefore, if our reactivity plots are normalized by the value of the reactivity at some reference conversion, all factors other than RSA will cancel out assuming that the diffusional limitations change very little with conversion. This analysis results in an experimental estimation of the variation of reactive surface area with conversion. This approach provides information about the variation of reactivity with conversion which was not provided by the raw kinetic data.

Figure 4.23 compares the evolution of surface area in the kinetic and diffusion control regimes. This was done by normalizing the reactivity plots by the value at 10% conversion for several runs and computing the average. This information will also be useful later in the development of a transient char combustion model, where the variation of char properties with conversion must be considered. The estimated variation of surface area with conversion was fairly uniform for the various runs. Focusing on the conversion range 0 - 10%, we see that at 750 °C, the curve begins very near the origin. This is an indication that at these early conversions, very little of the internal surface area was available for reaction. At this high temperature, oxygen is consumed quickly and does not reach a large portion of the internal pores until they become more accessible at higher conversions. In contrast, values of the normalized reactivity for the kinetic control regime, are considerably higher in this conversion range.
Figure 4.23  Averaged normalized reactivity plots for 28-32 mesh Illinois #6 char particles prepared at various heating rates and combusted at 750 °C in 33% O₂ and 450 °C in 21% O₂. HTT: 700 °C.
The peak in normalized reactivity at 750 °C attains much higher magnitudes. This is directly attributable to diffusion limitations. At this temperature, the available surface area at 10% conversion is quite low. As conversion progresses, more surface area becomes accessible. Since the reactivity at 750 °C is normalized by a smaller value, the peaks observed are much higher than those at 450 °C.

From figure 4.23, we see that peaks in reactivity are reached at very similar conversions in both the kinetic control and diffusion control regimes. This is in contrast to the theoretical studies of Bhatia and Perlmutter (Bhatia and Perlmutter 1981). Using a random pore model for description of non catalytic fluid solid reactions, they predicted that increasing diffusion limitations led to a shift in the maximum reaction rate to lower conversions. However, particle ignitions were not considered in their study since the model is geometric in nature, and assumes isothermal reaction. Furthermore, we have found that secondary ignitions and particles igniting at different times greatly affected the location of the maximum in reactivity.

4.6 Observations of Reacting Particles

The imaging capabilities of the TGA/VMi have been very useful in monitoring visual changes which occur in combusting char particles. In particular, we have been able to measure particle diameters as a function of conversion during combustion. Measurements of the particle diameters are made through analysis of digitized sequences of experiments obtained from video tape. Direct measurement of the changes in particle diameter can be very useful in modeling studies, since in most cases assumptions are made concerning the change in particle size.
The variation of particle diameter with conversion for various Illinois #6 char particles is presented in Figure 4.24. The particle diameters are normalized by the initial value to focus on the change in size. In most cases, the particle diameter at 90% conversion is between 50 and 70% of the original value. Furthermore, the various particles studied show fairly similar behavior in how the normalized diameter changes.

Measurements of the change in particle diameter with conversion were also made for chars combusting in the regime of diffusional limitations. Figure 4.25 includes data for chars combusted at 550 °C and 750 °C. In addition, measurements were also made for chars prepared from Pocahontas #3 coal which, like Illinois #6, is a bituminous coal but has a lower volatile and ash content.

Comparison of the normalized change in particle diameter to the data obtained at 450 °C (figure 4.24) shows that in the regime of diffusional limitations, the change in particle diameter is much less drastic. Char particle diameters generally shrink only 5 - 15 % in this regime. One possible explanation of this result is that at higher combustion temperatures, reaction rates are much higher within the particle as compared to the external surface due to intraparticle thermal gradients. This contention is supported by the models of Sotirchos and Amundson (1984a, 1984b, 1984c, 1984d), which showed that the center of char particles often exhibited much higher temperatures than the surface during ignition.

While studying the changes in particle diameter with conversion, we were also able to make other observations about the structure of reacting char particles with the aid of video microscopy. In some cases, when ignition occurred in char particles, we observed fusion, or melting of the
Figure 4.24  Changes in Illinois #6 28-32 mesh char particle diameter with conversion during combustion at 450 °C in 21% O₂. Other conditions HTT: 700 °C, various pyrolysis heating rates.
Figure 4.25 Changes in Illinois #6 and Pocahontos #3 28-32 mesh char particle diameters with conversion during combustion at 550 and 750 °C. Other conditions HTT: 700 °C, various pyrolysis heating rates.
residual ash. Ash fusion is a well known phenomena which contributes to fouling problems in pulverized combustors (Meyers 1981). In general, ash softens at a certain temperature (approximately 1310 °C for Pocahontas #3 coal and 1280 °C for Illinois #6) before eventually becoming fluid like in nature at higher temperatures (Vorres 1989).

Figure 4.26 shows a sequence of digital images from a combustion experiment in which a Pocahontas #3 char particle ignited and attained temperatures high enough to soften the ash. In frames B through D, ignition propagates across the particle from left to right heterogeneously. Because the ash content of these chars is fairly low, large cavities opened up in frame E as the ash softens and begins to fuse. In frame F, the hollow interior of the particle is exposed. It is likely that the hollow interior was formed during pyrolysis. However, the hollow interior of the particle may also be evidence that the center of the particle achieved higher temperatures and reacted first as predicted by the models of Sotirchos and Amundson.
Figure 4.26  Sequence of digital images from combustion experiment of Pocahontos #3 20-24 mesh char prepared at 20°C/sec and combusted at 750°C in 33% O₂ illustrating softening and fusion of the ash material due to high temperatures associated with ignition.
CHAPTER 5

EFFECTS OF PROCESS CONDITIONS ON DIRECT COAL COMBUSTION

5.1 Overview

In the preceding analysis of the ignition and reactivity of char particles, pyrolysis and combustion experiments were conducted sequentially in order to elucidate the effects of pyrolysis conditions on combustion. As discussed in chapter 1, these experiments are important considering the zones of high and low oxygen concentration which are present in industrial reactors. However, one major difference in conducting sequential experiments is that volatiles are completely removed and thus are not present during combustion. In true combustors, volatiles will be present and combustion of these volatiles can lead to homogeneous ignitions.

5.2.1 Effect of heating rate on coal reactivity

It is apparent that pyrolysis conditions such as heat treatment temperature and soak time do not have analogs in direct coal combustion experiments. On the other hand, conducting coal combustion experiments at various heating rates does produce a sort of analog to the effect of pyrolysis heating rate. This was illustrated in figure 3.2 of chapter 3, which shows devolatilization peaks in the coal reactivity plots very similar to peaks obtained in pyrolysis experiments conducted in a pure nitrogen atmosphere. It is quite interesting that peaks corresponding to both
pyrolysis and combustion are each visible in these reactivity plots. In addition, the fact that overlap occurs between the peaks leads to the suggestion that in a narrow range of conversions, these two processes occurred simultaneously.

Figure 5.1 presents the reactivity plots for multiple coal combustion experiments in which the sample was heated at 1.0, 10.0 and 20.0 °C/sec to a combustion temperature of 700 °C in 21% oxygen. The reactivities are quite repeatable and also show that higher combustion heating rates lead to higher reactivities. In general, the idea of conducting combustion experiments at different heating rates was to determine how well the observed effects of pyrolysis heating rate on char combustion translated to direct coal combustion experiments. However, comparison of the reactivity of coals combusted at different heating rates should be done cautiously. For coals which are combusted at very slow heating rates, significant reaction may occur before reaching the final combustion temperature. Because of this, observed differences in reactivity may be due more to the different reaction temperature than the effects of the heating rate on the internal structure of the particle.

Since primary devolatilization generally begins before 450 °C, it is practically impossible to avoid weight loss in a coal sample before reaching a final combustion temperature of 700 °C. In figure 5.2, the reactor temperature is plotted versus conversion for each of the heating rates of figure 5.1. From this plot we can see that the final combustion temperature of 700 °C is reached by about 40% conversion for heating rates of 10 and 20 °C/sec. Since Illinois #6 coal particles contain about 40% volatiles, we suspect that the combustion temperature was reached before significant heterogeneous reaction occurred. However, at a heating rate of 1 °C/sec,
Figure 5.1 Reactivity plots from multiple coal combustion experiments on 28-32 mesh sized Illinois #6 coal particles. Final combustion temperature: 700 °C, 21% O₂.
Figure 5.2  Plot of reactor temperature versus conversion for the combustion runs of figure 5.1.
almost complete conversion is achieved before reaching 700 °C. Therefore, the lower reactivity for combustion at 1 °C/sec is certainly due to the fact that combustion occurred at lower temperatures.

Faint ignitions were observed at both 10 and 20 °C/sec. However, we cannot rule out the possibility that more faint ignitions were undetected. Reactivity data was of little help because of the smooth reactivity curves. The observed differences in reactivity between combustion at 10 and 20 °C/sec may well be due to structural differences in the reacting particles that were caused by the different heating rates. This would agree well with the previously determined effects of pyrolysis heating rate on char reactivity. However, the fact that the final combustion temperature was reached earlier at 20 °C/sec, could have led to the observed difference in reactivity.

We also notice from figure 5.1 that as heating rate was increased, the distinction between the pyrolysis and combustion peaks became less clear. Matzakos (Matzakos 1991) and Ismail (Ismail 1994) found that at higher heating rates, devolatilization was shifted to higher temperatures. Thus, as heating rate is increased during a direct coal combustion experiment, we expect an increase in the overlap between pyrolysis and combustion.

5.2.2 Effect of combustion temperature on coal reactivity

Figure 5.3 presents the reactivity plots for a set of experiments designed to study the effects of combustion temperature on coal reactivity. Coal particles were combusted at 10 °C/sec in 21% oxygen to combustion temperatures of 500, 600, and 700 °C. At these conditions, the combustion temperature was easily reached before 40% conversion in all cases. Distinct peaks are again present corresponding to pyrolysis and combustion. For a
Figure 5.3  Reactivity plots of 28-32 mesh sized Illinois #6 coal particles heated at 10 °C/sec to different temperatures in 21%O₂.
final combustion temperature of 500 °C, no particle ignitions occurred and the combustion portion of the plot reveals very low reactivity. At 600 °C, one particle ignition was detected resulting in a peak in reactivity. Finally at 700 °C, 2 of the particles in the sample ignited and this curve, as expected, exhibits the highest reactivity. The ignitions observed in these experiments were fairly faint, perhaps due to the low oxygen concentration. As discussed in chapter 2, because of the smooth nature of the reactivity data, it is possible that other faint ignitions were undetected.

5.2.3 Effect of oxygen concentration on coal reactivity

As the oxygen concentration is increased in a coal combustion experiment, we certainly expect to see an increase in sample reactivity. Figure 5.4 presents the reactivity plots for coal combustion runs conducted in 21, 33, and 50 % oxygen. The reactivity plots clearly show an increase in reactivity with oxygen concentration. However, what is most interesting about the results presented here is the shape of the reactivity curves. As the oxygen concentration is raised to 50%, the pyrolysis and combustion peaks are essentially indistinguishable. This indicates that as oxygen concentration is increased, the pyrolysis and combustion stages overlap more. As indicated previously, when these two processes occur simultaneously, the likelihood of homogeneous ignitions is increased. Figure 5.5 shows that for a heating rate of 10 °C/sec, the combustion temperature of 700 °C is not reached before 40% conversion is achieved for oxygen concentrations higher than 21%. This indicates that heterogeneous reactions occur in a wide range of temperatures rather than only at the combustion temperature.
Figure 5.4 Reactivity plots of 20-24 mesh sized Illinois #6 coal particles heated at 10 °C/sec to a final combustion temperature of 700 °C in different oxygen concentrations.
Figure 5.5  Plot of reactor temperature versus conversion for the combustion runs of figure 5.4.
5.2.4 Ignition mechanism investigation

To study the effects of combustion conditions on the mechanism of coal particle ignitions, a number of coal combustion experiments were conducted for different particle sizes, combustion temperatures, and oxygen concentrations in the TGA/VMI. The heating rate was kept constant at 10 °C/sec while the oxygen concentration was varied between 21, 33, and 50%. For experiments with 28-32 mesh sized particles, 4 particles were placed in the pan. For experiments using 20-24 mesh sized particles, the sample size was limited to only 2 particles. These choices of sample size avoided situations where the combusting particles were in close proximity to one another. Combustion temperatures studied were in a range from 500 to 900 °C. However, it was noted that for the chosen heating rate of 10 °C/sec, final combustion temperatures above 800 °C could not be reached before significant combustion occurred.

The results of the ignition mechanism study are not quantitative in nature, since they involve observation of the location of light emissions in relation to the boundaries of the particles. To summarize the results, it was found that for the given restrictions in sample size, the majority of particle ignitions exhibited a heterogeneous mechanism. However, higher combustion temperatures increased the likelihood of homogeneous ignition as did increasing oxygen concentrations. It was apparent that of these two effects, oxygen concentration was most influential on the transition to a homogeneous mechanism. This agrees with the observation made in figure 5.4 that pyrolysis and combustion overlap more at higher oxygen concentrations. No conclusions were drawn on the effects of particle size on ignition mechanism, since the occurrence of homogeneous ignitions
were roughly the same for both 28-32 and 20-24 mesh sized Illinois #6 particles.

While the heterogeneous ignition mechanism was dominant for coal combustion experiments in which sample particles were not in close contact with each other, exactly the opposite was true for experiments in which many particles were placed adjacent to each other. In these experiments, the most commonly observed ignition sequence was one in which initial heterogeneous ignitions sparked extremely violent homogeneous ignitions of the volatiles present in the reactor. Visualization of this mechanism was presented earlier in figure 3.2.
CHAPTER 6

TRANSIENT CHAR IGNITION MODEL

6.1 Overview

The models of Sotirchos and Amundson (1984a, 1984b, 1984c, 1984d) illustrated the importance of considering a transient model in char combustion. The evolution of char properties with conversion significantly changes the solution structure of the char combustion problem. Sotirchos and Amundson did not have an accurate description of the pore structure of char particles. However, we can tackle the transient problem again using the structural data obtained from earlier studies in our lab.

6.2 Model Development

The combustion of carbon in oxygen involves the following heterogeneous reactions:

\[ C + \frac{1}{2}O_2 \rightarrow CO \quad (221.0 \text{ J/mol O}_2) \quad (6.1) \]

\[ C + O_2 \rightarrow CO_2 \quad (393.5 \text{ J/mol O}_2) \quad (6.2) \]

The relative amounts of CO and CO₂ produced in reactions 6.1 and 6.2 depend strongly on the reaction temperature. A direct relationship between the ratio of CO/CO₂ versus temperature has been developed by Arthur (Arthur 1951). It was found that CO is the primary reaction product at higher temperatures. At higher temperatures, the carbon surface undergoes endothermic reaction with CO₂:
\[ C + CO_2 \rightarrow 2CO \quad (-1.74 \text{ J/mol CO}_2) \quad (6.3) \]

From our experimental reactivity measurements, we have data on the rate of carbon reaction. To relate the carbon reactivity to the consumption of oxygen, we have utilized the stoichiometry of reactions 6.1 and 6.2. For example, the stoichiometry of reaction 6.1 indicates that two moles of carbon are consumed for each mole of oxygen. Reaction 6.3 has been neglected since it prevents simplifying assumptions about the reaction order. Utilizing our kinetic data and the stoichiometry of the reaction between oxygen and carbon, we have related the reaction of oxygen to the reaction of carbon:

\[ R_{O_2} = v_{O_2} \cdot R_C = \frac{(V_P^P_P f_c)_0 v_{O_2}}{M_c} A e^{-\left(\frac{E}{RT_s}\right)} C_S \quad (6.4) \]

where \( M_c \) is the molecular weight of carbon, \( v_{O_2} \) is the stoichiometric coefficient for oxygen in the chemical reactions with carbon. \( A \) and \( E \) are the pre-exponential factor and activation energy determined previously. The units of \( R_c \) are grams of carbon per initial grams of carbon per second [g C/(g_{initial} C \cdot \text{sec})]. In our experimental results, we have simply presented these units as inverse minutes, ignoring the grams of carbon per initial grams of carbon. Since this reactivity data was based on the initial mass of char present, the reactivity is multiplied by the product of initial particle volume and density. This product is then multiplied by the initial carbon content, \( f_{co} \) to obtain the ash free carbon mass.

The relative rates of formation of CO versus CO_2 are not only of importance due to the different heats of reaction. The stoichiometric
coefficient of oxygen in each reaction is different. Thus, the relative rates of these reactions determine the stoichiometric coefficient of oxygen. At high temperatures, where CO is the primary reaction product, $v_{O_2}$ is constant at $1/2$.

Since reactions 6.1 and 6.2 involve heterogeneous reaction of oxygen and carbon, model equations must be solved in both solid and gas phases. This particular model does not consider gas phase homogeneous reactions of oxygen with heterogeneous reaction products such as carbon monoxide. These reactions have been considered extensively by Sotirchos and Amundson.

### 6.2.1 Governing equations

The primary equations that make up the system are mass balances on reacting oxygen (6.5) and carbon (6.6), and a solid energy balance (6.7) which determines the particle temperature:

\[ V_p \varepsilon \frac{dC_s}{dt} = a_x k_g (C_f - C_s) - V_p \varepsilon R_{O_2} \eta \quad (6.5) \]

\[ \frac{d}{dt} (V_p \rho_p) = (V_p \rho_p)_0 R_c \quad (6.6) \]

\[ V_p \rho_s C_p_s (1 - \varepsilon) \frac{dT_s}{dt} = \sum_i (-\Delta H_i)_i R_{O_2} \eta - a_x h(T_s - T_f) - a_x \varepsilon (T^*_s - T_f^*) \quad (6.7) \]

with the initial conditions:

\[ T_{s,0} = T_s(0) \]
\[ C_{s,0} = C_s(0) \quad (6.8) \]
where $a_x$ and $V_p$ are the external surface area and volume of the char particle respectively; $C_{p_s}$ is the solid heat capacity and $\rho_s$ is the solid density. The porosity or void volume of the particle is given by $\varepsilon$. Subscript $s$ denotes solid properties and subscript $f$ denotes properties of the surrounding fluid. $k_g$ and $h$ are the mass and heat transfer coefficients respectively. In the radiation term of the energy balance, $e$ is the particle emissivity and $\sigma$ is the Boltzmann constant. The emissivity of the char particle was taken to be 0.9, the same value used by Sotirchos and Amundson. General values of the emissivity of Carbon are presented by Perry, et al. (Perry, et al. 1984). The exothermic heat of the reaction is denoted by $(-\Delta H_r)$, and $\eta$ is the effectiveness factor.

In these equations, we have neglected spatial variations in all properties. The equations are highly coupled since both the particle temperature and oxygen concentration determine the reaction rates, and reaction rate terms are found in both equations. In the energy balance, the reaction rate determines the amount of heat generated by the exothermic reaction.

### 6.2.2 Effectiveness factors

The effectiveness factor, $\eta$, was calculated by a method developed by Mingle and Smith (Mingle and Smith 1961) and outlined by Froment and Bischoff (Froment and Bischoff 1979). The method takes into account the strongly bimodal pore distribution that exists in char particles. Assuming the micropores are cylindrical and that the reactions are first order with respect to oxygen, the mass balance for reacting oxygen has the form:

$$D_\mu \frac{d^2C_\mu}{dz^2} = \frac{2}{r_\mu \rho_p S_g} k_o C_\mu \quad (6.9)$$
where $D_\mu$ is the micropore diffusion coefficient, $z$ is the axial coordinate, $r_\mu$ is the micropore radius, and $C_\mu$ is the oxygen concentration in the micropores. Boundary conditions for this equation assume micropores open to a macropore on each side with a symmetric concentration gradient:

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

(6.10)

where $L_\mu$ is the micropore length and $C_m$ is the concentration of oxygen in the macropores, located at the end of each micropore. If reaction 6.3 was also considered it is apparent that analytical solution of 6.9 would not be possible since the reaction order would no longer be 1. Solution of the micropore balance (6.9) with boundary conditions (6.10) yields an effectiveness factor for the micropores of the form:

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

(6.11)

where $\phi_\mu$ is the Thiele modulus for the micropores defined by:

$$\phi_\mu = L_\mu \sqrt{\frac{2k_o}{\rho_p S_g r_\mu D_\mu}}$$

(6.12)

where $k_o$ is the reaction rate constant and $S_g$ is the total surface area ($\text{cm}^2/\text{g}$). The micropore radius, $r_\mu$, is a parameter and was assigned an average value of 5Å. This value corresponds to the size separating the micropores from the sub-micropores. The micropore diffusion coefficient, $D_\mu$, was calculated using the micropore radius and assuming Knudsen
diffusion. The micropore length, $L_{\mu}$, was estimated by the ratio of the particle volume to macropore surface area as follows:

$$L_{\mu} = \frac{1}{(1-\varepsilon)S_{mg}} \quad (6.13)$$

where $S_{mg}$ is the macropore surface area per unit of solid volume (cm$^2$/cm$^3$ solid). The porosity, $\varepsilon$, has units of cm$^3$ void/cm$^3$ particle.

The oxygen balance for the macropores resembles an overall spherical particle balance:

$$D_{eff} \frac{d^2 C_m}{dr^2} = k_0 \eta_{\mu} C_m \quad (6.14)$$

where $D_{eff}$ is the effective diffusivity in the macropores, $r$ is the particle radius, and $\eta_{\mu}$ is the effectiveness factor obtained for the micropores. The boundary conditions for the macropores are:

$$\frac{d C_m}{dr} = 0 \ldots \ldots \ldots \ldots @ r = 0 \quad (6.15)$$

$$C_m = C_s \ldots \ldots \ldots \ldots @ r = R_p$$

where $C_s$ is the oxygen concentration at the particle surface, and $R_p$ is the particle radius. Solution of the macropore mass balance leads to an expression of the effectiveness factor for the macropores:

$$\eta_m = \frac{\tanh(\phi_m)}{\phi_m} \quad (6.16)$$

where the macropore Thiele moduli is defined by:

$$\phi_m = \frac{R_p}{3} \sqrt{\frac{k_0 \eta_{\mu}}{D_{eff}}} \quad (6.17)$$
In the macropores, the bulk diffusion coefficient was used for $D_{\text{eff}}$ since the macropore radii are typically larger than 1000 Å (Boissiere 1993). Finally, the overall effectiveness factor is determined as the product of the macro and micro effectiveness factors.

$$\eta = \eta_{\mu} \cdot \eta_{m} \quad (6.18)$$

### 6.2.3 Transport properties

To determine the heat and mass transfer coefficients found in equations 6.5 and 6.7, correlations for forced convection around a sphere were used (Bird, et al. 1960):

$$\frac{h(2R)}{k_f} = 2.0 + 0.6 \text{Re}^{1/2} \text{Pr}^{1/3} \quad (6.19)$$

$$\frac{k_g(2R)}{D_{AB}} = 2.0 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3} \quad (6.20)$$

where $\text{Re}$, $\text{Pr}$, and $\text{Sc}$ are the Reynolds, Prandtl, and Schmidt dimensionless numbers respectively, defined by:

$$\text{Re} = \frac{(2R) \nu_{\infty} \rho_f}{\mu_f} \quad (6.21)$$

$$\text{Pr} = \frac{C_p \mu_f}{k_f} \quad (6.22)$$

$$\text{Sc} = \frac{\mu_f}{\rho_f D_{AB}} \quad (6.23)$$

where $R$ is the particle radius and $\nu_{\infty}$ is the gas flow velocity. $C_p$, $\mu$, $\rho$, and $k$ are the heat capacity, viscosity, density, and thermal conductivity of the
fluid; and $D_{AB}$ is the binary diffusion coefficient. Pure component viscosity was calculated by a method proposed by Thodos and coworkers (Perry, et al. 1984). The mixture viscosity was then estimated by a series expression developed by Wilke (Perry, et al. 1984). Fluid heat capacity was determined as a function of temperature based on coefficients given by Felder and Rousseau (Felder and Rousseau 1978). Pure component thermal conductivity was calculated by averaging values obtained from the Eucken and modified Eucken correlation (Perry, et al. 1984). A similar series expression was used to calculate mixture thermal conductivity. The binary diffusion coefficient was estimated using the Fuller, Schettler, and Giddings relation (Perry, et al. 1984). Fluid density was determined by assuming ideal gas relations.

6.2.4 Solid properties

As mentioned earlier, consideration must be given to the dependence on conversion of solid properties such as particle size, surface area, and porosity. While many investigators make assumptions in determining these relationships, our experimental studies have been very useful in providing this information. Chapter 4 presented results on experiments designed to obtain information about the changes of particle diameter and surface area with conversion in both the kinetic control and diffusion limited regime. Since conditions which lead to particle ignitions are inherently in the diffusion limited regime, data on changes in normalized diameter from this regime were used.

To account for the variation in surface area with conversion, normalized reactivity data obtained previously for reacting chars in the kinetic control regime was used as input to the model. Kinetic control
regime data was used since diffusion control is accounted for by the effectiveness factors. As covered in chapter 4, normalized reactivity plots describe the change in internal surface area with conversion with respect the value at 10% conversion. In general, this variation of surface area could be taken to describe the change in reactive or total surface area. This depends on what value is assigned to the surface area at 10% conversion. Since measurements of the reactive surface area were not made, we have chosen to normalize reactivity by the total surface area, similar to many other investigators. To estimate the surface area at 10% conversion from initial data, it was assumed that the internal surface area was consumed uniformly with conversion in this range.

We must also take into account the presence of ash material in the char particle. In this study, we focused on chars prepared from Illinois #6 coal, which has a high ash content. Precursors of ash in char particles are clays and minerals such as quartz, pyrite, and calcite. As conversion proceeds, these minerals are oxidized to compounds such as SiO₂, CaO, Al₂O₃, Fe₂O₃, and a small amount of SO₃, which make up the majority of Illinois #6 ash present at late conversions (Vorres 1989). In determining the particle density and heat capacity, contributions must come from both the char carbon and ash material. As conversion progresses, the contribution due to ash becomes more significant.

Correlations developed by Kirov (Kirov 1965), were used for char and ash heat capacity dependence on temperature. True Illinois #6 char density has been measured by Ballal (Ballal 1985). By knowing the ash content of the char measured and the density of the ash, the contribution of the char carbon itself to the true density was determined to be 1.8 g/cc. Estimation of the true mineral and ash density for Illinois #6 chars is made
by determining the densities of the major components listed in the previous paragraph. Since the estimated true density for Illinois #6 char minerals (3.18 g/cc) and ash (3.32 g/cc) are similar, an average value was used (3.25 g/cc) instead of taking into account the gradual conversion of mineral to ash during combustion. Ash fusion at high temperatures was not taken into account in the current model.

6.3 Comparison with Experimental Results

To compare the model results with experimental data on char ignitions, it would be useful to have a definition of ignition that applies to the model results. Ignitions occur when the particle undergoes a transition from an unignited state to an ignited state. This transition is detected by sharp changes in particle temperature with time.

In the experimental case, ignitions were defined as visible emissions of light, or peaks in the reactivity data. These two phenomena resulted from particles reacting at temperatures much higher than the ambient. Unfortunately, our current experimental set-up does not allow for measurements of particle temperature. Furthermore, our reactivity measurements represent average reactivities for multiple particles while model results yield single particle reactivity. Choosing a model criterion for ignition which we could relate to experimental results, such as a minimum reactivity or temperature, would therefore be somewhat arbitrary.

Instead of choosing an arbitrary threshold for ignition, we will present data on maximum particle temperatures. Since maximum particle temperatures are achieved during ignition, maximum particle temperature
data should provide information about the relative frequency of ignition at various conditions.

Boissiere (Boissiere 1993) measured the particle size, macroporosity, and macropore surface areas of chars prepared from 28-32 mesh Illinois #6 coals under various pyrolysis conditions. Pyrolysis conditions such as heat treatment temperature, soak time, and gas composition, were identical to those utilized here. Macropore surface areas measured by Boissiere and Zygourakis (Boissiere 1993, Zygourakis 1993) utilized digital image processing techniques on char particle cross sections. Pyrolyzed char particles were embedded in an epoxy resin and cross sections were polished and exposed. The cross sections were imaged with a polarizing microscope.

Due to the limitations of the technique, only macropores having diameters larger than 2\(\mu\)m were detectable. Macropores are commonly defined as pores having diameters larger than 500 Å. Therefore, these surface areas do not correspond to traditional macropore values. It is expected that true macropore surface areas are larger than these values. In table 6.1, we again present the measurements of Boissiere (Boissiere 1993) obtained at different pyrolysis heating rates:

Table 6.1 Structural data for 28-32 mesh Illinois #6 chars. (Boissiere 1993)

<table>
<thead>
<tr>
<th>Heating Rate (°C/sec)</th>
<th>Radius (mm)</th>
<th>Macroporosity</th>
<th>Macropore SA (cm²/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.317</td>
<td>0.592 ± 0.030</td>
<td>865 ± 73</td>
</tr>
<tr>
<td>1.0</td>
<td>0.325</td>
<td>0.595 ± 0.025</td>
<td>1244 ± 98</td>
</tr>
<tr>
<td>10.0</td>
<td>0.407</td>
<td>0.648 ± 0.025</td>
<td>1040 ± 85</td>
</tr>
</tbody>
</table>
From this data, we were able to make direct relations between pyrolysis conditions and model parameters involving these char structural properties. Figure 6.1 shows the model results when the parameters listed in table 6.1 were used for a combustion run at 550 °C in 33% oxygen. From the plot of particle temperature versus conversion we see that chars prepared at 1.0 and 10.0 °C/sec exhibit the highest particle temperatures. Since higher particle temperatures lead to higher reactivities, these chars are more reactive. Confirmation of this is given in figure 6.2, which shows the associated reactivity plot for this run. At 550 °C, the model predicts a peak in reactivity for chars prepared at 1.0 °C/sec. This is in direct agreement with the experimental results at heating rates below 20 °C/sec.

In chapter 4, we explained the fact that chars with larger macropore surface areas exhibit higher reactivity in the diffusion control regime. From the data of table 6.1, we see that chars prepared at 1.0 °C/sec exhibited the highest macropore surface areas. Although chars prepared at 10.0 °C/sec are larger, the increase in macropore surface area accounts for the observed and predicted increases in reactivity.

It should be noted that since the model results are for individual particles, peaks in reactivity appear much higher than experimental values. This is because experimental reactivities are averages of all particles present. Thus, if four particles are reacting at a rate of 0.25 min⁻¹, and the fifth is igniting with a reactivity rate of 4.0 min⁻¹, the overall reactivity is only 1.0 min⁻¹. Due to the limitations of the TGA/VMI micro balance, it was not possible to accurately determine individual particle reactivities experimentally.
Figure 6.1  Model predictions of particle temperature versus conversion for chars with structural properties from table 6.1 combusted at 750 °C. 33% O₂.
Figure 6.2  Model predictions of reactivity of individual chars with structural properties from table 6.1 combusted at 550 °C. 33% O₂.
The same parameters were used to run the model for a combustion at 750°C in 33% oxygen. The particle temperature and reactivity plots are shown in figures 6.3 and 6.4 respectively. The same trends in reactivity are observed at 750 °C as those predicted at 550 °C. At 750 °C, diffusional limitations become more extreme. Therefore, the effect of macropore surface area becomes more important since higher macropore surface areas reduce the effects of diffusional limitations. For this reason, it is not surprising that the model predicts the same trends in reactivity at 750 °C.

Experimentally observed differences in reactivity for these heating rates were almost indistinguishable at 750 °C. This supports a contention that the diffusional limitations were underestimated by the model. However, it is not reasonable to suggest that all char particles exhibit the exact structural properties given by the table. At this point, we have not considered the standard deviations given in table 6.1. A consideration of these standard deviations will be given later.

As discussed in the beginning of this section, very sharp increases in particle temperature are attributed to the transition from the unignited to the ignited state. In figure 6.5, one of the particle temperatures obtained in figure 6.3 is plotted versus time. The sharp increase in particle temperature is evidence of the transition to the ignited branch of the solution structure.

It is important to note that the transition, or ignition, often occurs after significant conversion is achieved. Initially, the conditions are such that the particle reacts in the unignited state, perhaps in the multiplicity region of figure 1.1. However, as conversion progresses, the properties of the char change. Thus, the solution structure is modified until the particle no longer reacts in the multiplicity region, and must react in the ignited state.
Model predictions of particle temperature versus conversion for chars with structural properties from table 6.1 combusted at 750 °C. 33% O₂.
Figure 6.4  Model predictions of reactivity of individual chars with structural properties from table 6.1 combusted at 750 °C. 33% O₂.
Figure 6.5  Plot of particle temperature versus time for char prepared at 10.0 °C/sec and combusted at 750 °C. 33% O₂.
6.4 Parametric Study

To thoroughly determine the effects of model parameters, a parametric study was conducted. In this study, base values were chosen for each model parameter. To study the effects of a certain parameter, all other parameters were kept at their base value while the parameter of interest took values in a specified range. Any possible correlations among the parameters in this study were ignored in order to isolate the effect of each parameter. However, correlations between the particle radius, porosity, and macropore surface area are very important. The sensitivity of the model to individual parameters may change when correlations are taken into account. Table 6.2 summarizes the parameter choices:

Table 6.2 Base and range values for the parametric study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base Value</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion Temperature (°C)</td>
<td>550</td>
<td>450 - 750</td>
</tr>
<tr>
<td>Oxygen composition</td>
<td>33%</td>
<td>21 - 50%</td>
</tr>
<tr>
<td>Total Surface Area (m²/g)</td>
<td>530.8</td>
<td>200 - 1000</td>
</tr>
<tr>
<td>Macropore S.A. (cm²/cm³)</td>
<td>1200</td>
<td>700 - 2900</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.6</td>
<td>0.5 - 0.7</td>
</tr>
<tr>
<td>Particle radius (mm)</td>
<td>0.325</td>
<td>0.16 - 0.48</td>
</tr>
<tr>
<td>Micropore diameter (Å)</td>
<td>5.0</td>
<td>4.0 - 6.0</td>
</tr>
<tr>
<td>Gas velocity (cm/sec)</td>
<td>1.0</td>
<td>0.0 - 10.0 cm/sec</td>
</tr>
<tr>
<td>Ash content</td>
<td>17%</td>
<td>5 - 45%</td>
</tr>
</tbody>
</table>

With the exception of micropore radius, all base values for parameters describing physical properties of the coal were chosen based on
measurements made in our laboratory. Illinois #6 char surface area was measured by Ballal using CO$_2$ adsorption (Ballal 1985). Char particle radii, porosity, and macropore surface areas were measured by Boissiere and Zygourakis (Boissiere 1993, Zygourakis 1993). Since the macropores account for nearly all the internal porosity, we assumed that the measured values of macroporosity also correspond to total porosity. The chosen values for particle radii roughly correspond to values for chars prepared from (50-60), (28-32), and (20-24) mesh sized Illinois #6 coals. The gas velocity present in the TGA/VMI reactor was estimated to be approximately 1.0 cm/sec. The range of values chosen for the char ash content correspond to measurements from combustion experiments.

6.4.1 Combustion temperature

Figure 6.6 shows the effects of varying the combustion temperature on the ignition behavior of char particles. When chars having the base structural properties listed in table 6.2 were combusted at 450 °C in 33% oxygen, particle temperatures were approximately equal to the ambient. As the temperature was raised, the particles began to react at temperatures well above the ambient. As discussed previously, we decided not to define an arbitrary threshold for ignition to interpret the model results. Thus, we will discuss only the maximum particle temperatures, which should exhibit very similar trends to particle ignitions.

6.4.2 Oxygen composition

The effects of oxygen concentration are presented in figure 6.7. As expected, particle temperatures were increased at higher oxygen concentrations. For the base conditions chosen in this study, chars
Figure 6.6  Effects of combustion temperature on char ignition behavior. 33% O₂.
Figure 6.7  Effects of oxygen concentration on char ignition behavior. 550 °C.
combusted at 550 °C in 21% oxygen reacted at temperatures only slightly higher than the ambient. At higher oxygen concentrations, char particles reached higher temperatures. These higher particle temperatures are directly associated with higher reactivities. At 50% oxygen, particle temperatures greatly exceeded the ambient.

6.4.3 Total surface area

Chars with higher surface areas increase the accessibility of oxygen to reactive sites. Thus chars with higher surface areas exhibit increased reaction rates and these reactions generate more heat. This is supported by figure 6.8, showing the effects of increasing surface area on char particle ignitions. Particle temperatures were greatly increased in chars with higher surface areas.

6.4.4 Macropore surface area

In the regime of diffusion limitations, macropores act as major pathways allowing oxygen to reach the micropore surface area. Thus, we expect that chars with higher macropore surface area will exhibit higher reactivity and will ignite more often. Figure 6.9 confirms this effect, showing that chars with higher macropore surface areas exhibited much larger increases in particle temperature.

6.4.5 Porosity

Figure 6.10 indicates that higher porosity leads to less reactive chars. In a sense, this result is intuitive since more porous char particles have smaller solid volumes to accommodate internal reaction and heat generation. However, this result is quite misleading. Pyrolysis conditions
Figure 6.8  Effects of total surface area on char ignition behavior at 550 °C in 33% O\textsubscript{2}.
Figure 6.9  Effects of macropore surface area on char ignition behavior at 550 °C in 33% O₂.
Figure 6.10  Effects of porosity on char ignition behavior at 550 °C in 33% O₂.
which lead to highly porous chars also lead to increased particle radii and higher macropore surface areas. Since we have neglected correlations among the model parameters, the effects of particle radius and macropore surface area have been ignored.

6.4.6 Particle radius

As discussed previously, increasing particle size is expected to favor ignitions because of the trade off between heat generation inside the particle and heat removal from the surface. For spherical particles, the volume of the particle is proportional to \( R^3 \) while the external surface area is proportional to \( R^2 \). Thus, increasing the particle radius leads to more volume for heat generation with a smaller increase in heat transfer capacity. Figure 6.11 agrees with this prediction by showing that larger particles reached much higher temperatures. Just as before, we have neglected the associated effects of porosity and macropore surface area. Nonetheless, the purpose of this parametric study is to isolate the effects of individual parameters.

6.4.7 Micropore diameter

The size of the micropores of a char particle are instrumental in determining the degree of diffusional limitations encountered. This dependence is reflected in equation 6.12, which shows that the micropore Thiele modulus is inversely proportional to the micropore diameter. Since increasing Thiele moduli lead to greater diffusional limitations, smaller micropore diameters should have the same effect. Figure 6.12 shows this behavior for three different micropore diameters. The char with the
Figure 6.11  Effects of char particle radius on char ignition behavior at 550 °C in 33% O₂.
Figure 6.12  Effects of micropore diameter on char ignition behavior at 550 °C in 33% O₂.
largest micropore diameter was most accessible to oxygen and therefore exhibited the highest particle temperature.

6.4.8 Gas velocity

The velocity of the gas flowing past a reacting char particle certainly plays a key role in the removal of heat from the particle. Increased air velocities lead to greater heat removal rates and thus should lead to lower particle temperatures. This behavior is shown in figure 6.13, which shows that ignition was most favored by lower gas velocities.

6.4.9 Ash content

The effect of char ash content on ignition can be very complicated. In the present model, we have not accounted for any catalytic effects of ash in enhancing the rates of chemical reactions. Another effect of the presence of ash in char is a modification of the physical properties such as heat capacity and density. Illinois #6 ash has a much higher density and heat capacity than char. In addition, the difference in heat capacity is increased at higher temperatures. Also, since ash is inorganic in nature, including ash at the expense of reactive char should result in a decrease in char reactivity.

Figure 6.14 shows that the maximum particle temperature was achieved at an intermediate ash content of 18% before decreasing for higher ash contents. Initial increases in char reactivity with increasing ash content are likely due to the effect of heat capacity.Chars with higher heat capacity due to their higher ash content can achieve higher particle temperatures. This effect is eventually overtaken at very high ash contents where the reactivity decreases due to the large amounts of inert ash.
Figure 6.13  Effects of gas velocity on char ignition behavior at 550 °C in 33% O₂.
Figure 6.14  Effects of char ash content on char ignition behavior at 550 °C in 33% O₂.
6.5 Random Variation of Char Properties

As mentioned earlier, we do not propose that all chars produced at the specified heating rates exhibit the exact structural properties of table 6.1. Due to the heterogeneous nature of coal, we expect deviations from these values. For this reason, we have assumed that at each pyrolysis heating rate, the structural properties of the char varied according to a standard normal probability distribution. The mean of each distribution was taken to be the values in table 6.1. Standard deviations in particle radius, macropore surface area, and porosity given in table 6.1 were used for the distributions. For other model parameters, we assumed a standard deviation equal to 3% of the mean value in each case. In the case of ash content, we do have experimental data. Thus, the average ash content (17.8%) and standard deviation (9.74%) calculated from experimental results were used for the distribution.

To select the model parameters for a given run, multiple sets of pseudo random numbers were generated from the given probability distribution for each parameter. The data was set up to run the model 30 times, with char structural properties varying for each run. Average reactivities for each run were calculated by the same procedure used on experimental data. Calculating average reactivities for multiple model runs on individual particles effectively averages individual particle reactivities similar to what occurs in obtaining experimental reactivity.

It is important to note that in this analysis we have not necessarily preserved the correlations between char structural parameters. Although the correlations are preserved for the mean values in the distributions for each parameter, choosing random values from these distributions ignores any possible correlations.
In figure 6.15, the average reactivity data from the model runs and from experiments are presented for the 3 heating rates. As discussed earlier, for heating rates below 20 °C/sec, chars prepared at 1.0 °C/sec exhibited the highest reactivity when combusted at 550 °C. The random model results agree quite well with the experimental findings. Just as in the experimental results, the peak in reactivity is observed for chars prepared at 1.0 °C/sec. However, considering the standard deviations of table 6.1 leads to large differences in reactivity, as observed by the standard deviations of figure 6.15.

Figures 6.16a and 6.16b compare the number of experimentally detected ignitions with the average maximum achieved particle temperatures for combustion at 550 °C. Since we do not have experimental data on ignited particle temperatures, interpretation of the model results is limited to evaluating the predicted trends in particle ignitions rather than determining the actual number of particles which ignited. The model predicts little difference in average maximum particle temperatures for chars prepared at 1.0 and 10.0 °C/sec.

Figures 6.17a and 6.17b compare the number of experimentally detected ignitions with the average maximum achieved particle temperatures for combustion at 750 °C. Again, trends between model and experiment are in agreement. As discussed in chapter 3 however, ignition detection at 750 °C is much more difficult. The actual number of particle ignitions may be incorrect due to the inefficiency in detecting faint ignitions at 750 °C, but the trends should be preserved.
Figure 6.15 Comparison of average reactivity data between model and experiment at a combustion temperature of 550 °C. 33% O₂.
Figure 6.16a  Experimental data on particle ignitions at 550 °C. 33% O₂.

Figure 6.16b  Model predictions of maximum particle temperatures at 550 °C. 33% O₂.
Figure 6.17a  Experimental data on particle ignitions at 750 °C. 33% O₂.

Figure 6.17b  Model predictions of maximum particle temperatures at 750 °C. 33% O₂.
Figure 6.18 compares the average reactivity versus heating rate for model and experiment at a combustion temperature of 750 °C. Just as in section 6.3, the model results basically show the same trends observed at 550 °C. Chars prepared at 1.0 °C/sec again exhibit the highest reactivity. The model again predicts large variations in reactivity when allowing the initial char structural properties to vary randomly. Inclusion of these variations in the model leads to more similar reactivities for chars prepared at 1.0 and 10.0 °C/sec.

6.6 Extrapolation of Results to Higher Heating Rates

Unfortunately, structural data is not available for 28-32 mesh Illinois #6 chars prepared at heating rates above 10 °C/sec. However, based on what we have learned about the effects of various parameters and the trends observed below 20 °C/sec, we can make an educated attempt to explain the high reactivity of chars prepared at higher heating rates. Chars prepared at heating rates approaching 1000 °C/sec are expected to have much larger macropore surface areas. This is confirmed by the measurements of Zygourakis (Zygourakis 1993), who measured the structural properties of chars prepared at heating rates approaching 1000 °C/sec. As discussed in chapter 4, measurements were made on different coals and smaller mesh sizes. However, chars prepared at heating rates approaching 1000 °C/sec had much higher macropore surface areas as well as larger particle radii.
Figure 6.18  Comparison of average reactivity data between model and experiment at a combustion temperature of 750 °C. 33% O₂.
CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1.1 Detecting particle ignitions

The detection of coal and char particle ignitions, which is important in any coal or char reactivity study, was achieved by combining the video microscopy capabilities of the TGA/VMI reactor with digital image processing techniques. We found that to efficiently detect faint and strong particle ignitions during a multiple particle experiment, both video microscopy and reactivity measurements must be utilized. When multiple faint particle ignitions occurred during combustion, ignition detection was most difficult. Detecting char particle ignitions at high combustion temperatures (750 °C) was also found to be difficult due to the smooth nature of the reactivity curves.

Our approach allowed us to detect individual particle ignitions during a multiple particle experiment. We were also able to study particle interactions, which are extremely important in industrial reactors. Our experimental approach thus combined the advantages of single and multiple particle experiments.

Video microscopy was also very useful in identifying the ignition mechanism in reacting coal and char particles. Our findings show that the ignition of char particles typically occurs heterogeneously, while coal particles may ignite heterogeneously, homogeneously, or by a combination of both mechanisms. Particle interactions were found to play a key role in
the occurrence of homogeneous ignitions. Other transient phenomena such as multiple ignitions of a single particle were also detected. Video microscopy also allowed us to observe other structural changes occurring in reacting particles such as particle shrinkage and ash fusion.

7.1.2 Effects of heating rate on char ignition and reactivity

The previous studies of Boissiere (Boissiere 1993) determined that increasing pyrolysis heating rates lead to larger chars with more open macropore structures and larger macropore surface areas. Matzakos (Matzakos 1991) and Ismail (Ismail 1994) found that these structural features lead to chars which were more reactive at higher combustion temperatures.

In this study, we have focused on the effects of pyrolysis heating rate on char reactivity. The effects of pyrolysis heating rate were better quantified by calculating average reactivities and the percentage of particles which ignited. Furthermore, previously unattained reactivity data of chars prepared at heating rates approaching 1000 °C/sec has been studied. Our findings clearly show that higher pyrolysis heating rates lead to char particles which ignited more often and exhibited higher reactivity when combusted at temperatures existing in the diffusion limited regime. However, the greatest difference in reactivity was observed for chars prepared at 100 and 500 °C/sec in the hot stage reactor, rates which are much closer to those present in industrial combustors. Furthermore, difference in reactivity may be larger than detected due to inherent differences in the TGA/VMI and hot stage reactors.

7.1.3 Coal combustion experiments
Direct coal combustion experiments were conducted by heating coal particles in reactive atmospheres. The reactivity curves from these experiments clearly show peaks which correspond to pyrolysis and combustion. Experiments of this type were instrumental in observing a homogeneous ignition mechanism not previously observed in our laboratory. It was found that increasing oxygen concentrations, combustion temperatures, and the presence of multiple particles in close contact during combustion favored the homogeneous ignition mechanism.

7.1.4 Transient char ignition model

A transient model was developed to describe the combustion of single char particles in an oxygen containing atmosphere. Experimental results on the reaction kinetics, surface area evolution, and change in particle diameter with conversion were instrumental in the development of the model. The bimodal pore distribution of pores in char particles was taken into account in the estimation of diffusional limitations encountered by the particle. Values of the char structural properties such as particle radius, macroporosity, macropore surface area, and total internal surface area were obtained from measurements made on chars prepared in our laboratory. This allowed for direct relationships between these model parameters and experimental pyrolysis heating rates.

Model predictions on trends in char reactivity and ignition with heating rate agreed very well with experimental results. Unfortunately, char structural properties were not available for pyrolysis heating rates above 10 °C/sec. However, the model was very useful in determining the effects of various char properties and process conditions on the combustion behavior. Factors which increased the reactivity and ignition of char
particles were increasing combustion temperature, oxygen concentration, macropore and total surface area, particle radius, and micropore diameter. In contrast, higher values of porosity, ash content, and ambient velocity reduced the reactivity and ignition of char particles.

7.2 Recommendations for Future Work

Since it has been found that chars prepared at heating rates above 100 °C/sec are significantly more reactive when combusted in the diffusion limited regime, an extension of the char structural data on particle radius, macroporosity, and macropore surface area to these higher heating rates would be very useful. This information would be very useful in elucidating the features of chars prepared at these heating rates which lead to higher reactivities. Furthermore, these parameters could be utilized by a char combustion model to study the effects of extremely high heating rates on char reactivity and ignition behavior.

An investigation into possible thermal gradients in the mesh heating element of the hot stage should be made. With the use of two thermocouples, one for control, another for mesh temperature measurements, thermal gradients within the mesh could be measured. The use of two thermocouples may also be useful in the estimation of particle surface temperatures during ignition. Information on ignited particle temperatures would be extremely useful in verifying model results as well as defining a criteria for ignition.

Experiments to further study the role of particle interactions on coal particle ignition mechanism would also be useful. By making indentations in the hot stage mesh, coal particles could be placed at specified distances from each other. As discussed in chapter 5, homogeneous ignitions are
favored by the presence of multiple particles reacting while in close contact with one another. From these studies, a relationship could be determined between the occurrence of homogeneous ignitions and the number of particles or the particle spacing.

In addition, it is expected that combustion heating rate will have an important effect on ignition mechanism. Increasing the heating rate at which coal particles are combusted may lead to an overlap between the devolatilization and combustion stages. This would certainly lead to an increase in homogeneous ignitions by increasing the probability of having volatiles in close contact with combusting particles.

Many investigators have found a relation between the reactivity of coal and char particles and the emissions of NO\textsubscript{x} during combustion. This relation is likely due to the ability of the carbon surface to reduce NO\textsubscript{x}, as discussed in appendix A. Experiments could be carried out to investigate a relation between pyrolysis heating rate and the NO\textsubscript{x} emission levels from the resulting char during combustion.

The ignition models of Sotirchos and Amundson showed the importance of considering intraparticle thermal gradients. Our observations of particle ignitions which propagate across the particle surface from "hot spots" also indicate the importance of intraparticle heat conduction. To include these effects, future modeling efforts should consider a distributed model which accounts for spatial variations.
REFERENCES


M. W. Glass. (1987). *Stereological analysis of the macropore structure of chars produced under various pyrolysis conditions and the influence of macropore structure on char gasification rates in the presence of strong diffusional limitations* Ph.D., Rice University.


APPENDIX A

EMISSIONS OF NO\textsubscript{x} FROM COAL AND CHAR PARTICLES

Fossil fuel combustion is a primary source of many common atmospheric pollutants which contribute to problems such as global warming, acid rain, and photochemical smog. Among fossil fuels, coal is by far the most common fuel source used for electricity generation in the United States. Coal combustion introduces large quantities of CO, CO\textsubscript{2}, SO\textsubscript{x}, and NO\textsubscript{x} into the atmosphere.

Controlling the emissions of CO and CO\textsubscript{2} is certainly difficult since they are the primary reaction products of coal combustion. However, an increase in combustion efficiency would be an effective approach to reducing the emissions of CO and CO\textsubscript{2} per unit of energy generated.

Many pollution control strategies focus on the removal of NO\textsubscript{x} and SO\textsubscript{x} from the effluent gas streams of industrial reactors. However, it is more desirable to prevent formation of undesirable compounds rather than focus on treatment of those already formed. Preventing the production of SO\textsubscript{x} in coal combustors is commonly attempted through the use of a low sulfur content coal, or by cleaning the coal before combustion. Preventing the formation of NO\textsubscript{x}, however, is more difficult.

The formation of NO\textsubscript{x} in coal combustors occurs by two primary mechanism. NO\textsubscript{x} can be formed through the reaction of nitrogen present in air with oxygen through the Zeldovich mechanism (Clarke and Williams 1991):
\[ N_2 + O \rightarrow NO + N \]
\[ N + O_2 \rightarrow NO + O \]
\[ N_2 + O_2 \rightarrow 2NO \]

The overall reaction has a very high activation energy and thus requires high temperatures to be completed. NO\textsubscript{x} produced by this mechanism, called "thermal NO\textsubscript{x}", thus can be controlled by lowering combustion temperatures (Clarke and Williams 1991).

Another common source of NO\textsubscript{x} formation in coal combustion is a result of oxidation of nitrogen containing species present in the coal. Coal typically contains 1% by weight nitrogen. During devolatilization, some of the lower molecular weight nitrogen containing compounds are released and react with oxygen to form NO\textsubscript{x}. Other nitrogen compounds are retained in the char solid and can only be oxidized by heterogeneous reactions.

The formation of NO\textsubscript{x} through the oxidation of fuel-N has been found to be more dependent on oxygen concentration than combustion temperature. For this reason, low-NO\textsubscript{x} burners have been designed which utilize staged combustion. In the first stage, a low fuel-air ratio is used to reduce the amount of oxygen available to form NO\textsubscript{x}. In subsequent stages, combustion occurs at higher oxygen concentration to complete combustion of the char. In these low-NO\textsubscript{x} burners, conversion of fuel-N to NO has been identified as the primary source of NO (Pels, et al. 1993).

Wang and coworkers (Wang, et al. 1994) studied the comparison between NO production in coals versus chars. In particular, they found that the conversion of char-N to NO was comparable or lower than the
conversion of coal-N to NO. This result indicates that oxidation of nitrogen containing volatiles is more efficient than the oxidation of char-N to NO.

In fact, it is well known that the conversion efficiency of producing NO\textsubscript{x} through gas phase reactions with volatiles is much higher than production through heterogeneous oxidation of char bound nitrogen compounds (Clarke and Williams 1991). Lower conversion efficiencies of char bound nitrogen to NO\textsubscript{x} may be due to the capability of carbon to reduce NO:

\[ NO + C_s \rightarrow CO + \frac{1}{2} N_2 \]

Thus reduction of NO can occur at active sites occurring on the surface area of a coal or char particle. We therefore expect there to be a relationship between the surface area of a coal or char particle and its ability to reduce NO, effectively preventing the formation of NO.

As discussed in chapters 4 and 6, the reactivity of a char particle towards oxygen is strongly dependent on the available surface area for reaction. Thus, there should be a correlation between the reactivity of a coal or char particle towards oxygen and its ability to prevent the formation of NO. Independent studies by Wang and coworkers and Shimizu et al have confirmed these suggestions, showing that char-N to NO conversion is related to reactivity with more reactive samples yielding lower NO-N ratios (Shimizu, et al. 1992, Wang, et al. 1994).

The implications of these results are very important. Studies on the effects of process conditions in maximizing char reactivity not only provide a means to improve combustor efficiency, but also produce chars which lead to lower emissions of NO\textsubscript{x}. 