GASIFICATION OF COAL CHAR IN
OXYGEN AND CARBON DIOXIDE AT HIGH TEMPERATURES

by

GERALD MANDEL

SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE
DEGREES OF

BACHELOR OF SCIENCE

and

MASTER OF SCIENCE

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

May 1977

Signature of Author: ____________________________

Department of Chemical Engineering, May 1977

Certified by: ____________________________

Thesis Supervisor

Certified by: ____________________________

Thesis Supervisor

Accepted by: ____________________________

Chairman, Department Committee

(JUL 26 1977)
GASIFICATION OF COAL CHAR IN
OXYGEN AND CARBON DIOXIDE AT HIGH TEMPERATURES

by

GERALD MANDEL

Submitted to the Department of Chemical Engineering
in May, 1977 in partial fulfillment of the requirements
for the Degrees of Bachelor of Science and Master of Science.

ABSTRACT

Weight losses and changes in physical structure of a pulverized
Montana Rosabud coal char have been measured during gasification in
atmospheres of oxygen, carbon dioxide, and helium at temperatures between
1500 and 1825°K.

Data on the gasification kinetics were obtained in a muffle tube
furnace in which residence times were varied from 50 to 500 msec in a
laminar flow mode for oxidation experiments and from 0.5 to 3 minutes
in a crucible mode for the carbon dioxide reduction experiments. Devola-
tilization experiments in helium were run in both modes of operation with
residence times as long as 1 hour.

The results showed that the oxidation reaction was controlled by the
coupled effects of pore diffusion and reaction with the pore walls over
the entire range of conditions studied. The carbon dioxide reduction
reaction, however, was found to be kinetically controlled under similar
conditions.

Through a pore diffusion model, the intrinsic reactivity of the char
to these gases was extracted from the results yielding reaction orders of
0.26 for the oxidation reaction and 0.70 for the carbon dioxide reduction
reaction. Intrinsic reactivities, \( k_v \), expressed as the rate of carbon
consumption per unit total surface area, were then given by the empirical
relations

\[
-25,200/RT \quad k_v = 0.094 e^{-P \left( \frac{cm}{sec} \right) \left( \frac{g-moles}{cm^3} \right)^{0.74}}
\]

for the oxidation reaction, and

\[
-43,900/RT \quad k_v = 34.5 e^{-P \left( \frac{cm}{sec} \right) \left( \frac{g-moles}{cm^3} \right)^{0.30}}
\]

for the carbon dioxide reduction reaction.

Thesis Advisors: Jack B. Howard, Professor of Chemical Engineering
Adel F. Sarofim, Professor of Chemical Engineering
Department of Chemical Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139  
May 25, 1977

Professor Irving Kaplan  
Secretary of the Faculty  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139

Dear Professor Kaplan:

In accordance with the regulations of the faculty, I herewith submit a thesis, entitled "Gasification of Coal Char in Oxygen and Carbon Dioxide at High Temperatures," in partial fulfillment of the requirements for the degrees of Bachelor of Science and Master of Science in Chemical Engineering at the Massachusetts Institute of Technology.

Respectfully submitted,

Gerald Mandel

GM/pap
ACKNOWLEDGEMENTS

I give my deepest love and respect to my wife, Pam, to whom this work is dedicated. The brunt of the pressures and hardships associated with preparing a thesis are always shared by those who are closest to you, and this was no exception. Her continued compassion and understanding through the difficult times, of which there were many, go forever cherished.

I would like to express my sincere gratitude to Professor Howard and Professor Sarofim for their faith and encouragement during the menagerie of problems that arose. Their aid and guidance proved to be a most rewarding learning experience.

Special thanks are due also to Mr. Yih-Hong Song for the countless hours of enlightening discussion that prevailed, and for his invaluable assistance with some of the more complicated procedures. He too is to be specially recognized for his friendship and understanding while working closely together under pressured conditions.

Finally, I am greatly indebted to Phillips Petroleum Company for their funding of this research. Their work on the physical characterizations of the char is, in addition, very much appreciated.
# TABLE OF CONTENTS

I. INTRODUCTION ........................................... 11
   1.1 Background ........................................... 11
   1.2 Mechanisms of Coal Gasification ...................... 13
      1.2.1 Overview ........................................ 13
      1.2.2 Devolatilization ................................ 17
      1.2.3 Char Oxidation by Oxygen ......................... 19
      1.2.4 Carbon Dioxide Reduction by Char ................. 24
   1.3 Objectives ........................................... 29

II. APPARATUS AND PROCEDURES ............................. 32
   2.1 Experimental Apparatus ............................... 32
      2.1.1 The Furnace .................................... 34
      2.1.2 The Char Feeder ................................ 35
      2.1.3 Particle Collector ............................... 37
      2.1.4 Gas Preheat ..................................... 39
      2.1.5 Vacuum System .................................. 40
      2.1.6 Crucible Mode Adaptations ....................... 40
      2.1.7 Gas Flow Control and Measurement ............... 41
      2.1.8 Sample Weight Measurements ..................... 41
   2.2 Experimental Procedures ............................. 41
      2.2.1 Experimental Procedure for the Laminar Flow
            Experiments .................................... 41
      2.2.2 Procedure for the Crucible Experiments .......... 44
   2.3 Proximate Analysis ................................. 44
TABLE OF CONTENTS (Cont'd)

2.4 Experimental System Evaluations .......................... 46
  2.4.1 Residence Times ........................................ 46
  2.4.2 Particle Temperature and Heating Rates ............... 52
  2.4.3 Quenching Efficiency .................................. 54
  2.4.4 Collection Efficiency ................................. 57

III. RESULTS ....................................................... 60
  3.1 Data Analysis ................................................ 60
  3.2 Weight Loss by Ash Tracer ................................ 67
  3.3 Pyrolysis Results .......................................... 71
  3.4 Oxidation Results .......................................... 73
    3.4.1 Calculation of Initial Rates ......................... 74
    3.4.2 Approximate Particle Temperatures .................... 77
    3.4.3 Surface Oxygen Concentrations ....................... 80
    3.4.4 Apparent Kinetics .................................... 83
  3.5 Carbon Dioxide Reduction Results ......................... 86
    3.5.1 Calculation of Initial Rates ......................... 87
    3.5.2 Surface Carbon Dioxide Concentrations ............... 89
    3.5.3 Apparent Kinetics .................................... 91
    3.5.4 Langmuir-Hinshelwood Kinetics ...................... 95
  3.6 Summary of Oxidation and Carbon Dioxide Reduction Results 96

IV. DISCUSSION .................................................... 97
  4.1 Physical Changes During Reaction ........................ 97
TABLE OF CONTENTS (Cont'd)

4.2 Effectiveness Factors and Intrinsic Reactivity ........ 100
  4.2.1 Pore Diffusion Model for Oxidation Results ....... 101
  4.2.2 Pore Diffusion Model for Carbon Dioxide Reduction Results ............. 107
4.3 Evaluation of Results ............................................. 111
4.4 Comparison of Oxidation and Carbon Dioxide Reduction Results 115

V. CONCLUSIONS .............................................................. 117
VI. RECOMMENDATIONS ..................................................... 119

Appendix A. Results of Pyrolysis Experiments ................. 120
Appendix B. Results of Char Oxidation Experiments .......... 123
Appendix C. Results of Carbon Dioxide Reduction Experiments ... 125
Appendix D. Calculation of Binary Diffusion Coefficients for O₂-He and CO₂-He ................. 128
Appendix E. Calculation of Thermal Conductivities for O₂ and He Mixtures ......................... 131
Appendix F. Calculation of Effective Pore Diffusivities for O₂ and CO₂ ........................ 134
Appendix G. Characterization of Rosebud Char Samples ........ 138

REFERENCES ................................................................. 146
LIST OF FIGURES

1.1 Three Possible Kinetic Regimes in Heterogeneous Reaction of Porous Solid with Gas .......................... 16

2.1 Overall Scheme of Experimental Apparatus .................. 33

2.2 Char Feeder ............................................... 36

2.3 Particle Collector .......................................... 38

2.4 Axial Temperature Profile in Muffle Tube .................. 42

2.5 Hypothesized Particle Flow Field ......................... 49

3.1 Pyrolysis of Rosebud Char for Short Residence Times ...... 61

3.2 Summary of Results for Pyrolysis of Rosebud Char .......... 62

3.3 Oxidation of Rosebud Char by $O_2$ ....................... 63

3.4 Carbon Dioxide Reduction by Rosebud Char (1) ............. 65

3.5 Carbon Dioxide Reduction by Rosebud Char (2) ............. 66

3.6 Comparison of Weight Loss by Ash Tracer to Weight Loss by Direct Measurement .......................... 69

3.7 Arrhenius Plot of Apparent Kinetics for Oxidation Experiments 85

3.8 Arrhenius Plot for Carbon Dioxide Reduction Experiments ... 93

3.9 Evaluation of Langmuir-Hinshelwood Kinetic Constants ....... 94

4.1 Physical Changes of Char During Reaction ................ 98

4.2 Arrhenius Plot of Intrinsic Kinetics for Oxidation Experiments 105

D.1 Binary Diffusion Coefficients for $O_2$-He and $CO_2$-He ... 130

E.1 Thermal Conductivities of Pure Components Helium and Oxygen . 132

E.2 Thermal Conductivities of Helium and Oxygen Mixtures ......... 133

F.1 Effective Pore Diffusivities for the Representative Initial Chars ........................................... 137

G.1 Particle Size Distribution for the Raw Montana Rosebud Char 143
LIST OF FIGURES (Cont'd)

G.2 Particle Size Distribution for the Char from Run CPR-12 . . . 144
G.3 Particle Size Distribution for the Char from Run CPR-11 . . . 145
LIST OF TABLES

1.1 The Reactions of β-Graphite with Oxygen and Carbon Dioxide and Their Equilibrium Constants ........................................... 28
2.1 Collection Efficiency Summary .................................................. 58
3.1 Initial Rates of Reaction for Oxidation Experiments ................. 76
3.2 Approximate Particle Temperatures for Oxidation Experiments . 79
3.3 Oxygen Surface Concentrations for Oxidation Experiments ... 82
3.4 Apparent Kinetic Constants for Oxidation Reaction ................. 84
3.5 Initial Reaction Rates for Carbon Dioxide Reduction Experiments 88
3.6 Carbon Dioxide Surface Concentrations for Carbon Dioxide Reduction Experiments .......................................................... 90
3.7 Apparent Kinetic Constants for Carbon Dioxide Reduction Experiments .......................................................... 92
4.1 Intrinsic Kinetics for Oxidation Reaction ................................. 106
4.2 Intrinsic Kinetics for Carbon Dioxide Reduction Experiments . 110
A.1 Results of Rosebud Char Pyrolysis Experiments in Laminar Flow Mode ................................................................. 121
A.2 Results of Rosebud Char Pyrolysis Experiments in Crucible Mode 122
B.1 Results of Rosebud Char Oxidation Experiments ....................... 124
C.1 Results of Carbon Dioxide Reduction by Rosebud Char Experiments 126
F.1 Mean Pore Radii for the True InitialChars ............................... 136
G.1 Results of Proximate Moisture and Ash Analyses of the Rosebud Char as Received ...................................................... 140
G.2 Physical Properties of Rosebud Char Samples ........................... 141
G.3 Partial Ultimate Chemical Analyses of Rosebud Char Samples .. 142
Chapter I

INTRODUCTION

1.1 Background

In the United States alone total energy consumption has been increasing at 2.9% per year for the last 30 years (4.1% for the years 1960-1973). Rapidly dwindling natural gas reserves and the major dependence on foreign oil now pose a serious problem if we expect to meet our anticipated energy needs in even the next 10 years. One method of approach to this problem actively being sought is to develop and improve new and existing technologies which utilize coal to produce energy. Coal is by far the most plentiful of our domestic fossil resources with known reserves estimated to last 200 years at current growth rates.

The proposed uses of coal include gasification, liquefaction, magnetohydrodynamic power generation, and fluidized bed combustion to name a few. Of these, the fuel-to-fuel conversion of coal to gas is of particular interest for several reasons: 1) Many of the gasification processes currently under development have already reached at least the pilot plant stage such as Hygas, Texaco, Synthane, Cogas, and Bigas. 2) Research so far has shown great promise with the lack of serious faults in these processes and their applicability to large scale production of synthesis gas (CO and H₂) and synthetic natural gas (SNG). 3) While it appears that SNG prices will be considerably above those of current pipeline gas and liquified natural gas (LNG), these latter prices are certain to rise in the future, particularly with diminishing supplies, thus making the market much more competitive.
In most gasification systems, pulverized coal or coal char is exposed to a hot environment containing such species as $O_2$, $CO_2$, $H_2O$, $H_2$, $CO$, and $CH_4$. The reactions of char with $O_2$ and $CO_2$ are among the many complex homogeneous and heterogeneous reactions that occur. The carbon-oxygen reaction is important since it is generally used to produce the enthalpy supplied to the process. At the same time, however, $CO_2$, which is formed by this and other reactions, is undesirable since it not only acts as a diluent but inhibits the formation of hydrogen. $CO_2$ may be reduced, though, via reaction with char to produce $CO$ which is a desired product. It is therefore imperative to have an understanding of the reactivity of the coal or char with these gases for reasons of reactor design and process optimization.

The purpose of this research is to study in some detail the reactivity of a specified coal char with $O_2$ and $CO_2$. There have been numerous investigations in the past focussing on the reactions of non-porous particle geometries with both $O_2$ and $CO_2$. However, the non-homogeneous and porous nature of coal and coal char makes analogous modelling much more complicated. The following work approaches this complex problem from a somewhat pragmatic view. Rather than attempt to characterize the individual reactions that are believed to occur, "apparent reactivity" is defined accordingly by looking at the overall disappearance of solid material, which in this case is the coal char. Then, through theoretical modelling, an "intrinsic reactivity" is sought which may subsequently be compared to kinetic values obtained from the literature. It is hoped that this thesis will demonstrate a useful method for analyzing the complex kinetic systems encountered in gasification processes.
1.2 Mechanisms of Coal Gasification

1.2.1 Overview

Operating conditions among the many proposed coal gasification schemes may vary anywhere from 1100 to 3000°F and from 1 to 100 atm. However, all of these involve three basic steps similar in each. First, pulverized coal is devolatilized producing some amount of methane. Second, a portion of the devolatilized coal or char is reacted with steam to produce \( \text{H}_2 \) and CO. Third, the remaining char is gasified with the \( \text{H}_2-\text{CO}-\text{H}_2\text{O} \) to produce more methane.

Since \( \text{CH}_4 \) and/or \( \text{H}_2 \) enriched \( \text{H}_2-\text{CO} \) are the products of primary concern, a source of \( \text{H}_2 \) is required. Because the coal itself may have an \( \text{H}:\text{C} \) ratio of only 1.8 and \( \text{H}_2 \) alone is too costly to add to the process, steam is usually taken as the source of hydrogen by the following reactions:

\[
\begin{align*}
\text{C} + \text{H}_2\text{O}^{(v)} & = \text{CO} + \text{H}_2 & \Delta H = +32.5 \text{ kcal/g-mole} \quad (1.1) \\
\text{CO} + \text{H}_2\text{O}^{(v)} & = \text{CO}_2 + \text{H}_2 & \Delta H = -7.8 \text{ kcal/g-mole} \quad (1.2)
\end{align*}
\]

Unfortunately the carbon-steam reaction is highly endothermic. Although this is favorable from an equilibrium standpoint, it means that a substantial amount of heat or enthalpy must be put into the system. The heat needed is often provided by direct combustion of the char in the presence of oxygen as follows:

\[
\begin{align*}
\text{C} + \text{O}_2 & = \text{CO}_2 & \Delta H = -94.0 \text{ kcal/g-mole} \quad (1.3) \\
\text{C} + \frac{1}{2} \text{O}_2 & = \text{CO} & \Delta H = -26.6 \text{ kcal/g-mole} \quad (1.4)
\end{align*}
\]
\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H = -67.4 \text{ kcal/g-mole} \quad (1.5) \]

As the temperature or the fuel equivalence ratio \( \phi \) (see footnote) increases, CO becomes the primary product. \( \text{CO}_2 \) is the less desired product in spite of its high heat of formation, because the lower its partial pressure, the more readily reaction (1.2) will go to the right. \( \text{CO}_2 \) forms nonetheless via reactions (1.2), (1.3), and (1.5); but it may be removed by adsorption on calcined limestone or dolomite, or it may be reduced by the char to form CO when the residence time is sufficiently long or the gasification temperature is high.

Finally, the methanation reaction of char

\[ \text{C} + 2\text{H}_2 = \text{CH}_4 \quad \Delta H = -21.9 \text{ kcal/g-mole} \quad (1.6) \]

tends to be relatively slow and unfavorably affected by increased temperature. Nonetheless, it is important to maximize the yield of \( \text{H}_2 \) by reactions such as the water-gas shift reaction (1.2).

In all the gas-carbon reactions, three resistances occur in series:
1) diffusion of the reacting gas to the surface of the particles; 2) reaction at the particle surface; and 3) diffusion and reaction within the pores. As a result there are three regimes in which the reaction may be taking place depending upon which step is controlling, or which step

\[ \phi = \frac{\text{(fuel flow rate/air flow rate)}_{\text{actual}}}{\text{(fuel flow rate/air flow rate)}_{\text{stoichiometric}}} \]
is the slowest. Figure 1.1 shows approximately how the reaction regimes follow temperature as proposed by Wicke (1957). At sufficiently low temperature the reaction rate is so slow that the potential required for diffusion is insignificant and intrinsic kinetics are observed. This is the first regime. As temperature increases the diffusion rate increases slowly while the reaction rate rises exponentially. Concentration gradients within the pores become more severe until the rate of pore diffusion is much less than the rate of reaction. In this, the second regime, the concentration of reacting gas approaches zero before the center of the particle and the reaction is limited by the rate of pore diffusion. Furthermore, the observed activation energy is approximately the arithmetic average between that of the intrinsic reaction and that of diffusion or simply half the intrinsic activation energy ($E_{act}$ for diffusion is only about 1 to 3 kcal). As temperature is increased still further, the concentration difference between the bulk of the fluid and the outside of the particle becomes significant. In this third regime, the concentration of the reacting gas approaches zero at the outside surface and the reaction is bulk diffusion limited. In this regime, the activation energy is generally 1 to 3 kcal since the observed rate is merely that of diffusion; and the order of reaction appears to be first order regardless of the intrinsic kinetics since mass transfer is a first-order process. Understanding in which regime these reactions occur in a given system is necessary to determine how to adjust conditions for optimizing operations.
Figure 1.1 Three Possible Kinetic Regimes in Heterogeneous Reaction of Porous Solid with Gas (Wicke, 1957).
1.2.2 Devolatilization

When the pulverized coal first enters the hot environment the particles rapidly undergo devolatilization yielding a mixture of primary volatiles or tars consisting mainly of high molecular weight carbon species, plus a mixture of combustible gases containing CO, H₂, CH₄, and small amounts of other hydrocarbons. The remaining char consists of highly polymeric aromatics and unsaturated hydrocarbons and the ash. The amount of volatiles, their composition, and the rate at which they are released are all strongly dependent on many physical and chemical properties of the original coal.

Coals from different geographic locations not only vary widely in chemical composition, but have been demonstrated to exhibit large differences in physical behavior (Field et al., 1967) with respect to plastic behavior, melting, and swelling characteristics. Furthermore, any given coal sample is a heterogeneous mixture of organic and mineral matter whose structure is not well established. Even samples from the same seam may show great irregularities in shape and composition among particle sizes due to uneven breakage or the nonhomogeneity in composition.

The mechanism of devolatilization is not well understood despite numerous investigations in the area. Van Krevelen et al. (1951) studied the devolatilization mechanism by heating coals at 2°C/min. He observed that the volatile evolution occurred in two stages. The first stage occurred between 400-500°C in which mainly tars were released. The second stage took place above 500°C which saw the release of gases rich in hydrogen. Howard and Essenhigh (1967), upon studying the pyrolysis
of a Pittsburgh bituminous coal in a one-dimensional flame, also found that the evolution of volatiles appeared to occur as though the volatile matter existed as two different components. One evolved very rapidly and the other very slowly where the slower component represented about 15 percent of the total volatile matter.

Anthony et al. (1975) have studied the rapid devolatilization of Pittsburgh and Montana coals at temperatures up to 1100°C and heating rates of $10^4$ °C/sec under different atmospheres using an electrically heated screen. Under these conditions both coals devolatilized so rapidly that most of the weight loss occurred during heat-up. For the Montana lignite the devolatilization was found to be independent of heating rate, pressure, and particle size; but for the bituminous, a caking coal, volatile yields increased with decreasing pressure, decreasing particle size, and to a small extent, increasing heating rate. They also found that the kinetics and yields of the primary decomposition could be described by a set of independent first-order, parallel reactions represented by a Gaussian distribution of activation energies.

Findings that enhanced volatile yields are possible with higher temperatures and higher heating rates have important direct applications to gasification systems. Badzioch and Hawksley (1970) studied the kinetics of pyrolysis for 11 different coals at temperatures up to 1000°C and heating rates to $5 \times 10^4$ °C/sec. They found the total amount of volatiles to be sensitive to the heating rate as well as the final temperature. The amount of volatiles was determined by using ash as a tracer (see Section 3.2). Under these rapid heating conditions the volatile yield was 1.3 to
1.8 times higher than the difference between the proximate volatile matter in the coal and in the char. Kimber and Gray (1967a) found similar results by measuring weight loss directly to determine volatile yields. While most American coals contain a proximate volatile content of between 20 and 50 percent on a dry-ash-free (d.a.f.) basis, Kimber and Gray observed volatile yields as high as 70 percent d.a.f. at 1900°C and a heating rate of $10^6$ °C/sec with a coal having a proximate volatile content of only 38 percent d.a.f.

Increased volatile yield is of great importance in coal gasification since this would reduce the amount of char that must be gasified in the following steps thus increasing process efficiency. Therefore a good understanding of the complex pyrolysis mechanisms is needed. Several models have been proposed to describe this unusual behavior during rapid devolatilization (Jüntgen and Van Heek, 1968; Anthony, 1974; Kobayashi, 1972 and 1976) most of which involve some number and methods of combinations of first order reactions. However, the fit of data to these models must generally be done by determining a large number of adjustable parameters. It is apparent that further research in this area is warranted.

1.2.3 Char Oxidation by Oxygen

The carbon-oxygen reaction is currently of great importance in energy production, coal and char gasification, burnoff of carbon deposits on catalyst pellets, burnout of carbon particles in flames, and in many other industrial, commercial, and even residential applications. The ability to accurately predict the burning rate of a carbon body in oxygen
under various conditions has therefore been a topic of many investigations and is probably the best understood of the carbon-gas reactions.

One basis for describing the kinetics of the carbon-gas reactions is the Langmuir adsorption isotherm which was originally developed to explain the carbon-oxygen reaction (Langmuir, 1915). This theory assumes that there are active adsorption sites on the solid carbon surface which are filled by the chemisorption of oxygen; the rate of adsorption being proportional to the oxygen partial pressure \( (P_s) \) times the fraction of unoccupied active sites, \( (1 - \theta) \):

\[
\text{Rate}_1 = k_1 (1 - \theta) P_s \tag{1.7}
\]

where \( k_1 \) is the constant of proportionality. The chemisorbed sites are then made active again by the desorption of the oxygen carrying with it the underlying carbon atoms as CO or CO\(_2\). The rate of desorption is then simply proportional to the number of chemisorbed sites, \( \theta \):

\[
\text{Rate}_2 = k_2 \theta \tag{1.8}
\]

In (1.7) and (1.8) the values for \( k \) are generally of the form

\[
k = k_0 e^{-E/RT} \tag{1.9}
\]

Now at equilibrium, the rate of adsorption equals the rate of desorption. Solving for \( \theta \), the rate of reaction is then found to be
\[
\text{Rate} = \frac{k_1 k_2 p_s}{k_1 p_s + k_2}
\]  (1.10)

This relation indicates that for the two limiting cases, respectively,

when \( k_1 p_s \gg k_2 \); \( \text{Rate} = k_2 \)  (1.11)

when \( k_2 \gg k_1 p_s \); \( \text{Rate} = k_1 p_s \)  (1.12)

case (1.11) represents desorption control and (1.12) represents adsorption control. Tu et al. (1934) measured the combustion rates of spheres of brush carbon under varied conditions of temperature, oxygen partial pressure, and gas velocity. Reinterpretation of their results by Howard and Hottel revealed activation energies for adsorption, \( E_1 \), and desorption, \( E_2 \), to be 3.4 kcal/mole and 40 kcal/mole respectively. This indicates that at low temperatures, condition (1.11) exists and the reaction is zero order. At high temperatures condition (1.12) exists and the reaction becomes first order.

The Langmuir adsorption model has been demonstrated (Ergun and Menster, 1965; Walker et al., 1959) to show good agreement for the combustion of non-porous carbon particle geometries. However, most carbon materials of interest such as coal and coke are very porous in nature and require the combined kinetics of the boundary diffusion to the particle surface and the surface reaction, plus pore diffusion and reaction with the pore walls.
In the combustion of pulverized coal, the char burnout is considered to be the final stage although it may overlap to some extent with the volatile evolution. Howard and Essenhigh (1967) found, for instance, that ignition occurred on the particle surface at 1100°C before significant volatile release. But the period of rapid volatile evolution followed immediately, delaying further heterogeneous combustion in particles larger than about 65 microns until the rapid devolatilization had ceased. Furthermore, the period of char burnout is generally of much longer duration (on the order of 300 msec depending on particle size) than either the release of the major portion of volatiles or their combustion in the boundary layer (about 20 msec comparatively) (Mulcahy and Smith, 1969).

Initially the char combustion process was viewed as three steps in sequence: transport of oxygen (and other reactants) to the particle surface; reaction with the surface, including both chemisorption and desorption; and transport of products away. However, the latter step is unlikely to be controlling (Field et al., 1967) because there is a lack of evidence that the chemical reaction rate is inhibited by the presence of combustion products above 1000°K, and because the products will not significantly alter the diffusion rate of oxygen through what is largely inert diluent nitrogen (except as noted when there is a massive release of volatiles).

Evidence that under appropriate conditions char particle combustion occurs internally as well as externally has since introduced the need to admit pore diffusion and reaction to the list of steps in the char combustion process. Anson, Moles, and Street (1971) used microscopic analysis
and high-speed photography to study the structural changes of swelling bituminous coal particles during rapid heating in air. They found that the particles, in general, formed hollow spheres which burned internally as well as externally at nearly constant diameter until some advanced stage when the particles would fragment. Smith and Tyler (1972, 1974) found similar results upon studying the combustion rates of size-graded fractions of petroleum coke, anthracite, and a bituminous char. Their results showed that macropores developed during reaction and that the micropore volume decreased. They also found that reaction was only completely kinetically controlled for very small particles (about 25 microns and less).

To separate the effects of pore diffusion from "intrinsic" reactivity, Smith and Tyler (1974) used the method of Thiele (1939) as described by Satterfield (1975). This model employs the quantity referred to as the "effectiveness factor", \( \eta \), defined as the ratio of the actual reaction rate to that which would occur if all of the surface throughout the inside of the particle were exposed to the same temperature and oxygen partial pressure as that existing at the outside surface of the particle. As \( \eta \to 1 \), the combustion reaction becomes kinetically controlled. The general theoretical approach is to develop the mathematical equations describing the simultaneous mass transfer and chemical reaction occurring in the porous particles, and then, with the aid of some experimental data, determine the appropriate value for \( \eta \). This method of analysis is described in much detail in Chapter 4.
In summary, the present data indicate that the combustion of coal char in oxygen involves a complex combination of diffusion and kinetics phenomena. When reaction occurs simultaneously within the porous structure, concentration gradients are established which generally will give an average reaction rate below that which would occur were there no mass transfer limitations. As will later be demonstrated, such important observed characteristics of the reaction as the apparent activation energy depend strongly upon the magnitude of these concentration gradients. The modelling of such a system therefore requires analysis of pore diffusion effects and the extent to which they occur.

1.2.4 Carbon Dioxide Reduction by Char

Since carbon dioxide is a direct product of the carbon-oxygen reaction and an indirect product of the carbon-steam reaction through the water-gas shift, the secondary reaction of carbon dioxide with carbonaceous fuels is a major concern. In the production of synthesis gas, carbon gasification via the reaction with CO$_2$ is greatly encouraged:

\[ C + CO_2 = 2CO \quad \Delta H = +40.8 \text{ kcal/g-mole} \quad (1.13) \]

Paradoxically, there are times when the retardation of the carbon-gas reactions is necessary. When carbon is used as an electrode, it is desired that carbon not react with CO$_2$ produced in the reduction of ore, or the ambient atmosphere around it. The use of graphite as a moderating material in nuclear reactors has brought much attention to its reactivity with CO$_2$.
which may be used as a coolant. It is clear, therefore, that the carbon-carbon dioxide reaction has been studied extensively.

There have been several proposed mechanisms for the C-CO$_2$ reaction based on the techniques of Langmuir presented in Section 1.2.3 (Hinshelwood et al., 1946; Semechkova and Frank-Kamenetskii, 1940; Wu, 1949). All of these assume that either CO becomes adsorbed to retard the reaction or that the CO$_2$ dissociates at the carbon surface leaving an adsorbed O atom (to be distinguished from adsorbed CO) which acts to retard the reaction. In any case the general form of the rate of reaction is identical regardless of which mechanism is chosen:

$$\text{Rate} = \frac{K_1 \text{PCO}_2}{1 + K_2 \text{PCO}_2 + K_3 \text{PCO}}$$

(1.14)

It is seen from this equation that the C-CO$_2$ reaction will be zero order when $K_3 \text{PCO} \ll 1$ and $K_2 \text{PCO}_2 \gg 1$. At low temperatures the production of carbon monoxide is small and the first inequality is satisfied. At high carbon dioxide pressures the second inequality is also satisfied. On the other hand, at low temperature and low carbon dioxide pressure, $K_3 \text{PCO} \ll 1$ and $K_2 \text{PCO}_2 \ll 1$ and the reaction becomes first order. With increasing temperatures, investigators (Lewis et al., 1949; Wu, 1949) have found that the values for $K_2$ and $K_3$ drop off relatively quickly and again the reaction becomes first order with respect to carbon dioxide. As expected, however, the order of reaction will vary from zero to one, depending not only on temperature and pressure, but on the type of carbon reacted, its purity, and its physical shape and structure.
Ergun and Mentser (1965) have compared kinetic data on the reactions of CO$_2$ with relatively pure carbons and those with coke. They found that the activation energies of the reactions with the "pure" carbons were almost identical but reactivities varied by more than two orders of magnitude between a Ceylon graphite and an activated carbon. However, upon comparing these to a metallurgical coke, Ergun and Mentser found the latter to have a lower activation energy and thus become relatively less reactive as temperature increased. This they explained was due to a decrease in available active CO$_2$ adsorption sites with increasing temperature.

Golovina et al. (1962) studied the reaction of CO$_2$ with graphite spheres 15 mm in diameter over a temperature range of 1000 to 3200°C. They interestingly found that the rate of burning increased with temperature up to 1500°C, then decreased between 1500 and 2300°C, and then increased again above 2300°C. The gradual decrease in rate is believed due to the eventual build-up of adsorbed surface oxides with temperature. However, Golovina did not offer an explanation for the sudden increase in rate above 2300°C. Kimber and Gray (1967b), making similar discovery using size-graded charcoal particles, explained the phenomenon as being the result of reaction with oxygen from dissociated CO$_2$ molecules. (For example, at 2800°C, carbon dioxide is 50 percent dissociated.) They also found that at temperatures up to 2300°C the "true" reaction rate, expressed in terms of the external geometric surface area, was nearly two orders of magnitude smaller than the diffusion controlled rate. At 2300°C the true rate was found to be less than 0.003 g/(cm$^2$-sec-atm) while the calculated
diffusion (bulk) controlled rate was 0.18 g/(cm$^2$-sec-atm). Furthermore, even at the highest temperature investigated, 2800°K, the true rate was only about 0.01 compared to 0.26 for the calculated diffusion controlled rate at this temperature. Kimber and Gray admitted, though, that the measurement of the true rates at these temperatures was likely to be inaccurate due to the interference from the reaction with oxygen and might be as much as a factor of 10 higher than reported.

Von Fredersdorff and Elliot (1963) summarize the results found by other authors on the CO$_2$ reaction with porous carbons. Unfortunately, although there is much available data on the reaction of carbon dioxide with pure carbons, there is a scarcity of data concerning this reaction involving coal and coal char for temperatures greater than 1200°C. Insight into the reactivity of char with CO$_2$ might be realized nevertheless, by comparing C-O$_2$ data with C-CO$_2$ data and extrapolating to the case involving char. The C-O$_2$ and C-CO$_2$ reactions are summarized and values for their equilibrium constants at different temperatures are given in Table 1.1.

Relative rates for the carbon-gas reactions are given by Walker et al. (1959) for 800°C and 0.1 atm.: C-O$_2$, $1 \times 10^5$; C-H$_2$O, 3; C-CO$_2$, 1; C-H$_2$, $3 \times 10^{-3}$. Under these conditions, the C-O$_2$ reaction rate is five orders of magnitude larger than the C-CO$_2$ reaction. One would therefore expect that if CO$_2$ and O$_2$ were present together in about the same concentrations, the extent of carbon gasification by CO$_2$ would be negligible compared to the O$_2$. When considering the reactivity of a porous carbon such as coal char, however, an important factor is
Table 1.1  The Reactions of β-Graphite with Oxygen and Carbon Dioxide and Their Equilibrium Constants (Thring and Essenhig, in Lowry, 1963)

(1) \( C(\beta) + O_2(g) = CO_2(g) \) \( \Delta H = -94.0 \text{ kcal/g-mole} \)

(2) \( C(\beta) + \frac{1}{2} O_2(g) = CO(g) \) \( \Delta H = -26.6 \text{ kcal/g-mole} \)

(3) \( CO(g) + \frac{1}{2} O_2(g) = CO_2(g) \) \( \Delta H = -67.4 \text{ kcal/g-mole} \)

(4) \( C(\beta) + CO_2(g) = 2CO(g) \) \( \Delta H = +40.8 \text{ kcal/g-mole} \)

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>( \log_{10} K_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>300</td>
<td>+ 68.67</td>
</tr>
<tr>
<td>400</td>
<td>+ 51.54</td>
</tr>
<tr>
<td>500</td>
<td>+ 41.26</td>
</tr>
<tr>
<td>600</td>
<td>+ 34.40</td>
</tr>
<tr>
<td>700</td>
<td>+ 29.50</td>
</tr>
<tr>
<td>800</td>
<td>+ 25.83</td>
</tr>
<tr>
<td>900</td>
<td>+ 22.97</td>
</tr>
<tr>
<td>1000</td>
<td>+ 20.68</td>
</tr>
<tr>
<td>1100</td>
<td>+ 18.80</td>
</tr>
<tr>
<td>1200</td>
<td>+ 17.24</td>
</tr>
<tr>
<td>1300</td>
<td>+ 15.92</td>
</tr>
<tr>
<td>1400</td>
<td>+ 14.78</td>
</tr>
<tr>
<td>4000</td>
<td>+ 5.14</td>
</tr>
</tbody>
</table>
introduced. The data of Smith and Tyler (1974) show that above 1250°K, the C-O₂ reaction becomes diffusion controlled. Golovina et al. (1962) and Kimber and Gray (1976b) show, on the other hand, that the C-CO₂ reaction remains kinetically controlled even above 2800°K. This means that at high enough temperatures oxidation by O₂ may occur essentially only on the external surface of the particle whereas CO₂ may diffuse and react readily within the porous structure. Since the area within the pores may be three orders of magnitude larger than the external surface, gasification by the C-CO₂ reaction may in fact by significant at high enough temperatures.

1.3 Objectives

The reactions between carbon, oxygen, and carbon dioxide are among the most significant of the carbon-gas reactions with applications ranging from coke burnoff in chemical reactors to graphite-rod gasification in nuclear reactors. One of the major applications currently in the spotlight is the gasification of coal and coal char to produce synthesis gas and SNG. Knowledge of the rate limiting step in any given system involving a gas-solid reaction is very important whether it be in combustion, gasification, or catalysis. When analyzing laboratory data for purposes of large scale reactor design, it is imperative that the conditions be such that intrinsic kinetics are observed; the reason being that diffusional effects vary not only with temperature and pressure, but also with relative gas-solid velocities, particle sizes, and reactor dimensions. Furthermore, in analyzing data from any on-stream operation, knowing the
rate controlling step will make it possible to adjust reactor conditions to optimize through-put.

In light of the above considerations, the following objective were chosen for this investigation:

1. Obtain kinetic data on the overall reaction of pulverized coal char with oxygen and carbon dioxide by measuring weight loss of char versus residence time under the following conditions:

   Type of Char  A Montana Rosebud (produced at 1365°C)
   Particle Size  120-125 μm
   Temperature  1500 and 1750°C
   Pressure  ~ 1 atm

   Varied Residence Times
   Varied Concentrations of Oxidizing Gases

2. Determine apparent orders of reactions, activation energies and rate constants using kinetic data.

3. Calculate effectiveness factors for the system thus determining the extent of diffusion limitations.

4. Determine true orders of reactions, activation energies, and rate constants by applying the above information to an appropriate model.

   These objectives are met by performing experiments at varied residence times for at least two different oxidizing gas concentrations to determine reaction order and at two different temperatures to determine activation energy; the rate constants follow directly. In addition,
experiments using only an inert gas at the two temperatures are required to help isolate the effect of pyrolysis. Overall reaction rates are determined by plotting the trend in weight loss versus residence time and measuring the slope of the curves at specified points. Finally, calculation of the effectiveness factors and the "true" kinetic constants is done through the Thiele (1939) theory as demonstrated by Smith and Tyler (1974). Because of the enormous complexity that would be entailed in a rigorous theoretical approach to these problems, a somewhat empirical approach was decided as having more useful and direct application. In this way, fundamental analyses and established experimental techniques may be utilized to provide insight and general understanding of otherwise extremely complex gasification systems.
Chapter II
APPARATUS AND PROCEDURES

2.1 Experimental Apparatus

In choosing an appropriate apparatus to effectively carry out the required experiments, several considerations had to be taken into account: the furnace unit must be capable of reaching and accurately maintaining the desired temperatures under the types of atmosphere to be encountered; it must have a certain amount of flexibility to adapt to necessary modifications; a char feeding system is needed which can consistently control the feeding rate; and a collection system which can quickly quench the reaction yet be adaptable to the rest of the apparatus is necessary. With these considerations in mind, the overall system, depicted in Figure 2.1, was chosen as being especially well suited for the purposes of this research. The basic design for this system is given by Kobayashi (1976)

In brief, the apparatus consists of a tubular reactor/furnace which can be operated in either a "laminar-flow" mode or a "crucible" mode. In the laminar flow mode, used for the short residence time oxidation experiments (50-500 msec), char particles are injected from the top in a dispersed phase by a water cooled feeder probe. A main gas stream, sent coaxially through a honeycomb flow straightener to help counter convective currents, entrains the char particles carrying them downward through the furnace hot zone. The particles and about half the gas are sucked into a water cooled collecting probe by means of a vacuum. The remainder of the gas passes down the outside of the probe and is vented to the atmosphere. The reaction is quenched by the injection and mixing of a cold inert gas at
Figure 2.1 Overall Scheme of Experimental Apparatus.
the mouth of the probe. The char is trapped in a sintered bronze filter while the cooled gases pass through. The collector may be raised or lowered in the furnace in relation to the feeder tip, thus varying the residence time of the char particles.

The crucible mode is used for the longer residence time carbon dioxide and pyrolysis experiments (0.5 to 60 min). An alumina dish is used to hold a thin particle layer char sample which is raised into the furnace hot zone for a specified length of time with an alumina rod. Because the heating time is much slower in this mode of operation, the muffle tube is purged with an inert gas until the desired temperature is reached. Residence time is then controlled directly by the duration of the CO$_2$ main gas purge in the muffle tube.

2.1.1 The Furnace

The system in Figure 2.1 is centered around an ASTRO model 1000A furnace (ASTRO Industries, Inc., Santa Barbara, California). The heating is done by a 9 cm I.D., 30 cm long graphite resistance heating element. Thermal insulation around the outside is provided by a 10.5 cm I.D. graphite radiation shield packed with graphite fibre. The shell and chassis of the furnace, made of aluminum, are protected by a water cooled jacket. The heating element is shielded from the reaction zone by a 60 cm long, 6.5 cm I.D. aluminum oxide muffle tube. In addition, an inner ceramic muffle tube 38 cm long and 5 cm I.D. is used to support a 2.5 cm thick ceramic honeycomb flow straightener having a nominal pore diameter of 1.5 mm.

The furnace is equipped with a 14 KVA power supply (230V and 65A) and an automatic temperature controller and programmer. The programmer
allows temperature changes to be made at specified rates. This is particularly important when using the ceramic muffle tubes, since heating rates must be slow enough to avoid thermal shock to the material. The furnace temperature is controlled and monitored by a boron-graphite thermocouple located in the center of the furnace just outside the heating element. A 1.5 cm diameter quartz observation port bears visual access to the outside wall of the muffle tube. In this way, the temperature may also be checked by optical means such as with a pyrometer. The temperature immediately downstream of the honeycomb within the reaction zone is monitored by a platinum-rhodium thermocouple to indicate whether there is proper heating of the main gas or not. The maximum operating temperature is 1750°C with the aluminum oxide muffle tubes and is limited mainly by the properties of the material.

2.1.2 The Char Feeder

The char feeder, as shown in Figure 2.2, is used to control feed rates by the use of a mechanical vibrator, partial fluidization of the char particles, and an adjustable needle valve. The upper portion of the feeder is made of 9 cm long and 1.25 cm I.D. polished plexiglas in which up to a 3 gram pulverized char sample may be held. A 3 mm O.D. stainless steel needle valve extends axially through this part down to another smaller plexiglas portion which has been machined internally to form a cone-shaped funnel. The needle valve is hollow and has four equally spaced 0.254 mm diameter holes near the tip through which carrier gas passes radially. The carrier gas flows at high velocity (but low flow rates) through these holes to partially fluidize the char particles thus
Figure 2.2 Char Feeder
preventing clogging in the narrow region. The low carrier gas flow rates allowed by this arrangement (as small as 5 cc/min) helps insure high heating rates upon injection into the furnace. Feeding is further facilitated by an adjustable mechanical vibrator attached at the throat of the funnel. The particles are then carried by both gravity and the carrier gas through the innermost of three concentric stainless steel tubes to the furnace. The three tubes together have an outside diameter of 6 mm and an inside diameter of 1.5 mm. The annular space between the tubes is used for circulating water to cool the probe, the tip of which extends 2 cm below the honeycomb within the furnace hot zone.

The feed rate is therefore controlled by the opening of the needle valve, the strength of the vibrator, and the flow rate of the carrier gas. Feed rates can be adjusted between 0.01 gm/min and 1.0 gm/min with reasonable uniformity. For this study approximately 1 gm char samples are fed at 0.15 gm/min with carrier gas flow rates of about 30 cc/min.

2.1.3 Particle Collector

The particle collector, depicted in Figure 2.3, consists of three concentric copper tubes. The outside diameter dimension is 3.5 cm and the inside diameter of the innermost tube is 1.3 cm. As with the feeder, the annular spaces are used for water cooling. In addition, there are eight 3 mm tubes between the inner two tubes through which the cool quenching gas enters. The quenching gas is injected toward the axis through the porous bronze at the bevelled portion of the collection filters. The filters (manufactured specially by Thermet Inc., Gloucester, Massachusetts) are made of sintered bronze shot of 15 micron average size. The average
Figure 2.3 Particle Collector
pore size is about 5 microns. The bronze filters are 1.9 cm O.D. at the open end and 1 cm O.D. maximum in the straight section (this portion has a slight inward taper). The wall thickness is 1.5 mm. They have an overall length of 11.1 cm. A vacuum system draws the main gas, the char, and the quenching gas down through the center of the probe. The char is caught in the filter while the gases pass on through.

The quenching system, modelled after that of Kobayashi (1976), differs only in that the current system uses a gas quench instead of water. There are several important advantages in making this change. Large quantities of water (0.7 l/min) were needed because mixing with the hot gases at the probe mouth was otherwise poor. This required facilities for separating the gas from the water downstream. The water also forced the smaller particles through the porous filter which would quickly become clogged after only about 0.3 grams of coal had been fed. Plus the filters and collected sample needed to be dried in an oven for almost two hours before weighing. Quenching the reaction by injection of argon avoids these problems although substantial quantities of the gas are required. The reason the gas quench is feasible in the present system is that the quantity of hot main gas removed through the collector is much smaller compared to Kobayashi's system (3 l/min vs. 30 l/min). The water quench system may still be easily adapted for other applications.

2.1.4 Gas Preheat

The main gas enters the furnace through the top plate at room temperature. Heat transfer calculations showed that at the maximum temperature, 1750°K, and the maximum gas flow rate, 6 l/min STP, the gas would easily reach the furnace temperature before leaving the honeycomb. These
predictions were confirmed by measuring the gas temperature with a Pt-Rh thermocouple as it passed through the honeycomb. The system has nevertheless been equipped with a packed bed preheater for use with higher gas flow rates and for removal of O₂ traces in the CO₂ experiments. The preheater sets just upstream of the furnace main gas inlet and is comprised of a Lindberg model 55081-A tubular heater (120V, 8.5A) capable of reaching a temperature of 1000°C. The packed bed, made of about 5 mm alumina or copper pellets (depending on the application), is 30 cm in depth and contained in a 2.5 mm O.D. stainless steel tube.

2.1.5 Vacuum System

Suction for the drawing of gases through the collector probe is accomplished by the use of two Cenco "Megavac" pumps in parallel. These pumps (115V, 6A) are rated at 1/3 h.p., with individual capacities of 57 liters/minute max at 0 psig. The vacuum flow rate is simply controlled by a regulating valve. All vacuum lines are 1.3 cm diameter or larger to help minimize pressure drop.

2.1.6 Crucible Mode Adaptations

For the longer residence time pyrolysis or CO₂ experiments, a 3.5 cm alumina dish containing a char sample is raised into the furnace hot zone by a 70 cm long, 1 cm diameter alumina tube. Its rate of ascent and descent is controlled by an electrically operated linear actuator, thus avoiding thermal shock to the material. A Pt-Rh thermocouple may also be secured in the center of the tube to record the time-temperature history of the dish and sample during an experiment.
2.1.7 Gas Flow Control and Measurement

Flow rates for the main gases, quenching gas, and carrier gas are controlled by Matheson rotameters. The main gases used are He, O₂, and CO₂ and are controlled with rotameter model numbers 602 and 603. The quenching gas used is argon because of its high molecular weight, heat capacity, and inert qualities. Its flow rate is controlled by a model 605 Matheson rotameter. The flow rate of the carrier gas, helium, is controlled by a Matheson model 601 rotameter. Finally, the flow rates are kept constant throughout the experiment by maintaining a constant pressure inside the muffle tube. This is done mainly by adjusting the suction rate as necessary.

2.1.8 Sample Weight Measurements

All sample, crucible, and collection filter weights are measured on a Mettler model H34 analytical balance which claims an accuracy of ± 0.1 mg. The weighing chamber is supplied with calcium sulfate desiccant to curtail moisture adsorption.

2.2 Experimental Procedures

2.2.1 Experimental Procedure for the Laminar Flow Experiments

The furnace is heated at 250 to 350°C to the desired temperature by using the automatic temperature controller and programmer. The final temperature is checked with the platinum-rhodium thermocouple extending just below the honeycomb. Typical temperature profiles along the muffle tube axis are given in Figure 2.4 and are determined by moving a platinum-rhodium thermocouple along the axis from the bottom of the furnace. Once the furnace has reached the desired temperature, a pre-weighed bronze
Figure 2.4 Axial Temperature Profiles in Muffle Tube
filter is placed in the collector probe. About 1 gram of char is weighed and placed in the feeder with the needle valve closed. The quenching gas flow rate and vacuum are set to just counter each other at about 25 l/min so that the furnace pressure does not change rapidly as the probe is put into the muffle tube. The collector is then raised into the furnace and secured at a particular height. An O-ring, through which the probe is pushed, seals the muffle tube from the external atmosphere. The main gas is next adjusted to provide the desired oxidizing gas partial pressure using helium as a diluent. The total main gas flow rate is always 6 l/min STP with a maximum of 3 l/min being drawn into the collector for purposes of proper quenching. The remainder of the gas passes out the bottom of the furnace, its flow rate being controlled by a rotameter in conjunction with the vacuum control valve. As the main gas is being set, the furnace pressure is continuously monitored and maintained at a slight positive pressure (less than 1 psig) also by adjustment of the vacuum. Once the muffle tube has been purged for 2 min, the carrier gas is set at about 30 cc/min (only 1/2 of 1 percent of total main gas flow), and the needle valve and vibrator are adjusted so that the char feeds fairly consistently in 6-7 min or about 0.15 g/min. When the feeding is finished the main gas is turned off, and the collector probe is removed. The quenching gas and vacuum are then turned off and the filter is very quickly removed and weighed to avoid adsorption of moisture. Finally, the samples are stored in sealed glass vials to await further analyses.
2.2.2 Procedure for the Crucible Experiments

For the crucible mode of operation, the furnace is again first heated by the method just described. A thin layer of char particles (nominally a bed depth of not more than 0.5 mm), which average about 80 mg in mass, is spread on a preweighed alumina dish. This is then placed on an alumina plate attached to the tube which raises the sample into the furnace. Before exposing the sample to the hot environment, the muffle tube is evacuated three times and purged with helium (~4 l/min STP) to prevent contamination from the external atmosphere. The main gas is passed through the preheater maintained at about 900°C packed with copper pellets prior to entering the furnace to also remove any traces of oxygen.

The linear actuator is then turned on and the sample is brought to its desired position in the hot zone (generally taking 5 to 10 min). If pyrolysis experiments are being done, then the helium is left flowing at 4 l/min. If CO₂ experiments are being performed, then the helium is adjusted to its proper (predetermined) flow rate and the CO₂ is switched on to a preset value. Under these conditions, the total main gas flow rate may be 5 to 10 l/min STP depending on the CO₂ partial pressure desired. The lower the partial pressure, the higher the flow rate so as to minimize any diffusional limitations. When the experiment is completed, the CO₂ is turned off, the dish is lowered by the linear actuator, and the sample is placed in a desiccator to cool before weighing.

2.3 Proximate Analyses

Proximate moisture, volatile, and ash contents of the char samples give one form of characterization which can be very helpful in checking experimental accuracy. Due to the nature of the experiments, the size of the
char samples, and the available equipment, ASTM procedures have been modified to a small extent depending on the circumstances and procedures encountered.

Moisture content is determined using a Labline model 3620ST drying oven. Samples to be analyzed are placed in Coors ceramic crucibles of appropriate size such that the depth of particles do not exceed 5 mm. With the weights of the samples and crucibles recorded, they are placed in the oven which is controlled at 110°C. The oven is continuously purged with argon while the samples are being dried. At the end of 1 hour the samples are removed and placed in a desiccator to cool to room temperature before weighing.

Volatile content is determined in much the same manner as the time-resolved oxidation runs for short residence times by using only helium as the main gas at 6 l/min STP. Asymptotic values are determined in the crucible mode of operation as just described.

Ash content is found using a "home-made" brick-insulated furnace having four silicone carbide electrodes connected in parallel to a Variac. Preweighed char samples in crucibles are placed in the furnace at room temperature. The furnace is continuously purged with air. The Variac is then set to heat the furnace to 500°C in the first hour and then readjusted to reach 750°C by the end of the second hour. The samples are kept at 750°C until they reach constant weight. Finally they are removed and again placed in a desiccator to cool before weighing.

Because ash and moisture contents vary so widely among different coals and chars, it is more meaningful to report results such as weight loss on a dry-ash-free (d.a.f.) basis. It is therefore necessary to know the
moisture and ash contents for this purpose as well as for characterizing the char. Furthermore, the determination of proximate volatile contents at long residence times offers a means to check the time-resolved pyrolysis experiments by comparing the asymptotic values.

2.4 Experimental System Evaluations

The purpose of the experimental system just described is to obtain kinetic data on coal char oxidation. Three of the important parameters to be derived from this system are temperature, residence time, and extent of reaction. The complexity of the temperature and velocity profiles, however, necessitates that certain reasonable assumptions be made about the time-temperature histories of the char particles within the scope of this research. In addition, since the extent of reaction is determined directly by weight loss (instead of by gas analysis) certain checks on collection efficiencies must be made to help insure consistent and accurate results.

2.4.1 Residence Times

The length of time in which the char experiences the hot environment and gas concentrations is defined as its residence time. In the laminar flow mode, the residence time is therefore the time it takes from the moment the particle exits the tip of the feeder until it enters the mouth of the collector assuming reaction conditions are uniform throughout this region. The value of the residence time will depend solely upon the velocity of the particle as it falls from the feeder and becomes entrained in the main gas stream. But because of a stagnant boundary layer at the feeder wall and the fact that the bulk main gas stream is of different
velocity and viscosity than the carrier gas, the velocity profile of the
carrier gas, the particle is very complex. Kobayashi (1976), using essentially the same
system, has shown that the particles actually slow down rapidly upon
injection into the furnace, and then speed up. He was able to measure
velocities directly with a laser doppler anemometer through several
observation ports along the furnace axis which gave visual access to the
inside of the muffle tube. The major drawback of the current system is
the lack of these internal observation ports—the muffle tube being a
solid cylinder. As a result, direct particle velocity measurement is
not possible without some major modifications to the system.

The maximum average main gas velocity used in this investigation is
about 30 cm/sec at 1750°K. With a muffle tube diameter of 5 cm and a gas
kinematic viscosity of about 2 cm²/sec, the Reynolds number is only 75.
Therefore, it may be assumed that the flow is laminar (with negligible
back currents due to convective forces), and that the velocity profile is
parabolic. The average main gas velocity, \( <v \rangle_{main} \), is given by:

\[
<v_{z \text{ main}} > = \frac{2\pi R}{2\pi R} \int_0^R \int_0^{2\pi} v_{z \text{ rdrd} \theta} r \text{ rdrd} \theta
\]

If the char particles were evenly dispersed across the muffle tube,
then it would be expected that the average particle velocity would closely
coincide with this, overlooking the initial disturbance upon injection
into the furnace. However, due to the laminar flow conditions in the
muffle tube, the particles tend to remain centrally located along the
axis rather than spreading out over the entire diameter. Suppose instead the particles cover mainly the center, within 0.8 radius of the tube, as shown in Figure 2.5. The average particle velocity should then more closely coincide with the corresponding average main gas velocity in this region:

\[
\langle v \rangle_{z \text{ main}, 0.8R} = \frac{2\pi 0.8R}{2\pi 0.8R} \int_0^0 \int_0^0 v_r dr d\theta
\]

The velocity distribution for the parabolic profile is given by Bird, et al. (1960) as

\[
v_z = \frac{(P_0 - P_L)}{4\mu L} \left[ R^2 - r^2 \right]
\]

Substitution into equations (2.1) and (2.2) and integration gives:

\[
\langle v \rangle_{z \text{ main}} = 0.5JR^2
\]

\[
\langle v \rangle_{z \text{ main}, 0.8R} = 0.68JR^2
\]

where \( J = \frac{P_0 - P_L}{4\mu L} \). The indication is that the average particle velocity should be about 40% greater than the average main gas velocity. This is, in fact, the result found by Kobayashi (1976) upon his measurement of particle velocities. To avoid the problem of attempting to model exact flow fields and velocity distributions in such a complex system, particularly when it is not possible at this time to make experimental checks, the
Figure 2.5 Hypothesized Particle Flow Field
assumption is made, based on the findings of Kobayashi (1976), that the average particle velocity may be approximated by 1.4 times the average main gas velocity. This assumption is justifiable based on the great similarity between the two systems and the confirmed results he obtained. However, it should be noted that this becomes less accurate as the distance from the feeder becomes less.

On the basis of this assumption, the particle residence times may be computed straightforwardly. The two temperatures studied are 1500 and 1750 K. With the furnace pressure maintained at atmospheric, the ideal gas law is used to determine the main gas flow rates at the furnace temperature, \( \dot{V}_F \), within the muffle tube:

\[
\dot{V}_F = \dot{V}_o \frac{T_F}{T_o}
\]

The average main gas velocity is then simply \( \dot{V}_F \) divided by the muffle tube cross-sectional area, \( A_M \). Finally, the particle residence time is given by

\[
t_P = \frac{A_M}{1.4 \dot{V}_F} L
\]

where \( L \) is the distance between the feeder tip and the collector. With \( \dot{V}_o = 6 \) l/min and \( T_o = 300^\circ K \), the average particle velocities are computed to be 35.65 and 41.59 cm/sec at 1500 and 1750 K respectively.

In the crucible mode, the residence time is determined according to the time in which the \( CO_2 \) is on with the sample resting in the furnace hot zone. If the main gas moved through the muffle tube in plug flow then this
assumption would be valid for all residence times. However, in this mode of operation the main gas follows a more random flow pattern due to the disturbance created by the dish. By looking at the system as a well stirred reactor, an upper bound on the time it takes for the gas concentration to reach a certain percentage of the desired value may be found. In this way, a minimum residence time may be approximated to assure the sample is exposed to the proper conditions.

A mass balance on CO$_2$ leaving and entering the muffle tube gives:

$$\frac{dN_{AT}}{dt} = N_{AO} - N_{AF} = N_{AO} - N_{F} \frac{N_{AT}}{N_{T}}$$  \hspace{1cm} (2.6)

where $N_{AT}$ = moles of CO$_2$ in muffle tube,
$N_{AO}$ = moles of CO$_2$/unit time entering muffle tube,
$N_{AF}$ = moles of CO$_2$/unit time leaving muffle tube,
$N_{F}$ = total moles/unit time leaving muffle tube,
$N_{T}$ = total moles in muffle tube.

Solving equation (2.6) for the boundary condition that at $t = 0$, $N_{AT} = 0$, it is found that

$$P_{AT} = P_{AO} \left[ 1 - \exp \left( - \frac{T_{F}}{T_{O}} \frac{V_{O}}{V_{M}} t \right) \right]$$  \hspace{1cm} (2.7)

where $P_{AT}$ = partial pressure of CO$_2$ in muffle tube in atm
$P_{AO}$ = partial pressure of CO$_2$ at inlet in atm,
$V_{O}$ = total l/min leaving muffle tube = total l/min entering muffle tube,
$V_{M}$ = volume of muffle tube in liters.
With typical values of \( V_o = 5 \) l/min, \( P_{AO} = 0.2 \) atm, a muffle tube volume of \( \sim 0.75 \) l, and a furnace temperature of \( 1500^\circ \)K,

\[
P_{AT} = 0.2(1 - \exp(-33.3t)) \quad \text{or} \quad t = -0.03 \ln(1 - 5P_{AT})
\]

Therefore, in order for \( P_{AT} \) to reach 98% of \( P_{AO} \) or 0.196 atm, the residence time must be at least 0.12 min or 7.2 sec. When the \( CO_2 \) is turned off a similar decay in \( P_{AT} \) occurs. To get kinetic data in this manner, then, the actual residence time should be significantly above this value to validate the assumption that \( P_{AT} \) is constant.

2.4.2 Particle Temperature and Heating Rates

When a char particle is injected via a cold gas stream into a very hot environment, such as the furnace used, the particles experience rapid heating by both mixing and conduction from the hot gases and radiation from the muffle tube walls. While heating rates in such a system may be as high as \( 10^5 \) to \( 10^6^\circ \)C/sec (Kimber and Gray, 1967a; Kobayashi, 1976), a certain time is required for the particles to reach the furnace temperature. If the total residence time were short compared to the heating time, then an accurate knowledge of the particle temperature history during heating would be required. However, if the residence time is comparatively long, then isothermal conditions may be assumed.

Suppose the heating rate remains constant at the lower value of \( 10^5 \) ^\circ \)C/sec; it would take about 15 msec for the particle to reach 1750^\circ \)K from room temperature. At the fastest particle velocities encountered (with average main gas velocity equal to 30 cm/sec), this would correspond
to a distance of about 6 mm from the feeder tip or only four feeder
tube diameters downstream from the point of injection. Due to the decrease
in the driving force, the heating rate, in reality, will drop as the parti-
cle approaches the furnace temperature. Kobayashi (1976) found, however,
that even under his worst conditions, heating times were still only about
twice as long as this, or 30 msec. If the total residence times are kept
substantially above this length of time, then the assumption that the
particles experience isothermal conditions may be valid.

As shown previously, the carbon-oxygen reaction is highly exothermic
while the carbon-carbon dioxide reaction is highly endothermic. The
particle temperature, as a result, may not be the same as the gas temper-
ature even under isothermal, steady-state conditions. With the char-
oxygen reaction rates (see Chapter 3) on the order of $10^{-7}$ g-moles/(sec-
particle), the rate of heat generation via reaction (1.3) is about 0.01
cal/(sec-particle). As a rough calculation, the rate of heat loss from
the particle to the surrounding atmosphere (neglecting radiation loss)
may be expressed as

$$\dot{Q}_{\text{loss}} = h_t A_s (T_p - T_F) \quad (2.8)$$

where $h_t$ is the heat transfer coefficient, $A_s$ is the external surface
area per particle, and $T_p$ is the true particle temperature. Assuming the
gas velocity is zero relative to the particle, the Nusselt number equals
2.0 or
\[ h_t = \frac{\lambda}{r_s} \quad (2.9) \]

where \( \lambda \) is the thermal conductivity of the gas and \( r_s \) is the particle radius. For a 20\% mixture of \( O_2 \) in \( He \), the thermal conductivity at \( 1500^\circ K \) is about \( 8.7 \times 10^{-4} \) cal/(cm-sec-\(^\circ K\)). Therefore for a particle radius of 0.005 cm (50 \( \mu m \)), \( h_t \approx 0.174 \) cal/(cm\(^2\)-sec-\(^\circ K\)). At steady-state, \( Q_{loss} \) equals the heat generated by the chemical reaction. Substitution into (2.8) gives a value for \( T_P = 1680^\circ K \) or as much as \( 180^\circ K \) increase above the gas temperature. Unfortunately, this number is quite sensitive to not only the measured reaction rates, but to whether \( CO \) or \( CO_2 \) is the primary product. Furthermore, the lack of visual access to the inside of the muffle tube makes it impossible to make pyrometer or other optical measurements of the actual particle temperatures. In the case of the char-carbon dioxide reactions, the rates are several orders of magnitude smaller, and, as a result, there is little error in assuming \( T_P = T_F \). To make this assumption in the case of the char-oxygen reactions may result in significant error, however. This problem is therefore discussed further in Section 3.4.2.

### 2.4.3 Quenching Efficiency

In the laminar flow mode, the rate at which the reaction is quenched is as important as the rate at which the particle is heated upon injection. Again, rather than attempt to follow the temperature history as the particle cools, it will simply be shown that the time it takes the particle to reach its final quench temperature is small compared to the overall
residence time. Also, it is necessary to show that the amount of reaction which occurs in the collection filter for the duration of the experiment is negligible compared to that which occurs during the relatively short time the char is exposed to furnace temperature.

One of the assumptions in the data analysis is that the concentration of oxidizing gas in the bulk fluid remains essentially constant throughout the experiment. In other words, the amount of oxidizing gas consumed is negligible compared to the total. Take as an example an oxygen mole fraction of 0.5 in a 6 l/min main gas stream with a coal feed rate of 0.15 g/min. Assuming about 50% weight loss, there is only a 5% reduction in the oxygen concentration. The higher the main gas flow rate, the smaller the reduction in concentration. However, the main gas flow rate is limited by the quenching capacity of the collector. With perfect mixing, a simple heat balance on the quench system yields a final quench temperature of

$$T_q = \frac{V_F^T F + V_O^T O}{O_F^P + O_O^P}$$

(2.10)

where the superscripts refer to the furnace main gas and the quenching gas and the C's are their heat capacities. Assuming the heat capacities are about equal,

$$T_q = \frac{V_F^T + V_O^T}{O_F^O + O_O^O}$$

(2.11)

Therefore, with 3 l/min of main gas at 1750°K mixing with 25 l/min of
quenching gas at 300°K, $T_q$ equals 455°K. To check this approximation, a platinum-rhodium thermocouple is inserted from the bottom of the collector probe and extended up through the inside of a bronze filter in which a hole has been cut. Simulation of experimental conditions at 1750°K, (except no char is fed) reveal that the gas temperature at only 1 cm below the mouth of the probe is about 550°K with temperatures dropping to about 400°K at 3 cm and more below the probe mouth. It is evident that significant cooling is contributed by conduction from the cold walls of the probe itself. Because the mass flow rate of feeding char will be much less than that of the gas (0.15 g/min vs. 42 g/min), it is assumed its temperature should closely coincide. Therefore, for the small distance required, the quenching time must also be relatively short (about 20 msec). Furthermore, near the probe, the velocity streamlines become compressed and the velocities of the gas and particles increase. This acts to further decrease the time which it takes the particles to fall that 1 cm into the filter.

If 550°K is taken as an upper limit for the quench temperature, the question arises whether this quench temperature is low enough to prevent significant reaction in the filter for the duration of an experiment. Smith and Tyler (1974) give the true activation energy for the reaction of a porous brown coal char with oxygen to be 32.6 kcal/g-mole. Assuming the reaction rate may be expressed in the form

$$\text{Rate} = k_o e^{-\frac{E}{RT}} c_s^n$$ (2.12)
the total reaction occurring in 10 msec at 1500°K may be given as
\[ 1.9 \times 10^{-4} k_{o_s}^n \]. If an experiment takes 15 min or \( 9 \times 10^5 \) msec to run, then the total reaction occurring in the filter at 550°K over this length of time is only \( 1.2 \times 10^{-7} k_{o_s}^n \). This means less than 0.1% of the total reaction occurs within the filter. It is therefore reasonable to assume the 550°K quenching temperature is sufficient.

2.4.4 Collection Efficiency

Since the extent of reaction is determined directly by measuring the weight loss of a sample, it is necessary that the collection efficiency be consistent and high. When operating in the crucible mode, there is no problem; but for the laminar flow mode, particles may be lost to the muffle tube walls, through the filter pores, or they may just bypass the collector altogether. By varying gas flow rates at 1750°K and feeding inert alumina particles rather than char, experimental conditions can be determined which will maximize collection efficiency. The alumina particles (of about 75 µm in diameter) do not appreciably change weight at these temperatures so collection efficiency is measured directly. Table 2.1 summarizes the collection efficiency tests. It is seen that the percent recovery depends strongly upon the quenching gas flow rate and the amount of main gas drawn through the collector. If the fraction of the main gas that passes through the collector is too small, then some of the gas in the center of the muffle tube is forced toward the walls as it approaches the probe mouth, carrying particles with it. The ratio of the cross-sectional areas of the probe to the muffle tube is about 0.5 indicating that approximately one half of the main gas should be drawn into the
Table 2.1 Collection Efficiency Summary

<table>
<thead>
<tr>
<th>Total Main Gas Flow Rate</th>
<th>Main Gas Flow Rate Through the Collector</th>
<th>Quench Gas Flow Rate</th>
<th>Collection Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 l/min He</td>
<td>3 l/min He</td>
<td>1 l/min Ar</td>
<td>100.9%</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>20</td>
<td>98.4</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>30</td>
<td>94.2</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>40</td>
<td>85.4</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>10</td>
<td>4.1</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>20</td>
<td>65.0</td>
</tr>
<tr>
<td>10</td>
<td>3.3</td>
<td>38</td>
<td>26.7</td>
</tr>
<tr>
<td>20</td>
<td>10</td>
<td>0</td>
<td>(106)</td>
</tr>
</tbody>
</table>
probe to minimize the disturbance to the flow pattern. In addition, when quenching gas flow rates are too high, its momentum, as it is forced upward and outward through the walls of the collection filter, tends to blow the particles away before falling into the probe.

On the basis of these tests it is evident that a tradeoff exists between maximizing the main gas flow rate and minimizing the quenching gas flow rate while maximizing collection efficiency and minimizing the quench temperature. The conditions of a main gas flow rate of 6 l/min with 3 l/min drawn through the collector and a quenching gas flow rate of 25 l/min are therefore chosen as being optimum for the experiments as they have been designed. The collection efficiency is thus about 97% and is found to be very consistent over the entire length of the furnace hot zone.
Chapter III

RESULTS

3.1 Data Analysis

Data was taken for pyrolysis, oxidation, and carbon dioxide reduction experiments at 1500 and 1750°K. In addition, proximate moisture and ash analyses were made on some of the reacted samples as well as the raw char. To calculate weight loss on a dry-ash-free (d.a.f.) basis, the weighted average initial proximate ash content was used, 20.1%, from Table G.1. Because the moisture content of the char was less than 1%, it was assumed negligible in the calculations. Therefore, the d.a.f. weight loss was calculated by

$$
\% \text{WL}' = \frac{\left[1 - \frac{C_f}{C_i}\right]}{1 - f^A_i} \times 100
$$

(3.1)

where the ' represents the d.a.f. basis, the subscripts i and f stand for initial and final values, C is the weight of the char, and $f^A_i$ is the fraction of ash in the char.

Pyrolysis experiments were run for short residence times as well as long at both 1500 and 1750°K. These results are tabulated in Appendix A and are summarized in Figures 3.1 and 3.2.

Oxidation experiments were run at oxygen partial pressures of 0.2 and 0.5 atm at 1500°K and 0.2 atm at 1750°K in the laminar flow mode. These results are tabulated in Appendix B where the d.a.f. weight loss is found according to Equation (3.1). Figure 3.3 summarizes these results in plots.
Figure 3.1 Pyrolysis of Rosebud Char for Short Residence Times
Figure 3.3 Oxidation of Rosebud Char by $O_2$
of Retention vs. Residence Time where

\[
\% \text{ Retention}' = 100 - \% \text{ WL}'
\]  \hspace{1cm} (3.2)

Semi-log plots are used to increase the time in which a straight line can be drawn through the data. This will help improve the accuracy of measuring the initial slopes of the curves for calculating the initial rates of reaction (Section 3.4.1).

Carbon dioxide reduction experiments were run at 1500°K for carbon dioxide partial pressures of 0.048, 0.1, and 0.2 atm, and at 1750°K for 0.048 atm, all in the crucible mode. In these experiments the char samples are exposed to the high temperatures for about 2 minutes while being raised into the hot zone in an atmosphere of helium prior to the injection of carbon dioxide. As a result, there are important physical changes that occur in the char even before the experiment actually begins, and these changes vary with the furnace temperature. Figure 3.2 shows that significant volatile release occurs in the time it takes for the sample to reach its desired position in the hot zone. Therefore, this volatile loss must be accounted for in calculating the weight loss for the carbon dioxide experiments. The true d.a.f. weight loss for these experiments was then found by

\[
\% \text{ WL}' = \left\{1 - \frac{C_f - f_i^A C_i}{C_i (1 - f_i^A) (1 - f_i^{V*})} \right\} \times 100
\]  \hspace{1cm} (3.3)

where \( f_i^{V*} \) is the d.a.f. volatile content that was found at 1500 or 1750°K for a residence time between 1 and 15 minutes. The denominator
Figure 3.5 Carbon Dioxide Reduction by Rosebud Char (2)

\[ \Delta T_p = 1750^\circ K, \ P_g, CO_2 = 0.048 \ atm \]
\[ \Delta T_p = 1500^\circ K, \ P_g, CO_2 = 0.048 \ atm \]

Residence Time (minutes)

% Weight Loss, d.a.f.
in Equation (3.3) is the d.a.v.f. initial char; i.e., the char less the volatiles as well as the moisture and ash. Values of \( f_{\text{star}}^{\text{V}} \) are found (see Table A.2) according to Equation (G.1) by taking the weighted average volatile yields for runs numbered CPR-1, CPR-2, CPR-3, and CPR-12 at 1500°K; and runs numbered CPR-13, CPR-14, CPR-15, and CPR-16 at 1750°K. These particular runs at 1750°K are used for this purpose because the sample sizes and residence times are comparable to the CO\(_2\) runs, and the results from Table A.2 indicate that these factors may influence the weight loss. Values for \( f_{\text{star}}^{\text{V}} \) at 1500 and 1750°K are therefore found to be 0.149 and 0.283 respectively. The tabulated results for the carbon dioxide reduction experiments are given in Appendix C and are summarized in Figures 3.4 and 3.5.

Finally, the physical and chemical analysis of the raw char as well as selected reacted samples were supplied by Phillips Petroleum Co. of Bartlesville, Oklahoma. The results of these characterizations are tabulated in Appendix G.

3.2 Weight Loss by Ash Tracer

When collection efficiency is uncertain or known to be poor, the extent of reaction or true d.a.f. weight loss has, in the past, been found by the method of using ash as a tracer (Badzioch and Hawksley, 1970; Howard and Essenhigh, 1967; and Kobayashi, 1976). If for the moment, it is assumed that the total ash in the char particles does not change during reaction, then it is possible to measure the extent of reaction on a d.a.f. basis merely by finding the percentage of ash in the initial char and
that in the collected char, regardless of the collection efficiency:

\[
\% \text{ WL}_{\text{AT}} = \left( 1 - \frac{f_{\text{i}}^{\text{A}}}{f_{\text{i}}^{\text{F}}} \right) \times 100
\]  

Some of the problems associated with this method are that 1) the ash is not evenly distributed among the various particle sizes; 2) chemical interaction during heating can alter the ash composition; and 3) at high temperatures, significant ash loss can occur because of vaporization and decomposition of metal sulfates. Padia (1976) studied the behavior of ash in pulverized coal during combustion and found that for temperatures up to 1830°K, ash losses are mainly due to the decomposition of CaSO₄ that may be initially present in coal or formed during combustion. At about 1950°K, Padia found that silica, in its more volatile form, SiO, volatilizes to contribute to the loss of ash. Kobayashi (1976) studied the accuracy of the ash tracer method in some depth and found ash loss to be as high as 15% at 1750°K for a Montana lignite. These effects naturally depend on the coal or char used as well as with the temperature and residence time.

As a means of "checking" the observed weight loss measurements for the oxidation and carbon dioxide reduction experiments, the d.a.f. weight loss was also calculated by using ash as a tracer for some runs. These values are given in Appendices B and C and summarized in Figure 3.6. For the oxidation runs, the observed weight loss is seen to be consistently 10 to 15 percent higher than the weight loss as determined by ash tracer.
Figure 3.6  Comparison of Weight Loss by Ash Tracer to Weight Loss by Direct Measurement
But, for the carbon dioxide runs, there is less than 5 percent difference at 1500°C and 20 to 35 percent difference at 1750°C. This indicates that considerably more ash is "lost" at 1750°C and that there exists a strong dependence on residence time as well as temperature. It is seen that the 1500°C oxidation runs lie to the right of the 1500°C CO₂ runs in Figure 3.6. However, this may be explained by the smaller ash particles and droplets, that form on the char surface at these temperatures, which can come free of the char particles in the turbulent action within the collection filters during the oxidation experiments. This ash can then become trapped within the porous structure of the filters. While its weight is included in the final char weight, it does not get collected for purposes of ash analysis. In the CO₂ experiments, the sample is held motionless in an alumina dish so there is no escape for the ash save for vaporization or chemical reaction. The ash loss may be calculated by

\[
\%\ AL = \left[1 - \frac{f^A_i}{f^A_{C_i}}\right] \times 100
\]  

(3.5)

where the fraction numerator is the ash collected and the denominator is the initial ash in the char. Combining this with Equations (3.1) and (3.4) gives

\[
\%\ AL = \left[1 - \frac{1 - \frac{\%WL'}{100}}{1 - \frac{\%WL}{100}} (1 - f^A_i)\right] \times 100
\]  

(3.6)
Therefore, with \( \%WL' = 60\% \), \( \%WL'_{AT} = 25\% \), and \( \frac{A}{f_i} = 0.2 \), the ash loss is 35\% at 1750\(^{\circ}\)K; and with \( \%WL' = 85\% \), \( \%WL'_{AT} = 80\% \), and \( \frac{A}{f_i} = 0.2 \), the ash loss is only about 10\% at 1500\(^{\circ}\)K. Padia (1976) has found that for residence times of about 30 minutes, a Pittsburgh bituminous coal lost only about 5\% of its ASTM ash content at 1750\(^{\circ}\)K while a Montana lignite coal lost about 20\% under the same conditions. It is apparent that the type of coal or char and its ash composition greatly effect the amount of ash that is lost at these temperatures. Deriving weight loss measurements strictly on the basis of using ash as a tracer can therefore give erroneous results, particularly at high temperatures, unless the loss of ash is taken into account.

3.3 Pyrolysis Results

The pyrolysis results from Figure 3.1 show that there is initially a rapid evolution of volatiles which begins to level off by about 100 msec. Due to the restrictions of the current system, however, only limited data could be taken in this initial region. For the short residence times, the d.a.f. weight losses appear to coincide very closely at both 1500 and 1750\(^{\circ}\)K between 10 and 15 percent d.a.f. Figure 3.2 shows how they deviate at long residence times. While there is negligible change at 1500\(^{\circ}\)K between 500 msec and 5 min, an asymptotic value does not appear to have been reached even after 1 hour at 1750\(^{\circ}\)K. As was noted in Chapter 1, other investigators (Van Krevelen et al., 1951; and Howard and Essenhigh, 1967) have found that the devolatilization appeared to occur in two stages: an initial rapid devolatilization followed by a much slower "degassing" mechanism. The first stage generally accounted for the
largest portion of volatile loss by weight. The deviation of the 1750°K results from the 1500°K results at long residence times seems to be larger than would be expected on this basis although not unreasonable. A portion of this weight loss, after all, should be attributed to ash loss. These results imply that high activation energy reactions are occurring which contribute to the loss of volatiles over a long period of time at a constant temperature. This is therefore in agreement with the observations of other authors (Anthony, 1974; Jüntgen and Van Heek, 1968; and Kobayashi, 1976) that the complex devolatilization mechanism may be described as a system of two or more reactions with different activation energies.

Where the sample size, and hence the bed depth, were varied at 1750°K for residence time of about 5 min, there is consistently a 3 to 4 percent higher weight loss for the small sample sizes where only a thin layer of particles (about 2 particle layers) are spread over the alumina dish (see Table A.2). The larger samples were placed in much smaller crucibles with resulting bed depths as high as 100 particle layers. Observance of this behavior has been noted in the past by numerous authors (Anthony, 1974; Kobayashi, 1976; and Van Krevelen et al., 1951) and is attributed by most to secondary reactions occurring between escaping volatiles and the char surfaces in the bed, leading to additional char formation. The smaller the sample size and bed depth, the less opportunity the volatiles have to contact the char, resulting in a higher weight loss. While this effect is not known to be large, except in extreme cases, Kobayashi (1976) found such "additional" char deposits to amount to 2 or 3 percent of the
total bed weight for a pulverized Pittsburgh bituminous coal under conditions very similar to the present study.

3.4 Oxidation Results

The curves in Figure 3.3 show the results of the oxidation experiments. It is seen that the reactivity of the char decreases with the extent of burnout, and for the experiments run at 0.2 atm of oxygen at either temperature, the d.a.f. weight loss appears to level off considerably below 100%. This is evidence of a protective ash layer build up on the particle’s surface which inhibits diffusion of oxygen inward to gasify the unreacted char at the center of the particle.

The oxidation results, as given, actually represent the total d.a.f. weight loss due both to pyrolysis as well as oxidation. There are several reasons for presenting the data in this manner. First, there is an absence of data resolution in the critical initial stages of volatile evolution. This makes "subtracting-out" the volatile loss more of guesswork than anything else; this is opposed to the case of the carbon dioxide reduction experiments where long residence time resolution was very good. Second, the oxidation reaction is clearly dominant over the devolatilization in terms of contributing to particle weight loss. Third, runs numbered RPR-152 and RPR-153 from Table C.1 interestingly show that the weight loss after 500 msec in the presence of He and CO₂ is considerably less than the weight loss found in pure helium under the same conditions (10% compared to 15%). This may be due to some physical resistance imposed on the volatiles, or be the result of a chemical interaction. While the number of runs taken to support this observation was limited, if this were
actually the case, similar effects would be expected in the presence of oxygen. Therefore, accurately separating the volatile release from the actual oxidation mechanisms becomes virtually impossible without performing extensive gas analyses.

As will be discussed in the following section, the initial rates of reaction will be derived by measuring the slopes at the beginning of these curves. The true effect of separating the volatile loss from the data as it is presented, would be to put an inflection point near the beginning of the curve for d.a.f. weight loss by oxidation only. This then would increase the "initial" oxidation rate at the point of inflection relative to the initial rate as the curve now stands. But, on the basis of the above argument, it is not likely that any significant error will be imposed by analyzing the data as it is currently presented.

3.4.1 Calculation of Initial Rates

To gain information about the kinetics of the overall oxidation mechanism, the rate of reaction under the different conditions must be evaluated. The rate of reaction is identical to the rate of disappearance of char (taken on a d.a.f. basis) when examining the overall reaction. Because the retention of char is given as a dimensionless quantity, the slope of a tangent to any curve at any time in Figure 3.3 will be of the form

\[
\text{Slope} = \frac{d[\ln(\% \text{ Retention}')] }{dt} = \frac{1}{C_i} \frac{dc'}{dt}
\]  

(3.7)
where \( C_i^t \) is the initial d.a.f. char and \( \frac{dC_i^t}{dt} \) is the rate of disappearance of d.a.f. char. By expressing \( C_i^t \) as the initial mass of one char particle, the rate of reaction per particle may be given as

\[
\text{Rate} = -\frac{4}{3} \pi r B \rho \frac{1}{M_c} \frac{d[\ln(\text{Retention}')]}{dt} \quad (3.8)
\]

where \( \rho_B \) is the bulk density of the char and \( M_c \) is the molecular weight of carbon. Expressing the rate in this form is particularly convenient for many of the calculations to follow. However, other useful forms of the rate expression are:

\[
\text{Rate}_{A_P} = -\frac{1}{A_p} \frac{1}{M_c} \frac{d[\ln(\text{Retention}')]}{dt} \quad (3.9)
\]

\[
\text{Rate}_{A_S} = -\frac{1}{3} r B \rho \frac{1}{M_c} \frac{d[\ln(\text{Retention}')]}{dt} \quad (3.10)
\]

where Equation (3.9) gives the rate per unit of total surface area and Equation (3.10) gives the rate per unit external surface area. These two forms are useful when examining rates at varying extents of reaction and comparing true relative reactivities.

Table 3.1 thus gives the initial rates of reaction in terms of Equations (3.8), (3.9), and (3.10) as determined from the slopes of the tangents to the curves shown in Figure 3.3. Values for \( r_s \), \( \rho_B \), and \( A_p \) are given in Table G.2 for the raw char.
Table 3.1 Initial Rates of Reaction for Oxidation Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_F (^\circ\text{K}) )</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g, O_2} ) (atm)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>( \rho_B ) (g/cm(^3))</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>( A_p ) (cm(^2)/g)</td>
<td>(1.65 \times 10^6)</td>
<td>(1.65 \times 10^6)</td>
<td>(1.65 \times 10^6)</td>
</tr>
<tr>
<td>( r_s ) (cm)</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>( \frac{d[\ln(% \text{ Retention})]}{dt} ) (sec(^{-1}))</td>
<td>-3.838</td>
<td>-9.210</td>
<td>-6.486</td>
</tr>
<tr>
<td>Rate ( \frac{g\text{-moles}}{\text{sec\times particle}} )</td>
<td>(1.45 \times 10^{-7})</td>
<td>(3.47 \times 10^{-7})</td>
<td>(2.45 \times 10^{-7})</td>
</tr>
<tr>
<td>Rate ( \frac{g\text{-moles}}{cm^2\times sec} ) (A_p)</td>
<td>(1.94 \times 10^{-7})</td>
<td>(4.65 \times 10^{-7})</td>
<td>(3.28 \times 10^{-7})</td>
</tr>
<tr>
<td>Rate ( \frac{g\text{-moles}}{cm^2\times sec} ) (A_s)</td>
<td>(3.20 \times 10^{-4})</td>
<td>(7.68 \times 10^{-4})</td>
<td>(5.41 \times 10^{-4})</td>
</tr>
</tbody>
</table>
3.4.2 Approximate Particle Temperatures

In Section 2.4.2 it was shown that for the char-oxygen reactions the actual particle temperature is likely to be considerably above the gas temperature. Without the ability to directly measure the particle temperature, an approximation may be made to compensate if it is known what the primary product of the reaction is.

The rate of heat generation within a particle is given by

\[ \dot{Q}_{\text{gen}} = \text{Rate} \cdot \Delta H_r \tag{3.11} \]

where Rate is the rate of reaction and \( \Delta H_r \) is the heat of reaction. The rate of heat loss by a particle is governed by the combined effects of the heat loss by convection and the heat loss by radiation

\[ \dot{Q}_{\text{loss}} = h_t A_s (T_p - T_F) + 4\sigma A \frac{T_{\text{AVE}}^3}{s} (T_p - T_F) \tag{3.12} \]

where \( h_t \) is the external heat transfer coefficient between the particle surface and the main gas, \( A_s \) is the external surface area of the particle, \( \sigma \) is the Stefan-Boltzmann constant, and \( T_{\text{AVE}} \) is the arithmetic average temperature between the particle and the main gas. At steady-state, \( \dot{Q}_{\text{gen}} \) equals \( -\dot{Q}_{\text{loss}} \). Therefore, combining equations (3.11) and (3.12) and solving for \( T_p \) gives

\[ T_p = T_F - \frac{\text{Rate} \cdot \Delta H_r}{A_s (h_t + 4\sigma T_{\text{AVE}}^3)} \tag{3.13} \]
However, as is evident from this equation, the particle temperature depends on $\Delta H_r$, or, in other words, on whether CO or CO$_2$ is the primary product. Referring back to Equations (1.3) and (1.4), $\Delta H_r = -94.0$ kcal/g-mole when CO$_2$ is the product and $\Delta H_r = -26.6$ kcal/g-mole when CO is the primary product. Obviously, a large difference is made depending on what the major product actually is. Ayling and Smith (1972) measured particle temperatures of size graded semi-anthracite coal during combustion at gas temperatures of 1400 to 1800$^\circ$K using a two-color optical pyrometer. They found that the measured particle temperatures coincided very closely with what would be calculated if CO were the primary product based on their observed rates of reaction. Ayling and Smith also found calculated particle temperatures to exceed the gas temperature by as much as 400$^\circ$K with CO as the primary product and as much as 1200$^\circ$K with CO$_2$ as the primary product. They admitted, however, that the calculated particle temperature is rather sensitive to the measured particle density and particle size (and hence the observed reaction rates). On this basis, with the lack of direct particle temperature measurement and gas analyses, the primary product is assumed to be CO.

Assuming a Nusselt number $\approx 2.0$, $h_t = \lambda_g/r_s$, where $\lambda_g$ is the thermal conductivity of the gas to be calculated at $T_{AVE}$ (see Appendix E). Therefore Equation (3.13) becomes

$$T_p = T_F + \frac{26.6 \times 10^3 \text{ Rate}}{4\pi r_s^2 \left( \frac{\lambda_g}{r_s} + 4\sigma T_{AVE}^3 \right)}$$

(3.14)

For given rates, $T_p$ may be found by an iterative solution assuming values
Table 3.2 Approximate Particle Temperatures for Oxidation Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_P \ (°K) )</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g,O_2} \ (atm) )</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>( r_s \ (cm) )</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>Rate ( \frac{g\text{-moles}}{\text{sec-particle}} )</td>
<td>( 1.45 \times 10^{-7} )</td>
<td>( 3.47 \times 10^{-7} )</td>
<td>( 2.45 \times 10^{-7} )</td>
</tr>
<tr>
<td>( \lambda \ \frac{cal}{g \text{ cm-sec-}°K} )</td>
<td>( 8.68 \times 10^{-4} )</td>
<td>( 5.57 \times 10^{-4} )</td>
<td>( 9.78 \times 10^{-4} )</td>
</tr>
<tr>
<td>( T_P \ (°K) )</td>
<td>1552</td>
<td>1678</td>
<td>1824</td>
</tr>
<tr>
<td>( T_{AVE} \ (°K) )</td>
<td>1526</td>
<td>1589</td>
<td>1787</td>
</tr>
</tbody>
</table>
for $T_{\text{AVE}}$. Table 3.2 gives values for the particle temperatures using Equation (3.14) and the initial rates from Table 3.1.

3.4.3 Surface Oxygen Concentrations

To apply the reaction rates to a power law kinetic expression of the form of Equation (2.12)

$$\text{Rate} = k_a (c_s)^n$$  \hspace{1cm} (3.15)

a correction for the diffusion of oxygen to the particle surface must be made to determine the true value of the surface concentration, $c_s$. A mass balance on an external spherical shell in the "boundary" region leads to

$$\frac{d}{dr} (r^2 N_r) = 0$$  \hspace{1cm} (3.16)

where $N_r$ is the mole flux of $O_2$ per unit area through an external shell of radius $r$. From Fick's First Law, $N_r$ may be given as

$$N_r = \frac{-gD}{\alpha + c_r} \frac{dc_r}{dr}$$  \hspace{1cm} (3.17)

$$\alpha = \frac{P}{RT_{\text{AVE}}}$$  \hspace{1cm} (3.18)

where $c_r$ is the oxygen concentration at radius $r$; $D_g$ is the binary gas diffusion coefficient for, in this case, oxygen-helium; $P$ is the total system pressure; and $R$ is the gas constant. Substitution into Equation (3.16) gives
\[
\frac{d}{dr} \left( \frac{r^2}{r + c_r} \right) \frac{dc_r}{dr} = 0
\] (3.19)

Realizing that the total rate of O\textsubscript{2} transport to the particle surface equals half of the observed reaction rate when CO is the primary product, Equation (3.19) may then be solved using the following boundary conditions:

**B.C. 1** \( N_r = \frac{-\alpha D_g}{\alpha + c_r} \frac{dc_r}{dr} = -\frac{1}{2} \frac{\text{Rate}}{4\pi r_s^2} \) at \( r = r_s \)

**B.C. 2** \( c_r = c_g \) at \( r = \infty \)

where \( c_g \) is the oxygen concentration at the outer edge of the boundary layer evaluated at \( T_{\text{AVE}} \). This gives

\[
c_r = (\alpha + c_g)e^{-\frac{\text{Rate}}{8\pi \alpha D_g} - \alpha}
\] (3.20)

And at the surface \( r = r_s \) and \( c_r = c_s \), giving

\[
c_s = (\alpha + c_g)e^{-\frac{\text{Rate}}{8\pi \alpha D_g} - \alpha}
\] (3.21)

Therefore for the rates given in Table 3.1, values of \( c_s \) for oxygen may be found at the experimental conditions used. These values are summarized in Table 3.3.
Table 3.3 Oxygen Surface Concentrations for Oxidation Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_F ) (°K)</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g, O_2} ) (atm)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>( T_{AVE} ) (°K)</td>
<td>1526</td>
<td>1589</td>
<td>1787</td>
</tr>
<tr>
<td>( c_g ) (g-moles/cm³)</td>
<td>(1.60 \times 10^{-6})</td>
<td>(3.84 \times 10^{-6})</td>
<td>(1.36 \times 10^{-6})</td>
</tr>
<tr>
<td>( a ) (g-moles/cm³)</td>
<td>(7.99 \times 10^{-6})</td>
<td>(7.67 \times 10^{-6})</td>
<td>(6.82 \times 10^{-6})</td>
</tr>
<tr>
<td>( r_s ) (cm)</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>( D_g ) (cm²/sec)</td>
<td>11.2</td>
<td>12.1</td>
<td>14.6</td>
</tr>
<tr>
<td>Rate (g-moles/sec-particle)</td>
<td>(1.45 \times 10^{-7})</td>
<td>(3.47 \times 10^{-7})</td>
<td>(2.45 \times 10^{-7})</td>
</tr>
<tr>
<td>( c_s ) (g-moles/cm³)</td>
<td>(1.50 \times 10^{-6})</td>
<td>(3.56 \times 10^{-6})</td>
<td>(1.23 \times 10^{-6})</td>
</tr>
</tbody>
</table>
3.4.4 Apparent Kinetics

With the information from Tables 3.1, 3.2, and 3.3, the apparent reaction order, \( n \), rate constants, \( k_{ao} \), and activation energy, \( E_a \), may be found for the oxidation of the Rosebud char. Assuming \( k_{ao}, E_a, \) and \( n \) are constant over the range of conditions explored, applying Equation (3.15) to the three sets of conditions gives three equations and three unknowns:

\[
\begin{align*}
\text{Rate}_1 &= k_{ao} e^{-E_a/RT_p \left( c_{S1} \right)^n} \\
\text{Rate}_2 &= k_{ao} e^{-E_a/RT_p \left( c_{S2} \right)^n} \\
\text{Rate}_3 &= k_{ao} e^{-E_a/RT_p \left( c_{S3} \right)^n}
\end{align*}
\]

These may then be solved simultaneously for any of the three unknowns.

Solving for the apparent reaction order gives

\[
\ln \frac{\text{Rate}_1}{\text{Rate}_2} + \frac{TP_3}{TP_1} \ln \frac{\text{Rate}_2}{\text{Rate}_3} + \frac{TP_3}{TP_2} \ln \frac{\text{Rate}_3}{\text{Rate}_1} - \ln \frac{c_{S1}}{c_{S2}} - \frac{TP_3}{TP_1} \ln \frac{c_{S2}}{c_{S3}} - \frac{TP_3}{TP_2} \ln \frac{c_{S3}}{c_{S1}} = 0
\]

Once \( n \) is known, the three rate constants, \( k_{a1}, k_{a2}, \) and \( k_{a3} \), are found by substituting into Equations (3.22)
Table 3.4 Apparent Kinetic Constants for Oxidation Reaction

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_F ) (°K)</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g, O_2} ) (atm)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>( T_P ) (°K)</td>
<td>1552</td>
<td>1678</td>
<td>1824</td>
</tr>
<tr>
<td>( c_s ) (g-moles/cm(^3))</td>
<td>(1.50 \times 10^{-6})</td>
<td>(3.56 \times 10^{-6})</td>
<td>(1.23 \times 10^{-6})</td>
</tr>
<tr>
<td>( R_{Ap} ) (g-moles/cm(^2)-sec)</td>
<td>(1.94 \times 10^{-7})</td>
<td>(4.65 \times 10^{-7})</td>
<td>(3.28 \times 10^{-7})</td>
</tr>
<tr>
<td>( k_{a} ) (cm/sec) (g-moles/cm(^3))(^{1-n})</td>
<td>(9.05 \times 10^{-4})</td>
<td>(12.59 \times 10^{-4})</td>
<td>(17.35 \times 10^{-4})</td>
</tr>
<tr>
<td>( k_{ao} ) (cm/sec) (g-moles/cm(^3))(^{1-n})</td>
<td>(7.21 \times 10^{-2})</td>
<td>(7.22 \times 10^{-2})</td>
<td>(7.19 \times 10^{-2})</td>
</tr>
</tbody>
</table>

\[ k_{ao} \approx 7.2 \times 10^{-2} \left( \text{cm/sec} \right) \left( \text{g-moles/cm}^3 \right)^{0.37} \]

\[ n = 0.63 \]

\[ E_a = 13.5 \ \frac{\text{kcal}}{\text{g-mole}} \ (\text{from Figure 3.7}) \]
Figure 3.7 Arrhenius Plot of Apparent Kinetics for Oxidation Experiments

\[ k = 10^4 \times \left( \frac{cm^3 \text{ sec}}{g \text{ moles} \cdot cm} \right) \frac{1}{T-1} \]
\[ k_{ao}e^{-\frac{E_a}{RT_p}t_p} = k_{aj} \]  

(3.24)

where \( j = 1, 2, \) or \( 3. \) Finally, rearranging equation (3.24) gives

\[ \ln k_{aj} = \frac{-E_a}{R} \frac{1}{T_p} + \ln k_{ao} \]  

(3.25)

Therefore, plotting \( \ln k_{aj} \) versus \( \frac{1}{T_p} \) should give a reasonably straight line whose slope is \( \frac{-E_a}{R} \) and intercept is \( \ln k_{ao} \). These results are summarized in Table 3.4 and Figure 3.7.

3.5 Carbon Dioxide Reduction Results

The results for the carbon dioxide reduction experiments presented in Figures 3.4 and 3.5 yield straight lines in the initial stages of burnout on a linear plot. Reaction rates are clearly much slower than the oxidation rates and particle temperatures may therefore be assumed equal to the furnace temperature. Furthermore, there does not appear to be the ash layer diffusion limitation that is seen for the oxidation experiments. This is probably due to the large difference in the intrinsic reactivities of the two gases with the char.

The data from the carbon dioxide experiments is presented on a true d.a.f. basis where the loss of volatiles is essentially accounted for. While there is still a slow release of volatiles during the experiment, this amount is seen to be small from Figure 3.2 for the time interval between 5 and 15 minutes.
3.5.1 Calculation of Initial Rates

The curves in Figures 3.4 and 3.5 are given in terms of d.a.f. weight loss as opposed to d.a.f. retention. Therefore, the slope of a tangent to any curve here will be

\[
\text{Slope} = \frac{d(\% \text{ WL'})}{dt} = -\frac{1}{c_i} \frac{dc'}{dt} \times 100
\]  

(3.26)

As with the oxidation experiments, by expressing \( C_i \) as the initial mass of one char particle (d.a.f.), the rate of reaction per particle may be given in the following forms analogous to Equations (3.8), (3.9), and (3.10):

\[
\text{Rate} = + \frac{4}{3} \pi r^3 \rho B \frac{1}{M_c} \frac{d(\% \text{ WL'})}{dt} \times \frac{1}{100}
\]  

(3.27)

\[
\text{Rate}_{Ap} = + \frac{1}{M_{Ap}} \frac{d(\% \text{ WL'})}{dt} \times \frac{1}{100}
\]  

(3.28)

\[
\text{Rate}_{As} = + \frac{1}{3} \pi r^3 \rho B \frac{1}{M_c} \frac{d(\% \text{ WL'})}{dt} \times \frac{1}{100}
\]  

(3.29)

In the oxidation experiments, because the particles are not exposed to the furnace temperatures until the start of an experiment, the initial char is represented by the raw char in terms of its physical and chemical characteristics. In the carbon dioxide experiments, however, the char is exposed to the furnace temperature for several minutes prior to the injection of the CO\(_2\). As a result, there is considerable alteration in the physical structure of the true initial char, which depends mainly
Table 3.5 Initial Reaction Rates for Carbon Dioxide Reduction Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_p$ (°K)</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>$P_{g,CO_2}$ (atm)</td>
<td>0.048</td>
<td>0.1</td>
<td>0.2</td>
<td>0.048</td>
</tr>
<tr>
<td>$\rho_B$ (g/cm$^3$)</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
<td>0.37</td>
</tr>
<tr>
<td>$A_p$ (cm$^2$/g)</td>
<td>$1.02 \times 10^6$</td>
<td>$1.02 \times 10^6$</td>
<td>$1.02 \times 10^6$</td>
<td>$0.2 \times 10^6$</td>
</tr>
<tr>
<td>$r_s$ (cm)</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
</tr>
<tr>
<td>$\frac{1}{100} \times \frac{d(% \text{ WL}')}{dt}$ (sec$^{-1}$)</td>
<td>$5.49 \times 10^{-3}$</td>
<td>$9.26 \times 10^{-3}$</td>
<td>$14.93 \times 10^{-3}$</td>
<td>$7.94 \times 10^{-3}$</td>
</tr>
<tr>
<td>Rate $\frac{\text{g-moles}}{\text{sec-particle}}$</td>
<td>$2.48 \times 10^{-10}$</td>
<td>$4.18 \times 10^{-10}$</td>
<td>$6.74 \times 10^{-10}$</td>
<td>$2.50 \times 10^{-10}$</td>
</tr>
<tr>
<td>Rate$_{A_p}$ $\frac{\text{g-moles}}{\text{cm}^2\text{-sec}}$</td>
<td>$4.49 \times 10^{-10}$</td>
<td>$7.57 \times 10^{-10}$</td>
<td>$12.20 \times 10^{-10}$</td>
<td>$33.08 \times 10^{-10}$</td>
</tr>
<tr>
<td>Rate$_A$ $\frac{\text{g-moles}}{\text{cm}^2\text{-sec}}$</td>
<td>$5.05 \times 10^{-7}$</td>
<td>$8.52 \times 10^{-7}$</td>
<td>$13.74 \times 10^{-7}$</td>
<td>$5.10 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
on the furnace temperature. The initial physical characteristics of the char at 1500 and 1750°K may therefore be represented by runs numbered CPR-12 and CPR-11 respectively from Table G.2. It is seen here that while there is little variation among the particle sizes for the raw char, CPR-12, and CPR-11, the specific surface areas differ quite markedly. Therefore, when comparing the reactivities of the char from the CO₂ experiments, the reaction rates should be of the form Rateₐp.

Table 3.5 gives the initial rates of reaction in terms of Equations (3.27), (3.28), and (3.29) as determined from the slopes of the tangents to the curves shown in Figures 3.4 and 3.5. Values for rₛ, ρₜₜ, and Aₚ are given in Table G.2 according to runs CPR-12 and 1500°K and CPR-11 at 1750°K.

3.5.2 Surface Carbon Dioxide Concentrations

Since the stoichiometry of the C-CO₂ reaction indicates that one CO₂ molecule reacts with one C atom, the rate of CO₂ transport to the particle surface will equal the observed rate of char disappearance. Therefore, Equation (3.21) may be modified slightly to calculate the surface concentration of carbon dioxide:

\[
cₛ = (α + cₑ) e^{-\frac{\text{Rate}}{4πrtₛₜₒₜ}} - α
\]  

(3.30)

where \(α = \frac{P}{RTₚ}\), \(cₑ\) is the carbon dioxide concentration in the main gas evaluated at \(Tₚ\), and \(Dₕ\) is the binary gas diffusion coefficient for a carbon dioxide-helium mixture from Appendix D.
Table 3.6 Carbon Dioxide Surface Concentrations for Carbon Dioxide Reduction Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_F$ $(^\circ K)$</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>$P_{g,CO_2}$ (atm)</td>
<td>0.048</td>
<td>0.1</td>
<td>0.2</td>
<td>0.048</td>
</tr>
<tr>
<td>$c_g$ (g-moles/cm$^3$)</td>
<td>$3.90 \times 10^{-7}$</td>
<td>$8.12 \times 10^{-7}$</td>
<td>$16.25 \times 10^{-7}$</td>
<td>$3.34 \times 10^{-7}$</td>
</tr>
<tr>
<td>$a$ (g-moles/cm$^3$)</td>
<td>$8.12 \times 10^{-6}$</td>
<td>$8.12 \times 10^{-6}$</td>
<td>$8.12 \times 10^{-6}$</td>
<td>$6.96 \times 10^{-6}$</td>
</tr>
<tr>
<td>$r_s$ (cm)</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
</tr>
<tr>
<td>$D_g$ (cm$^2$/sec)</td>
<td>8.7</td>
<td>8.7</td>
<td>8.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Rate (g-moles/sec-particle)</td>
<td>$2.48 \times 10^{-10}$</td>
<td>$4.18 \times 10^{-10}$</td>
<td>$6.74 \times 10^{-10}$</td>
<td>$2.50 \times 10^{-10}$</td>
</tr>
<tr>
<td>$c_s$ (g-moles/cm$^3$)</td>
<td>$\approx 3.90 \times 10^{-7}$</td>
<td>$\approx 8.12 \times 10^{-7}$</td>
<td>$\approx 16.25 \times 10^{-7}$</td>
<td>$\approx 3.34 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
Values of $c_s$ for carbon dioxide at the experimental conditions used are then calculated from the rates given in Table 3.5. These results are summarized in Table 3.6.

3.5.3 Apparent Kinetics

The apparent reaction order, $n$, the rate constants, $k_a$, and the activation energy, $E_a$, may be found for the carbon dioxide reaction, assuming power law kinetics, from the information in Tables 3.5 and 3.6. Because $T_{P_1} = T_{P_2} = T_{P_3}$ from Table 3.6, $k_{a_1} = k_{a_2} = k_{a_3}$. Therefore, $n$ may be found directly by

$$n_{ij} = \frac{\ln \frac{\text{Rate}_{Apj}}{\text{Rate}_{Api}}}{\ln \frac{c_{s_j}}{c_{s_i}}}$$

(3.31)

where $n$ should turn out to be about the same when using conditions 1 and 2, 2 and 3, or 1 and 3 for $i$ and $j$. With $n$ known, the $k_a$'s are found by

$$k_{a_j} = \frac{\text{Rate}_{Apj}}{(c_{s_j})^n}$$

(3.32)

where $j = 1, 2, 3, \text{ or } 4$. Finally, the apparent activation energy may be found by plotting $\ln k_{a_j}$ versus $1/T_{P_j}$ according to Equation (3.25). These results are summarized in Table 3.7 and Figure 3.8.
Table 3.7 Apparent Kinetic Constants for Carbon Dioxide Reduction Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_F ) (°K)</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g,CO_2} ) (atm)</td>
<td>0.048</td>
<td>0.1</td>
<td>0.2</td>
<td>0.048</td>
</tr>
<tr>
<td>( c_s ) (g-moles/cm(^3))</td>
<td>3.90 \times 10^{-7}</td>
<td>8.12 \times 10^{-7}</td>
<td>16.25 \times 10^{-7}</td>
<td>3.34 \times 10^{-7}</td>
</tr>
<tr>
<td>( R_A ) (g-moles/cm(^2)-sec)</td>
<td>4.49 \times 10^{-10}</td>
<td>7.57 \times 10^{-10}</td>
<td>12.20 \times 10^{-10}</td>
<td>33.08 \times 10^{-10}</td>
</tr>
<tr>
<td>( k_a ) (cm/sec) ( (\text{g-moles/cm}^3) )(^{1-n})</td>
<td>1.38 \times 10^{-5}</td>
<td>1.39 \times 10^{-5}</td>
<td>1.38 \times 10^{-5}</td>
<td>11.30 \times 10^{-5}</td>
</tr>
<tr>
<td>( k_{ao} ) (cm/sec) ( (\text{g-moles/cm}^3) )(^{1-n})</td>
<td>34.41</td>
<td>34.66</td>
<td>34.41</td>
<td>34.37</td>
</tr>
</tbody>
</table>

\[
k_{ao} \approx 34.5 \left( \frac{\text{cm}}{\text{sec}} \right) \left( \frac{\text{g-moles}}{\text{cm}^3} \right)^{0.30}
\]

\[
n_{12} = 0.71 \\
n_{23} = 0.69 \\
n_{13} = 0.70
\]

\[
n_{\text{AVE}} = 0.70
\]

\[
E_a = 43.9 \frac{\text{kcal}}{\text{g-mole}} \quad \text{(from Figure 3.8)}
\]
Figure 3.8 Arrhenius Plot for Carbon Dioxide Reduction Experiments
Figure 3.9 Evaluation of Langmuir-Hinshelwood Kinetic Constants

Slope = $8.75 \times 10^7$ g-moles/cm$^2$-sec-atm

$K_1 = 1.14 \times 10^{-8}$ g-moles/g-moles

Intercept = $4.1 \times 10^8$ atm$^{-1}$

$K_2 = 4.67$ atm$^{-1}$

$\frac{1}{P_{g, CO_2}}$ (atm$^{-1}$)

$\left( \frac{\text{cm}^2}{\text{g-moles}} \right) \times 10^{-6}$
3.5.4 Langmuir-Hinshelwood Kinetics

In Section 1.2.4 the char-carbon dioxide reaction was modelled according to the Langmuir-Hinshelwood mechanism (Hinshelwood et al., 1946)

\[ \text{Rate}_{\text{AP}} = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}_2} + K_3 P_{\text{CO}}} \quad (3.33) \]

If it is assumed that the adsorption of CO is negligible, then Equation (3.33) becomes

\[ \frac{\text{Rate}_{\text{AP}}}{K_1 P_{\text{CO}_2}} = \frac{1}{1 + K_2 P_{\text{CO}_2}} \quad (3.34a) \]

or

\[ \frac{1}{\text{Rate}_{\text{AP}}} = \frac{1}{K_1 P_{\text{CO}_2}} + \frac{K_2}{K_1} \quad (3.34b) \]

Therefore, the Langmuir-Hinshelwood constants \( K_1 \) and \( K_2 \) may be found by plotting \( 1/\text{Rate}_{\text{AP}} \) versus \( 1/P_{\text{CO}_2} \) for conditions 1, 2, and 3 (where the \( K \)'s are considered constant). Here, \( P_{\text{CO}_2} \) is the partial pressure of \( \text{CO}_2 \) at the particle surface. These results are plotted in Figure 3.9 from the values in Table 3.7.

3.6 Summary of Oxidation and Carbon Dioxide Reduction Results

The oxidation results show initial reaction rates to vary from about \( 2 \times 10^{-7} \) to \( 5 \times 10^{-7} \) g-moles/(cm\(^2\)-sec) based on the total particle surface areas. Particle temperatures are found to exceed the gas temperature
by as much as 178°K at the maximum rate observed. Due to the relatively
high thermal conductivity of the helium in the main gas stream, the par-
ticle temperatures are kept substantially lower than would otherwise be
experienced for the same reaction rates. Surface oxygen concentrations
are found not to be more than 10% lower than that in the free stream
(which occurs at 1750°K). The apparent kinetics show a reaction order
of 0.63 and an activation energy of 13.5 kcal/g-mole. Frequency, or
pre-exponential, factors for the rate constants are then calculated
to be about $7.2 \times 10^{-2} \text{(cm/sec)}(\text{g-moles/cm}^3)^{0.37}$.

The carbon dioxide reduction results show initial rates to vary
between about $5 \times 10^{-10}$ to $3 \times 10^{-9} \text{ g-moles/(cm}^2\text{-sec)}$ based on the total
particle surface areas. These rates are therefore two to three orders
of magnitude slower than the oxidation rates. The effect of this is to
maintain particle temperatures very near the gas temperatures and to give
essentially no change in carbon dioxide concentrations between the par-
ticle's surface and the main gas. The apparent kinetics yield a reaction
order of 0.70 and a much higher activation energy of 43.9 kcal/g-mole.
The pre-exponential factors are then found to be approximately $34.5
\text{(cm/sec)}(\text{g-moles/cm}^3)^{0.30}$. The Langmuir-Hinshelwood constants are shown
to be $K_1 = 1.16 \times 10^{-2} \text{ g-moles/(g-sec-atm)}$ and $K_2 = 4.67 \text{ atm}^{-1}$. While
the plot of $1/\text{Rate}$ versus $1/P_g\text{CO}_2$ does not appear to fall on a very
straight line, the magnitudes of the constants do not change appreciably
by altering the line to fall through any two of the points. The apparent
change in slope may actually be due to a gradual shift in order as a
result of the more than factor of 4 difference between the highest and
lowest CO$_2$ partial pressure investigated (see Section 1.2.4).
Chapter IV
DISCUSSION

4.1 Physical Changes During Reaction

When comparing the oxidation results with those from the carbon dioxide reduction experiments, it is necessary to study, at least in some detail, the physical changes that occur in the char during reaction. This is also particularly important when considering how the reaction proceeds within the porous structure. Figure 4.1 shows graphically the results of Table G.2 in plots of $\frac{A_p}{A_{pi}}$ and $\frac{\theta_p}{\theta_{pi}}$ versus d.a.f. weight loss, where the subscript $i$ refers to the values given for the initial chars. While the information in Appendix G is somewhat incomplete, it is still possible to draw several key conclusions on the basis of the data that has been given and the observed behavior at different stages of reaction.

The initial char for the oxidation experiments is represented by the raw char as received. Figure 4.1 (a) shows that the total char surface area for these experiments decreases with the extent of burnout. At the same time Figure 4.1 (b) shows a small trend toward increasing porosity with increasing weight loss. Similarly, the pyrolysis runs CPR-12 and CPR-11 show a sharp decrease in surface area with only a small increase in porosity after sustained residence times at high temperatures in an inert atmosphere. Such behavior may be explained by a partial collapse of the internal micro-pore structure which accounts for a large part of the surface area but only a small part of the total pore volume. This similarity in the changing physical structure of the char during
(a) Variation of Total Surface Area with Extent of Reaction

(b) Variation of Porosity with Extent of Reaction

- Δ Oxidation Experiments
- O CO₂ Reduction Experiments
- □ Pyrolysis Experiments

Figure 4.1 Physical Changes of Char During Reaction
oxidation and devolatilization indicates that the oxidation reaction is occurring essentially on the external surface of the particle with little penetration of oxygen into the porous interior. Smith and Tyler (1974), upon studying the combustion of size graded fractions of a pulverized Australian brown coal in oxygen partial pressure of 0.1 and 0.2 atm, found that above 1250°K the reaction became pore diffusion controlled for particles greater than about 50 μm in diameter. In the present study, the raw char has a mean diameter of about 120 μm; it has about the same porosity; and temperatures are 250 to 500°K higher. From these results, it is therefore reasonable to assume that the oxidation data are representative of pore diffusion control, and that reaction is occurring under the conditions of the second regime as described in Chapter 1.

The large difference between the oxidation rates and the carbon dioxide reduction rates suggests that the CO₂ reaction is much less diffusion controlled than the oxidation reaction under these experimental conditions. There is, unfortunately, significantly less information on the reacted CO₂ samples; however, the surface area measurements actually give considerable insight into determining the controlling mechanism. Runs numbered CPR-12 and CPR-11 represent the initial chars for the CO₂ experiments at 1500 and 1750°K respectively. From Figure 4.1 (a) it can be seen that the surface area actually increases with the extent of reaction which is just the reverse of the oxidation results. Furthermore, at 1500°K and only 50% burnout, the char having reacted with CO₂ shows surface areas of more than twice the initial char. This is therefore evidence of significant penetration and reaction by the carbon dioxide
within the internal porous structure of the char particles. Kimber and Gray (1976b) studied the reactivity of 35 μm charcoal particles in CO₂ and found that at temperatures up to 2300°K, the true reaction rate was at least two orders of magnitude smaller than the calculated diffusion controlled rate. Based on these findings, it is apparent that the reduction of carbon dioxide by char is to a large extent kinetically controlled for the experimental conditions presently under study.

Thus, characterization of the physical changes, or lack of changes, which occur in the char particles during reaction actually give a reasonable description of the controlling reaction mechanism.

4.2 Effectiveness Factors and Intrinsic Reactivity

In Sections 3.4.3 and 3.5.2, the external diffusion of reactants to the particle surface was compensated for by determining the actual surface concentrations. Still, in order to distinguish the intrinsic reaction kinetics, the extent to which pore diffusion limits the reaction must be understood. This is done by defining an effectiveness factor, η, as in Section 1.2.3, where

\[
\eta = \frac{\text{Observed Rate}}{\text{Rate in Absence of any Pore Diffusion Limitations}} \tag{4.1}
\]

Therefore,

\[
\eta = \frac{\text{Rate}}{V k_c c^m_s v_s} \tag{4.2}
\]
where \( \text{Rate} \) is the observed reaction rate, \( V_s \) is the volume of the particle, \( m \) is the intrinsic reaction order, and \( k_v \) is the intrinsic rate constant expressed per unit volume of particle. By defining the Thiele diffusion modulus, \( \phi_s \), such that

\[
\phi_s = r_s \sqrt{\frac{k_v}{D_{eff}} c_s^{m-1}}
\]  \hspace{1cm} (4.3)

where \( D_{eff} \) is the effective pore diffusivity, Equation (4.2) may be written in the form

\[
\eta^2 \phi_s = \frac{3 \text{ Rate}}{4\pi r_s^2 D_{eff} c_s}
\]  \hspace{1cm} (4.4)

by substituting for \( k_v \).

When the reaction rate is sufficiently small the reactant thoroughly penetrates the particle and the reaction is therefore kinetically controlled with \( \eta \) approaching a value of one. As the rate increases, the reactant concentration approaches zero at or before the center of the particle. In this, the second regime, the reaction is pore diffusion controlled and \( \eta \) decreases in magnitude. Upon determining the value for \( \eta \), Equation (4.4) can then be used to calculate \( \phi_s \) and the intrinsic rate constants.

4.2.1 Pore Diffusion Model for Oxidation Results

In Section 4.1, it was shown that the oxidation reaction under the studied conditions is pore diffusion controlled. To determine the value
for \( \eta \), and hence \( \phi_s \), for this regime, a shell mass balance within the particle is done analogous to the method used in determining the external surface reactant concentrations. The main difference here is that reaction occurs within the shell, or within the porous structure, instead of being used only as a boundary condition. Therefore, to make possible an analytical solution, a flat-plate geometry will be assumed along with constant gas density. This gives the shell balance in the form:

\[
D_{\text{eff}} \frac{d^2 c_p}{dx^2} = k_v \frac{c_p^m}{v_p}
\]  

(4.5)

where \( c_p \) is the reactant concentration within the porous structure at a distance \( x \) from the center of the particle. It is convenient as well as informative to put Equation (4.5) in dimensionless terms by defining the following dimensionless variables

\[
\xi = \frac{c_p}{c_s} \quad \psi = \frac{x}{x_s} \quad \phi_L = x_s \sqrt{\frac{k_v}{D_{\text{eff}} \frac{c_s^{m-1}}{v_p}}}
\]

where \( x_s \) is the distance from the particle's center to the surface, and \( \phi_L \) is the analogous Thiele modulus for the flat-plate geometry. Substituting these into Equation (4.5) yields

\[
\frac{d^2 \xi}{d\psi^2} = \phi_L^2 \xi^m
\]

(4.6)

with boundary conditions
B.C. 1 \[ \xi = 1 \text{ at } \psi = 1 \]

B.C. 2 \[ \frac{d\xi}{d\psi} = 0 \text{ at } \psi = 0 \]

Solving Equation (4.6) for \( \frac{d\xi}{d\psi} \), utilizing the second boundary condition, gives

\[
\frac{d\xi}{d\psi} = \phi_L \left( \frac{2}{m + 1} \right)^{1/2} \left( \xi^{m+1} - \xi_o^{m+1} \right)^{1/2}
\]

(4.7)

where \( \xi_o \) is the dimensionless concentration at the center of the particle.

But for pore diffusion control \( \xi_o \to 0 \) and Equation (4.7) reduces to

\[
\frac{d\xi}{d\psi} = \phi_L \left( \frac{2}{m + 1} \right)^{1/2} \frac{m+1}{\xi^{2}}
\]

(4.8)

Now at steady-state, the rate of reaction must equal the flux of reactant to the surface. Therefore,

\[
\frac{1}{A_s} \text{ Rate} = D_{\text{eff}} \frac{dc_p}{dx} \bigg|_{x=x_s}
\]

(4.9)

where \( A_s \) is the external surface area. And in dimensionless form

\[
\gamma_s = \frac{d\xi}{d\psi} \bigg|_{\psi=1}
\]

(4.10)

where \( \gamma_s = \frac{x_s}{A_s D_{\text{eff}} C_s} \text{ Rate} \) is the dimensionless reaction rate. Since \( \xi = 1 \) at \( \psi = 1 \), substituting Equation (4.10) into (4.8) yields
\[ \gamma_s = \phi_L \left( \frac{2}{m + 1} \right)^{1/2} \] (4.11)

Analogous to Equation (4.2), the effectiveness factor is given in dimensionless terms as

\[ \eta = \frac{\gamma_s}{\phi_L^2 \beta_s} \] (4.12)

where \( \beta_s = \frac{A_s x_s}{V_s} \) (which, for the flat-plate geometry is equal to unity). Therefore, substituting for \( \gamma_s \) and solving for \( \eta \phi_L^2 \) gives

\[ \eta \phi_L^2 = \phi_L \beta_s \left( \frac{2}{m + 1} \right)^{1/2} \] (4.13)

Furthermore, the right-hand-side of this equation is seen to equal

\( \left( \frac{2}{m + 1} \right) \beta_s^2 \frac{1}{\eta} \). Thus, for the case in which the reaction is pore diffusion limited

\[ \eta \phi^2 + \left( \frac{2}{m + 1} \right) \beta_s^2 \frac{1}{\eta} \] (4.14)

Finally, combining Equations (4.2), (4.4), and (4.14) yields

\[ \text{Rate}_{A_s} = \left[ \left( \frac{2}{m + 1} \right) D_{eff} k_c v_s c^{m+1} \right]^{1/2} \] (4.15)

where \( \text{Rate}_{A_s} \) is the observed reaction rate per unit external surface area. Here it is seen that the apparent reaction order, \( n \), takes on the value \( m + \frac{1}{2} \). In addition, by expressing the temperature dependence of \( k_c \) and
Figure 4.2 Arrhenius Plot of Intrinsic Kinetics for Oxidation Experiments
Table 4.1 Intrinsic Kinetics for Oxidation Reaction

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_F ) (°K)</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>( P_{g, O_2} ) (atm)</td>
<td>0.2</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>( T_p ) (°K)</td>
<td>1552</td>
<td>1678</td>
<td>1824</td>
</tr>
<tr>
<td>( c_s ) ( \frac{g\text{-moles}}{cm^3} )</td>
<td>( 1.50 \times 10^{-6} )</td>
<td>( 3.56 \times 10^{-6} )</td>
<td>( 1.23 \times 10^{-6} )</td>
</tr>
<tr>
<td>( A_p ) ( \frac{cm^2}{g} )</td>
<td>( 1.65 \times 10^6 )</td>
<td>( 1.65 \times 10^6 )</td>
<td>( 1.65 \times 10^6 )</td>
</tr>
<tr>
<td>( \rho_B ) ( \frac{g}{cm^3} )</td>
<td>0.50</td>
<td>0.50</td>
<td>0.50</td>
</tr>
<tr>
<td>( r_s ) (cm)</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
<tr>
<td>( \text{Rate}_{AS} ) ( \frac{g\text{-moles}}{cm^2\text{-sec}} )</td>
<td>( 3.20 \times 10^{-4} )</td>
<td>( 7.68 \times 10^{-4} )</td>
<td>( 5.41 \times 10^{-4} )</td>
</tr>
<tr>
<td>( D_{eff} ) ( \frac{cm^2}{sec} )</td>
<td>0.0640</td>
<td>0.0665</td>
<td>0.0695</td>
</tr>
<tr>
<td>( \eta )</td>
<td>0.238</td>
<td>0.245</td>
<td>0.125</td>
</tr>
<tr>
<td>( \phi_s )</td>
<td>15.88</td>
<td>15.45</td>
<td>30.14</td>
</tr>
<tr>
<td>( k_v ) ( \text{sec}^{-1} \frac{g\text{-moles}}{cm^3} )</td>
<td>21.96</td>
<td>40.97</td>
<td>74.21</td>
</tr>
<tr>
<td>( k_v ) ( \frac{cm}{sec} \frac{g\text{-moles}}{cm^3} ) ( \text{1-m} )</td>
<td>( 2.66 \times 10^{-5} )</td>
<td>( 4.97 \times 10^{-5} )</td>
<td>( 9.00 \times 10^{-5} )</td>
</tr>
<tr>
<td>( k_{vo} ) ( \frac{cm}{sec} \frac{g\text{-moles}}{cm^3} ) ( \text{1-m} )</td>
<td>( 9.41 \times 10^{-2} )</td>
<td>( 9.52 \times 10^{-2} )</td>
<td>( 9.42 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

\[ k_{vo} \propto 9.4 \times 10^{-2} \text{ (cm/sec)(g-moles/cm}^3)_{0.74} \]

\[ m = 0.26 \]

\[ E_v = 25.2 \text{ kcal/(g-mole)} \] (from Figure 4.2)
In Arrhenius form, the apparent activation energy, $E_a$, is seen to equal $\frac{E_v + E_d}{2}$ where $E_v$ and $E_d$ are the intrinsic and diffusional activation energies respectively. Since $E_v$ is generally much larger than $E_d$, $E_a$ equals approximately $E_v/2$.

In Section 3.4.4, the apparent order for the oxidation reaction was found to be 0.63. Therefore, the true order of reaction is $m = 0.26$. And solving Equation (4.15) for $k_v$ gives

$$k_v = 0.63 \frac{(\text{Rate}_A)^2}{D_{eff}^{1.26} s}$$

Equation (4.2) then gives the effectiveness factors for the oxidation reactions as

$$\eta = \frac{3}{r_s} \left( \frac{cD_{eff}}{0.63 \text{ Rate}_A} \right)$$

The intrinsic kinetic constants and effectiveness factors for the oxidation reactions are given in Table 4.1 and Figure 4.2. $k_v$ is put into the same units as $k_a$ for comparison by dividing by the quantity $\rho_B \rho_P$. Values for $D_{eff}$ are determined in Appendix F assuming Knudsen diffusion in fine pores.

4.2.2 Pore Diffusion Model for Carbon Dioxide Reduction Results

The carbon dioxide reduction reaction appeared to be largely kinetically controlled based on the evidence from the physical analyses on the reacted samples. Therefore the observed kinetics should essentially be
equivalent to the intrinsic kinetics. To show that this is in fact the situation, and that the values for \( \eta \) are close to unity for each of the conditions studied, a shell mass balance is again done within the particle. In spherical coordinates this yields

\[
D_{\text{eff}} \left[ \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{dc_p}{dr} \right) \right] = k_v c_p^m
\]  

(4.18)

or, in dimensionless form

\[
\frac{1}{\psi^2} \left[ \frac{d}{d\psi} \left( \psi^2 \frac{d\xi}{d\psi} \right) \right] = \phi_s \xi^m
\]  

(4.19)

with boundary conditions

B.C. 1 \( \xi = 1 \) at \( \psi = 1 \)

B.C. 2 \( \frac{d\xi}{d\psi} = 0 \) at \( \psi = 0 \)

In Section 3.5.3, the apparent order of reaction was found to equal 0.70. Therefore, if intrinsic kinetics were observed, \( m \) would also equal 0.70. However, for purposes of demonstrating the validity of the assumption that the effectiveness factors are close to unity, it will be assumed that \( m = 1 \). In this way, Equation (4.19) may readily be solved analytically and in closed form.

Thus, with \( m = 1 \), Equation (4.19) may be solved using the boundary conditions to yield
\[ \xi = \frac{1}{\psi} \frac{\sinh \phi_s \psi}{\sinh \phi_s} \]  

(4.20)

With the dimensionless reaction rate represented by Equation (4.10), \( \gamma_s \) may be written as

\[ \gamma_s = \frac{\phi_s}{\tanh \phi_s} - 1 \]  

(4.21)

And finally, combining Equations (4.12) and (4.21) yields

\[ \eta = \frac{3}{\phi_s} \left[ \frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \right] \]  

(4.22)

This gives the value for \( \eta \) assuming a first-order reaction and spherical particles. As \( \phi_s \) becomes large, \( \tanh \phi_s \rightarrow 1 \) and \( \frac{1}{\phi_s} \ll 1 \), so \( \eta \rightarrow \frac{3}{\phi_s} \).

This is precisely the limit that is reached by combining Equations (4.13) and (4.14) for a spherical geometry with \( m = 1 \).

Since \( \gamma_s \) may be calculated from known or observed quantities, Equation (4.21) may be solved by trial and error to find \( \phi_s \). With this, \( \eta \) is then found directly from Equation (4.22). Table 4.2 shows these results for the assumption \( m = 1 \). It is seen that even for the conditions of highest severity, \( \eta \) is very close to unity. Therefore, if \( \eta \approx 1 \) and \( m = 0.70 \), Equation (4.2) yields values for \( k_v \)

\[ k_v = \frac{3 \, \text{Rate}_{AS}}{r_s^{0.70}} \]  

(4.23)
Table 4.2 Intrinsic Kinetics for Carbon Dioxide Reduction Experiments

<table>
<thead>
<tr>
<th>Experimental Set No.</th>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_F ; (^oK))</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
<td>1750</td>
</tr>
<tr>
<td>(P_{g,CO_2} ; (atm))</td>
<td>0.048</td>
<td>0.1</td>
<td>0.2</td>
<td>0.048</td>
</tr>
<tr>
<td>(C_{s_s} ; (g\text{-mole}_{cm^3}))</td>
<td>(3.90 \times 10^{-7})</td>
<td>(8.12 \times 10^{-7})</td>
<td>(16.25 \times 10^{-7})</td>
<td>(3.34 \times 10^{-7})</td>
</tr>
<tr>
<td>(A_p ; (cm^2/g))</td>
<td>(1.02 \times 10^6)</td>
<td>(1.02 \times 10^6)</td>
<td>(1.02 \times 10^6)</td>
<td>(0.2 \times 10^6)</td>
</tr>
<tr>
<td>(\rho_B ; (g/cm^3))</td>
<td>0.53</td>
<td>0.53</td>
<td>0.53</td>
<td>0.37</td>
</tr>
<tr>
<td>(r_s ; (cm))</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
<td>0.00625</td>
</tr>
<tr>
<td>(\text{Rate}<em>{A_s} ; (g\text{-mole}</em>{cm^2\text{-sec}}))</td>
<td>(5.05 \times 10^{-7})</td>
<td>(8.52 \times 10^{-7})</td>
<td>(13.74 \times 10^{-7})</td>
<td>(5.10 \times 10^{-7})</td>
</tr>
<tr>
<td>(D_{eff} ; (cm^2/sec))</td>
<td>0.0900</td>
<td>0.0900</td>
<td>0.0900</td>
<td>0.719</td>
</tr>
<tr>
<td>(\phi_s)</td>
<td>0.524</td>
<td>0.471</td>
<td>0.422</td>
<td>0.200</td>
</tr>
<tr>
<td>(\eta)</td>
<td>0.982</td>
<td>0.986</td>
<td>0.988</td>
<td>0.997</td>
</tr>
<tr>
<td>(k_v ; (sec)^{-1}(g\text{-mole}_{cm^3})^{1-m})</td>
<td>7.427</td>
<td>7.499</td>
<td>7.441</td>
<td>8.360</td>
</tr>
<tr>
<td>(k_v ; (cm/sec)(g\text{-mole}_{cm^3})^{1-m})</td>
<td>(1.38 \times 10^{-5})</td>
<td>(1.39 \times 10^{-5})</td>
<td>(1.38 \times 10^{-5})</td>
<td>(11.30 \times 10^{-5})</td>
</tr>
<tr>
<td>(k_{vo} ; (cm/sec)(g\text{-mole}_{cm^3})^{1-m})</td>
<td>34.41</td>
<td>34.66</td>
<td>34.41</td>
<td>34.37</td>
</tr>
</tbody>
</table>

\(k_{vo} \approx 34.5 \; (cm/sec)(g\text{-mole}/cm^3)^{0.30}\)

\(n = 0.70\)

\(E_v = 43.9 \; \text{kcal/(g-mole)}\)
This expression is, of course, identical to the apparent rate expression so that \( k_v = k_a \). \( k_v \) is again put into the same units as \( k_a \) by dividing by \( \rho B_A p \). This means also that \( E_a = E_v \) from Figure 3.8. These results are summarized in Table 4.2.

4.3 Evaluation of Results

**Oxidation Results:**

In Section 4.2 the intrinsic reactivity of the Rosebud char was determined through the development of a pore diffusion model. Effectiveness factors for the oxidation experiments ranged from 0.25 to as low as 0.13, indicating that the observed reactivity was, to a large extent, limited by pore diffusion and reaction with the pore walls. For this reason, the apparent activation energy, 13.5 kcal/g-mole, was about half what would be observed if the reaction were kinetically controlled.

Smith (1971) studied the kinetics of combustion of size-graded pulverized carbon fuels at temperatures between 1200 and 2270°K. He too found pore diffusion to be limiting throughout this temperature range with apparent activation energies varying from 16 to 18 kcal/g-mole for a bituminous coal char and petroleum coke respectively. This would then correspond to intrinsic activation energies of 32 and 36 kcal/g-mole. Other studies (Smith and Tyler, 1974; Field et al., 1967) have similarly given intrinsic activation energies ranging from 35 to 55 kcal/g-mole for the combustion of pulverized coals and coal chars. Although the value of \( E_v \), 25.2 kcal/g-mole, found in the present study is somewhat lower than these previously reported values, it is still reasonably consistent when
compared to results reported on other types of carbons. Thring and Essenhigh (1963) summarize the activation energies given by other authors for the combustion of carbons with values ranging from 17.5 to 85 kcal/g-mole.

If pore diffusional effects and corrected particle temperatures have been properly accounted for, then several factors may still be responsible for lowering the activation energy. First, the method of measuring the reaction rates obviously possesses a number of uncertainties. Although there was only small scatter in the data for the most part, this was magnified by the fact that relatively few sets of data were actually taken from which the rates were measured. Furthermore, the calculation of residence times for the laminar flow mode, though not totally speculative, may be somewhat inaccurate due to the lack of direct measurement. However, if the error is linear and not too severe, the effect on the activation energy should be small. Second, because the volatile loss was incorporated into the measured weight loss, the true weight loss due to oxidation would be somewhat lower thus affecting the measured initial rates. And third, the relatively high proximate ash content of the char might have a significant effect in catalyzing the reaction. For instance, Mulcahy and Smith (1969) report that for highly purified carbons, the intrinsic activation energy is about 60 kcal/g-mole at around 1000°C. They suggest that the discrepancy between this and the values reported on unpure carbons is the result of a catalytic effect by the ash and trace minerals which are inherent in the latter.
The present oxidation results might further be put into perspective by comparing the intrinsic reactivity with that found by Smith and Tyler (1974) for a pulverized Australian brown coal. Upon studying the combustion of 22 \(\mu\)m to 89 \(\mu\)m particles in oxygen partial pressures of 0.1 to 0.2 atm over a temperature range of 630 to 1812\(^\circ\)K, they too found a value for \(m\) between 0.2 and 0.3; but they went on to calculate the intrinsic rate constants assuming a zero order reaction. With this approximation, they determined \(E_v\) to be 32.6 kcal/g-mole and the pre-exponential factor as 1.34 g/(cm\(^2\)-sec) based on the total particle surface area. Thus, at 1552\(^\circ\)K, this yields an absolute reaction rate of \(3.44 \times 10^{-5}\) g/(cm\(^2\)-sec) or \(2.86 \times 10^{-6}\) g-moles/(cm\(^2\)-sec). This may be compared with the rate of reaction calculated at \(T_p = 1552^\circ K\) from Table 4.1 for \(m = 0.26\), since the oxygen partial pressure is within the range studied by Smith and Tyler. Therefore, the rate is calculated as \(8.14 \times 10^{-7}\) g-moles/(cm\(^2\)-sec) which differs only by a factor of 3.5. Assuming a surface partial pressure of 0.2 atm, the rates would coincide at a temperature of about 1050\(^\circ\)K.

Therefore, the present results show good agreement among those reported by other authors for the combustion of pulverized fuels. While the intrinsic activation energy appears a little bit low, this may be explained by the high mineral content in the char which is likely to have a catalytic effect on the reaction. Overall reaction rates are nevertheless comparable to those found by Smith and Tyler (1974) for a pulverized Australian coal over a fairly wide range in temperature.
Carbon Dioxide Reduction Results:

Effectiveness factors for the carbon dioxide reduction experiments were shown to be above 0.98 under all the conditions investigated. Thus, the observed reaction was essentially kinetically controlled and the calculated apparent kinetics were equivalent to the intrinsic kinetics. The activation energy was therefore determined to be 43.9 kcal/g-mole for the overall disappearance of carbon from Figure 3.8. It was found for the oxidation reaction that the activation energy for pure carbons was generally much higher than that for coals and coal chars. This also appears to be the case for the carbon dioxide reaction. Walker et al. (1959) discuss the results found by several authors on the activation energies for the carbon-carbon dioxide reaction and suggests a value of about 86 kcal/g-mole for carbons of "medium" to high purity. Ergun and Mentser (1965) also find equivalent activation energies for a variety of comparatively pure carbons, but their value is only about 59 kcal/g-mole. While relatively little work has been done at high temperatures for the reaction of unpure carbons with carbon dioxide, von Fredersdorff and Elliott (1963) summarize the values found by other authors giving a range of 32.5 kcal/g-mole for anthracite to 61.7 kcal/g-mole for a New England coke. Although again there has been reported a rather wide range of activation energies, the results from the present study seem to show good agreement with the trend.

Modelling by power law kinetics, in addition, showed a reaction order of 0.7. Strickland-Constable (1947) studied the CO₂ reaction kinetics on carbon filaments at pressures of only about 1 mm Hg and found
the reaction order to be 0.7 at about 1400°K and unity above about 2000°K. However, von Fredersdorff and Elliott (1963) give the results of several authors showing the order to depend greatly on the CO₂ partial pressures and type of carbon, as well as the temperature. The relatively strong dependence on partial pressure gives support to modelling by the Langmuir-Hinshelwood mechanism in the case of the C-CO₂ reaction. Values for K₁ and K₂ in Equation (3.34a) may be calculated from the data given by von Fredersdorff and Elliott. Ranges of 5.38 × 10⁻⁴ to 2.51 × 10⁻¹ g-moles/(g-sec-atm) for K₁ and 0.245 to 130 atm⁻¹ for K₂ are then determined at a temperature of 1500°K for the various purities of carbons reported. From Figure 3.9, K₁ is given as 1.16 × 10⁻² g-moles/(g-sec-atm) and K₂ as 4.67 atm⁻¹. Both values lie well within this range, thus yielding comparable reaction rates. Although insufficient data was taken to determine the activation energies of the Langmuir-Hinshelwood kinetic constants, the carbon dioxide reduction results on a whole show very good agreement with those reported in the literature.

4.4 Comparison of Oxidation and Carbon Dioxide Reduction Results

The observed absolute reaction rates for the oxidation and carbon dioxide reduction reactions have been found to differ by as much as three orders of magnitude under the conditions studied. This, of course, is not surprising from the information given previously in Chapter 1 for the relative reactivities of carbon with oxygen and carbon dioxide. Those results were based on rates per unit surface area exposed to the reactant gas. In the present study, however, it was shown that the oxidation reaction occurs mainly in a shell near the external surface
of the char particle, whereas the carbon dioxide thoroughly penetrates the porous structure. Thus, the carbon dioxide reaction has significantly greater surface area per particle of char available to it. Furthermore, by changing the particle sizes it is clear that the oxidation rate, which varies with approximately the square of the radius, will not change in magnitude equivalent to the carbon dioxide reduction rate which varies with the cube of the radius. The major advantage of the current analysis is the defining of intrinsic reactivity as either per unit external surface area or per unit total surface area which may be used in conjunction with effectiveness factors to make possible the extrapolation of reaction rates for different particle sizes.

In addition to the changes in rate with particle size, the changes in reactivity with the extent of reaction are also of interest. While rates were not calculated at later stages of reaction, examining the alteration in physical structure indicates that still greater surface area becomes available to carbon dioxide as the reaction proceeds. The oxidation results, on the other hand, show that the apparent reactivity drops off markedly far prior to complete burnout. In other words, the intrinsic reactivity for the carbon dioxide reduction reaction appears to increase further relative to the char oxidation by $O_2$ as the reactions proceed toward completion. This comparison of reactivities is particularly interesting because it emphasizes the true effect of pore diffusion and reaction with the pore walls on limiting rates.
Chapter V

CONCLUSIONS

Upon studying the reactivity of a Montana Rosebud coal-char with oxygen and carbon dioxide at temperatures of 1500 to 1825°C, the following conclusions are made:

1. Oxidation Results

   i) Reaction rates were found to be sufficiently high to raise particle temperatures as much as 180°C above furnace gas temperature with the assumption that CO was the primary product of reaction.

   ii) Observing the physical changes occurring in the char at various stages of reaction revealed that penetration of oxygen into the porous structure was limited largely by pore diffusion and reaction with the pore walls. These observations were confirmed through the development of a pore diffusion model which gave effectiveness factors between 0.245 and 0.125 over the entire range of conditions studied.

   iii) From the model, an intrinsic reaction order was found to be 0.26. This information was used to calculate an activation energy of 25.2 kcal/g-mole which yielded an overall intrinsic reactivity for the char to be

\[
k_v = 0.094 e^{-25,200/RT} \left( \frac{\text{cm}}{\text{sec}} \right)^{0.74} \left( \frac{\text{g-moles}}{\text{cm}^3} \right)
\]

expressed as the rate of carbon consumption per unit total surface area.
2. **Carbon Dioxide Reduction Reaction**

i) Reaction rates were found to be 2 to 3 orders of magnitude slower than the oxidation rates under similar reaction conditions. Thus, particle temperatures and surface reactant concentrations remained essentially unchanged from the main gas properties.

ii) Notable changes in the physical structure of the char during reaction indicated that the carbon dioxide penetrated well into the porous structure. Through an appropriate pore diffusion model, effectiveness factors were found to exceed 0.98 for all conditions studied, indicating, in fact, that the reaction was essentially kinetically controlled.

iii) Power law kinetics therefore yielded an intrinsic reaction order of 0.7. This was then used to determine an activation energy of 43.9 kcal/g-mole giving an overall intrinsic reactivity of

\[ \chi_v = 34.5 e^{-43,900/RT} P^{0.30} \left( \frac{\text{cm}}{\text{sec}} \right)^{1/3} \left( \frac{\text{g-moles}}{\text{cm}^3} \right) \]

expressed as the rate of carbon consumption per unit total surface area.

iv) Modelling of the reaction by the Langmuir-Hinshelwood mechanism yielded values for the constants \( K_1 = 1.16 \times 10^{-2} \) g-moles/(g-sec-atm) and \( K_2 = 4.67 \) atm\(^{-1}\) neglecting adsorption by CO, thus showing very good agreement with previous results.
Chapter VI

RECOMMENDATIONS

1) A practical technique should be developed for measuring particle velocities and residence times under experimental conditions.

2) Modifications to the system should be made so that direct visual access to the inside of the muffle tube is possible and particle temperature measurements can be made.

3) Similar experiments on at least one other particle size should be done in order to give a good check of the theory.

4) The apparent changes in reactivity during reaction should be investigated in some detail. In this way, a plot of the ratio of reaction rate to initial reaction rate versus weight loss may be constructed.

5) Addition of a pore-size-distribution model may greatly enhance the accuracy of the theory particularly at later stages of burnout when pore sizes may begin to change considerably.

6) Gas analyses for CO and CO$_2$ should be made to not only add a check on closing the carbon balance, but also to confirm the notion of a primary reaction product.
Appendix A. Results of Pyrolysis Experiments

Tables A.1 and A.2 summarize the results of the pyrolysis experiments in the laminar flow and crucible modes respectively. Residence times for the laminar flow mode are defined accordingly in Chapter 2. Residence times for the crucible experiments are defined by the length of time in which they are held at the peak of the linear actuator cycle. Dry-ash-free weight losses are calculated based on a proximate ash content of 20.1%. Because of the low moisture content (∼1%), it is assumed negligible in calculating the d.a.f. weight losses.
Table A.1 Results of Rosebud Char Pyrolysis Experiments in Laminar Flow Mode

<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°K)</th>
<th>Char Fed (g)</th>
<th>Char Collected (g)</th>
<th>Apparent Weight Loss (%)</th>
<th>D.A.F. Weight Loss (%)</th>
<th>Residence Time (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPR-101</td>
<td>1500</td>
<td>0.7625</td>
<td>0.6843</td>
<td>10.26</td>
<td>12.82</td>
<td>356</td>
</tr>
<tr>
<td>PPR-102</td>
<td>1500</td>
<td>1.0061</td>
<td>0.9006</td>
<td>10.49</td>
<td>13.11</td>
<td>356</td>
</tr>
<tr>
<td>PPR-103</td>
<td>1500</td>
<td>0.8729</td>
<td>0.8032</td>
<td>7.98</td>
<td>10.00</td>
<td>213</td>
</tr>
<tr>
<td>PPR-104</td>
<td>1500</td>
<td>0.7872</td>
<td>0.7109</td>
<td>9.69</td>
<td>12.12</td>
<td>213</td>
</tr>
<tr>
<td>PPR-107</td>
<td>1500</td>
<td>0.6247</td>
<td>0.5595</td>
<td>10.44</td>
<td>13.05</td>
<td>500</td>
</tr>
<tr>
<td>PPR-108</td>
<td>1500</td>
<td>0.7173</td>
<td>0.6179</td>
<td>13.86</td>
<td>17.32</td>
<td>500</td>
</tr>
<tr>
<td>PPR-109</td>
<td>1500</td>
<td>0.7340</td>
<td>0.6784</td>
<td>7.57</td>
<td>9.47</td>
<td>70</td>
</tr>
<tr>
<td>PPR-111</td>
<td>1500</td>
<td>0.6137</td>
<td>0.5577</td>
<td>9.12</td>
<td>11.41</td>
<td>426</td>
</tr>
<tr>
<td>PPR-112</td>
<td>1500</td>
<td>0.8731</td>
<td>0.8183</td>
<td>6.28</td>
<td>7.85</td>
<td>426</td>
</tr>
<tr>
<td>PPR-114</td>
<td>1500</td>
<td>0.8506</td>
<td>0.7244</td>
<td>14.84</td>
<td>18.55</td>
<td>283</td>
</tr>
<tr>
<td>PPR-115</td>
<td>1500</td>
<td>0.9116</td>
<td>0.8535</td>
<td>6.37</td>
<td>7.97</td>
<td>283</td>
</tr>
<tr>
<td>PPR-117</td>
<td>1500</td>
<td>0.9627</td>
<td>0.8881</td>
<td>7.75</td>
<td>9.69</td>
<td>356</td>
</tr>
<tr>
<td>PPR-118</td>
<td>1500</td>
<td>0.8543</td>
<td>0.7468</td>
<td>12.58</td>
<td>15.73</td>
<td>500</td>
</tr>
<tr>
<td>PPR-120</td>
<td>1500</td>
<td>0.5623</td>
<td>0.5135</td>
<td>8.68</td>
<td>10.85</td>
<td>213</td>
</tr>
<tr>
<td>PPR-121</td>
<td>1750</td>
<td>0.7438</td>
<td>0.6663</td>
<td>10.42</td>
<td>13.02</td>
<td>305</td>
</tr>
<tr>
<td>PPR-122</td>
<td>1750</td>
<td>0.7501</td>
<td>0.6702</td>
<td>10.65</td>
<td>13.31</td>
<td>305</td>
</tr>
<tr>
<td>PPR-123</td>
<td>1750</td>
<td>0.7409</td>
<td>0.6569</td>
<td>11.33</td>
<td>14.17</td>
<td>428</td>
</tr>
<tr>
<td>PPR-124</td>
<td>1750</td>
<td>0.7078</td>
<td>0.6561</td>
<td>7.30</td>
<td>9.13</td>
<td>183</td>
</tr>
<tr>
<td>PPR-125</td>
<td>1750</td>
<td>0.7117</td>
<td>0.6725</td>
<td>5.51</td>
<td>6.88</td>
<td>60</td>
</tr>
<tr>
<td>PPR-126</td>
<td>1750</td>
<td>0.7285</td>
<td>0.6630</td>
<td>8.99</td>
<td>11.24</td>
<td>243</td>
</tr>
</tbody>
</table>
Table A.2 Results of Rosebud Char Pyrolysis Experiments in Crucible Mode

<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°K)</th>
<th>Initial Char (g)</th>
<th>Final Char (g)</th>
<th>Apparent Weight Loss (%)</th>
<th>D.A.F. Weight Loss (%)</th>
<th>Residence Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPR-1</td>
<td>1500</td>
<td>0.3072</td>
<td>0.2706</td>
<td>11.91</td>
<td>14.89</td>
<td>5</td>
</tr>
<tr>
<td>CPR-2</td>
<td>1500</td>
<td>0.2691</td>
<td>0.2370</td>
<td>11.93</td>
<td>14.91</td>
<td>5</td>
</tr>
<tr>
<td>CPR-3</td>
<td>1500</td>
<td>0.1761</td>
<td>0.1549</td>
<td>12.04</td>
<td>15.05</td>
<td>5</td>
</tr>
<tr>
<td>CPR-12</td>
<td>1500</td>
<td>1.0495</td>
<td>0.9242</td>
<td>11.94</td>
<td>14.92</td>
<td>5</td>
</tr>
<tr>
<td>CPR-6</td>
<td>1750</td>
<td>0.3693</td>
<td>0.2993</td>
<td>18.95</td>
<td>23.69</td>
<td>5</td>
</tr>
<tr>
<td>CPR-7</td>
<td>1750</td>
<td>0.3909</td>
<td>0.3140</td>
<td>19.67</td>
<td>24.59</td>
<td>5</td>
</tr>
<tr>
<td>CPR-8</td>
<td>1750</td>
<td>0.2875</td>
<td>0.2341</td>
<td>18.57</td>
<td>23.22</td>
<td>5</td>
</tr>
<tr>
<td>CPR-11</td>
<td>1750</td>
<td>1.5516</td>
<td>1.2598</td>
<td>18.81</td>
<td>23.51</td>
<td>5</td>
</tr>
<tr>
<td>CPR-13</td>
<td>1750</td>
<td>0.0817</td>
<td>0.0641</td>
<td>21.54</td>
<td>26.93</td>
<td>1</td>
</tr>
<tr>
<td>CPR-14</td>
<td>1750</td>
<td>0.0810</td>
<td>0.0627</td>
<td>22.59</td>
<td>28.24</td>
<td>5</td>
</tr>
<tr>
<td>CPR-15</td>
<td>1750</td>
<td>0.0765</td>
<td>0.0592</td>
<td>22.61</td>
<td>28.27</td>
<td>15</td>
</tr>
<tr>
<td>CPR-16</td>
<td>1750</td>
<td>0.0851</td>
<td>0.0649</td>
<td>23.74</td>
<td>29.67</td>
<td>0*</td>
</tr>
<tr>
<td>CPR-17</td>
<td>1750</td>
<td>0.0799</td>
<td>0.0577</td>
<td>27.78</td>
<td>34.73</td>
<td>60</td>
</tr>
</tbody>
</table>

* reached hot zone and brought down immediately.
Appendix B. Results of Char Oxidation Experiments

Table B.1 summarizes the results of the Rosebud char oxidation experiments with oxygen at the various temperatures and partial pressures. These experiments were all run in the laminar-flow mode of operation with residence times, as defined in Chapter 2, varying between 50 and 500 msec. Dry-ash-free weight losses were calculated using a proximate ash content of 20.1%. Because of the low moisture content of the char, it is assumed negligible in calculating the d.a.f. weight losses.
<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°K)</th>
<th>$P_{O_2}$ (atm)</th>
<th>Char Fed (g)</th>
<th>Char Collected (g)</th>
<th>Apparent Weight Loss (%)</th>
<th>D.A.F. Weight Loss (%)</th>
<th>D.A.F. Weight Loss by Ash Tracer (%)</th>
<th>Residence Time (msec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPR-136</td>
<td>1500</td>
<td>0.2</td>
<td>0.9346</td>
<td>0.5411</td>
<td>42.10</td>
<td>52.63</td>
<td></td>
<td>213</td>
</tr>
<tr>
<td>TPR-137</td>
<td>1500</td>
<td>0.2</td>
<td>1.0005</td>
<td>0.4362</td>
<td>56.40</td>
<td>70.50</td>
<td></td>
<td>356</td>
</tr>
<tr>
<td>TPR-138</td>
<td>1500</td>
<td>0.2</td>
<td>1.0104</td>
<td>0.4121</td>
<td>59.21</td>
<td>74.02</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>TPR-139</td>
<td>1500</td>
<td>0.2</td>
<td>0.9459</td>
<td>(0.5449)</td>
<td>(42.39)</td>
<td>(52.99)</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>TPR-140</td>
<td>1500</td>
<td>0.2</td>
<td>1.0292</td>
<td>0.4793</td>
<td>53.43</td>
<td>66.79</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>TPR-141</td>
<td>1500</td>
<td>0.2</td>
<td>1.1837</td>
<td>0.8412</td>
<td>28.93</td>
<td>36.17</td>
<td></td>
<td>143</td>
</tr>
<tr>
<td>TPR-142</td>
<td>1500</td>
<td>0.2</td>
<td>0.9561</td>
<td>0.3506</td>
<td>63.33</td>
<td>79.16</td>
<td></td>
<td>356</td>
</tr>
<tr>
<td>TPR-143</td>
<td>1500</td>
<td>0.2</td>
<td>0.9115</td>
<td>0.4766</td>
<td>47.71</td>
<td>59.64</td>
<td></td>
<td>45.63</td>
</tr>
<tr>
<td>TPR-144</td>
<td>1500</td>
<td>0.5</td>
<td>0.9093</td>
<td>(0.3264)</td>
<td>(64.10)</td>
<td>(80.13)</td>
<td>(59.62)</td>
<td>213</td>
</tr>
<tr>
<td>TPR-145</td>
<td>1500</td>
<td>0.5</td>
<td>0.8861</td>
<td>0.2053</td>
<td>76.83</td>
<td>96.04</td>
<td></td>
<td>356</td>
</tr>
<tr>
<td>TPR-146</td>
<td>1500</td>
<td>0.5</td>
<td>0.8597</td>
<td>0.1931</td>
<td>77.54</td>
<td>96.92</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>TPR-147</td>
<td>1500</td>
<td>0.5</td>
<td>0.9127</td>
<td>0.1826</td>
<td>79.99</td>
<td>99.99</td>
<td></td>
<td>500</td>
</tr>
<tr>
<td>TPR-148</td>
<td>1500</td>
<td>0.5</td>
<td>0.7747</td>
<td>0.1694</td>
<td>78.13</td>
<td>97.67</td>
<td></td>
<td>283</td>
</tr>
<tr>
<td>TPR-149</td>
<td>1500</td>
<td>0.5</td>
<td>0.9558</td>
<td>0.2607</td>
<td>72.72</td>
<td>90.91</td>
<td></td>
<td>213</td>
</tr>
<tr>
<td>TPR-150</td>
<td>1500</td>
<td>0.5</td>
<td>0.7264</td>
<td>0.2779</td>
<td>61.74</td>
<td>77.18</td>
<td></td>
<td>143</td>
</tr>
<tr>
<td>TPR-151</td>
<td>1500</td>
<td>0.5</td>
<td>0.8125</td>
<td>0.3650</td>
<td>55.08</td>
<td>68.85</td>
<td></td>
<td>143</td>
</tr>
<tr>
<td>TPR-128</td>
<td>1750</td>
<td>0.2</td>
<td>0.8510</td>
<td>0.3024</td>
<td>64.47</td>
<td>80.58</td>
<td></td>
<td>428</td>
</tr>
<tr>
<td>TPR-129</td>
<td>1750</td>
<td>0.2</td>
<td>0.8064</td>
<td>0.3807</td>
<td>52.79</td>
<td>65.99</td>
<td></td>
<td>56.25</td>
</tr>
<tr>
<td>TPR-130</td>
<td>1750</td>
<td>0.2</td>
<td>0.7954</td>
<td>(0.2078)</td>
<td>(73.87)</td>
<td>(92.34)</td>
<td>(82.14)</td>
<td>365</td>
</tr>
<tr>
<td>TPR-131</td>
<td>1750</td>
<td>0.2</td>
<td>0.8828</td>
<td>0.3202</td>
<td>63.73</td>
<td>79.66</td>
<td></td>
<td>365</td>
</tr>
<tr>
<td>TPR-132</td>
<td>1750</td>
<td>0.2</td>
<td>0.8280</td>
<td>0.3272</td>
<td>60.48</td>
<td>75.60</td>
<td></td>
<td>243</td>
</tr>
<tr>
<td>TPR-134</td>
<td>1750</td>
<td>0.2</td>
<td>0.7875</td>
<td>0.2889</td>
<td>63.31</td>
<td>79.14</td>
<td></td>
<td>305</td>
</tr>
<tr>
<td>TPR-135</td>
<td>1750</td>
<td>0.2</td>
<td>0.9517</td>
<td>0.5021</td>
<td>47.24</td>
<td>59.05</td>
<td></td>
<td>45.35</td>
</tr>
</tbody>
</table>
Appendix C. Results of Carbon Dioxide Reduction Experiments

Table C.1 summarizes the results of the carbon dioxide reduction experiments at the temperatures and carbon dioxide partial pressures used. These experiments were carried out in the crucible mode of operation to accommodate the longer residence times of 30 seconds to 3 minutes with exception to runs numbered RPR-152 and RPR-153. In the longer residence time experiments, the loss of volatiles prior to the start of the carbon dioxide purge is taken into account assuming 14.9% and 28.3% d.a.f. volatile loss for the 1500°F and 1750°F experiments respectively. The column marked "D.A.V.F. Initial Char" therefore gives the true initial d.a.f. char. Again 20.1% proximate ash content is used and the moisture content of the char is assumed negligible.
Table C.1 Results of Carbon Dioxide Reduction by Rosebud Char Experiments

<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°K)</th>
<th>P&lt;sub&gt;CO₂&lt;/sub&gt; (atm)</th>
<th>Initial Char (g)</th>
<th>D.A.V.F Initial Char (g)</th>
<th>D.A.F. Final Char (g)</th>
<th>D.A.F. Weight Loss (%)</th>
<th>D.A.F. Weight Loss by Ash Tracer (%)</th>
<th>Residence Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPR-178</td>
<td>1500</td>
<td>0.048</td>
<td>0.0817</td>
<td>0.0556</td>
<td>0.0383</td>
<td>31.11</td>
<td>75.20</td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-179</td>
<td>1500</td>
<td>0.048</td>
<td>0.0781</td>
<td>0.0531</td>
<td>0.0195</td>
<td>63.28</td>
<td></td>
<td>2.25</td>
</tr>
<tr>
<td>RPR-180</td>
<td>1500</td>
<td>0.048</td>
<td>0.0852</td>
<td>0.0579</td>
<td>0.0479</td>
<td>17.27</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-181</td>
<td>1500</td>
<td>0.048</td>
<td>0.0775</td>
<td>0.0527</td>
<td>0.0278</td>
<td>47.25</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>RPR-182</td>
<td>1500</td>
<td>0.048</td>
<td>0.0785</td>
<td>0.0534</td>
<td>0.0359</td>
<td>32.77</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-184</td>
<td>1500</td>
<td>0.048</td>
<td>0.0762</td>
<td>0.0518</td>
<td>0.0432</td>
<td>16.60</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-185</td>
<td>1500</td>
<td>0.048</td>
<td>0.0788</td>
<td>0.0536</td>
<td>0.0114</td>
<td>78.73</td>
<td>75.20</td>
<td>3.0</td>
</tr>
<tr>
<td>RPR-186</td>
<td>1500</td>
<td>0.048</td>
<td>0.0772</td>
<td>0.0525</td>
<td>0.0395</td>
<td>24.76</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>RPR-162</td>
<td>1500</td>
<td>0.1</td>
<td>0.0768</td>
<td>0.0522</td>
<td>0.0216</td>
<td>58.62</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-163</td>
<td>1500</td>
<td>0.1</td>
<td>0.0821</td>
<td>0.0558</td>
<td>0.0172</td>
<td>69.18</td>
<td>66.55</td>
<td>1.5</td>
</tr>
<tr>
<td>RPR-164</td>
<td>1500</td>
<td>0.1</td>
<td>0.0789</td>
<td>0.0536</td>
<td>0.0374</td>
<td>30.22</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-165</td>
<td>1500</td>
<td>0.1</td>
<td>0.0717</td>
<td>0.0488</td>
<td>0.0009</td>
<td>98.16</td>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td>RPR-166</td>
<td>1500</td>
<td>0.1</td>
<td>0.0841</td>
<td>0.0572</td>
<td>0.0089</td>
<td>84.44</td>
<td>79.12</td>
<td>2.25</td>
</tr>
<tr>
<td>RPR-167</td>
<td>1500</td>
<td>0.1</td>
<td>0.0736</td>
<td>0.0500</td>
<td>0.0209</td>
<td>58.20</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-168</td>
<td>1500</td>
<td>0.1</td>
<td>0.0839</td>
<td>0.0570</td>
<td>0.0420</td>
<td>26.32</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-169</td>
<td>1500</td>
<td>0.1</td>
<td>0.0753</td>
<td>0.0512</td>
<td>0.0170</td>
<td>66.80</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>RPR-154</td>
<td>1500</td>
<td>0.2</td>
<td>0.0705</td>
<td>0.0479</td>
<td>0.0009</td>
<td>98.12</td>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td>RPR-155</td>
<td>1500</td>
<td>0.2</td>
<td>0.0616</td>
<td>0.0419</td>
<td>0.0088</td>
<td>79.00</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-156</td>
<td>1500</td>
<td>0.2</td>
<td>0.0877</td>
<td>0.0596</td>
<td>0.0368</td>
<td>38.26</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-157</td>
<td>1500</td>
<td>0.2</td>
<td>0.0837</td>
<td>0.0569</td>
<td>0.0327</td>
<td>42.53</td>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>RPR-158</td>
<td>1500</td>
<td>0.2</td>
<td>0.0811</td>
<td>0.0551</td>
<td>0.0246</td>
<td>55.35</td>
<td></td>
<td>0.75</td>
</tr>
<tr>
<td>RPR-159</td>
<td>1500</td>
<td>0.2</td>
<td>0.0763</td>
<td>0.0519</td>
<td>0.0154</td>
<td>70.33</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>RPR-160</td>
<td>1500</td>
<td>0.2</td>
<td>0.0758</td>
<td>0.0515</td>
<td>0.0077</td>
<td>85.05</td>
<td>79.70</td>
<td>1.5</td>
</tr>
<tr>
<td>RPR-161</td>
<td>1500</td>
<td>0.2</td>
<td>0.0804</td>
<td>0.0547</td>
<td>0.0028</td>
<td>94.88</td>
<td>90.42</td>
<td>2.25</td>
</tr>
</tbody>
</table>
Table C.1 (continued)

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RPR-152</td>
<td>1500</td>
<td>0.5</td>
<td>0.8407</td>
<td>0.6055</td>
<td>9.86</td>
<td>500*</td>
<td></td>
</tr>
<tr>
<td>RPR-153</td>
<td>1500</td>
<td>0.5</td>
<td>1.0112</td>
<td>0.7314</td>
<td>9.47</td>
<td>500*</td>
<td></td>
</tr>
<tr>
<td>RPR-170</td>
<td>1750</td>
<td>0.048</td>
<td>0.0762</td>
<td>0.0211</td>
<td>51.72</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>RPR-171</td>
<td>1750</td>
<td>0.048</td>
<td>0.0714</td>
<td>0.0210</td>
<td>48.66</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>RPR-172</td>
<td>1750</td>
<td>0.048</td>
<td>0.0785</td>
<td>0.0054</td>
<td>88.00</td>
<td>56.55</td>
<td></td>
</tr>
<tr>
<td>RPR-173</td>
<td>1750</td>
<td>0.048</td>
<td>0.0816</td>
<td>0.0366</td>
<td>21.63</td>
<td>56.55</td>
<td></td>
</tr>
<tr>
<td>RPR-174</td>
<td>1750</td>
<td>0.048</td>
<td>0.0781</td>
<td>0.0302</td>
<td>32.44</td>
<td>11.72</td>
<td></td>
</tr>
<tr>
<td>RPR-175</td>
<td>1750</td>
<td>0.048</td>
<td>0.0687</td>
<td>0.0294</td>
<td>25.38</td>
<td>11.72</td>
<td></td>
</tr>
<tr>
<td>RPR-176</td>
<td>1750</td>
<td>0.048</td>
<td>0.0849</td>
<td>0.0195</td>
<td>59.88</td>
<td>24.44</td>
<td></td>
</tr>
<tr>
<td>RPR-177</td>
<td>1750</td>
<td>0.048</td>
<td>0.1001</td>
<td>0.0022</td>
<td>96.16</td>
<td>24.44</td>
<td></td>
</tr>
</tbody>
</table>

*msec
Appendix D. Calculation of Binary Diffusion Coefficients for O₂–He and CO₂–He (Perry and Chilton, 1973)

Perry and Chilton (1973) give the following correlation for calculating binary gas diffusion coefficients:

$$D_{12} = \frac{BT^{3/2}}{P r_{12}^2 I_D} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{3/2}$$

$$B = \left( 10.7 - 2.46 \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \right) \times 10^{-4}$$

where $D_{12}$ = binary diffusion coefficient, cm²/sec

$T$ = absolute temperature, °K

$P$ = absolute pressure, atm

$M_1, M_2$ = molecular weights

$r_{12}$ = collision diameter, Å. $r_{12} = \frac{(r_o)_1 + (r_o)_2}{2}$

$I_D$ = collision integral, function of $\kappa \frac{T}{\epsilon_{12}}$. $\frac{\epsilon_{12}}{\kappa} = \sqrt{\frac{\epsilon_1}{\kappa} \left( \frac{\epsilon_2}{\kappa} \right)}$

<table>
<thead>
<tr>
<th>gas</th>
<th>$r_o$</th>
<th>$\frac{\epsilon}{\kappa}$</th>
<th>$M$</th>
<th>$\frac{\kappa T}{\epsilon_{12}}$</th>
<th>$I_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>2.70</td>
<td>6.03</td>
<td>4</td>
<td>40</td>
<td>0.2980</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>0.2878</td>
</tr>
<tr>
<td>O₂</td>
<td>3.433</td>
<td>113.2</td>
<td>32</td>
<td>60</td>
<td>0.2798</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>0.2732</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>0.2676</td>
</tr>
<tr>
<td>CO₂</td>
<td>3.996</td>
<td>190</td>
<td>44</td>
<td>40</td>
<td>0.2980</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50</td>
<td>0.2878</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>0.2798</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>70</td>
<td>0.2732</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>0.2676</td>
</tr>
</tbody>
</table>

For the O₂–He System:

$r_{12} = 3.0665$

$\frac{\epsilon_{12}}{\kappa} = 26.127$

For the CO₂–He System:

$r_{12} = 3.348$

$\frac{\epsilon_{12}}{\kappa} = 33.848$
On the basis of this information, Figure D.1 has been made to show how $D_{O_2-He}$ and $D_{CO_2-He}$ vary with temperature.
Figure D.1 Binary Diffusion Coefficients for $O_2$-He and $CO_2$-He
Appendix E. Calculation of Thermal Conductivities for O₂ and He Mixtures

Figure E.1 has been constructed from values of the thermal conductivities for helium and oxygen at various temperatures as given by Powell et al. (1972) and Perry and Chilton (1973). To determine the thermal conductivities of gas mixtures, Perry and Chilton give the following simplified expression:

\[
\lambda_g = \frac{\sum y_i \lambda_i (M_i)^{1/3}}{\sum y_i (M_i)^{1/3}} \quad \text{(E.1)}
\]

where \( \lambda_i \), \( y_i \), and \( M_i \) are the thermal conductivity, mole fraction, and molecular weight respectively of the individual species. From this information, Figure E.2 is developed to show how the thermal conductivities for various mole fractions of helium and oxygen vary with temperature.
Figure E.1 Thermal Conductivities of Pure Components Helium and Oxygen
Figure E.2 Thermal Conductivities of Helium and Oxygen Mixtures
Appendix F. Calculation of Effective Pore Diffusivities for $O_2$ and $CO_2$
(Satterfield, 1975; and Wheeler, 1951)

If the mean free path of a molecule is about equal to, or greater than, a pore radius of the char particle, then Knudsen, or self, diffusion may be assumed. The char particle is actually likely to have a rather wide pore-size distribution, but without a detailed analysis it will suffice to simply determine an average pore radius. Wheeler (1959) gives the following expression for the calculation of a mean pore radius:

$$\bar{r}_p = \frac{2\theta \sqrt{\tau}}{A_p \rho_B} \quad (F.1)$$

Assuming a tortuosity, $\tau$, of 2.0, the mean pore radii of the true initial chars may be found using the values of $\theta_p$, $A_p$, and $\rho_B$ for runs numbered CPR-12, CPR-11, and the raw char given in Table G.2. These are summarized in Table F.1. The mean free paths of $O_2$ and $CO_2$ at 1 atm are both on the order of $10^{-4}$ and $10^{-3}$ cm at 1500 and 1750$^\circ$K respectively. Since these are nearly two orders of magnitude larger than any corresponding value of $\bar{r}$ in Table F.1, Knudsen diffusion is assumed. Satterfield (1975) gives the following relations for determining the effective pore diffusivities based on Knudsen diffusion:

$$D_{\text{eff}} = D_K \frac{\theta_p}{\tau} \quad (F.2)$$

$$D_K = 9700 \frac{r}{p} \sqrt{\frac{\theta_p}{M}} \quad (F.3)$$
where $D_K$ is the Knudsen diffusion coefficient and $M$ is the molecular weight of the gaseous reactant species. From this information, Figure F.1 was made to show how the effective pore diffusivities vary with temperature for the different experiments that were run.
Table F.1  Mean Pore Radii for the True Initial Chars

<table>
<thead>
<tr>
<th>Type of Experiment</th>
<th>Oxidation Experiments</th>
<th>Carbon Dioxide Reduction Experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td>True Initial Char</td>
<td>True Initial Char = Raw Char</td>
<td>1500°K True Initial Char = CPR-12</td>
</tr>
<tr>
<td>( \theta_p )</td>
<td>0.745</td>
<td>0.779</td>
</tr>
<tr>
<td>( A_p ), cm(^2)/g</td>
<td>1.65 \times 10^6</td>
<td>1.02 \times 10^6</td>
</tr>
<tr>
<td>( \rho_B ), cm(^3)/g</td>
<td>0.50</td>
<td>0.53</td>
</tr>
<tr>
<td>( r_p ), cm</td>
<td>2.55 \times 10^{-6}</td>
<td>4.08 \times 10^{-6}</td>
</tr>
</tbody>
</table>
Appendix G. Characterization of Rosebud Char Samples

The char used in this investigation was provided by Foster-Wheeler Corp., of Livingston, New Jersey. It was prepared from a pulverized sample of a Montana Rosebud coal which had been sieved between 200 and 150 mesh screens (75 to 105 \( \mu \text{m} \)). The particles were injected in a dispersed phase into a muffle tube furnace at 1365\(^{\circ}\)K containing an atmosphere of 41\% CH\(_4\), 45\% H\(_2\)O, and 14\% CO\(_2\) with a total system pressure of about 1 atm. Residence times were on the order of 150 msec. The char was collected and stored under an argon atmosphere until the time of its use.

The char, as received from Foster-Wheeler, was analyzed for ASTM proximate moisture and ash contents by the methods described in Section 2.3. Weighted average values for these proximate analyses were calculated by

\[
\text{Weighted Average} = \frac{\sum C_i \cdot \%X}{\sum C_i}
\]  

(G.1)

where \( C_i \) is the initial char weight, \( \%X \) is the percent proximate content in \( C_i \). The quantities are summed over the number of runs that were made.

Physical analyses of the raw char, as well as reacted char samples from selected experiments, were performed by Phillips Petroleum Co. of Bartlesville, Oklahoma. Values for the total specific surface area, \( A_p \), bulk density, \( \rho_B \), and skeletal density, \( \rho_p \), for these samples are given in Table G.2. The porosity, or void fraction, \( \epsilon_p \), was calculated by the relation...
\[ \theta_p = 1 - \frac{\rho_B}{\rho_p} \]  

(G.2)

Particle size distributions were determined by examination of scanning electron micrographs. These distributions are given in Figures G.1, G.2, and G.3 for the raw char, CPR-12, and CPR-11 respectively. For the oxidation experiments, in which reaction occurred mainly in a shell near the external surface of the particle, the average particle diameter, \( d_p \), for the initial char, which is represented by the raw char, is given by an external area median. For the carbon dioxide reduction experiments, on the other hand, the reaction occurred throughout the particle. Therefore, the average particle size for the initial char, CPR-12 at 1500°F and CPR-11 at 1750°F, is given by a volume (or mass) median.

Finally, a partial ultimate chemical analysis for the raw char, CPR-12, and CPR-11, was also done by Phillips Petroleum Co. These results are given in Table G.3 for carbon, hydrogen, and nitrogen.
Table G.1: Results of Proximate Moisture and Ash Analyses of the Rosebud Char as Received

<table>
<thead>
<tr>
<th>Run Number</th>
<th>Initial Char Mass (g)</th>
<th>ASTM Proximate Moisture Content (%)</th>
<th>ASTM Proximate Ash Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APR-1</td>
<td>0.2835</td>
<td>0.99</td>
<td>21.83</td>
</tr>
<tr>
<td>APR-3</td>
<td>0.2698</td>
<td>0.93</td>
<td>20.31</td>
</tr>
<tr>
<td>APR-6</td>
<td>0.3230</td>
<td>1.02</td>
<td>19.50</td>
</tr>
<tr>
<td>APR-7</td>
<td>0.2763</td>
<td>0.94</td>
<td>19.11</td>
</tr>
<tr>
<td>APR-8</td>
<td>0.3000</td>
<td>0.87</td>
<td>19.33</td>
</tr>
<tr>
<td>APR-9</td>
<td>0.2451</td>
<td>0.94</td>
<td>20.93</td>
</tr>
<tr>
<td>Weighted Average</td>
<td>0.95</td>
<td></td>
<td>20.13</td>
</tr>
</tbody>
</table>
Table G.2  Physical Properties of Rosebud Char Samples

<table>
<thead>
<tr>
<th>Run Number</th>
<th>T (°K)</th>
<th>Type of Atmosphere</th>
<th>Residence Time (msec, min)</th>
<th>D.A.F. Weight Loss (%)</th>
<th>( A_p^+ ) (m²/g)</th>
<th>( \rho_B^+ ) (g/cm³)</th>
<th>( \rho_p^+ ) (g/cm³)</th>
<th>( \theta_p )</th>
<th>dₛ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Char</td>
<td>1500</td>
<td>He</td>
<td>5 min</td>
<td>14.92</td>
<td>165</td>
<td>0.50</td>
<td>1.96</td>
<td>0.745</td>
<td>120</td>
</tr>
<tr>
<td>CPR-12</td>
<td>1750</td>
<td>He</td>
<td>5 min</td>
<td>23.51</td>
<td>102</td>
<td>0.53</td>
<td>2.40</td>
<td>0.779</td>
<td>125</td>
</tr>
<tr>
<td>CPR-11</td>
<td>1750</td>
<td>0.2 O₂</td>
<td>143 msec</td>
<td>36.17</td>
<td>155</td>
<td>0.37</td>
<td>1.71</td>
<td>0.784</td>
<td>125</td>
</tr>
<tr>
<td>TPR-141</td>
<td>1500</td>
<td>0.2 O₂</td>
<td>283 msec</td>
<td>(52.99) low</td>
<td>123</td>
<td>0.47</td>
<td>2.12</td>
<td>0.778</td>
<td></td>
</tr>
<tr>
<td>TPR-139</td>
<td>1500</td>
<td>0.2 O₂</td>
<td>356 msec</td>
<td>70.50</td>
<td>96.8</td>
<td>0.44</td>
<td>2.21</td>
<td>0.801</td>
<td></td>
</tr>
<tr>
<td>TPR-137</td>
<td>1500</td>
<td>0.2 O₂</td>
<td>143 msec</td>
<td>68.85</td>
<td>122</td>
<td>0.46</td>
<td>2.16</td>
<td>0.787</td>
<td></td>
</tr>
<tr>
<td>TPR-135</td>
<td>1500</td>
<td>0.2 O₂</td>
<td>123 msec</td>
<td>59.05</td>
<td>126</td>
<td>0.42</td>
<td>2.14</td>
<td>0.804</td>
<td></td>
</tr>
<tr>
<td>TPR-132</td>
<td>1750</td>
<td>0.2 O₂</td>
<td>243 msec</td>
<td>75.60</td>
<td>61.1</td>
<td>0.42</td>
<td>2.14</td>
<td>0.804</td>
<td></td>
</tr>
<tr>
<td>RPR-178</td>
<td>1500</td>
<td>0.048 CO₂</td>
<td>0.048 CO₂</td>
<td>31.11</td>
<td>181</td>
<td>42.53</td>
<td>44.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RPR-182</td>
<td>1500</td>
<td>0.048 CO₂</td>
<td>0.048 CO₂</td>
<td>30.22</td>
<td>167</td>
<td>42.53</td>
<td>44.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

+ Analyses made by Phillips Petroleum Co., Bartlesville, Oklahoma.
Table G.3  Partial Ultimate Chemical Analyses of Rosebud Char Samples†

<table>
<thead>
<tr>
<th></th>
<th>Weight Percent as Received</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Raw Char</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.90</td>
</tr>
<tr>
<td></td>
<td>75.01</td>
</tr>
<tr>
<td>CPR-12 (1500°K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>74.00</td>
</tr>
<tr>
<td></td>
<td>74.97</td>
</tr>
<tr>
<td></td>
<td>75.60</td>
</tr>
<tr>
<td>CPR-11 (1750°K)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>82.52</td>
</tr>
<tr>
<td></td>
<td>82.73</td>
</tr>
</tbody>
</table>

† Analyses made by Phillips Petroleum Co., Bartlesville, OK.
Figure G.1 Particle Size Distribution for the Raw Montana Rosebud Char

Total Sample Size = 97 particles
Figure G.2 Particle Size Distribution for Char from Run CPR-12

Total Sample Size = 247 particles

Median Frequency = 45 μm
Median Area = 95 μm
Median Mass = 125 μm
Frequency Median = 45 μm

Area Median = 100 μm

Mass Median = 125 μm

Particle Diameter (μm)

Total Sample Size = 201 particles

Figure G.3 Particle Size Distribution for Char from Run CPR-11
REFERENCES


Thiele, E. W., "Relation Between Catalytic Activity and Size of Particle,"

Thring, M. W., and Essenhigh, R. H., in H. H. Lowry, ed., Chemistry of

Tu, C. M., Davis, H., and Hottel, H. C., Ind. Eng. Chem., 26, p. 749,
1934.


Van Krevelen, D. W., Van Heerden, C., and Huntjens, F. J., "Physico-
chemical Aspects of the Pyrolysis of Coal and Related Organic


Wheeler, A., "Reaction Rates and Selectivity in Catalyst Pores," Advances


Wu, P. C., "The Kinetics of the Reaction of Carbon with Carbon Dioxide,"