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**FATE OF SULFUR IN A
HIGH PERFORMANCE POWER SYSTEM'S
HIGH TEMPERATURE ADVANCED FURNACE**

**A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville**

**Samuel Albert Morton III
December 1998**

For my Family
and Friends

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ABSTRACT

In an era of ever decreasing fossil fuel resources and increasing awareness of the environmental ramifications of their use, it becomes necessary to investigate improved methods to use these resources in the generation of electric power. To further these ends a national research program, Combustion 2000, was developed by the Department of Energy(DOE) with the goal of decreasing negative environmental impact while increasing the efficient use of valuable fossil fuel resources, namely coal. A portion of this program, the High Performance Power System(HIPPS), was proposed and developed by Foster Wheeler Development Corporation(FWDC). This proposal consisted of a combined cycle power generation system, within which the coal would be first pyrolyzed and the remaining char sent to a combustor. A part of the purpose of the pyrolyzer was to remove nearly 50 % of the sulfur present in the coal by subjecting it to high temperatures while in the presence of a limestone sorbent. This process would cause the formation of calcium sulfide from the sulfur and limestone and thereby capture the sulfur, which would then be removed from the system. During the later design phase of the HIPPS project the packed bed pyrolyzer was switched from containing a limestone-sorbent bed, into which the coal would be injected, to containing a sand bed, into which the coal and the required sorbent would be injected. This redesign changed the path of the calcium sulfide from removal after pyrolysis, to being combusted along with the char in the High

Temperature Advance Furnace(HITAF), as it was now impossible to separate the calcium sulfide from the char.

This work was primarily concerned with the fate of sulfur in the HITAF combustor. Due to the limited information with regards to the combustion of a mixture of char and calcium sulfide several series of tests were undertaken. These tests were designed to study the both the combustion of char and the oxidation of calcium sulfide simultaneously, with the ultimate goal of predicting the fate of sulfur in the HIPPS HITAF. An additionally desired outcome from this research was the development of a relationship between the conversion of the carbon in the char and the overall conversion of sulfur. During the course of this investigation the various effects of equilibrium, temperature, and product inhibition were evaluated and any possible relation to the HIPPS HITAF performance was discussed.

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LIST OF SYMBOLS

A	Ideal Gas Heat Capacity Correlation Constant	
B	Ideal Gas Heat Capacity Correlation Constant	
C	Ideal Gas Heat Capacity Correlation Constant	
C_C	Concentration of Carbon	$\frac{\text{mol}}{\text{volume}}$
C_{C0}	Initial Concentration of Carbon	$\frac{\text{mol}}{\text{volume}}$
C_p°	Constant Pressure Ideal Gas Heat Capacity	$\frac{\text{Btu}}{\text{lb} \cdot ^\circ \text{F}}$
C_S	Concentration of Sulfur	$\frac{\text{mol}}{\text{volume}}$
C_{S0}	Initial Concentration of Sulfur	$\frac{\text{mol}}{\text{volume}}$
D	Ideal Gas Heat Capacity Correlation Constant	
E	Activation Energy	$\frac{\text{calories}}{\text{mol}}$
I	Integration Constant for Equation 3.9	
J	Integration Constant for Equation 3.10	

K	Equilibrium Constant	
MW _C	Molecular Weight of Carbon	$\frac{\text{gram}}{\text{gram mol}}$
N _C	Moles of Carbon	mol
R	Universal Gas Constant	$\frac{\text{calories}}{\text{mol} \cdot \text{K}}$
T	Temperature	°F, °C, K
W _C	Mass of Carbon	grams
W _{C0}	Initial Mass of Carbon	grams
W _S	Mass of Sulfur	grams
W _{S0}	Initial Mass of Sulfur	grams
X _C	Overall Fractional Conversion of Carbon	
X _S	Overall Fractional Conversion of Sulfur	
a	algebraic constant	
b	algebraic constant	
k	rate constant	$\frac{1}{\text{min} \cdot \text{mol}^a}$

$\bar{k}$	average rate constant over temperature range	$\frac{1}{\text{min} \cdot \text{mol}^\alpha}$
k_o	frequency factor	$\frac{1}{\text{min} \cdot \text{mol}^\alpha}$
$-r_c$	Rate of Carbon Disappearance	$\frac{\text{mol}}{\text{min}}$
t	Time	min, sec
ΔG°	Standard State Gibbs Free Energy of Reaction	$\frac{\text{J}}{\text{mol}}$
ΔG_{298}°	Standard State Gibbs Free Energy of Reaction at 298.15 Kelvin	$\frac{\text{J}}{\text{mol}}$
ΔH°	Standard State Heat of Reaction	$\frac{\text{J}}{\text{mol}}$
ΔH_{298}°	Standard State Heat of Reaction at 298.15 Kelvin	$\frac{\text{J}}{\text{mol}}$
α	Constant	
Φ	Function Relating Sulfur Conversion to Carbon Conversion	

LIST OF ABBREVIATIONS

ANL	Argonne National Laboratory
CEA	Chemical Equilibrium and Applications
DOC	United States Department of Commerce
DOE	United States Department of Energy
FETC	Federal Energy Technology Center
FGD	Flue Gas Desulfurization
FWDC	Foster Wheeler Development Corporation
GT	Gas Turbine
HHV	Higher Heating Value
HITAF	High Temperature Advanced Furnace
HIPPS	High Performance Power System
HRSG	Heat Recovery Steam Generator
IR	Infrared
J	Joule(s)
JANAF	Joint Army-Navy-Air Force
KJ	KiloJoule(s)
LEBS	Low-Emission Boiler System
m ³	cubic meter(s)
mg	milligram(s)
min	minute(s)

mol	gram-mole(s)
NASA	National Aeronautics and Space Administration
PETC	Pittsburgh Energy Technology Center
psia	pounds per square inch absolute
ppm	parts per million
sec	second(s)
TGA	Thermogravimetric Analyzer
UTSI	University of Tennessee Space Institute
wt. %	weight percent

CHAPTER I

INTRODUCTION

Foster Wheeler's High Performance Power System

In an era of ever shrinking fossil fuel resources, coupled with increasing awareness of environmental damage due to the current use of these fuels, it is imperative to investigate new methods of using these resources. Of great concern to the future is the use of coal to produce electricity, which is the currently favored method in the United States because of its abundance. It is necessary to develop more efficient processes that use coal to produce electricity, while improving the environmental acceptability at the same time, a pair of goals that are not often compatible. To further these goals the United States Department of Energy (DOE) has lead an initiative called Combustion 2000. Combustion 2000 is directed at the commercial generation of electricity from coal, as the current plants display a less than desirable efficiency and suffer from large costs to retrofit in order to become more environmentally friendly. The Combustion 2000 project is being implemented in two different steps, first the Low-Emission Boiler System (LEBS) and second the High Performance Power System (HIPPS), with increased efficiency and decreased environmental impact.

The project of concern to this thesis is that of the HIPPS process, and in particular the

program which is being lead by Foster Wheeler Development Corporation (FWDC). Foster Wheeler's concept is a combined cycle power generation system, within which the coal is first pyrolyzed, releasing a fuel gas to used to operate a turbine cycle, and the remaining char is sent to a steam cycle combustor along with the turbine exhaust as the preheated oxidizer. The overall process is designed to have an efficiency of more than 50 percent, which would satisfy the efficiency goal of the HIPPS. The remaining goal, reduced environmental impact, is to be met by the advanced design of the system, planned to reduce deleterious emissions by about a factor of ten.

Statement of Problem

The main focus of this thesis is the ultimate fate of sulfur in the HIPPS process. Sulfur that is found naturally in coal has to be removed from the final plant output, so that the SO_x -emission requirement can be met. The conceptual sulfur removal process in the FWDC HIPPS concept is a binary process, the first step being the capture of sulfur released in the pyrolyzer with the coal fuel gases, and the second being the hindering of sulfur release during the combustion process. Pyrolysis heats the coal in a reducing, or oxygen starved, environment which releases the volatiles, some carbon monoxide and the some of the sulfur. This sulfur is captured by utilizing its reaction with calcium oxide, introduced to the pyrolyzer as a "sorbent" with the coal, to form calcium sulfide. This prohibits the release of sulfur species with the volatiles, thereby allowing for the production of a "clean" fuel gas. After separating the fuel gas from the solid char,

remaining sorbent, and calcium sulfide, the solids are sent to a furnace where entrained combustion occurs to power the steam cycle. This furnace is called a high temperature advanced furnace (HITAF). This process utilizes the energy evolved from the combustion of the char to heat air and steam to drive separate power generation systems.

It is proposed in the HIPPS concept that the sulfur emission levels will be met due to the fact that minimal amounts of sulfur species are released in this process, because most of the sulfur will be bound as calcium sulfide. It is also believed that calcium sulfide will not decompose or oxidize to form sulfur dioxide in the char combustor and can then be disposed of along with the remaining ash, as CaSO_4 . The difficulty with this concept is that there is little information concerning the oxidation of calcium sulfide in a combustion process. When coupled with the fact that preliminary tests and the available literature indicate that only part of the sulfur is thermally released in the pyrolyzer for calcium sulfide capture, it becomes evident that further investigation is required.

It is therefore necessary to investigate the HIPPS hypothesis, that most of the sulfur is released in the pyrolyzer and will be captured as calcium sulfide, and this compound will not oxidize during combustion of the char in the HITAF, to form sulfur dioxide. Also only the little remaining sulfur in the char that did not get absorbed by lime in the pyrolyzer will be released in the HITAF in the form of sulfur dioxide. If this hypothesis proves true, the HIPPS exhaust will require only minimal desulfurization prior to release to the atmosphere to meet SO_x -emission guidelines.

Objectives of This Investigation

This investigation into the fate of sulfur has two main objectives: (1) determine that there does not exist, in significant amounts, two very different forms of sulfur in the HIPPS char, and (2) to determine if any HITAF oxidation of calcium sulfide will occur to form primarily sulfur dioxide. The first objective is directly related to the combustion of the char and therefore can be determined by studying the combustion behavior of the char and its subsequent evolution of sulfur dioxide . The second objective can be met by verifying, through a series of bench-scale experiments, that the calcium sulfide does not oxidize to sulfur dioxide in an entrained particle combustion situation similar to that proposed in the HIPPS process.

CHAPTER II

LITERATURE REVIEW

Department of Energy's Combustion 2000 Initiative

The United States is blessed with an abundance of fossil fuel resources of which coal is by far the most plentiful. In the mid 1990's, electric utilities consumed about 800 million tons of coal per year , or about 85 percent of the total coal used in the United States. Of the electricity generated at that time, 55 percent was generated with coal (Ruth "Combustion 2000" 4). As communities and industries grow, the demand for electric power will no doubt increase. Although most new coal-fired capacity will not be built in the U.S. until after the year 2000, the Department of Energy predicts that 42 gigawatts of electric power capacity will be added between 1995 and 2010 to satisfy the growing demand for power (Ruth "Combustion 2000: advanced..." 77). It is this growing demand coupled with the predicted retirement of aging power plants that drives the Department of Energy's Combustion 2000 initiative.

Combustion 2000 is a long-term, cost-shared, federally-funded research and development effort with the goal of advancing coal-fired electric power generation technology into the 21st century (Ruth "Combustion 2000: Planning..." 4). The Combustion 2000 initiative is composed of two major areas of investigation. The first area is the Low-Emission

Boiler System, which is concerned with the development of a more environmentally friendly direct-fired pulverized coal-based power generation system. The second area is the High Performance Power System, which is concerned with the development of a more efficient and environmentally friendly indirect-fired combined-cycle based power generation system. A comparison of the requirements for each project can be seen in Table 2.1 (Ruth "Combustion 2000: advanced..." 77).

High Performance Power System (HIPPS)

The High Performance Power System is a coal-fired, combined-cycle system with the goal of producing electric power from coal with nearly a 30 percent greater thermal efficiency than conventional coal power plants. In this system, only clean gas is

Table 2.1 Combustion 2000 Project Objectives

Objective	LEBS	HIPPS
Environmental Performance		
SO _x (mg/m ³)	125	75
NO _x (mg/m ³)	125	75
Particulates (mg/m ³)	13	4
Efficiency Based on (HHV - total %)	42	> 47
Cost of electricity	Comparable to current	10 % lower than current

Source: Lawrence A. Ruth, "Combustion 2000: advanced coal firing for the next century.", May 1995

expanded in a gas turbine, which protects the turbine blades from corrosive damage. This is done by heating air for the turbine indirectly in a High Temperature Advanced Furnace (HITAF). Natural gas or a clean coal derived fuel gas is used to increase the temperature of the preheated turbine inlet air, which is then expanded in the gas turbine, producing nearly half of the overall cycle's power. To increase the thermal efficiency, heat is recovered from the furnace flue gas and the turbine exhaust to drive a conventional Rankine steam cycle (Figueroa et al. 2).

As can be seen in Table 2.1, the requirements for the HIPPS concept are quite stringent. The overall desire to generate power at an efficiency of greater than 47 percent while at the same time reducing emissions and cost is quite daunting. Current coal-fired power generation facilities function with an overall efficiency of about 35 percent and produce emissions at nearly ten times the levels mandated for the HIPPS concept. Two different HIPPS projects are currently underway, the first headed by United Technologies and the second headed by Foster Wheeler Development Corporation. It is with the Foster Wheeler HIPPS concept that this work at the University of Tennessee Space Institute (UTSI) is concerned.

The Foster Wheeler HIPPS project differs from the United Technologies' HIPPS project in one major area. The Foster Wheeler project utilizes a pyrolyzer to partially gasify the coal and produce both char and pyrolysis gas for use as fuel sources. The pyrolyzer char is then burned in the HITAF and provides the energy needed by the Rankine cycle and to

partially heat the gas turbine inlet air. Final air heating is provided by the pyrolysis gas to heat the air to the required temperature. There are two main subsystems in the Foster Wheeler HIPPS project, the aforementioned pyrolyzer and the HITAF. A schematic of the overall commercial system concept can be seen in Figure 2.1.

The first subsection in the FWDC's concept is the pyrolyzer, which is a circulating fluidized bed reactor that operates under reducing conditions. The pyrolyzer operates at about 240 psia and 1700 °F at substoichiometric conditions, which are required to convert the coal to a fuel gas and a solid char. The fuel gas is then used to generate electricity in a gas turbine combustor. Prior to firing, the fuel gas is cooled to 1100 °F. This cooling allows for the removal of the alkali compounds generated during the pyrolysis process. The HIPPS char is a mixture of coal char, which is mainly fixed carbon and ash, and the sorbent material. The sorbent is introduced into the pyrolyzer to capture the sulfur that is released during pyrolysis. The sorbent introduced into the pyrolyzer will remove nearly 90 percent of the sulfur species released during the process. This sulfur species removal process, when used in tandem with a downstream additional sulfur species removal scheme, can achieve the required SO_x emission standards. Any entrained char or sorbent in the fuel gas stream is separated by means of a cyclone separator. The char/sorbent mixture removed from the pyrolyzer is then fired in the second subsection of the HIPPS process, known as the HITAF.

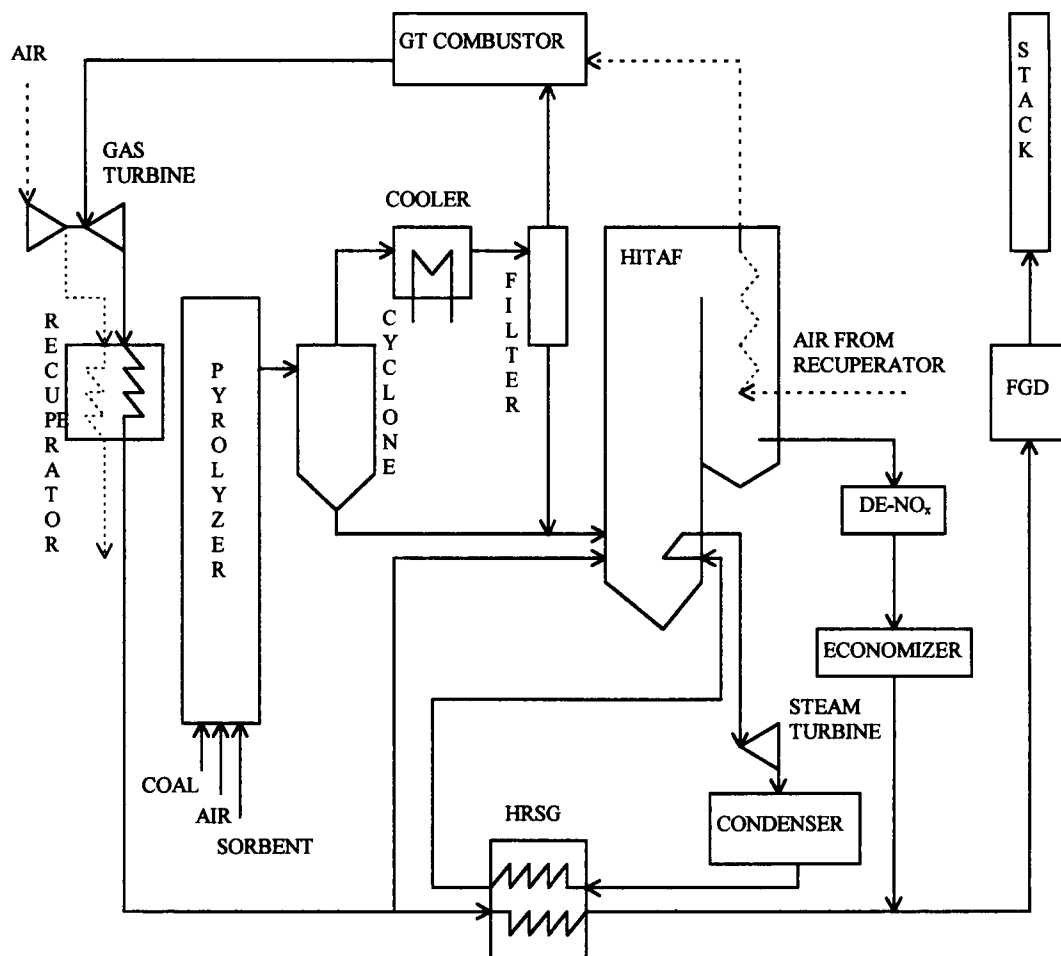


Figure 2.1 HIPPS Commercial Plant Design Schematic

Source: Nehrozoglu et al, "Engineering Development of Coal-Fired High-Performance Power Systems." Advanced Coal-Based and Environmental Systems 1997 Conference Pittsburgh: 22-24 July 1997. Online Posting: http://www.fetc.doe.gov/publications/proceedings/97ps/ps97_toc.html (19 Feb. 1998)

This HITAF is a combination air heater/boiler. The char/sorbent mixture is combusted in the HITAF, which contains both steam and air heat exchangers. The HITAF operates between 1400 °F and 2500 °F, and heats the air for the gas turbine to about 1400 °F. A steam cycle system is also included in the HITAF, within which the vaporization and superheating of the steam are performed. Before the heated air is carried to a gas turbine, it is heated to 2350 °F. After exiting the gas turbine, the hot gas is passed back through a recuperator to maximize the thermal performance of this design. If necessary, the exhaust gas from the HIPPS plant can be further desulfurized to meet the stringent SO_x emission standards.

Chemical and Physical Properties of Coal

To understand the behavior of coal and coal char, it is necessary to ask the question, “What is the chemical and physical composition of coal?” This question seems simple. However, it leads to a complex and often confusing answer. Coal once was thought to be an impure form of elemental carbon even after evidence was discovered to suggest that it was composed of various compounds of carbon. In order to answer the question concerning the composition of coal, it is necessary to obtain an understanding of the carbon framework, or the way the carbon atoms are connected (Elliot and Yohe 27). This understanding should include knowledge about the types, bonding, and amounts of elements attached to the carbon frame and how their inclusion in the coal structure affects its various properties.

Coal is composed primarily of five elements; carbon, oxygen, hydrogen, sulfur, and nitrogen. Carbon is by far the most plentiful element in coal, comprising 70 to 85 percent of its weight. Next most plentiful is oxygen comprising 8 to 22 percent of the overall weight of the coal. All coals contain oxygen, and the amounts decrease as the rank of a coal increases (Elliot and Yohe 34). Hydrogen comes after oxygen and carbon, in terms of amounts, comprising 4 to 7 percent of the coal by weight. The vast bulk of the hydrogen found in coal is bound directly to the carbon atoms because single and clustered aromatic rings represent an important component of the carbon frame. As the rank of coal increases, the amount of hydrogen found in aromatic rings increases while at the same time a decrease in the amount of aliphatic hydrogen is noted. The remaining hydrogen is found connected to the other elements of significance, oxygen, nitrogen, and sulfur (Elliot and Yohe 33). Following hydrogen is sulfur, comprising from fractions of a percent to a very unusual value of 11 percent by weight. Sulfur exists in two major forms, organic sulfur and inorganic sulfur. Organic sulfur is chemically bound to the carbon frame directly and is included in the composition of the coal molecule. Inorganic sulfur is bound to other mineral compounds and is mainly physically intermixed with the other impurities of the coal aggregate. Organic sulfur is mixed throughout the coal and is difficult to remove by physical coal-cleaning methods. Organic sulfur exists primarily in the same type of structures that are found in the amino acids of animal and plant proteins. Inorganic sulfur is mainly found in the form of iron pyrite, FeS_2 . In some situations, such as weathered coal from outdoor stockpiles, the inorganic sulfur is also

found to be in the form of mineral sulfates. Unlike organic sulfur, inorganic sulfur can be removed by physical cleaning methods. The last of the major elements is nitrogen, comprising 1 to 2 percent of the total weight of the coal. Nitrogen is not remarkable in the manner of its inclusion in coal, as the basic nitrogen structure found in proteins has not been greatly affected by the process of coalification (Elliot and Yohe 35-36). The remaining bulk of the coal is comprised of minerals. These minerals were either part of the original organic structures of the plants and animals or were introduced later on by other methods as the coal formed. The main minerals found in coal are kaolinite, detrital clay, pyrite, and calcite, which give rise to silicon, aluminum, iron, and calcium oxides and to lesser degrees magnesium, sodium, potassium, manganese, phosphorus, and sulfur compounds (Elliot and Yohe 36). Table 2.2 gives a listing of elemental values measured for a variety of coals of different ranks.

The HIPPS coal char is, in essence, pyrolyzed coal, and is similar in composition and structure. The HIPPS char has undergone a pyrolysis process very similar to the carbonization process of coking. HIPPS char contains the same elements as coal with little variation in their incorporation in the char. The char still contains carbon, oxygen, hydrogen, sulfur, and nitrogen, however a few changes in composition are worthy of comment. The most noticeable changes from the pulverized coal is the increase in the ash component, which is mostly due to the addition of the sorbent material, and the absence of volatiles. The sorbent material is limestone or dolomite, but

Table 2.2 Elemental Compositions of Some Typical Coals with Different Ranks

Coal	State	Seam	Overall Composition (mass %)				
			Carbon	Oxygen	Hydrogen	Sulfur	Nitrogen
Lignite	North Dakota	Coteau	72.38	20.53	5.30	0.67	1.12
Subbituminous B	Colorado	Unnamed	77.69	14.98	5.24	0.49	1.60
High-volatile C bituminous	Illinois	5	81.41	7.89	5.64	3.50	1.56
High-volatile B bituminous	Illinois	6	81.96	10.23	4.98	1.18	1.65
High-volatile A bituminous	Pennsylvania	Pittsburgh	82.92	6.34	5.91	3.03	1.80
Medium-volatile bituminous	West Virginia	Sewell	89.47	3.49	4.93	0.45	1.66
Low-volatile bituminous	West Virginia	Pocahontas 3	91.36	2.07	4.60	0.73	1.24
Anthracite	Pennsylvania	Lykens	94.88	1.78	1.83	0.84	0.67

Adapted from Martin A. Elliot and G. Robert Yohe,
 "The Coal Industry and Coal Research and Development in Perspective," Chemistry of Coal Utilization,
 John Wiley and Sons, 1981

for the sake of simplicity it is considered to be mainly calcium oxide, CaO. The ash component is also increased by the carbonization process in that natural oxygen in the coal is transferred to mineral oxides present in the coal itself. Another change, is the decrease in the levels of organic and pyritic sulfur, however the overall level of sulfur does not change significantly. The pyrolysis process utilized in the HIPPS concept introduces sufficient amounts of the sorbent to capture a large percentage of the released sulfur species. This captured sulfur is transferred to the ash component in the form of calcium sulfide, CaS. A comparison between the HIPPS design coal, a Pittsburgh No. 8 coal, and the HIPPS char after the pyrolysis has occurred can be seen in Table 2.3. It is evident from this table that as a result of the pyrolysis process there has been a marked decrease in the levels of volatile matter, moisture, and hydrogen. The volatile matter and the moisture are driven off by the high temperatures required to form the char, and the hydrogen is transformed into various gaseous compounds, mainly methane, CH₄. The most noticeable change is the increase in the level of ash materials, which is possibly due to two factors: (1) the addition of calcium oxide to capture the released sulfur species, and (2) the further oxidation of some of the mineral components of the coal. It should be noted that in the ultimate analysis of the HIPPS char a negative value is listed for the weight percent of oxygen. A possible interpretation is that the oxygen was determined by difference calculation, that is after adding up the rest of the measured constituents whatever remains is oxygen, and therefore, it may represent an accumulation of the experimental errors.

Table 2.3 Comparison of HIPPS Design Coal to HIPPS Char

	Pittsburgh No. 8	HIPPS Char
Proximate Analysis		
(weight %)	(as received)	(as received)
Fixed Carbon	48.15	59.63
Volatile Matter	35.91	5.25
Ash	9.94	34.26
Moisture	6.00	0.86
Total	100.00	100.00
Ultimate Analysis		
(weight %)		
Carbon	69.36	67.36
Oxygen	11.41	-7.99
Hydrogen	5.18	0.37
Sulfur	2.89	4.65
Nitrogen	1.22	1.05
Ash (ignited basis)	9.94	34.56
Total	100.00	100.00
Ash Analysis		
(weight %)		
Silicon Dioxide	47.86	30.69
Ferric Oxide	24.08	11.86
Aluminum Oxide	22.19	13.53
Potassium Oxide	1.49	1.08
Titanium Dioxide	1.29	0.69
Calcium Oxide	1.29	23.82
Sulfur Trioxide	0.80	17.16
Magnesium Oxide	0.60	0.88
Sodium Oxide	0.30	< 0.1
Phosphorus Pentoxide	0.10	0.20
Nickel Oxide	NIL	0.10
Total	100.00	100.00

Adapted from Foster Wheeler Development Corporation (FWDC),
"Fuel Analysis", FWDC, 26 Aug. 1997, 1

Forms of Sulfur Compounds in Coal/Coal Char

As mentioned earlier, there are two main categories of sulfur in coal. However, sulfur is usually found in three forms: (1) organic, (2) pyritic, and (3) secondary sulfates . Organic sulfur is left over from the biological material that over time formed coal, and as such is not simply physically bound to the coal structure, it is chemically bound. Organic sulfur is the primary sulfur form in those coals of low overall sulfur content. As the overall level of sulfur increases, the amount of organic sulfur can increase to as much as one percent of the overall weight of the coal. As mentioned earlier, organic sulfur cannot be removed by ordinary physical methods. The first form of inorganic sulfur is that of the iron sulfides, or pyrite and marcasite. Pyrites are normally physically bonded to the coal, and can occur in clumps, bands, or as finely scattered particles. Larger pyrite particles can be separated by conventional means, but finer particles are more elusive and require special treatment. The second form of inorganic sulfur, and the last main form of sulfur in coal, is mineral sulfates. Sulfates are usually found in such small amounts as to be of little or no concern to the use of the coal. Sulfates can be removed, should the need exist, by simple physical methods. The sulfur composition of the HIPPS char is different from that of raw coal, as can be seen in Table 2.4. The most obvious difference between the HIPPS char and the various coals is the forms of sulfur that are present in the HIPPS Char. The raw coals have pyritic sulfur and organic sulfur of varied levels, while the HIPPS char has organic sulfur but no pyritic sulfur. The sulfur that was bound up in the

Table 2.4 Comparison of Sulfur Contents of Various Coals and HIPPS Char

	Coals (by seam)			
	Upper Freeport	Wyodak Anderson	Illinos #6	Pittsburgh
Pyritic Sulfur	1.77	0.17	2.81	1.37
Sulfate Sulfur	0.01	0.03	0.01	0.01
Organic Sulfur	0.54	0.43	2.01	0.81
Sulfide Sulfur	0.00	0.00	0.00	0.00
Overall Sulfur	2.32	0.63	4.83	2.19
				0.66
	Coals (by seam)			HIPPS Char
	Blind Canyon	Lewiston-Stockton	Beulah-Zap	
Pyritic Sulfur	0.24	0.16	0.14	0.00
Sulfate Sulfur	0.03	0.03	0.03	0.00
Organic Sulfur	0.35	0.52	0.63	2.04
Sulfide Sulfur	0.00	0.00	0.00	2.61
Overall Sulfur	0.62	0.71	0.80	4.65

note Values given are in percent of overall dry weight

Adapted from Argonne National Laboratory (ANL). Argonne Premium Coal Sample Analytical Data. Argonne, Illinois (1 Aug. 1996)
Online posting: <http://www.anl.gov/PCS/report/part2.html> (9 May 1998)

&

FWDC, "Fuel Analysis", FWDC, 26 Aug. 1997, 1

pyrite has been transferred to calcium sulfide. This is due to the addition of the sorbent material, calcium oxide, and its subsequent capture of the released sulfur species during the pyrolysis process. From the data given in this table, the level of total sulfur seems to have apparently increased, but this is not actually true. The process of pyrolysis causes a decrease in overall mass by a loss of volatiles, and by this concentrates the sulfur, which explains the seeming increase in sulfur. The last step in determining the possible fate of sulfur in the HIPPS process is to understand the behavior of the aforementioned sulfur compounds in a pyrolysis and combustion environment.

Behavior of Sulfur Compounds

The behavior of the four pertinent sulfur compounds is of great importance to the HIPPS concept. In the HIPPS process the sulfur species pass through two different process environments; (1) pyrolysis (reducing), and (2) combustion (oxidizing). The fate of sulfur species in the pyrolysis section of the HIPPS concept has been determined by actual pyrolysis testing. Foster-Wheeler has performed feasibility trials on the pyrolysis section and that information, in the form of char analysis and char samples, has been passed on to UTSI to assist in evaluating the HITAF section. With this information in mind, a brief discussion of the behavior of sulfur compounds in a combustion environment would assist in the understanding the fate of sulfur species in the HITAF section.

The behavior of organic sulfur in a combustion environment is of particular importance to the HIPPS process, as nearly half of the total sulfur in the HIPPS char is in this form. The combustion of coal leads to the oxidation of the chemically bound sulfur. This oxidation of organic sulfur is an involved and complex process, and through a complicated series of reactions gets converted to sulfur dioxide, SO₂. Equations 2.1 through 2.3 show a few of the possible reactions involved in this process.

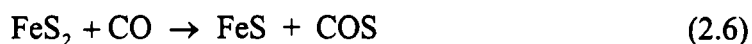


Pyritic sulfur has been studied extensively due to its influence on corrosion and slag formation. Pyritic sulfur decomposes in three different ways depending on the gaseous environment. In the absence of air, the pyrites decompose to iron, iron sulfide, and sulfur. Equations 2.4 and 2.5 show the steps involved in this thermal decomposition.



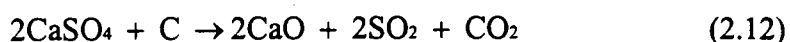
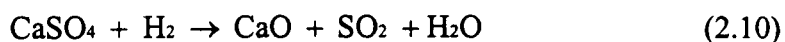
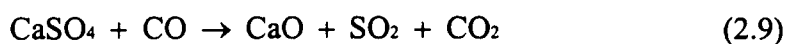
The second way is by decomposition in an air rich environment. During this process the additional oxidation of sulfur to sulfur dioxide and iron to iron oxide, FeO_x, further complicates matters. The third way is in a reducing environment which is similar to that of the pyrolysis process. Sulfur species evolved under reducing conditions can form

sulfides if it migrates through the ash or slag deposits (Reid 1402). The HIPPS pyrolysis section is under reducing conditions and the vaporization of iron sulfide and its subsequent capture by the calcium oxide sorbent is a possible reason for the lack of any pyritic sulfur in the analysis of HIPPS char as shown in Table 2.4. The following equation shows possible reactions leading to the formation of calcium sulfide from the sulfur species released during pyrolysis.



Since the vast bulk of pyritic sulfur is most likely transformed to mineral sulfides during the pyrolysis, the fate of pyrites is of consequence only in the pyrolyzer.

The third form of natural sulfur in coal, mineral sulfates (CaSO_4 or FeSO_4), is usually of little importance in either a pyrolysis or combustion process. In a reducing environment, like the HIPPS pyrolyzer, calcium sulfate can undergo a large number of reactions, shown in equations 2.9 through 2.12.



As can be seen from these reactions the only sulfur product from this reaction is sulfur dioxide, but, due to the initially low levels of CaSO_4 , in the coal, it is of little concern. Budnikoff and Syrkin investigated the thermal decomposition of calcium sulfate in an air environment. Their research showed that calcium sulfate remained stable until around 2500 °F, at which temperature there was an almost complete conversion of CaSO_4 to SO_2 and CaO (Swift et al. 7). This temperature is well beyond the maximum HITAF combustion temperature and when coupled with the insignificant initial levels of CaSO_4 , discounts any serious evolution of sulfur containing compounds by this means.

Calcium sulfide, which is only found in the HIPPS char, is perhaps the most relevant form of sulfur for the HITAF section of the HIPPS project. The oxidation of calcium sulfide to form calcium sulfate, naturally found as gypsum, has been thoroughly investigated as a means of producing sulfur dioxide. There are a large number of reactions that could possibly occur with CaS and air, but two main reactions have been determined to be most probable (Swift "Decomposition of Calcium Sulfate in a..." 323). They can be seen in equations 2.13 and 2.14.



From Loebach's investigations of the oxidation of calcium sulfide, it can be seen that the decisive factor, concerning the most likely of the two previous reactions is the

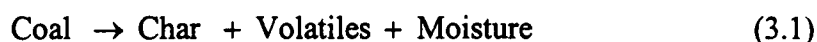
temperature at which they occur. For lower temperatures, up to about 1800 °F, the second reaction appears to have the highest probability of completion, while the first reaction is dominant above this temperature (Loebach 76). The HITAF's highest temperature is designed to be 2400 °F, however the average operating temperature may be approximately 1900 °F. Due to the fact that the range of operating temperatures may overlap the transition temperature for the above two reactions, it is possible that one or both reactions may assume dominance and this uncertainty leads to the investigation undertaken in this thesis.

CHAPTER III

COAL CHAR / CALCIUM SULFIDE OXIDATION BEHAVIOR

Reactions of Concern

The HIPPS concept is concerned with a combination of two processes. As mentioned earlier the first process, pyrolysis, is very similar to the process by which coke is manufactured. This process concerns the heating of coal to elevated temperatures in an environment that hinders the combustion of the coal. The pyrolysis process involves the thermal decomposition of the coal, during which there is a marked decrease in volatiles, moisture, and bulk density.



As with all coal-based processes, the evolution of gaseous sulfur compounds is of concern. In the pyrolysis process, the pyritic, sulfur compounds will also thermally decompose thereby releasing sulfur to form hydrogen sulfide, H_2S , and/or sulfur dioxide, SO_2 . The HIPPS concept remedies this problem by introducing a sorbent, limestone, into the coal as it enters the pyrolyzer. When the pyritic sulfur is released it migrates through the coal/sorbent mixture and reacts with the sorbent to form calcium sulfide, CaS .



The main drawback of this reaction is that the sulfur, while being captured, is not removed from the system. The char/sorbent/calcium sulfide mixture is transferred to the second step in the HIPPS system, the HITAF. The purpose of the HITAF is to combust this char mixture and transfer the heat evolved into an air stream and a steam cycle. These two cycles in turn are used to actually produce a nearly half of the electricity generated by the HIPPS concept.

In order to determine the fate of sulfur species in the HITAF, one must first determine the sulfur containing compounds present before the combustion process occurs, and then determine the sulfur containing compounds after combustion. Before the combustion process the sulfur is in two main forms, organic sulfur and mineral sulfur. The organic sulfur is chemically bound to the char and will therefore be directly affected by the combustion process. The mineral sulfur is not only composed of the calcium sulfide from the pyrolysis process, but contains small amounts of pyritic sulfur that did not decompose in the previous step. The possible sulfur containing compounds that result from the combustion process are greatly dependent on the combustion conditions of the HITAF. However, the main sulfur compound resulting from the combustion of char is sulfur dioxide. In the HIPPS concept, it was originally proposed that the calcium sulfide would remain unchanged throughout the combustion process or would be separated from the

char and disposed of in a suitable landfill or will oxidize to CaSO_4 and then disposed of in a suitable landfill with combustor ash.

In order to determine the possible levels of sulfur dioxide released from the combustion process, the chemical reactions that best represent the release of sulfur must be defined. The first and most obvious reactions are concerned with the combustion of the char itself. Since the char is a heterogeneous compound, it is difficult to determine an exact chemical formula for its combustion, but, for the purposes of this investigation, it is appropriate to assume that the char is in effect mostly fixed carbon. This is valid assumption since the char is at least 60 percent carbon and as such will display similar behavior to fixed carbon in a combustion situation. The reason the char combustion is so important is that the organic sulfur, chemically bound to the char, will be released as the char combusts. This released sulfur will form sulfur dioxide in the manner shown in the following equation.



For this reason, the following two combustion reactions can be used to describe the char combustion and can be directly correlated to the release of organic sulfur.



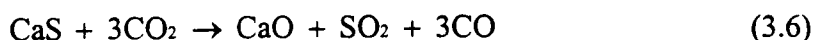
The first reaction is for complete combustion of carbon and is the desired reaction. The second reaction is considered incomplete combustion. The first reaction is favored at higher temperatures and will be the most likely carbon combustion reaction in the HITAF.

The next two reactions are concerned with the combustion of calcium sulfide.



As can be seen, both of these reactions are similar to the previous carbon combustion reactions and, indeed, will behave in much the same manner. The second reaction is the most desirable from the view point of the HIPPS concept as there is no sulfur dioxide produced or released and the calcium sulfate can then be disposed of with the ash in a landfill.

While the reactions of calcium sulfide and oxygen are of the most concern, there exists several other reactions concerned with the decomposition of calcium sulfide. Of these reactions the following two are considered the most likely to occur.



The first reaction is concerned with the decomposition of calcium sulfide by its reaction with carbon dioxide. As seen earlier, carbon dioxide will be abundant in the HITAF process as it is the desired product of the carbon combustion. The second reaction is concerned with the reaction of calcium sulfide and calcium sulfate, the latter of which is a product of one of the previously mentioned calcium sulfide combustion reactions. Neither of these two reactions is desirable as they both produce sulfur dioxide as a product. The first reaction is especially undesirable because it also produces carbon monoxide, which is a sign of incomplete combustion.

Thermodynamic Analysis of Oxidation

An investigation of the role of thermodynamics is required to satisfactorily determine the fate of sulfur species in the HIPPS HITAF process. The first step toward determining the thermodynamic effects on sulfur dioxide formation can be carried out by investigating the potential equilibrium compositions of the system. There are two main methods to determine the equilibrium compositions of a system, through determination of equilibrium constants or by the minimization of free energy.

Computational Determination of Equilibrium Compositions

The determination of equilibrium compositions using the equilibrium constant method requires the use of reactions to describe the system. The initial steps in this method require the calculation of equilibrium constants for each reaction to be considered. The

calculation of equilibrium constants is straightforward. Equilibrium constants are a function of temperature only and, as a first step, are calculated at a standard temperature, 298.15 K, for each reaction. Since the standard Gibbs energy of each reaction, ΔG° , is related to equilibrium constants by the following equation:

$$\Delta G^\circ = -RT \ln K \quad (3.8)$$

where R is the universal gas constant and T is the absolute temperature in Kelvin. Once this equilibrium constant has been found for each reaction, it is possible to determine equilibrium constants for each reaction over the full range of HITAF temperatures, 1400 °F to 2400 °F. This is done by determining a generalized equation describing the equilibrium constant as a function of temperature. The effects of temperature on equilibrium constants are related to the standard heats of reaction, ΔH_{298}° , for each reaction. Additionally, ΔH° is related to the heat capacities of each component involved in each of the reactions. The following two equations show this relationship:

$$\ln K = \int \frac{\Delta H^\circ}{RT^2} dT + I \quad (3.9)$$

$$\Delta H^\circ = \int \Delta C_p^\circ dT + J \quad (3.10)$$

where I and J are integration constants that must be determined. The change in ideal gas heat capacity, ΔC_p° is calculated using constants that can be found in almost any

compilation of thermodynamic data. The following equation shows how to calculate the heat capacity of each component:

$$\frac{C_p^\circ}{R} = A + BT + CT^2 + \frac{D}{T^2} \quad (3.11)$$

From the previous three equations, it is possible to determine the generalized equation of the equilibrium constants for each reaction. First equation 3.11 is substituted into equation 3.10, and then equation 3.10 is substituted into equation 3.9. Next the substituted form of equation 3.9 is integrated, resulting in the following equation:

$$\ln K = -\frac{J}{RT} + \Delta A \ln T + \frac{\Delta B}{2}T + \frac{\Delta C}{6}T^2 + \frac{\Delta D}{2T^2} + I \quad (3.12)$$

Once this equation has been determined all that remains before calculation is the determination of both of the integration constants. This can be done by first integrating equation 3.10 and solving for J using the reference value of ΔH° at 298 K. The remaining constant, I, can be determined by solving equation 3.12 for I using the value of $\ln K$, calculated from equation 3.8, and the value for J determined previously. From this it is possible to determine the feasibility of this method of determining the equilibrium compositions. Figure 3.1 shows the behavior of $\ln K$, for each reaction, as a function of temperature, over the HITAF temperature range. Table 3.1 shows the determined values of ΔH_{298}° , ΔG_{298}° , K_{298} , I, and J for each reaction of concern..

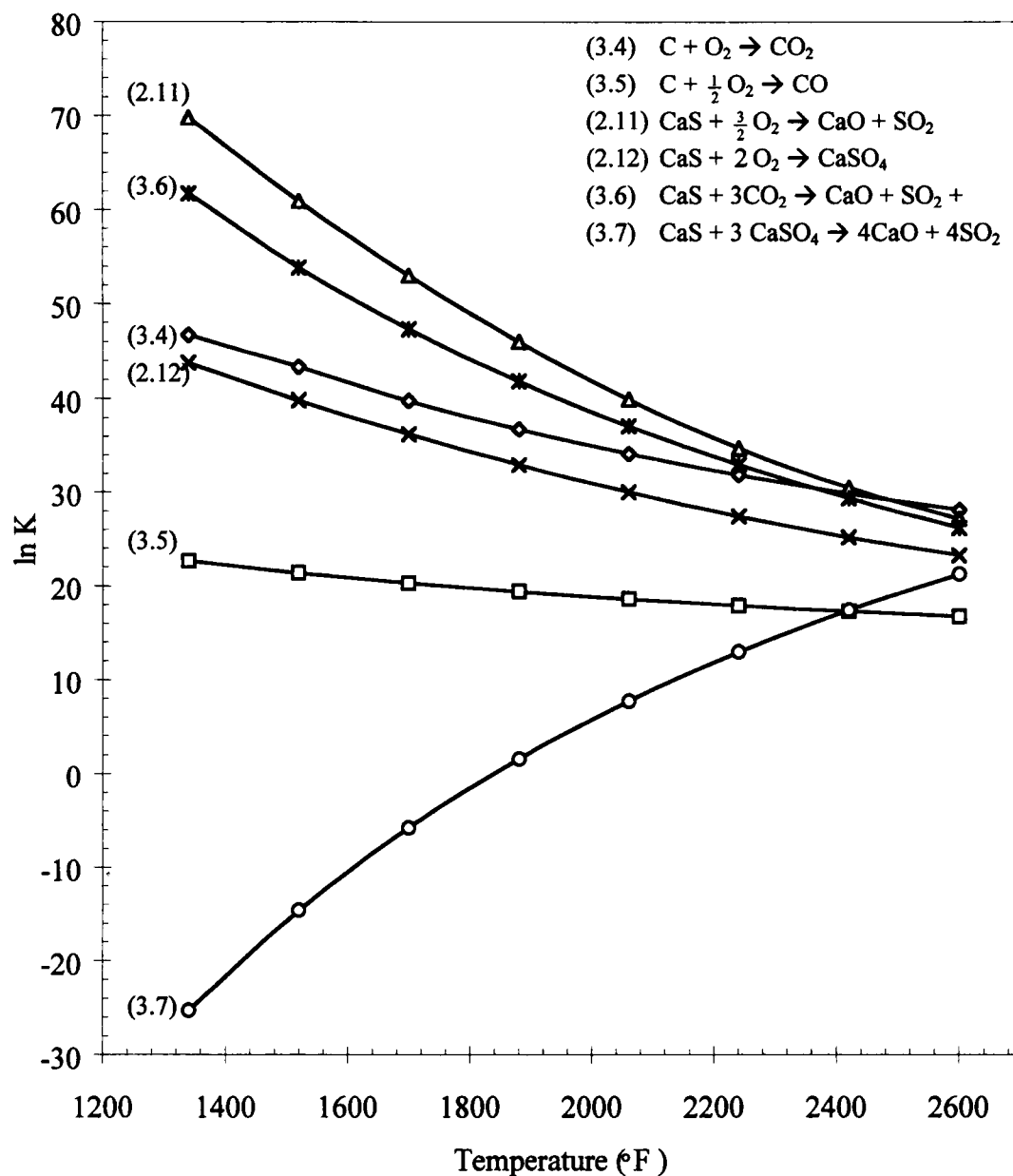


**Figure 3.1 Equilibrium Constants as a Function of Temperature
for the Six Reactions of Interest in the HITAF**

Table 3.1 Thermodynamic Data for the Reactions of Concern*

Reaction	ΔG_{298}° (J/mol)	ΔH_{298}° (J/mol)	K_{298}	I	J (J/mol)
$C(s) + O_2 \rightarrow CO_2$	-394648	-393777	1.070×10^{69}	.1333	-47363
$C(s) + \frac{1}{2} O_2 \rightarrow CO$	-137361	-110599	1.080×10^{24}	10.6267	-13577
$CaS(s) + \frac{3}{2} O_2 \rightarrow CaO(s) + SO_2$	-430738	-453599	3.774×10^{68}	-38.1244	-55493
$CaS(s) + 2 O_2 \rightarrow CaSO_4(s)$	-832335	-939644	2.126×10^{35}	-46.0043	-112721
$CaS(s) + 3CO_2 \rightarrow CaO(s) + SO_2 + 3CO$	-664629	-725248	2.691×10^{116}	-53.2327	-88981
$CaS(s) + 3 CaSO_4(s) \rightarrow 4CaO(s) +$	774053	1004053	5.698×10^{-145}	-14.4846	116189

* Compounds are gas phase unless otherwise indicated.

It is known from thermodynamics that an exothermic reaction displays a decrease in $\ln K$ as temperature increases. From Figure 3.1, it can be seen that the first five of the six reactions of concern are exothermic, and the sixth is endothermic. Also, it is evident that there is a large magnitude change in the values of the equilibrium constants for the six reactions. As a result, any attempt to use the equilibrium constant method of determining equilibrium concentrations/compositions would prove to be difficult due to the intense nature of the calculations and the large variation in the values of the constants. Because of this the second method was chosen in this work.

The second method, which involves a minimization of free energy, does not require the identification of reactions in order to determine equilibrium concentrations/compositions. Minimization of free energy treats each component independently and computer code currently exists utilizing this method. The code used for the determination of equilibrium

compositions, "Chemical Equilibrium and Applications" (CEA), was developed by Sanford Gordon and Bonnie J. McBride for the National Aeronautics and Space Administration (NASA). The equilibrium program was developed in part to assist in the determination of chemical rocket combustion conditions, however the same methodology can also be applied in the determination of the HIPPS HITAF combustion situation.

The program can determine equilibrium compositions for a wide variety of situations. The input situation utilized in this thesis was for a set reaction temperature and pressure. For a given temperature and pressure situation, the CEA program utilizes a minimization of total Gibbs free energy to determine equilibrium composition. Table 3.2 lists the calculated equilibrium compositions as determined by the CEA program, for the temperature range predicted in the HITAF. A complete listing of inputs to and outputs from the CEA program can be seen in Appendix I.

From the data in Table 3.2, it is possible to forecast, that based on equilibrium conditions, there will be a production of sulfur dioxide at the high end of the HITAF temperature range. In the literature, Swift indicates from other's experimentation, that the oxidation of calcium sulfide will follow the theoretical equilibrium behavior (Swift et al. 36). This would be further supported by the larger equilibrium constant calculated for reaction 2.13, when compared to the equilibrium constant for reaction 2.14. From the thermodynamic data it is expected that carbon dioxide will be favored over carbon monoxide as a product of char combustion.

Table 3.2 Equilibrium Gas Compositions
Determined by Minimization of Gibbs Free Energy*

		Temperature (°F)					
	Input Gas	1400	1600	1800	2000	2200	2400
Gaseous Phase Components							
N₂	0.8290	0.8270	0.8270	0.8270	0.8268	0.8254	0.8241
O₂	0.1387	0.0324	0.0324	0.0323	0.0323	0.0327	0.0329
CO₂	0.0323	0.1317	0.1329	0.1329	0.1329	0.1327	0.1325
H₂O	0.0000	0.0042	0.0042	0.0042	0.0042	0.0042	0.0042
SO₂	0.0000	0.0000	0.0000	0.0000	0.0001	0.0011	0.0020
NO	0.0000	0.0000	0.0001	0.0001	0.0002	0.0004	0.0008
Condensed Phase Components							
CaCO₃		0.0014	0.0000	0.0000	0.0000	0.0000	0.0000
CaO		0.0000	0.0014	0.0014	0.0015	0.0026	0.0035
CaSO₄		0.0020	0.0020	0.0020	0.0020	0.0009	0.0000

* Listed values are mole fractions of components.

Effects of Reactor Conditions on Equilibrium Compositions

There are three main factors relating to the reactor conditions that can affect the conditions at equilibrium. The first is temperature, which as indicated earlier is readily evident in the changing values of the equilibrium constants. As the temperature increases, there will be more complete combustion; however, the production of sulfur dioxide and nitrogen oxides also increase. This increase is undesirable. Unfortunately in order to reach the HIPPS efficiency goals a high temperature in the HITAF is required. For this reason the altering of the temperature range will have little justifiable positive effects on the equilibrium compositions. The second factor is pressure. As a system's pressure increases, reactions tend to favor condensed liquid and solid phase products. This would be beneficial, as a increase in pressure would hinder the production of sulfur dioxide and nitrogen oxides. Unfortunately, the pressure of the system will also affect the combustion process by hindering the rate of formation of desired gaseous compounds, and therefore again negatively affect the efficiency of the HIPPS process. The third consideration is the residence time of the particles in the HITAF. The residence time of the particles is related to the temperature profile of the HITAF, with the hottest zone being at the inlet nozzle, and the coolest toward the end of the combustor. The residence time is a function of the vitiated air flow rate, where a high flow rate will force the particles to exit the higher temperature zones faster. The negative side to this factor is also related to the combustion process, for as the particles exit the high temperature zones faster the efficiency of the HIPPS process decreases due to poor/incomplete combustion caused by the reduced residence time in the high temperature zone.

Combustion Kinetics of Calcium Sulfide and Organic Sulfur

The kinetics concerning the formation of sulfur dioxide is of great interest with regards to the fate of sulfur species in the HIPPS process. As indicated earlier, sulfur dioxide is formed from two main sources in the HIPPS process. The first source being organic sulfur released during the combustion of the char in the HITAF, and the second being the oxidation of calcium sulfide. The oxidation of organic sulfur was shown in equation 3.3, and can be directly related to the oxidation of the char. The oxidation of calcium sulfide is most likely equilibrium controlled, and, as shown in equations 2.11 and 2.12, will occur during the combustion process. The effects of organic sulfur derived sulfur dioxide may drive the oxidation of calcium sulfide toward the solid product, calcium sulfate. However the extent of this effect is unknown and may not occur to a beneficial extent. For this reason, the important kinetics is that of the char combustion reaction, for which the desired reaction is shown in equation 3.4, and its respective sulfur dioxide production.

The reaction of carbon with oxygen to produce carbon dioxide is dependent on the amount of solid carbon present and the level of oxygen available in the gas stream. When excess oxygen is present, the reaction is limited only by the amount of carbon. Since two different kinetic situations exist in the planned experiments, both kinetics must be evaluated to more fully understand the production of sulfur dioxide and the ultimate fate of sulfur in the HITAF. The first type of kinetics to be investigated is that of a fixed bed process, in which the solid reactant is stationary, but the products are removed from the

reaction area. The second type of kinetics to be investigated is that for entrained particle flow. To simplify this investigation both types of kinetics will be developed as a batch process. This is justifiable for the fixed bed reactor because, despite the fact that the oxygen stream is flowing through the system, it is to be in such an excess as to have little negative effect on the combustion processes under investigation. The justification for the use of batch for entrained particle flow is because as the particles travel through the reactor, they are in contact with their own gaseous environment/cloud throughout the reactor, therefore simulating a potential batch reactor behavior.

The reaction of carbon and oxygen is a well studied reaction and the literature indicates that it is first order when oxygen is in excess. The first step in determining the kinetics is the development of a material balance. A general material balance is as follows:

$$\text{Input} + \text{Generation} = \text{Output} + \text{Accumulation} + \text{Disappearance} \quad (3.13)$$

From this material balance it is possible to eliminate terms that are negligible for each of the kinetics to be studied. For these investigations, the input and output terms are negligible, since the reaction is based on batch of solid carbon. The material balance for the fixed bed kinetics is as follows:

$$\overset{0}{\cancel{\text{Input}}} + \overset{0}{\cancel{\text{Generation}}} = \overset{0}{\cancel{\text{Output}}} + \text{Accumulation} + \text{Disappearance} \quad (3.14)$$

Upon evaluation of the remaining terms, it is found that the disappearance term represents the loss of carbon due to chemical reaction, and the accumulation term represents the rate of accumulation of carbon in the reactor. The disappearance term is found to be:

$$\text{Disappearance} = -r_C W_C \quad (3.15)$$

where $-r_C$ has the units of $\frac{\text{moles carbon}}{(\text{sec onds})(\text{grams carbon})}$ and W_C has the units of grams carbon. The accumulation term is found to be :

$$\text{Accumulation} = \frac{dN_C}{dt} \quad (3.16)$$

where N_C represent the moles of carbon in the bed at any time t . Substitution of equations 3.15 and 3.16 back into equation 3.14 yields the following:

$$0 = -r_C W_C + \frac{dN_C}{dt} \quad (3.17)$$

Since $-r_C$ is the specific reaction rate for the combustion of carbon, it is desirable to rearrange the above equation to solve for it as:

$$-r_C = \left(\frac{1}{W_C} \right) \frac{dN_C}{dt} \quad (3.18)$$

It is possible now to relate the mass of carbon, W_C , present to that of the mass of the carbon initially present. This is as follows:

$$W_C = W_{C0}(1 - X_C) \quad (3.19)$$

$$\frac{dW_C}{dt} = -W_{C0} \frac{dX_C}{dt} \quad (3.20)$$

where W_{C0} is the initial mass of carbon and X_C is the overall conversion of carbon. The mass of carbon in the reactor can also be related to the moles of carbon present. This is simply done as follows:

$$W_C = MW_C(N_C) \quad (3.21)$$

$$\frac{dW_C}{dt} = MW_C \frac{dN_C}{dt} \quad (3.22)$$

where MW_C is the molecular weight of carbon. Equation 3.22 can now be rearranged and substituted into equation 3.18, which leads to the following:

$$-r_C = \left(\frac{1}{(W_C)(MW_C)} \right) \frac{dW_C}{dt} \quad (3.23)$$

Substitution of equations 3.19 and 3.20 into equation 3.23 yields the following equation, which is in terms of the initial mass of carbon and the conversion of carbon:

$$-r_c = -\left(\frac{1}{(MW_c)(W_{c0}(1 - X_c))}\right)(W_{c0})\frac{dX_c}{dt} \quad (3.24)$$

After removal of cancelled terms, equation 3.24 gives:

$$-r_c = -\left(\frac{1}{(MW_c)(1 - X_c)}\right)\frac{dX_c}{dt} \quad (3.25)$$

which relates the specific rate of carbon combustion to the conversion of carbon at any time t .

Due to the small size of the particles and the elevated temperatures of the HITAF, it is logical to assume that there will be little mass transfer limitations to inhibit the conversion of carbon to carbon dioxide, and therefore, the rate of combustion will most likely remain constant. Since the specific rate is assumed constant, it is possible to determine the conversion of the carbon at any time t . Solving equation 3.25 by separation of variables yields an equation for carbon conversion as a function of time. This is as follows:

$$(-r_c)(MW_c)dt = -\left(\frac{1}{(1 - X_c)}\right)dX_c \quad (3.26)$$

$$(-r_c)(MW_c)t = \ln(1 - X_c) \quad (3.27)$$

$$X_C = 1 - e^{-(r_c)(MW_C)t} \quad (3.28)$$

Equation 3.28 shows the conversion of carbon as a function time, assuming a constant rate of reaction. It is now possible to determine an empirical relation for the production of sulfur dioxide from the combustion of char by relating it to the above conversion of carbon, which requires three main assumptions: (1) the conversion of carbon is directly related to the actual conversion of char, (2) the sulfur is homogeneously distributed in the char, and (3) the released sulfur species is in the monatomic form, S. From this equation 3.28 becomes:

$$X_S = \Phi X_C \quad (3.29)$$

where X_S is the extent of sulfur conversion at time t , determined by the empirical relation to X_C . This allows for the determination of sulfur remaining in the char at any give time by the following equation:

$$W_S = W_{S0} (1 - X_S) \quad (3.30)$$

where W_S is the mass of sulfur present and W_{S0} is the sulfur that was present initially. Once the conversion of char has been found, it will then be possible to determine the expected levels of sulfur dioxide produced by the char combustion. It is also possible to separate the levels of sulfur dioxide produced by organic sulfur from the sulfur dioxide produced from the oxidation of calcium sulfide. This is due to indications in the literature that calcium sulfide decomposes to measurable sulfur dioxide above 1750 °F.

Using another function relating the conversion of sulfur as a function of time and temperature, the levels of organic sulfur can be determined and subsequently subtracted.

$$X_{S\text{-organic}} = f(t, T) \quad (3.31)$$

$$X_{S\text{-sulfide}} = X_{S\text{-total}} - X_{S\text{-organic}} \quad (3.32)$$

This hypothesis will be verified during the bench-scale tests and used during the study of entrained particle flow. It is during the entrained particle flow experiments that the function relating X_s to X_c will be determined. This will be done by performing a series of tests at various temperatures with a set gas and char flow rate, thereby minimizing the factors affecting char combustion. Once this is completed a relation between the combustion of char and the production of sulfur dioxide, from both sources, can be finalized.

CHAPTER IV

EXPERIMENTAL METHODS

Sulfur Content in HIPPS Char

An analysis of the HIPPS char, by FWDC, was provided with the char sample itself , therefore only a cursory analysis was required before testing could begin. The proximate, ultimate, and ash analyses provided with the char are shown in Table 2.3. The first test of the HIPPS char was undertaken in a LECO SC132 Sulfur Determinator, which calculated a percentage sulfur by weight, when the sample was combusted at 2400 °F in pure oxygen. From these tests it is possible to verify the total sulfur in the HIPPS char, as reported in the analysis from FWDC. The LECO SC132 functions by combusting the sample, HIPPS char, rapidly in a pure oxygen environment releasing sulfur. The sulfur combines with oxygen to form sulfur dioxide, SO_2 . The combustion gases are then sent to an infrared (IR) detection tube, which determines the levels of sulfur dioxide in the air. Sulfur dioxide absorbs a specific wavelength of the IR spectrum and the detector determines the levels of sulfur dioxide in the gases by determining the decrease in the relative intensity of the detected IR light. Once the amount of sulfur dioxide in the gas has been determined the value at that time increment is output to the display/printer. When the sample has been completely combusted, the LECO SC132 calculates the total sulfur in the sample using an integration of the IR detector outputs and the initial weight

of the sample. These values are then output to and printed by the display/printer. A simplified schematic of the LECO SC132 can be seen in Figure 4.1.

After the verification of the total sulfur as reported by FWDC, further tests were undertaken in the LECO SC132. These tests were designed to show the amounts of sulfur dioxide produced during combustion of HIPPS char samples at various temperatures, in pure oxygen or air. The data measured during this portion demonstrated the amounts of sulfur dioxide detected over a period of time, however the values listed are dimensionless due the fact that the exact flow rate of the gas through the LECO was not known, and as such were only qualitative. Despite the qualitative nature of this data, it is considered valuable in that it shows the effects of temperature on rate and overall amounts of sulfur dioxide formed. These tests were performed for three different materials, a commercially simulated char, calcium sulfide, and an actual sample of the FWDC provided HIPPS char. The commercial char is different from the HIPPS char in that it was generated by physically mixing a char with appropriate levels of sorbent and calcium sulfide. Its inclusion in these test was to determine whether or not the calcium sulfide was made less reactive by the thermal conditions of the pyrolyzer, as the commercial char's calcium sulfide did not undergo such treatment.

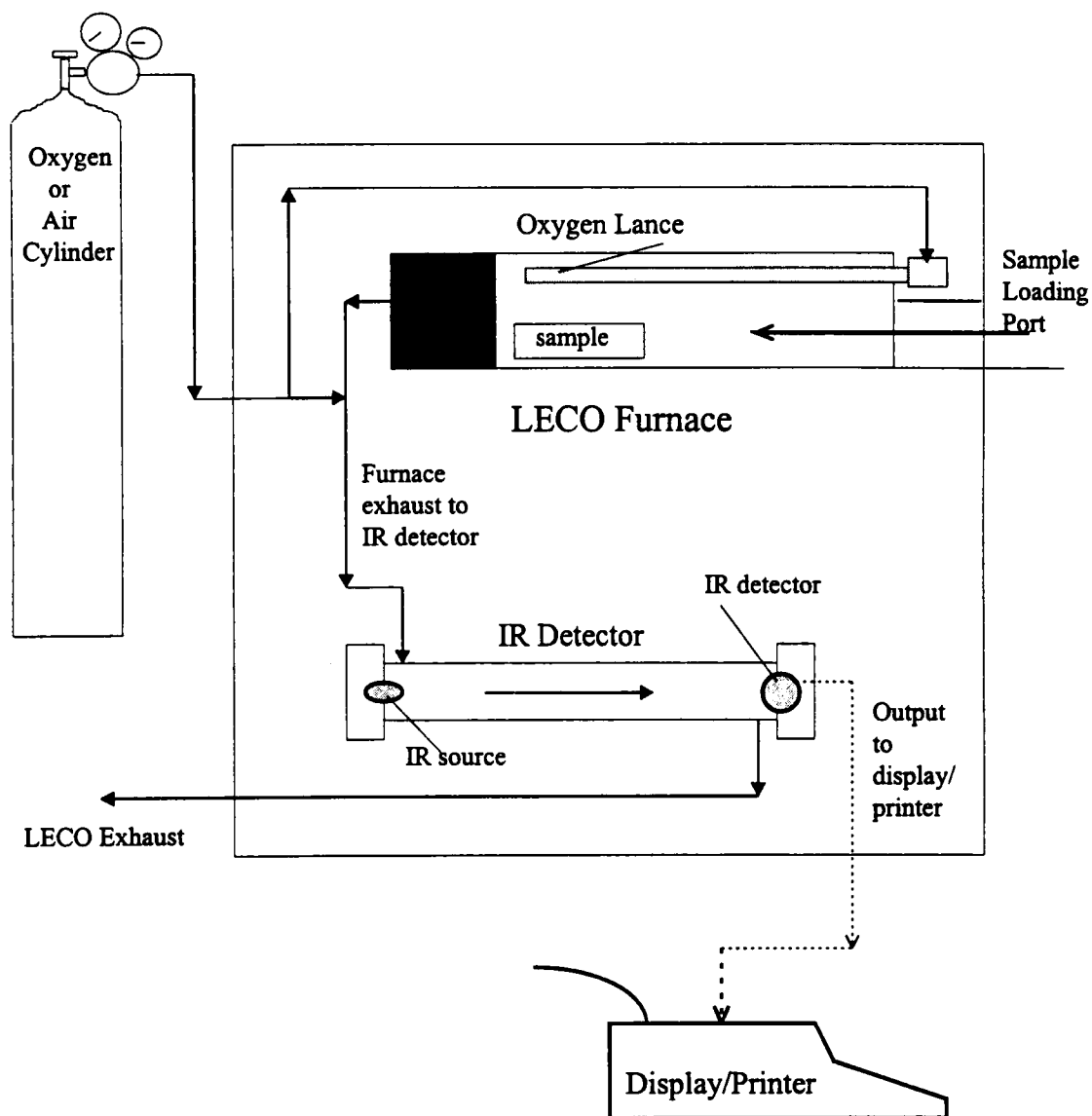


Figure 4.1 Simplified Schematic of LECO SC132 Sulfur Determinator

Thermogravimetric Analysis

The next series of tests was performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. In these tests the previous sample materials and one additional mixture of calcium sulfide, CaS, and calcium sulfate, CaSO₄, were tested to determine the weight loss versus temperature in various gaseous environments: argon, oxygen, carbon dioxide, and air. The TGA determines the weight loss over a period of time through use of its internal microbalance, and correlates that to the temperature of the TGA furnace at each time step.

The temperature of the TGA is easily controlled, and a specific heating rate is input prior to the test. As the temperature increases, the sample loses or gains weight based on the reaction with the gas in contact with the sample. These TGA tests show the effects of the certain reactions pertinent to the HIPPS HITAF combustion environment. A schematic of the Perkin-Elmer TGA 7 can be seen in Figure 4.2. Additionally a diagram of the TGA 7 furnace is shown in Figure 4.3.

Bench-Scale Oxidation Studies

Once the initial experiments regarding sulfur dioxide evolution and weight loss in the TGA were determined, several series of bench-scale batch mode experiments were performed to determine the combustion behavior of the HIPPS char. In the first phase of these bench-scale experiments a reactor, with sealable ends, was heated to various

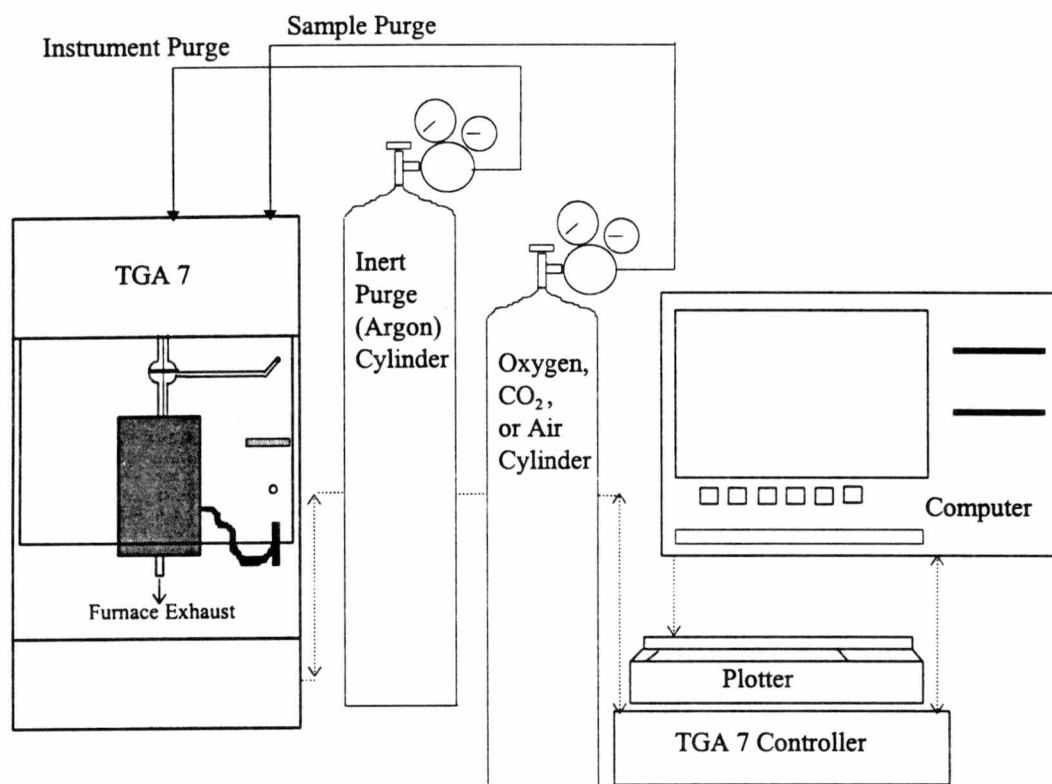


Figure 4.2 Schematic of the Perkin-Elmer TGA 7

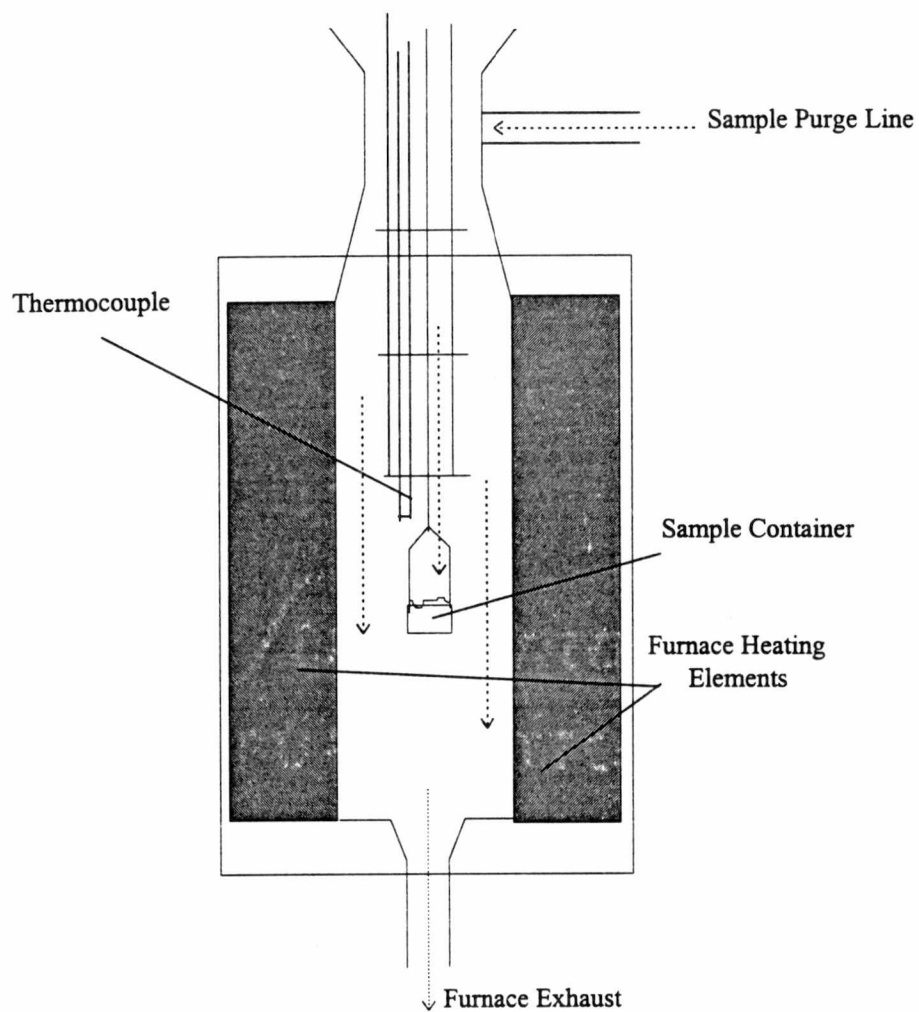
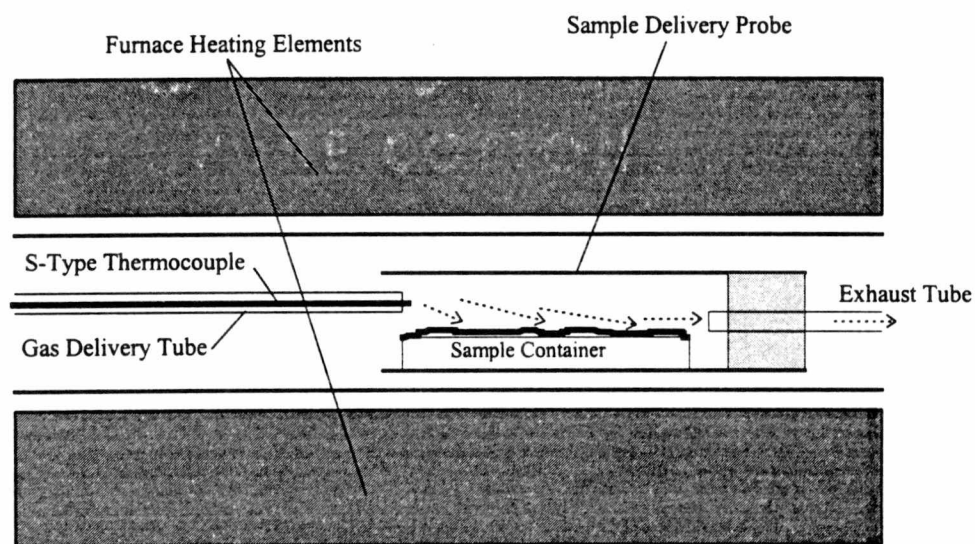
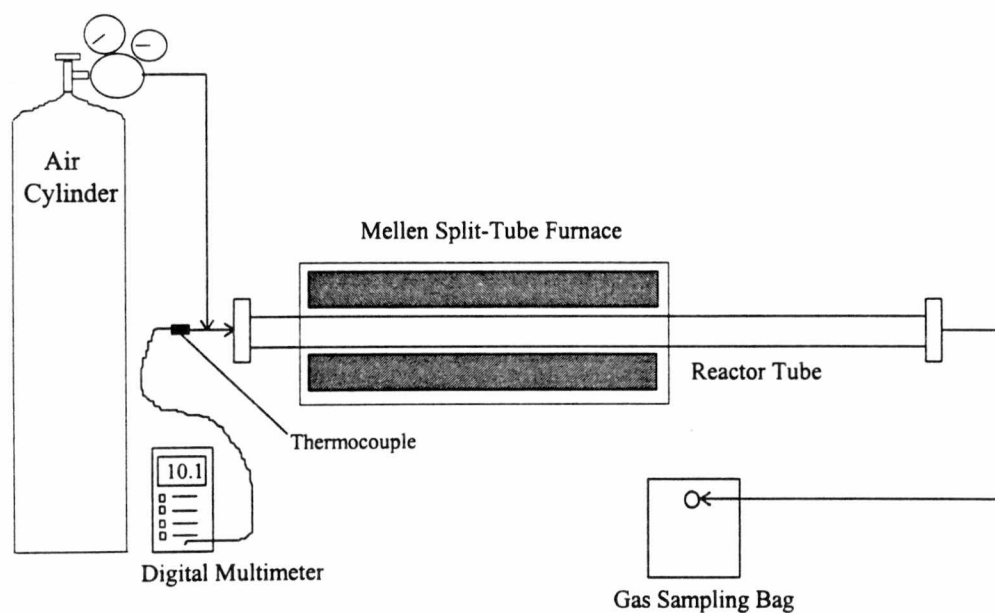


Figure 4.3 Schematic of the TGA 7 Furnace

temperatures in a Mellen Model TS-2200-231-3 split-tube furnace. The reactor tube, $2\frac{3}{4}$ -inches in outer diameter and five feet long, was composed of silicon carbide and was manufactured by INEX Incorporated. The reactor tube was fitted with flanged ends by INEX during the manufacturing process, which allowed for the ends to be sealed and the internal gaseous environment to be controlled. This tube was selected over stainless steel, due to its thermal characteristics. Once the desired temperature was reached and stabilized, a sample weighed on a Mettler PM2000 analytical balance, was inserted in the reactor tube and air, representative of the HIPPS input air, was passed over it and through the tube. The sample was introduced to the reaction zone by another silicon carbide tube, $1\frac{1}{2}$ -inches outer diameter and six inches long, which was fitted to a long tube of $\frac{3}{8}$ -inch diameter stainless steel tubing. A schematic of the bench-scale apparatus and the sample delivery probe are shown in Figure 4.4. The char is combusted and the off gases were passed down the tube and through a exit port in the end cap. These exhaust gases were then captured in gas sampling bags and tested in a SRI 8610C gas chromatograph. The purpose of these experiments was to determine concentrations and rates of combustion gases, such as carbon monoxide and carbon dioxide, produced in the reactor. This data showed the consumption of oxygen during combustion of the HIPPS char and the effects of temperature on the combustion process. The range of temperatures, 1400 °F to 2400 °F, investigated spans the temperatures proposed for in the HIPPS HITAF operations.



Cut-away view of Combustion Zone

**Figure 4.4 Schematic of Bench-Scale Oxidation Studies
(Phase 1 Experiments)**

The second phase of the bench-scale experiments was undertaken in a similar manner to the first phase of bench-scale tests. The purpose of the second phase experiments was to determine the rates and levels of sulfur dioxide formed during the combustion process. Several methods of detection were proposed and investigated, such as measurement of electrical conductivity, pH, and an online SO₂ analyzer. The electrical conductivity option was discarded because a suitable conductivity probe was not available and the construction of one was prohibitive. The pH alternative was discarded due to the minimal effect on the pH of a hydrogen peroxide solution that the expected levels of sulfur dioxide expected would have. For this reason an Enerac 2200 Boiler Gas Analyzer was chosen. This option was chosen as it was available on site and was simple to use with LabVIEW software extracting the various levels of carbon dioxide, carbon monoxide, nitrogen oxides, oxygen, and sulfur dioxide simultaneously present. However during testing of the apparatus it was determined that the Enerac 2200 was not functioning well and it was sent back for recalibration. During this down time, an alternative choice of analyzers was presented. The idea was to utilize the analysis capabilities of the LECO SC132's IR detector by passing the bench-scale apparatus' exhaust through the detector where the LECO furnace interfaces with the detector. While this alternative was readily available and functional, it required a calibration to determine a correlation between the display/printer readout and actual sulfur dioxide concentrations. A schematic of this set-up is shown in Figure 4.5.

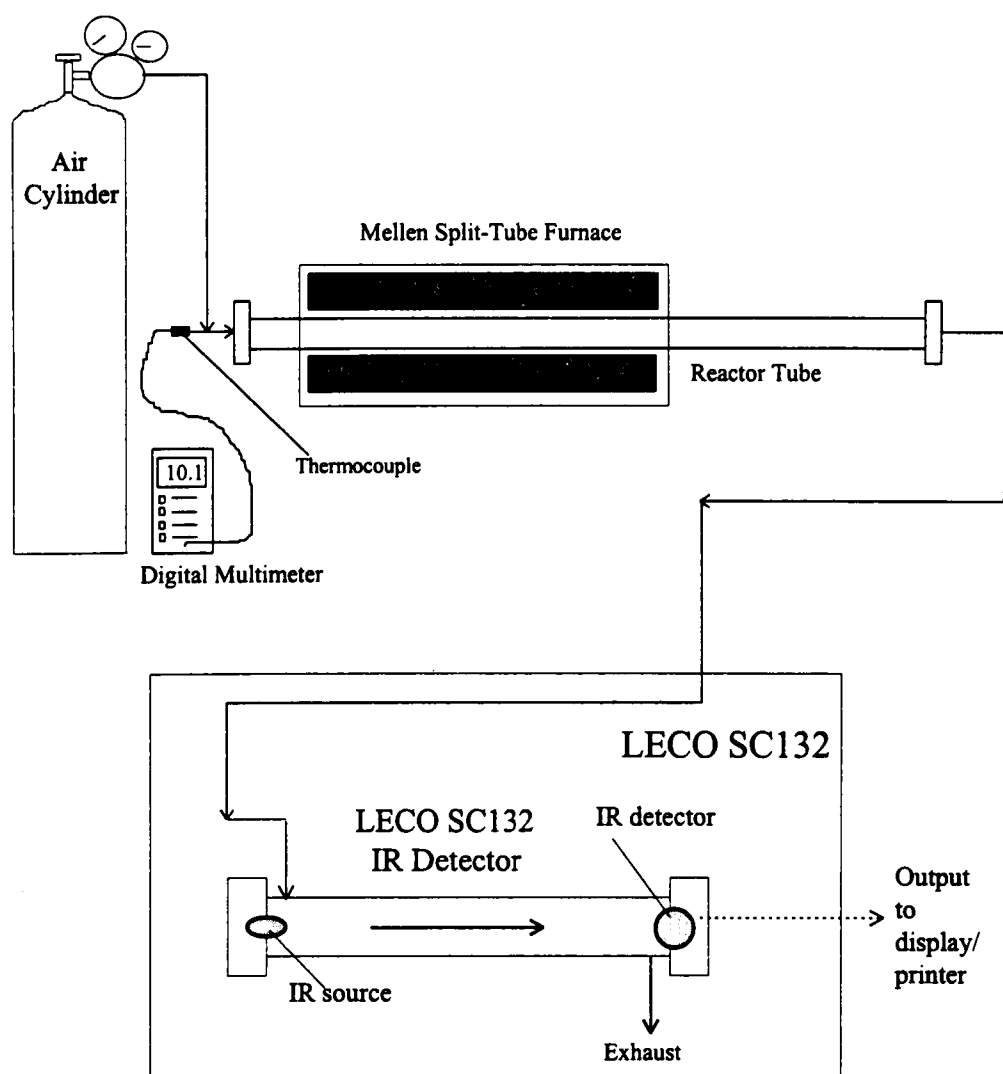


**Figure 4.5 Schematic of Bench-Scale Oxidation Studies
(Phase 2 Experiments)**

After the completion of the initially planned Phase 2 tests, it was determined later on that additional testing would be beneficial to understand the effects of combustion on sulfur dioxide production. These additional tests were designed to study the effects of the isothermal conditions on the combustion of char and resulting production of sulfur dioxide. The same apparatus used in the initial portion of Phase 2 was used to perform these experiments, with one major addition, the exhaust port from the LECO SC132 was routed into a gas sampling bag. This allowed for the capture of the combustion gases which were then tested in the SRI 8610 gas chromatograph used in earlier tests.

The third phase of the bench-scale tests involved a total redesign of the apparatus. In order to more effectively simulate the combustion conditions in the HITAF, the orientation of the apparatus had to be changed from horizontal to vertical. In the HITAF, the char would enter the combustor furnace and be entrained in the gas flow as it passes through, only being separated from the gas flow at the exit of the furnace. The Phase 1 and 2 experiments were not designed to simulate such entrainment of the char, and therefore, may not be adequate to determine the fate of sulfur species from the oxidation of calcium sulfide. This was based on the literature which indicates that the oxidation of calcium sulfide can be equilibrium dependent, and the Phase 1 and 2 experiments may not have allowed for the system to reach equilibrium. In the Phase 1 and 2 experiments, the gas flowed over the char sample which removed the sulfur dioxide that formed from calcium sulfide to oxidize to sulfur dioxide instead of calcium sulfate as sulfur dioxide

was not present to retard the forward reaction. Also, it is known that calcium sulfate is not the thermodynamically favored product at the lower temperatures. To counter this, the apparatus from the previous experiments was reoriented vertically and the char was entrained in the gas stream prior to entering into the heated zone of the furnace. The INEX reactor was replaced with a $\frac{3}{4}$ -inch outer diameter, 316 stainless steel tube, which allowed for a small enough area to insure that the char was forced downward at the gas velocity and not solely due to gravitational forces. The char was introduced into the gas stream through a separatory funnel. A vibrator was used to ensure that the char flowed smoothly through the funnel's stopcock and into the gas stream. This also allowed for better control of the char flow rate. After passing through the furnace, any ash or remaining char was separated from the gas stream and the gas was passed to the LECO IR detector to measure the levels of sulfur dioxide produced. A schematic of this set-up is shown in Figure 4.6.

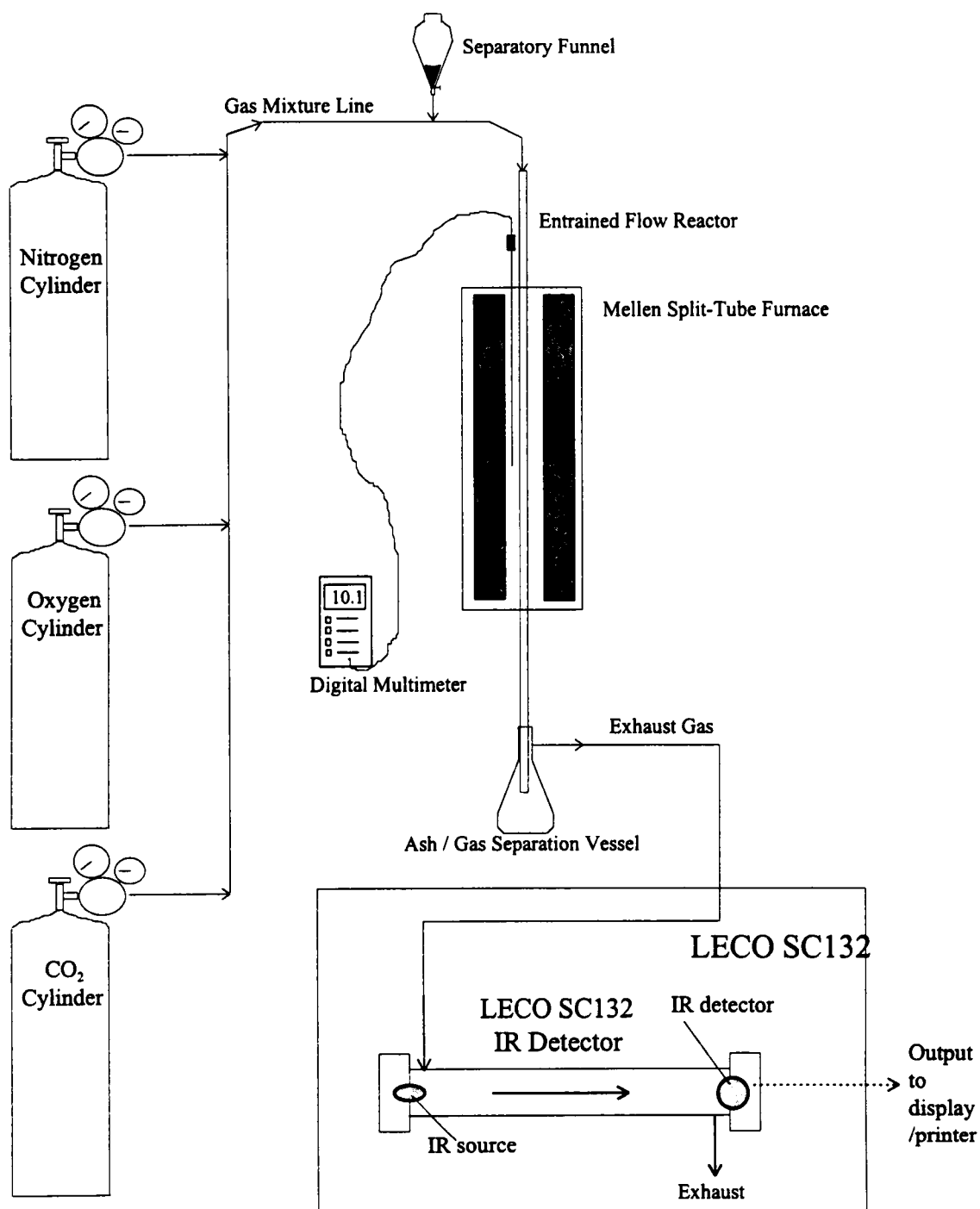


**Figure 4.6 Schematic of Bench-Scale Oxidation Studies
(Phase 3 Experiments)**

CHAPTER V

RESULTS AND DISCUSSION

Listing of Experiments

A listing of the conducted experiments is shown in Table 5.1. From this point on the experiment being discussed will be referred to by its respective number found in this table.

Analysis of HIPPS Char

The HIPPS char, provided by FWDC, was first analyzed to compare the amounts of sulfur, ash, volatiles, moisture, and fixed carbon to the respective amounts reported by FWDC, which can be seen in Table 2.3. As indicated in the previous chapter, the first test, Test 1.1, performed on this HIPPS char was undertaken with the intention of verifying the amounts of sulfur, as reported by FWDC. This measurement was performed using the LECO SC132 Sulfur Determinator, and gave a value of 4.61 wt. % sulfur. This value closely matched the value, 4.66 wt. % sulfur, reported by FWDC. The next two tests, Test 1.2 and 1.3, were undertaken to verify the reported values for the weight percent of ash, moisture, volatiles, and fixed carbon in the HIPPS char. A TGA analysis for the amount of ash in the char resulted in a value of 35.42 wt. % ash, which corresponded to a value of 34.26 wt. % ash as reported by FWDC. This analysis was

Table 5.1 Listing of Experiments Performed

Experiment Section	Test ID Number	Description of Experiment
Analysis of Char	1.1	Determination of sulfur in HIPPS char
	1.2	Determination of ash content in HIPPS char
	1.3	Determination of moisture and volatiles
LECO Analysis	2.1	Calcium sulfide at 1000 °F in pure oxygen
	2.2	Calcium sulfide at 1500 °F in pure oxygen
	2.3	Calcium sulfide at 2000 °F in pure oxygen
	2.4	Calcium sulfide at 2500 °F in pure oxygen
	2.5	Commercial char at 1500 °F in pure oxygen
	2.6	Commercial char at 2000 °F in pure oxygen
	2.7	Commercial char at 2500 °F in pure oxygen
	2.8	HIPPS char at 1500 °F in pure oxygen
	2.9	HIPPS char at 2000 °F in pure oxygen
	2.10	HIPPS char at 2500 °F in pure oxygen
	2.11	HIPPS char at 1800 °F in air
	2.12	HIPPS char at 2000 °F in air
	2.13	HIPPS char at 2200 °F in air
	2.14	HIPPS char at 2400 °F in air
TGA Analysis	3.1	Calcium sulfide under argon
	3.2	Calcium sulfide under carbon dioxide
	3.3	HIPPS char under carbon dioxide
	3.4	Calcium sulfide under air
	3.5	HIPPS char under air
	3.6	Calcium sulfide/calcium sulfate mixture under argon

Table 5.1 (continued)

Experiment Section	Test ID Number	Description of Experiment
Bench-Scale Tests		
Phase 1		<i>Non-Isothermal Tests</i>
	4.1	Combustion of HIPPS char at 1700 °F
	4.2	Combustion of HIPPS char at 1900 °F
	4.3	Combustion of HIPPS char at 2100 °F
		<i>Non-Isothermal Tests</i>
	4.4	Combustion of HIPPS char at 1350 °F
Phase 2a	4.5	Combustion of HIPPS char at 1725 °F
	4.6	Combustion of HIPPS char at 2035 °F
	4.7	Combustion of HIPPS char at 2140 °F
Phase 2b		<i>Isothermal Tests</i>
	4.8	Combustion of HIPPS char at 1350 °F
	4.9	Combustion of HIPPS char at 1500 °F
	4.10	Combustion of HIPPS char at 1650 °F
	4.11	Combustion of HIPPS char at 1900 °F
		<i>Isothermal Tests</i>
Phase 3		
	4.12	Entrained HIPPS char combustion at 2000 °F

performed under a pure oxygen environment to ensure 100 % combustion of the fixed carbon. It is important to note that the ash value resulting from this test also includes the solid products of any calcium sulfide combustion. A plot of this TGA run can be seen in Figure 5.1. Next to determine the amount of volatiles and moisture present in the char, a second TGA run was performed under an inert, argon, environment which resulted in a value of 1.13 wt. % volatiles, and a value of 0.625 wt. % moisture. The moisture value differs slightly from a reported value of 0.86 wt. % moisture from FWDC. However the value determined for the volatiles differs significantly from the reported value of 5.25 wt. % volatiles from FWDC. The value of 1.13 wt. % volatiles will be used in this thesis, due to the fact that some of the volatiles from the original char could have been lost during storage and/or handling. A plot of this TGA run can be seen in Figure 5.2. There are two distinct regions of weight loss shown on this plot. The first region is attributed to the loss of moisture. The second region of weight loss, occurring at approximately 1067 °F, was attributed to the loss of volatiles. Next to determine the amounts of fixed carbon a few assumptions were made:

- The levels of oxygen, nitrogen, and hydrogen are represented by the volatiles, since they are essentially depleted by pyrolysis.
- The carbon can be determined by difference calculation, as shown in equation 5.1.

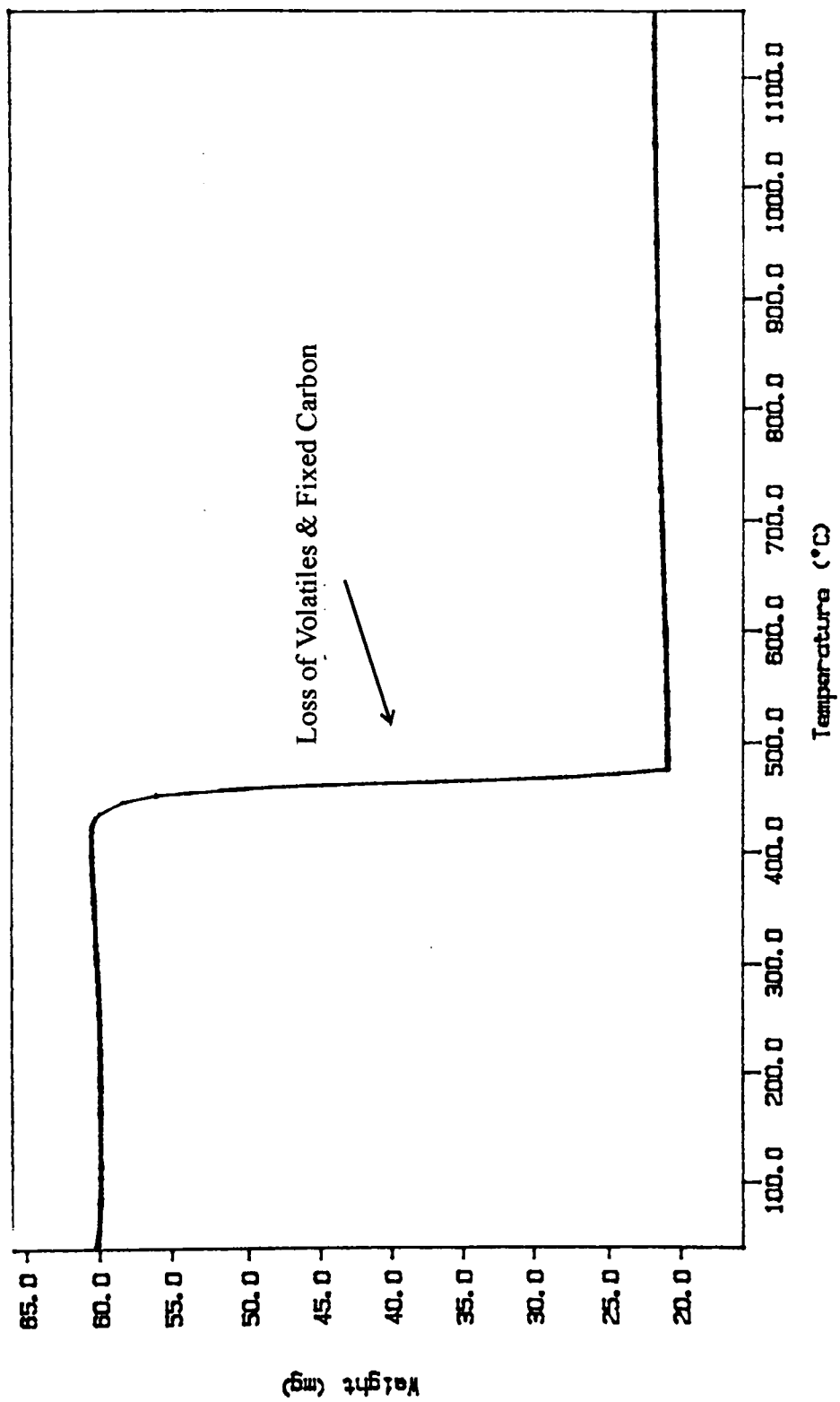


Figure 5.1 Determination of Ash Content in HIPPS Char

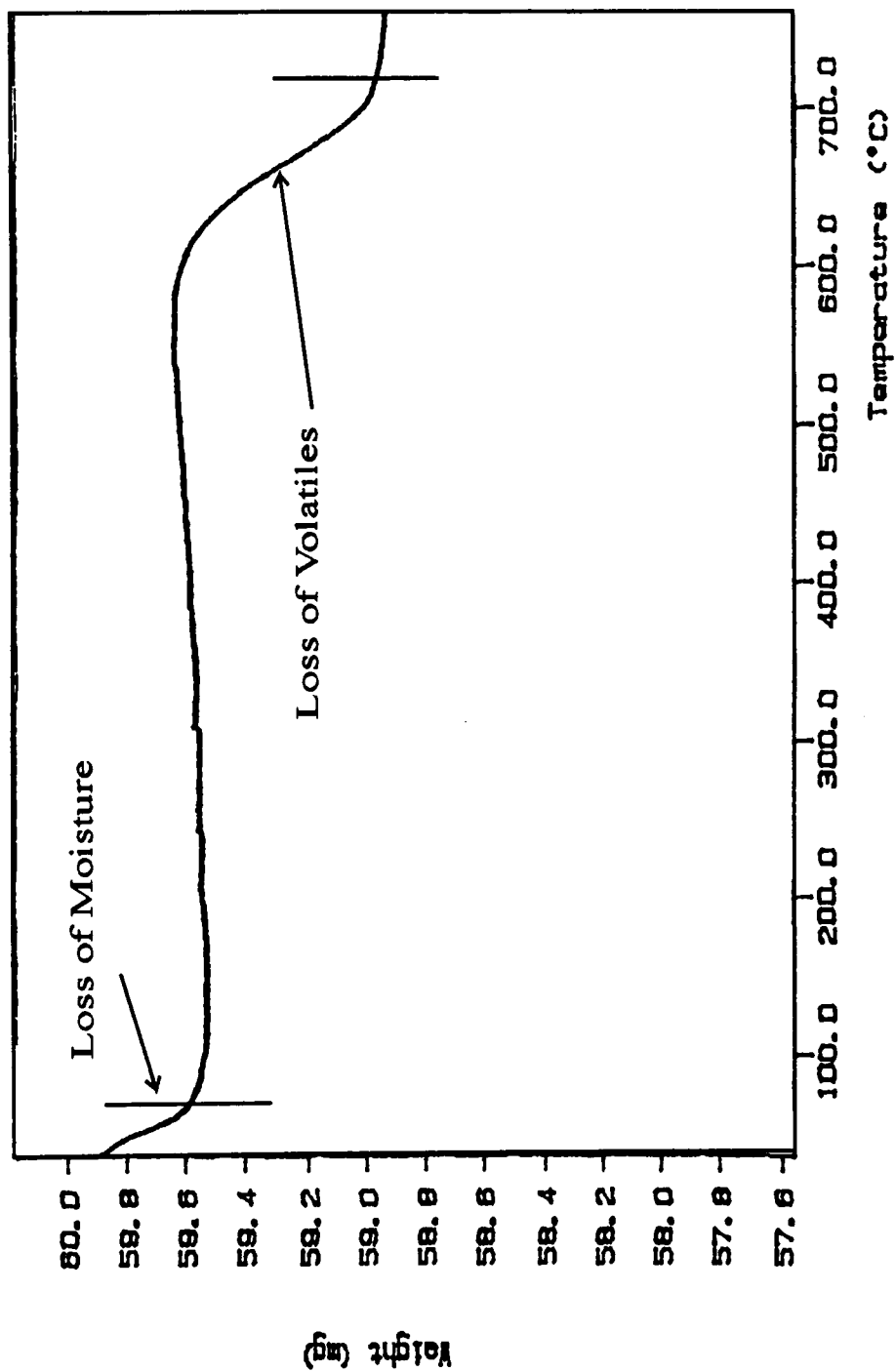


Figure 5.2 Determination of Volatiles and Moisture Content in HIPS Char

$$\text{Total} - \text{Ash} - \text{Moisture} - \text{Volatiles} - \text{Sulfur} = \text{Carbon} \quad (5.1)$$

The values for ash, moisture, volatiles, and sulfur as determined for the HIPPS char can be seen in Table 5.2.

As indicated in the previous section the first testing performed was done with the LECO SC132. The primary reason for this testing was the verification of the percent of sulfur in the HIPPS char, however during testing an additional source of information was derived from the LECO SC132. As explained in the previous chapter, during the process of determining the levels of sulfur in a sample the LECO SC132 outputs values to the display/printer device. These values are representative of the levels of sulfur in the IR detector at any give time. From this it is possible to qualitatively determine the effects of temperature on sulfur species production and the resulting levels of sulfur dioxide

Table 5.2 Analysis of HIPPS Char

HIPPS Char Component	Weight Percent
Sulfur	4.61
Ash	35.42
Moisture	0.63
Volatiles	1.13
Fixed carbon	58.22

produced at certain temperatures. These tests were performed under pure oxygen and under air, which is 21 vol. % oxygen, to determine the effect of available oxygen on the production of sulfur dioxide. Tests 2.1 through 2.10, under pure oxygen, were performed at four successively higher temperatures using three different sample materials, calcium sulfide, the commercially generated char, and the HIPPS char. The samples were tested at 1000 °F, 1500 °F, 2000 °F, and 2500 °F which are considered representative of the HIPPS HITAF temperature range, with the obvious exception of the 1000 °F test.

The first material tested in this manner was calcium sulfide and the results for the first three temperatures can be seen in Figure 5.3. The fourth temperature, 2500 °F, produced high levels of sulfur dioxide that at one point even exceeded the detection limits of the Leco SC132 IR detector. The values for the 2500 °F test, Test 2.4, can be seen in Figure 5.4. From these two figures it is possible to determine the four important characteristics of the combustion of calcium sulfide.

- The first characteristic is the time at which the production of sulfur dioxide initiated.
- The second characteristic is the time at which the sulfur dioxide production peaked, as indicated by the maximum reported number on the LECO SC132 display/printer.

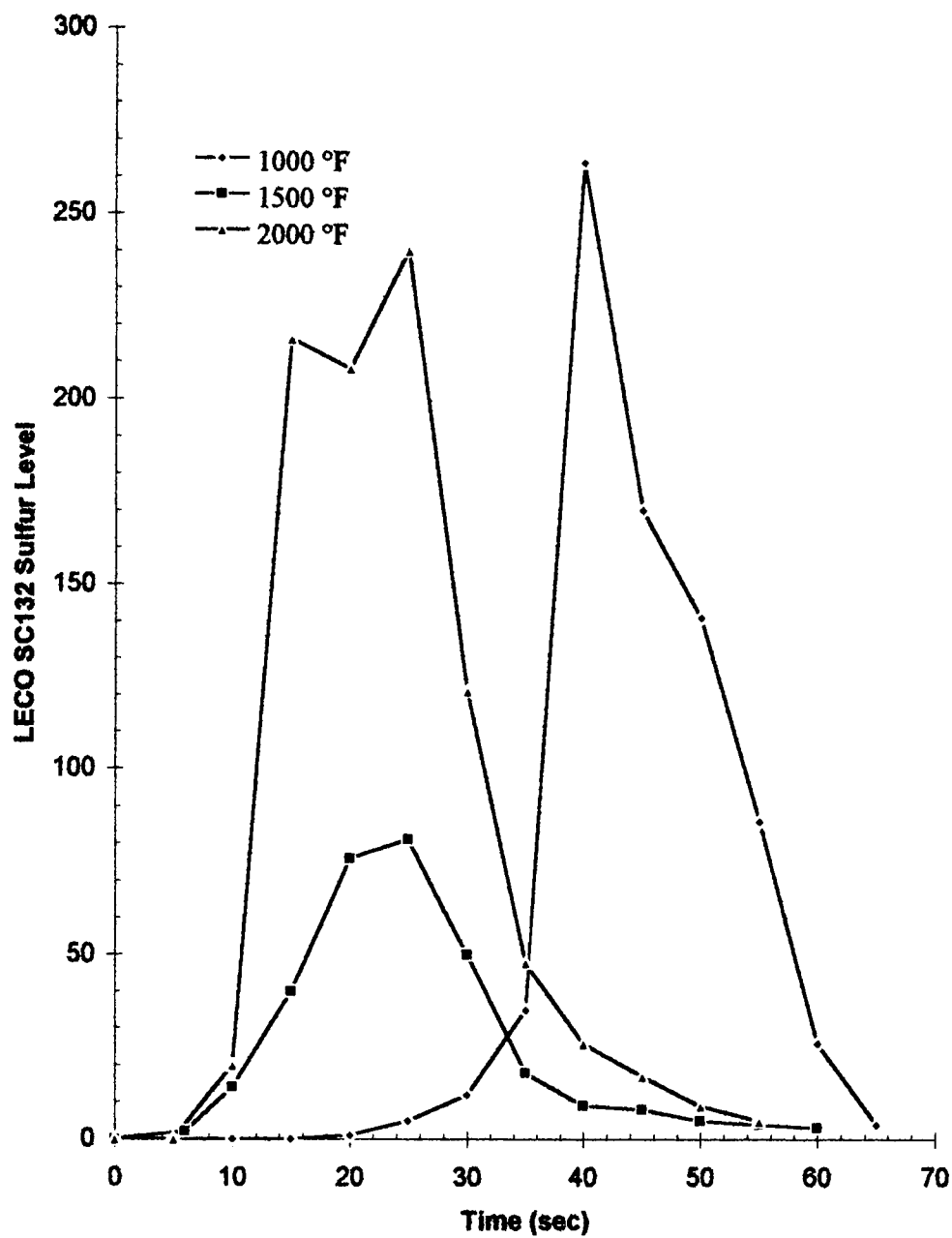


**Figure 5.3 Oxidation of Calcium Sulfide in Pure Oxygen
at 1000 °F, 1500 °F, and 2000 °F**

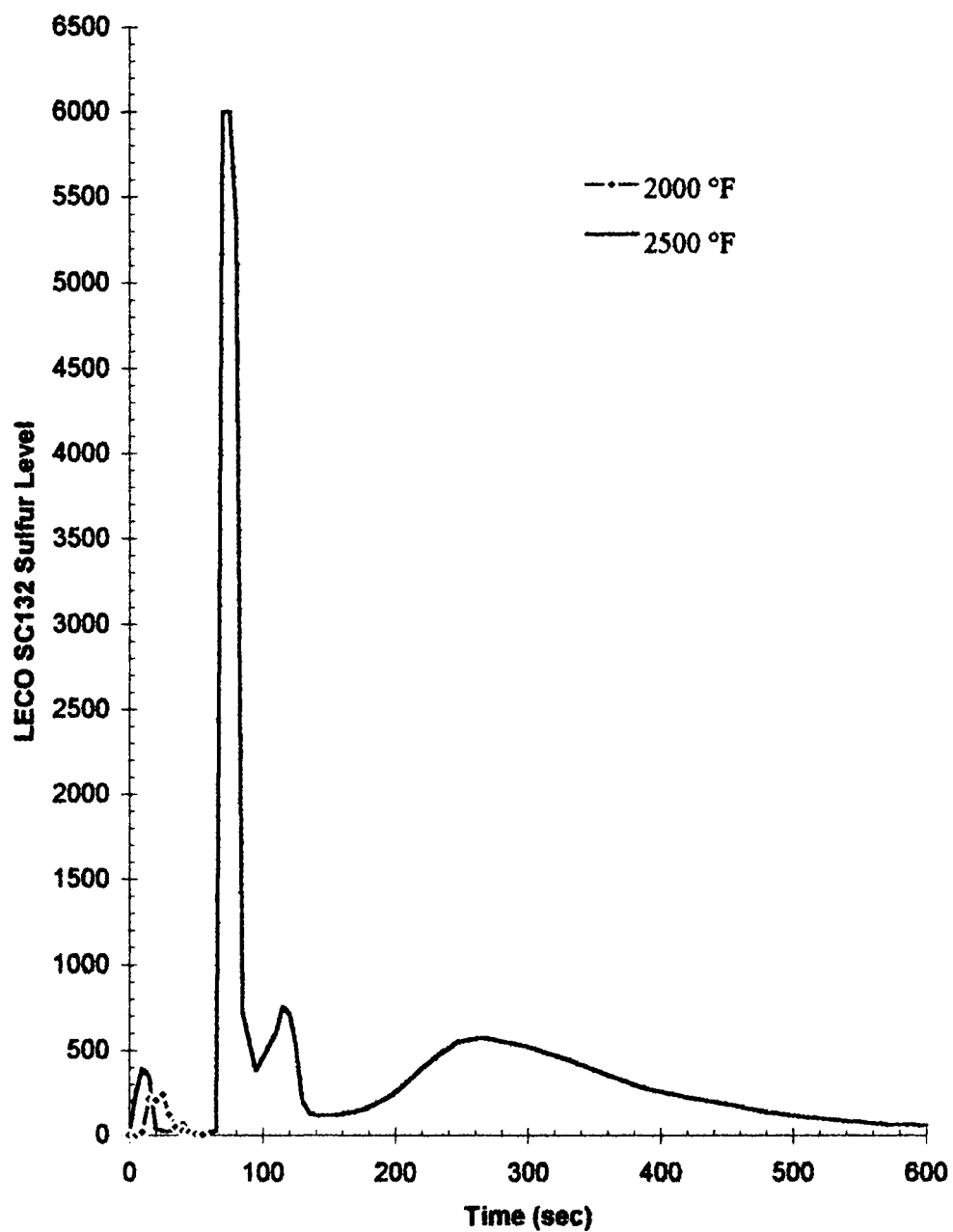


**Figure 5.4 Oxidation of Calcium Sulfide in Pure Oxygen
at 2000 °F and 2500 °F**

- The third characteristic is the time at which the production of sulfur dioxide declined to a negligible rate.
- The last characteristic is that of the maximum, or peak value for the production of sulfur dioxide.

These characteristics, for each of the temperatures, can be seen in Table 5.3. It can be seen from the plots that as the temperature increased from 1500 °F to 2500 °F, the peak levels of sulfur dioxide produced increased dramatically. It should be noted here that the observed decrease in the production of sulfur dioxide from calcium sulfide, going from 1000 °F to 1500 °F is probably anomalous and could have been an error in the experiment or in the manual recording of the data. The large amount of sulfur dioxide was produced at high temperature as expected. At these temperatures, the sulfur species combusted so rapidly and to such a degree that it exceeded the detection limits of the IR detector. The literature indicates that in the temperature range of 1500 °F to 2000 °F and in high excess of oxygen, calcium sulfide will primarily form calcium sulfate, however as the amount of available oxygen decreases the calcium sulfide will increasingly favor the production of sulfur dioxide. This particular observation was investigated further in the TGA tests.

**Table 5.3 Effects of Temperature
on the Oxidation of Calcium Sulfide in Pure Oxygen**

	Temperature (°F)			
	1000	1500	2000	2500
Initial Time of Measurable Sulfur Dioxide Production (<i>sec</i>)	20	6	10	5
Time of Peak Sulfur Dioxide Production (<i>sec</i>)	40	25	25	70 - 75
Time of Last Measurable Sulfur Dioxide (<i>sec</i>)	65	60	55	600
Peak Value Measured for the Production of Sulfur Dioxide (<i>LECO Reading</i>)	264	81	240	6000+

The second material tested in this series was the commercial char, described in the previous section. This was tested in the same manner as the one employed in the previously mentioned calcium sulfide tests. The value in testing the commercially generated char is found in its differences from the HIPPS char. The carbon contents are roughly the same for both chars, and therefore the forms of organic sulfur are believed to be similar. This allows for the closer analysis of the effects of oxygen on the calcium sulfide in the char. The main reason for this is that the commercial char was produced separately from the calcium sulfide, which was added after pyrolysis. On the other hand the calcium sulfide in the HIPPS char was generated at the same time as the char, and therefore, may show different reactivity towards the oxygen introduced during combustion. If the pyrolysis process has any kind of hindering effect on the subsequent evolution of sulfur dioxide from the calcium sulfide, then it should be obvious in the magnitudes of the times and levels of sulfur dioxide production as mentioned in the calcium sulfide test. The first of the chars to be analyzed was the commercial char. It was tested at the same temperature increments as in the calcium sulfide tests. The results from these tests, Tests 2.5 through 2.7, can be seen in Figure 5.5. Next the HIPPS char was tested, Tests 2.8 through 2.10, at the same temperatures to compare the results with the commercial char tests. The results from these HIPPS char tests can be seen in Figure 5.6. A comparison of the commercial char and the HIPPS char, for the values of the previously mentioned characteristics is given in Table 5.3. From earlier testing it was determined that the HIPPS char contained 4.65 wt. % sulfur, and the commercial char

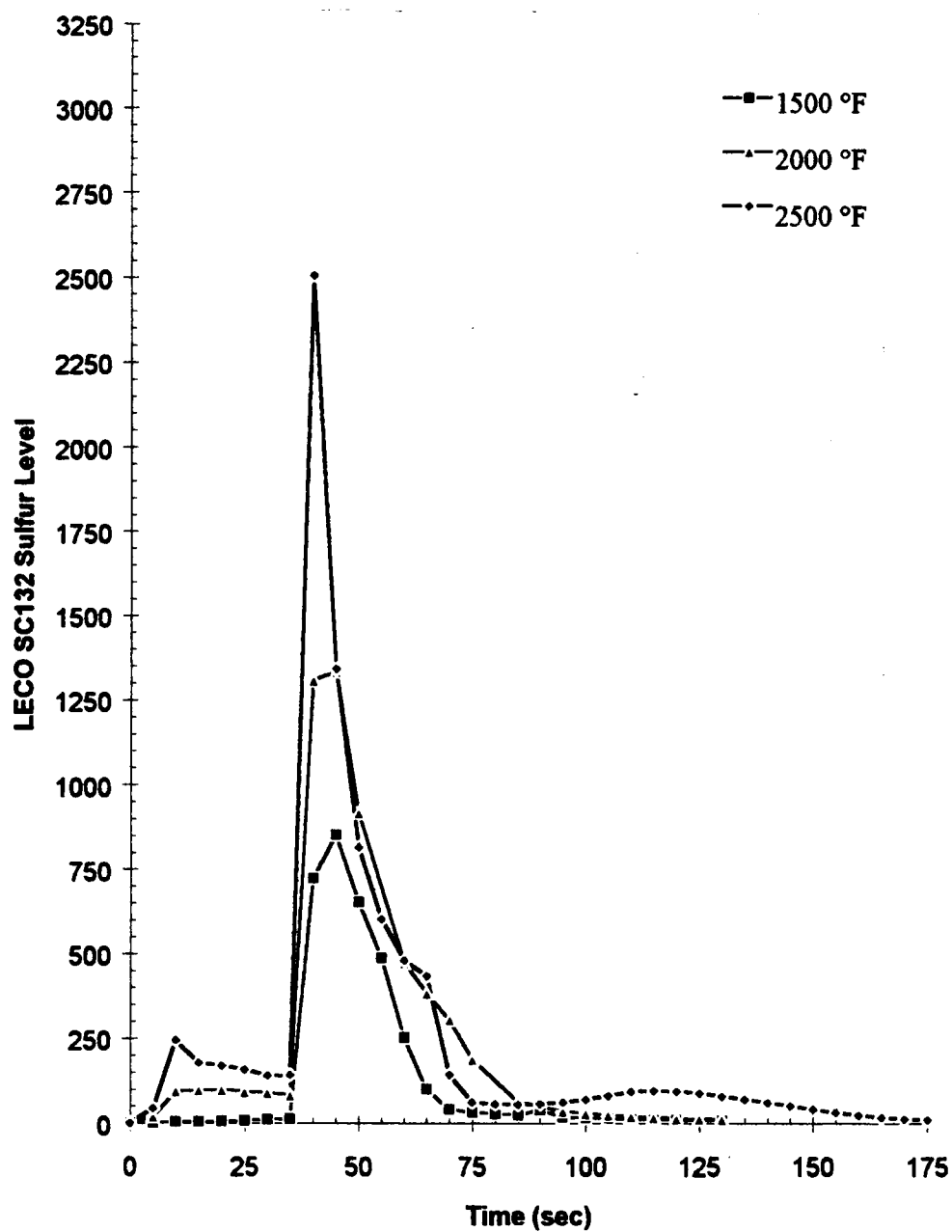


**Figure 5.5 Oxidation of Commercial Char in Pure Oxygen
at 1500 °F, 2000 °F, and 2500 °F**

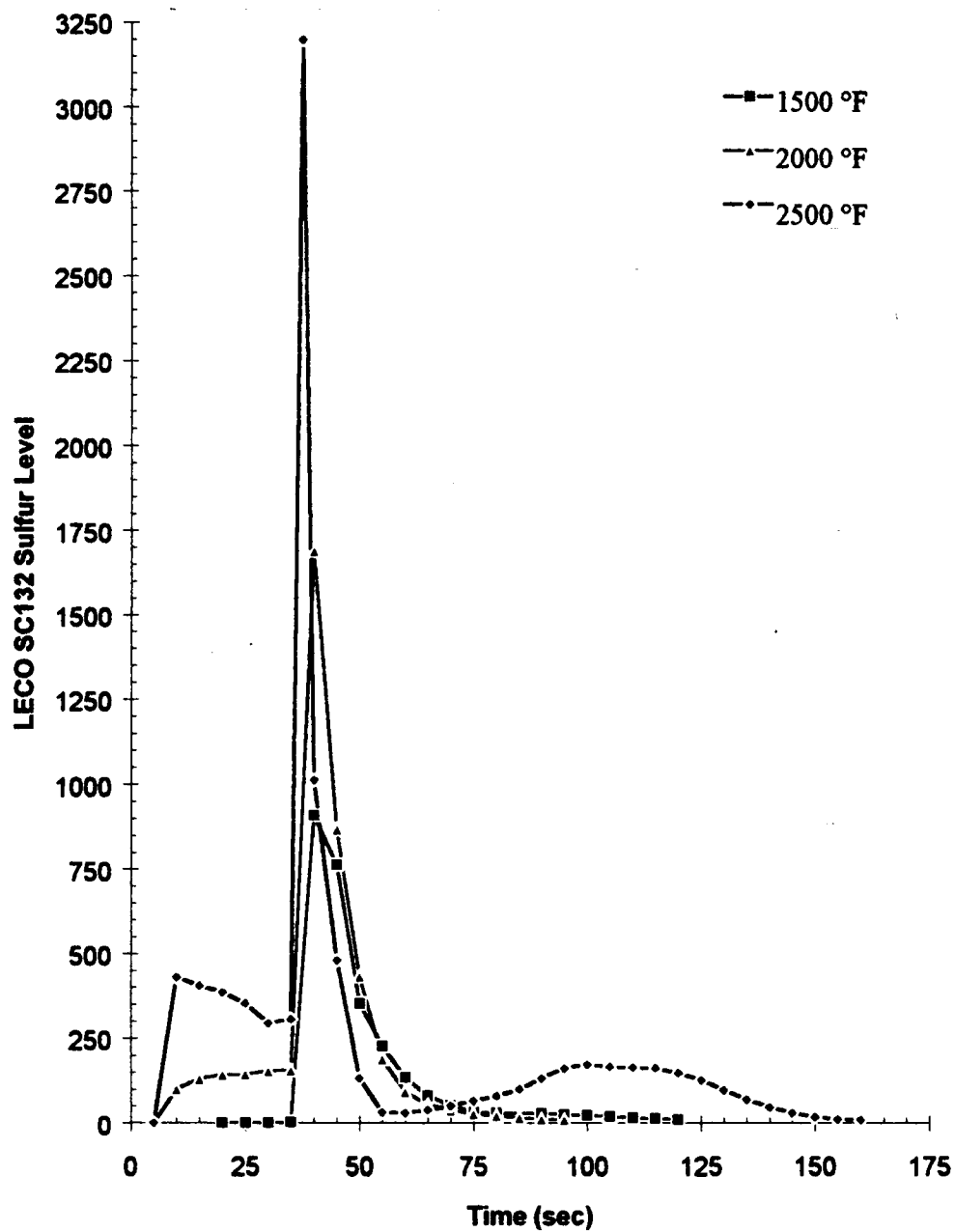


**Figure 5.6 Oxidation of HIPPS Char in Pure Oxygen
at 1500 °F, 2000 °F, and 2500 °F**

contained 3.85 wt. % sulfur. From Figure 5.5 and 5.6 it is obvious that the two chars behaved in a very similar manner. This observation is further supported by the various characteristic values listed in Table 5.3. There are consistently higher values listed for the evolution of sulfur dioxide from the HIPPS char, which can most likely be attributed to the slightly higher levels of sulfur contained in the char. There was negligible sulfur dioxide produced during the 1000 °F run, and for this reason it is not included in the reported data. From 1500 °F to 2500 °F, the levels of gaseous sulfur species increased as was expected from the similar information obtained for the calcium sulfide tests. While not all the sulfur dioxide produced in these experiments could have come from the oxidation of calcium sulfide, there were sufficient levels of sulfur dioxide produced to warrant further investigation. From the behavior of the two chars it was concluded that the effects of the pyrolysis process on the reactivity of calcium sulfide was negligible.

Next, a few experiments were carried out to determine the effect of oxygen concentration on the production of sulfur dioxide from the HIPPS char. These additional tests, Tests 2.11 through 2.14, were performed under an air environment, at the following temperatures: 1800 °F, 2000 °F, 2200 °F, and 2400 °F. These temperatures fall within the portion of the HIPPS HITAF temperature range during which the oxidation of the calcium sulfide is most likely to form sulfur dioxide. The results from these additional tests are shown in Figure 5.7. The characteristic values similar to the ones mentioned earlier in Table 5.2 and 5.3, for these air oxidation tests are shown in Table 5.4. From

**Table 5.4 Comparison of the Effects of Temperature
on the Oxidation of Commercial Char and
HIPPS Char in Pure Oxygen**

	Commercial Char			HIPPS Char		
	Temperature (°F)					
	1500	2000	2500	1500	2000	2500
Initial Time of Measurable Sulfur Dioxide Production (sec)	5	5	5	25	10	10
Time of Peak Sulfur Dioxide Production (sec)	45	45	40	40	40	37.5
Time of Last Measurable Sulfur Dioxide (sec)	130	130	175	120	95	160
Peak Value Measured for the Production of Sulfur Dioxide (LECO Reading)	853	1334	2506	910	1690	3199

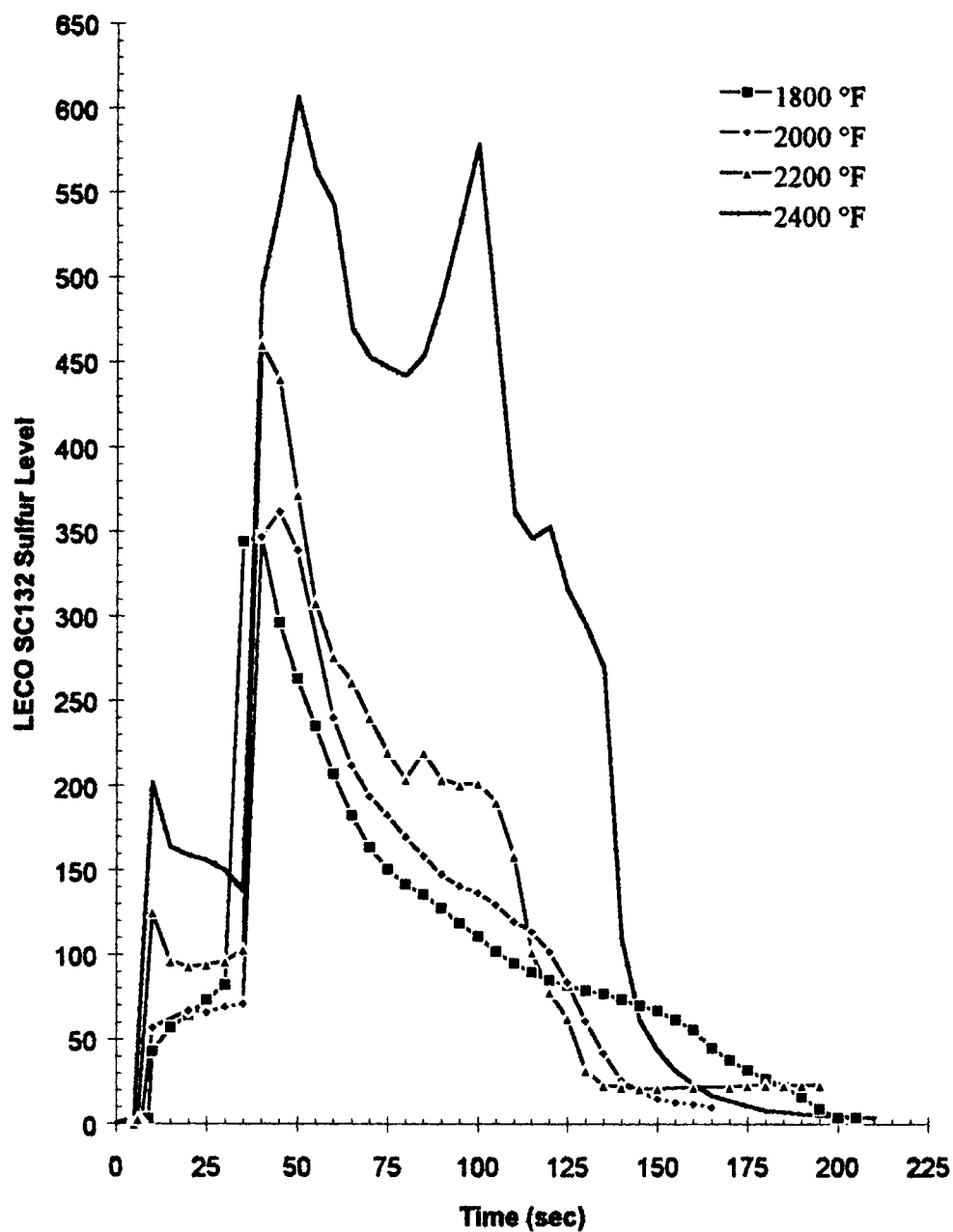


**Figure 5.7 Oxidation of HIPPS Char in Air
at 1800 °F, 2000 °F, 2200 °F, and 2400 °F**

Figure 5.7 and Table 5.5 the effects of temperature on the production of sulfur dioxide can be seen. As the temperature increases the peak levels of sulfur dioxide increase, and the time for initial measurable sulfur dioxide production decreases. An interesting result was observed for the 2400 °F run, where a double peak in the sulfur dioxide levels occurred. A possible explanation for this is the presence of two forms of sulfur, organic and inorganic sulfide, requiring different times to reach peak levels of sulfur dioxide production. A similar dual peak was also evident in the 2000 °F run. A comparison of the oxidation of HIPPS char in pure oxygen and in air with 21 vol. % oxygen, can be seen in Figure 5.8. It is evident from this figure that a lower level of oxygen introduced to the system would lead to lower levels of sulfur dioxide evolution, and subsequently would result in a lower amount of calcium sulfide converted to sulfur dioxide. From Figures 5.6 and 5.7 the approximate levels of sulfur converted to both sulfur dioxide and/or calcium sulfide can be determined. This determination depends on the assumption that at the highest available temperature run the measured production of sulfur dioxide represents the conversion of at least 99.9 percent of the total sulfur initially present. Separately analyzing the oxidation of char in air and pure oxygen it is possible to determine these conversions for each. Table 5.6 shows the estimated conversion of sulfur to calcium sulfate and sulfur dioxide for Tests 2.8 through 2.14. The first set of values for the oxidation in pure oxygen seem to be reasonable and most likely are a good representation of the actual levels of sulfur dioxide and calcium sulfate produced during this process. However the second set of data, for the oxidation of char in air appear to

**Table 5.5 Effects of Temperature
on the Oxidation of HIPPS Char in Air**

	Temperature (°F)			
	1800	2000	2200	2400
Initial Time of Measurable Sulfur Dioxide Production (<i>sec</i>)	9	7	6	5
Time of Peak Sulfur Dioxide Production (<i>sec</i>)	40	45	40	50
Time of Last Measurable Sulfur Dioxide (<i>sec</i>)	205	165	195	210
Peak Value Measured for the Production of Sulfur Dioxide (<i>LECO Reading</i>)	347	362	460	607

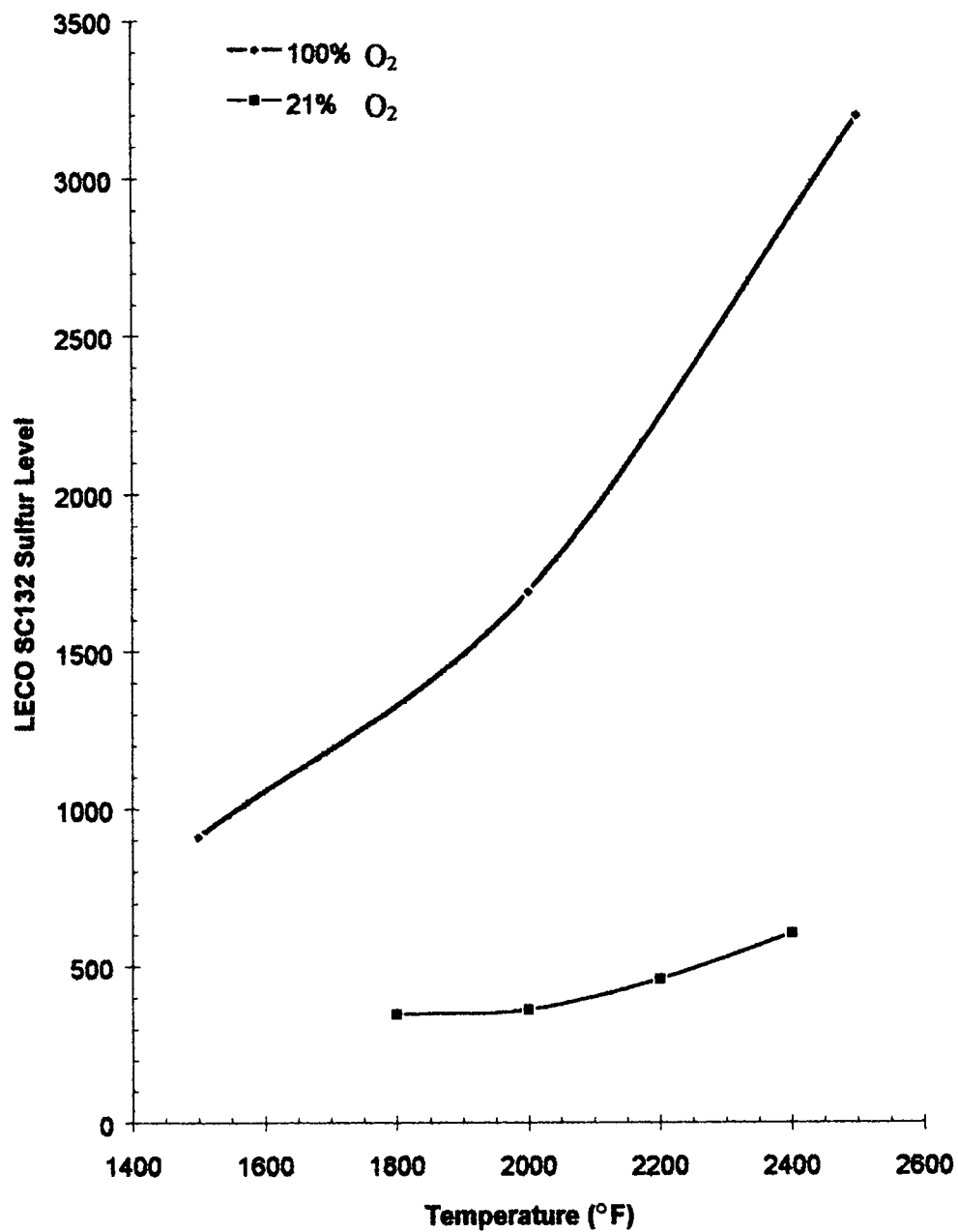


Figure 5.8 Comparison of Peak Levels of Sulfur Dioxide Evolution in Pure Oxygen and Air for HIPPS Char

Table 5.6 Comparison of the Estimated Conversion of Sulfur to Calcium Sulfate and Sulfur Dioxide During the Oxidation of HIPPS Char in Air and Pure Oxygen

Temperature (°F)				
	1500 °F	2000 °F	2500 °F	
<i>Pure Oxygen</i>				
Estimated % Conversion to Sulfur Dioxide	39.4	61.3	99.9	
Estimated % Conversion to Calcium Sulfate	60.6	38.7	0.1	
	1800 °F	2000 °F	2200 °F	2400 °F
<i>Air</i>				
Estimated % Conversion to Sulfur Dioxide	41.3	38.6	49.4	99.9
Estimated % Conversion to Calcium Sulfate	58.7	61.4	50.6	0.1

have unusually large, but consistent amounts of calcium sulfate being produced for the first three temperatures. This is unusual in that the highest temperature test abruptly varies from the previous three tests. It is therefore possible that in actuality the overall levels of sulfur converted are less than 99.9 percent in the highest temperature test.

Results from Thermogravimetric Analysis

With the first group of tests relating to the LECO SC132 completed a series of thermogravimetric analyses was performed to study the effects of various gas atmospheres on the thermal and reactive decomposition of calcium sulfide. These tests were performed on samples of calcium sulfide and HIPPS char, for the following gases: argon, carbon dioxide, and air. The first gas, argon, was chosen to investigate only the thermal decomposition of the samples. The first test in argon, Test 3.1, shown in Figure 5.9, was performed on a sample of calcium sulfide. It can be seen from this test that calcium sulfide starts thermally decomposing at approximately 1470 °F (800 °C) and the decomposition is completed at approximately 1967 °F (1075 °C). This thermal decomposition accounts for a loss of about 22.0 percent of the original weight of the sample. It is also evident from Figure 5.9 that the loss of moisture, volatiles, and impurities accounts for a decrease of approximately 7.2 percent from the original weight. Assuming that the thermal decomposition accounted for complete release of the sulfur species, then whatever remained represented the calcium. Knowing from calculations that the calcium consists of approximately 51.6 percent of the original weight of the

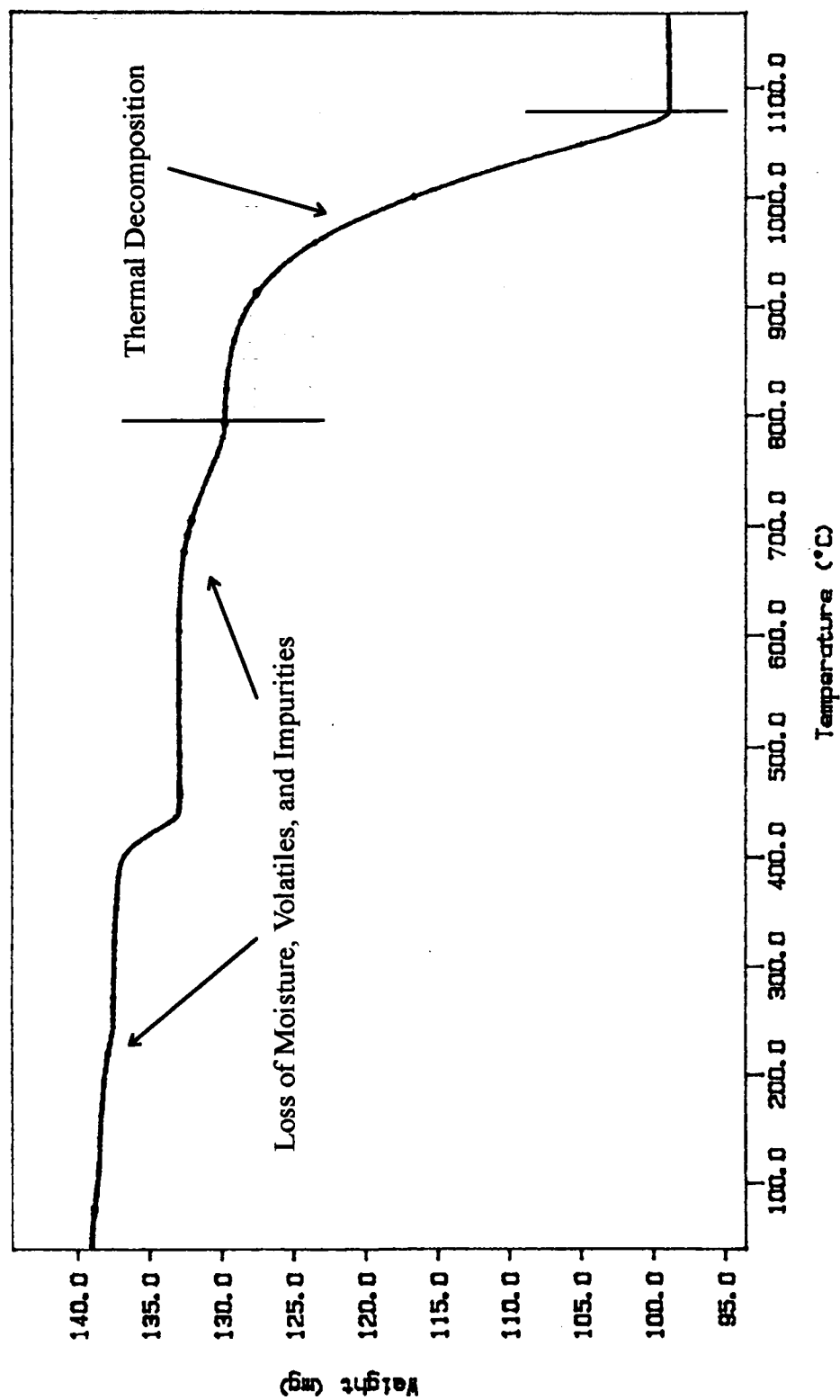


Figure 5.9 Thermogravimetric Analysis of Calcium Sulfide in Argon

sample, then sulfur must be 41.3 percent of the weight of the original sample. It is then evident, from difference calculations, that 46.8 percent of the original sulfur remained in the sample. This is a confusing development because, as is visible from the plot, the thermal decomposition seemed to stop abruptly and the sample weight remained constant until the completion of the run. Another possible explanation for this observation is that the original sample probably contained CaS_x instead of pure CaS , and these other forms of calcium and sulfur compounds probably have different temperatures of thermal decomposition. If this is true then it is difficult to determine whether the thermal decomposition observed is actually that of CaS , or one or more forms of the CaS_x type compounds. Despite this it is still valuable to know that some thermal decomposition did occur, and that the possibility that it was partly due to CaS cannot be ruled out at this point.

The next sample to be examined in argon was the HIPPS char, however since it was tested earlier during the primary analysis of the char it was not repeated. From Figure 5.10 it is possible to see that some thermal decomposition did occur, starting at approximately 1290 °F (700 °C) and continuing through the end of the TGA run at approximately 2190 °F (1200 °C). The thermal decomposition observed in this figure represents a weight loss of approximately 1.71 percent of the original sample weight. Assuming that the lost material is sulfur, which must be from the calcium sulfide as the organic forms of sulfur will not be removed by this method, then it represents a loss of

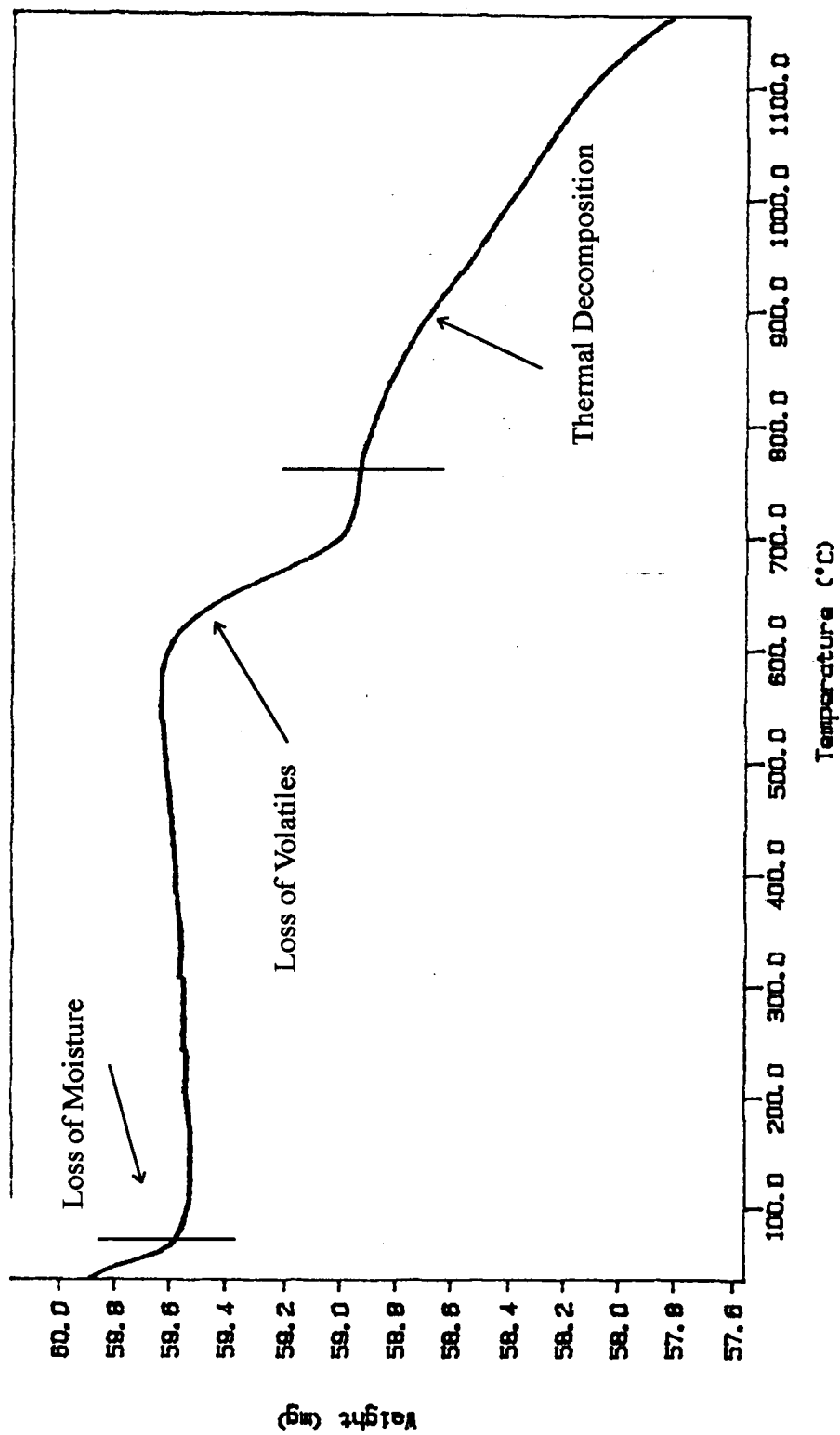


Figure 5.10 Thermogravimetric Analysis of HIPPS Char in Argon

approximately 65.8 percent of the sulfide sulfur initially present in the HIPPS char sample tested. This thermal decomposition of calcium sulfide was also observed during Test 4.11 in the isothermal bench-scale tests and will be discussed later in this chapter.

Next, the behavior of the sample in a carbon dioxide atmosphere was investigated. In addition to observing the weight loss it was possible to assume that the observations would also be an indication of the previously mentioned reaction of calcium sulfide and carbon dioxide (e.g. Equation 3.6). The results from this test, Test 3.2, are shown in Figure 5.11. It is readily obvious from this figure that some weight loss occurred. The first area of weight loss can be attributed to the loss of moisture, volatiles, and impurities. This amounts to a loss of approximately 5.8 wt. % of the original sample. The second area of weight loss, starting at approximately 1600 °F (875 °C) and continuing through the end of the run, is most likely due to a combination of thermal decomposition and reaction with carbon dioxide to form sulfur dioxide, carbon monoxide, and calcium oxide. This amounts to a combined loss of approximately 24.5 wt. % of the original sample. It is not possible to separate the loss due to thermal decomposition from the loss due to reaction with carbon dioxide from this analysis. To further complicate this, the uncertainty regarding the actual composition of the calcium sulfide sample makes any assumption impossible. Despite this it is important to note that the earlier thermal decomposition of calcium sulfide accounted for a loss of only about 22.0 percent of the original sample weight, which even if assumed to have occurred to the same degree in

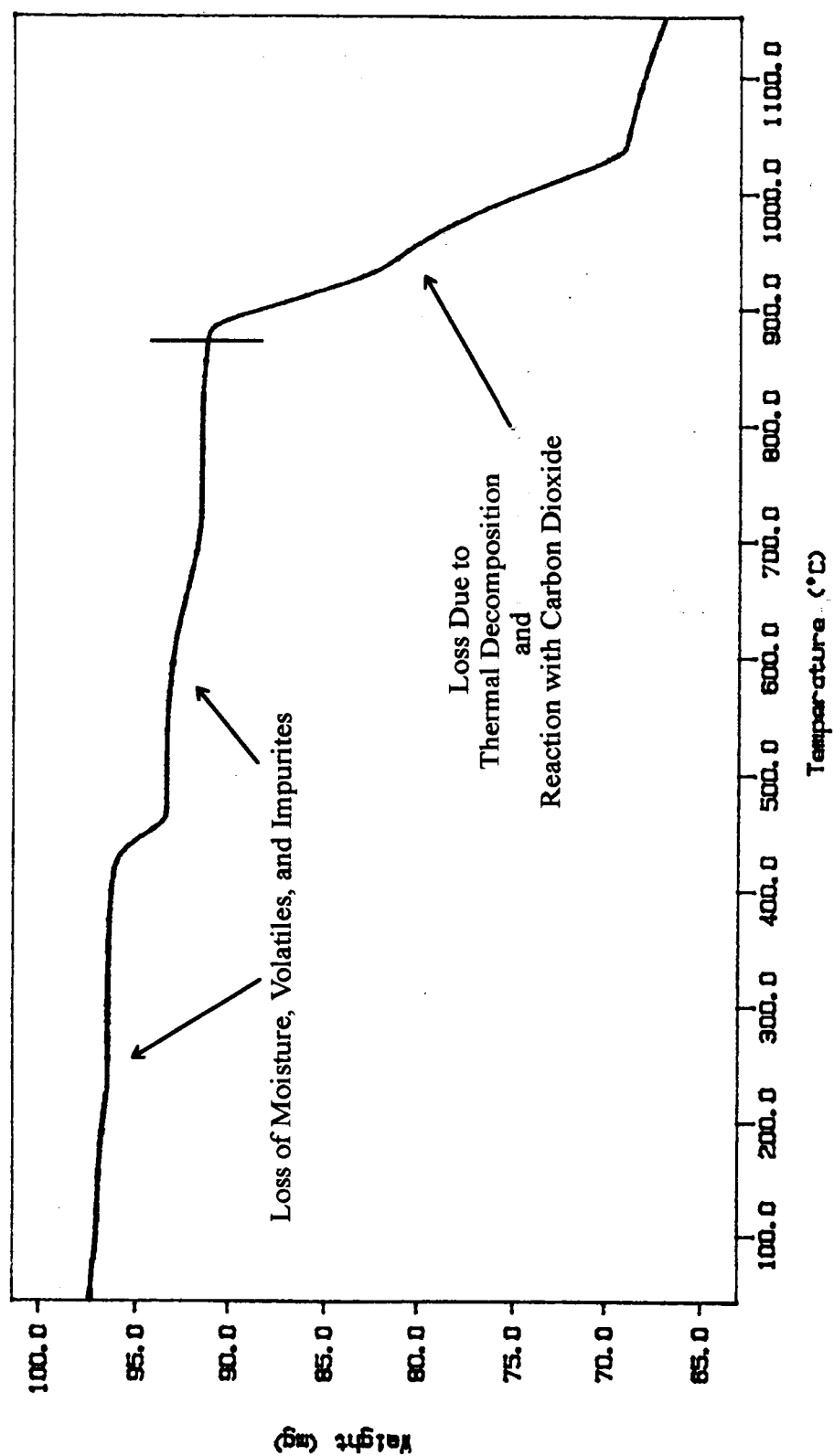


Figure 5.11 Thermogravimetric Analysis of Calcium Sulfide in Carbon Dioxide

this test, would leave a loss equivalent to 2.6 percent of the original weight to be attributed to the reaction with carbon dioxide. The reaction between calcium sulfide and carbon dioxide produces calcium oxide which results in a much less pronounced weight loss when compared to the loss from thermal decomposition. Most likely the 24.52 percent loss seen here represents a more complicated combination of the two, and therefore, only the fact that it occurs can be confirmed at present.

The next sample to be analyzed in carbon dioxide was the HIPPS char, Test 3.3. As can be seen in Figure 5.12, there are three distinct areas of weight loss. The first area, as in all the previous TGA test can be attributed to the loss of moisture, and accounts for a loss of approximately 2.4 wt. % of the original sample. This amount is larger than the corresponding loss of moisture as observed in the test of the HIPPS char under argon. This result is easily explained, the increase in moisture was most likely from the room air and the high humidity present in the South during the spring and early summer, when this test was undertaken. The second area of weight loss is due to the loss of the volatiles. This decrease accounts for a loss of approximately 1.6 wt. % of the original sample. Testing under argon resulted in a loss of 1.1 wt. % of the original sample. This difference can be explained by the fact that coal and coal char are very heterogeneous compounds, and such a slight increase in volatiles is well within an expected variance. The third area of weight loss occurs starting at approximately 1290 °F (700 °C) and continues through the end of the run. Like the second area of weight loss observed in the calcium

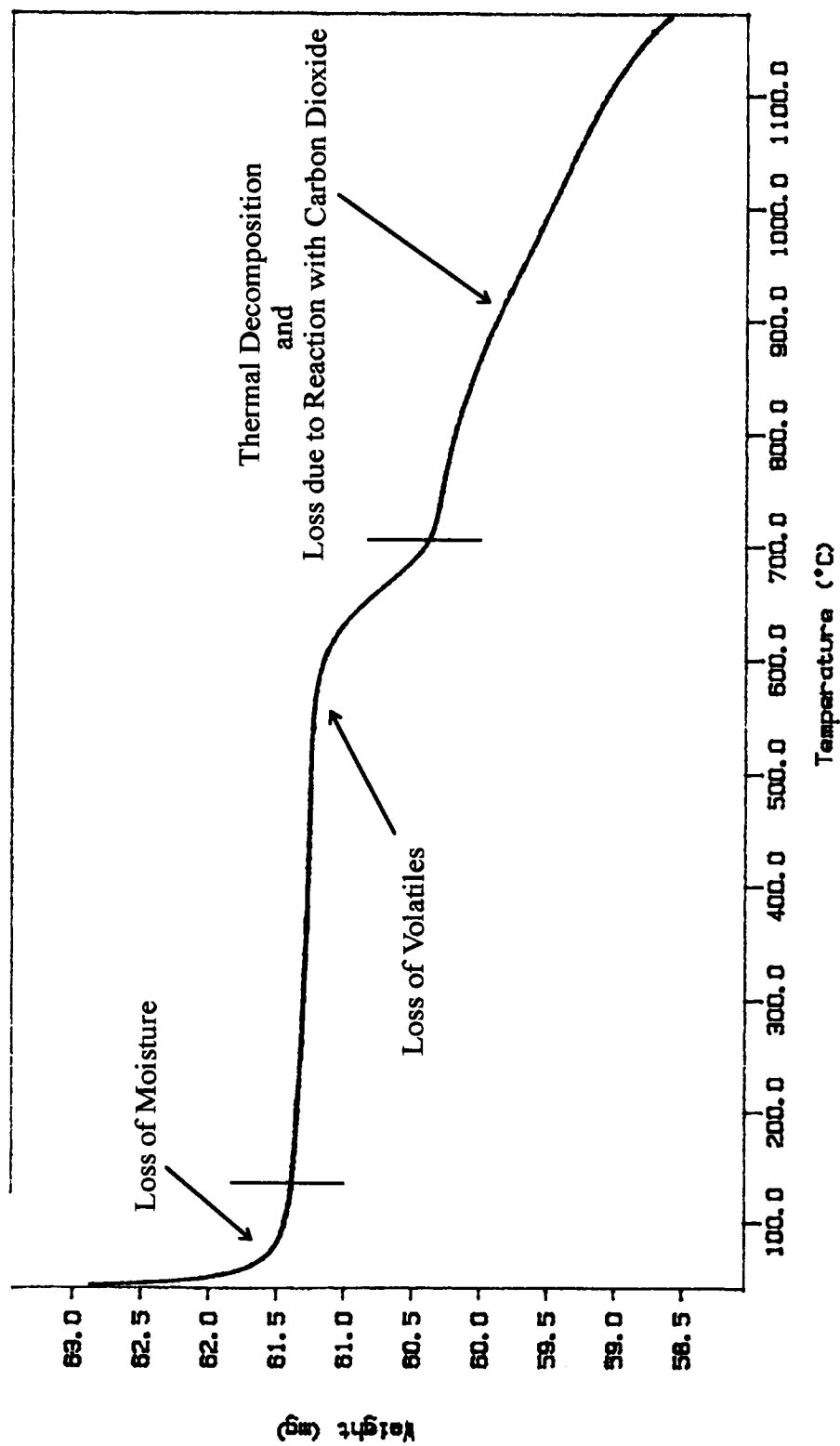


Figure 5.12 Thermogravimetric Analysis of HIPPS Char in Carbon Dioxide

sulfide-argon test, Test 3.1, a combination of thermal decomposition and loss due to reaction with carbon dioxide probably can explain this particular loss in the HIPPS char-carbon dioxide test, Test 3.3. This decrease accounts for a loss of approximately 2.90 percent of the weight of the original sample. From the previously observed thermal decomposition, accounting for a loss of 1.71 wt. %, it is obvious that the reaction with carbon dioxide accounts for a little less than 50 percent of this weight loss. This is dependent on the assumption that the thermal decomposition occurs to the same degree as observed earlier. However, as mentioned in the calcium sulfide-carbon dioxide test, Test 3.3, the likely explanation includes a probable combination of thermal decomposition and the reaction of carbon with carbon dioxide. This reaction of carbon with carbon dioxide is known in the literature as the Boudouard Reaction and can be represented by the following equation:



This reaction, having a ΔH_{298}° of 172.5 KJ/mol, is endothermic, and therefore, will be favored at high temperatures. From this it is likely that a portion of the third area of weight loss, primarily seen at higher temperatures, is probably due to a combination of equation 3.10, as mentioned in the calcium sulfide-carbon dioxide tests, and equation 5.1. Therefore it is possible, as shown in equation 3.10, that sulfur dioxide is being produced during this period of weight loss too.

The next set of TGA tests, Tests 3.4 and 3.5, was performed under an air environment. The purpose was to study the weight loss due to oxidation of calcium sulfide and the combustion of HIPPS char. The first material tested was again the calcium sulfide, Test 3.4. From Figure 5.13, it is evident that there are three areas of changing weight, two areas of weight loss and one area of weight gain. The first area of change, attributable to the loss of moisture, volatiles, and impurities, accounts for a loss of approximately 4.3 wt. % of the original sample. The next area of change, an increase starting at approximately 860 °F (460 °C), is most likely due to the formation of calcium sulfate. This formation was anticipated from the literature, which indicated that up to 1800 °F calcium sulfate will be the favored product from the oxidation of calcium sulfide. This formation of calcium sulfate increased the weight to approximately 101.3 percent of the weight of the original sample. This indicates that the formation of calcium sulfate replaced the weight loss seen in the first area of change, and added an additional weight equal to 1.3 wt. % of the original sample to the sample. The third area of change, a decrease that starts at approximately 1796 °F (980 °C) , can be attributed to the loss of weight due to the oxidation of remaining calcium sulfide to form sulfur dioxide. This decrease accounted for a loss of approximately 6.5 wt. % from the point of greatest weight, measured during the formation of calcium sulfate, and an overall loss of approximately 5.4 wt. % from the initial weight of the sample. This test is perhaps the most valuable of all the TGA runs as it confirms the earlier predictions from the literature, by showing physically the initial increase of weight from the formation of calcium sulfate and the final loss of

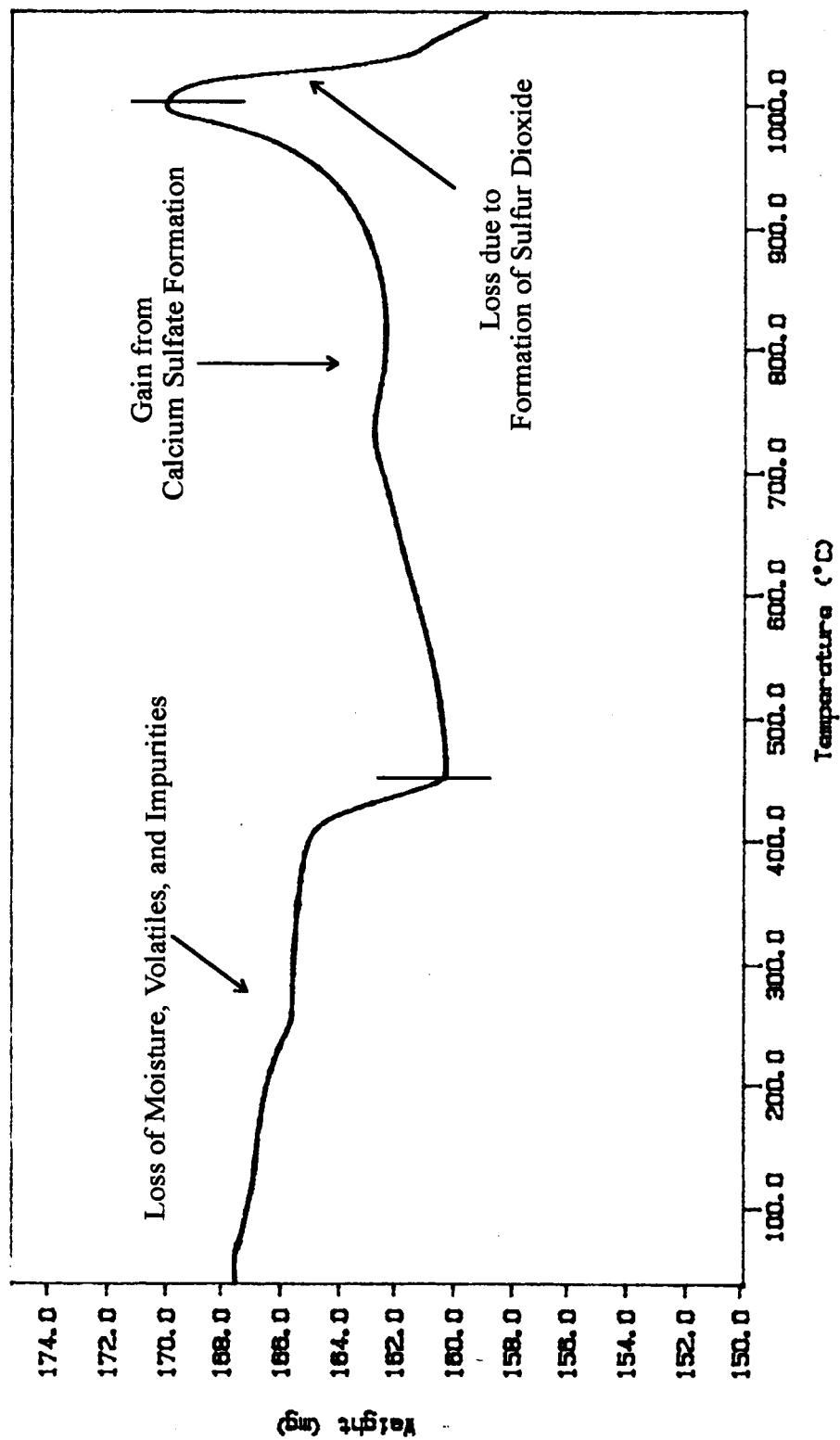


Figure 5.13 Thermogravimetric Analysis of Calcium Sulfide in Air

weight due to the possible formation of sulfur dioxide. It is also evident from this figure that a temperature of approximately 1800 °F is of great importance in determining the fate of sulfur in the HIPPS concept.

The final sample tested, Test 3.5, under air was the HIPPS char itself. As can be seen from Figure 5.14, it is obvious that the expected oxidation of the fixed carbon can be attributed to the bulk of the weight loss, however additional areas of gain and loss were also seen in the same temperature range corresponding to the formation of calcium sulfate and sulfur dioxide as seen in the previous test. The loss of weight due to carbon oxidation was not as steep a decline as was observed in the pure oxygen test, Test 1.2, and is most likely due to the lower level of oxygen, 21.0 vol. % present in air. This decrease accounts for a loss of approximately 64.1 wt. % of the original sample. This is slightly different from the loss of fixed carbon observed in the pure oxygen test, and therefore, this decrease must also include the loss of moisture and volatiles. Since the char is of a very heterogeneous nature it is possible to assume that this accounts for the possible difference in the observed carbon combustion weight loss values. The next change is the increase of weight, most likely due to the formation of calcium sulfate, which was also observed in the previous test with calcium sulfide. This increase accounts for a gain of approximately 2.1 percent of the original weight of the sample, measured from the completion of the char combustion. The final change occurs at approximately 1970 °F (1075 °C), and can be attributed to the loss of weight from the oxidation of the

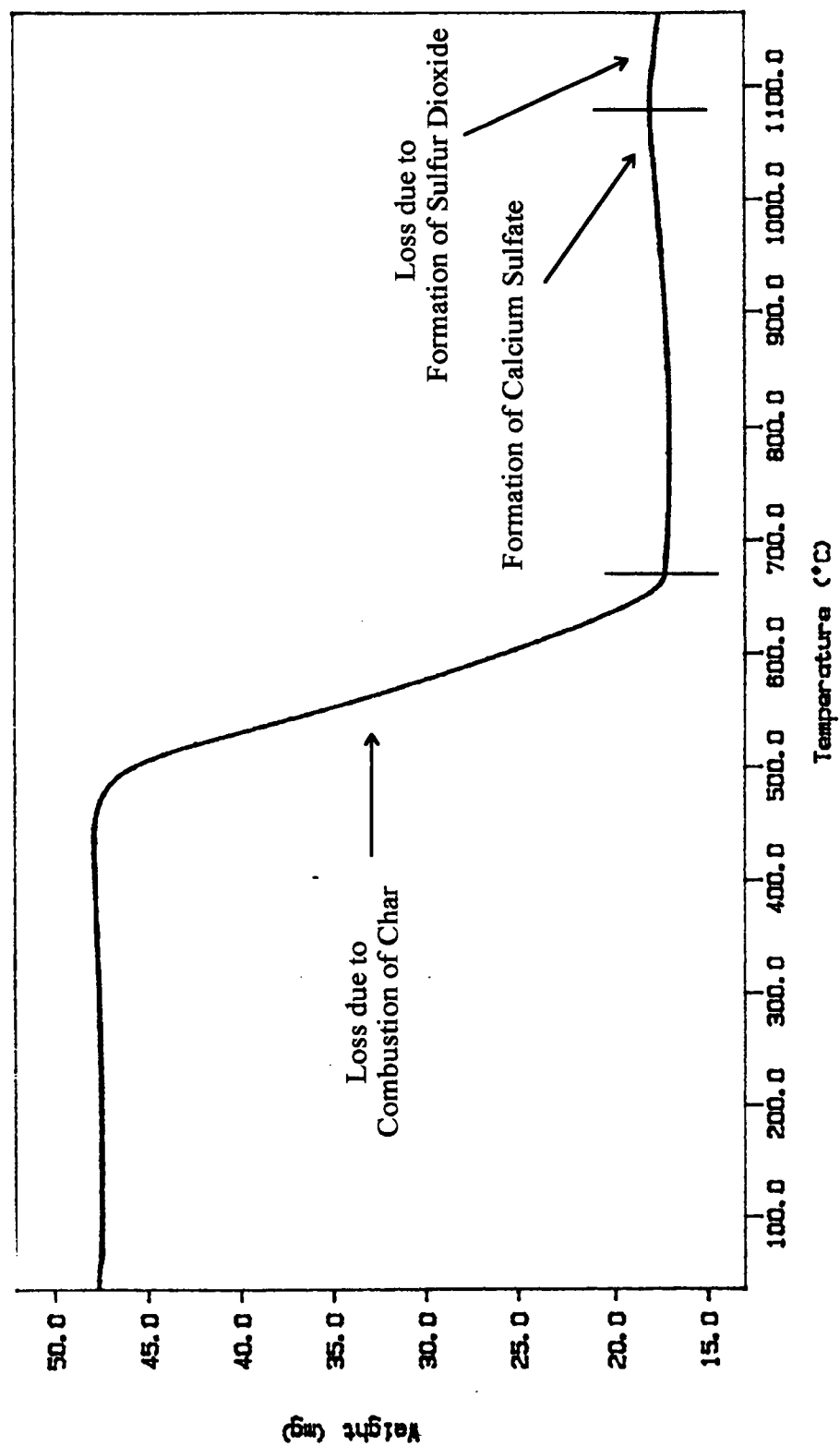


Figure 5.14 Thermogravimetric Analysis of HIPPS Char in Air

remaining calcium sulfide to form sulfur dioxide. This decrease accounts for a loss of approximately 1.5 percent of the weight of the original sample, as measured from the peak level of gain from formation of calcium sulfate reaction. It is interesting to note that the transition temperature between the formation of calcium sulfate and sulfur dioxide production has shifted from approximately 1790 °F for pure calcium sulfide, to about 1970 °F for the calcium sulfide in the HIPPS char.

One last TGA test, Test 3.6 was performed to investigate the possible reaction between calcium sulfate and calcium sulfide, following equation 3.7. This run is shown in Figure 5.15, and it is readily apparent that weight loss occurs in two main regions. The first region of weight is attributable to the loss of moisture and impurities, and accounts for a loss of approximately 12.0 percent of the weight of the original sample. This value is considerably higher than that observed in the calcium sulfide-argon test, however it is not believed to be due to a reaction between the calcium sulfide and the calcium sulfate. Instead it is probably due to the fact that the calcium sulfate was actually in the hydrated form, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. This was known in advance and was assumed to have no effect on the possible reaction between these two calcium compounds as the water of hydration would be driven off long before any possible reaction between calcium species could occur. The second region of weight loss, initiating at approximately 1470 °F (800 °C), is attributable to the thermal decomposition of calcium sulfide, also observed in the calcium sulfide-argon test. This decrease accounts for a loss of approximately 28.8

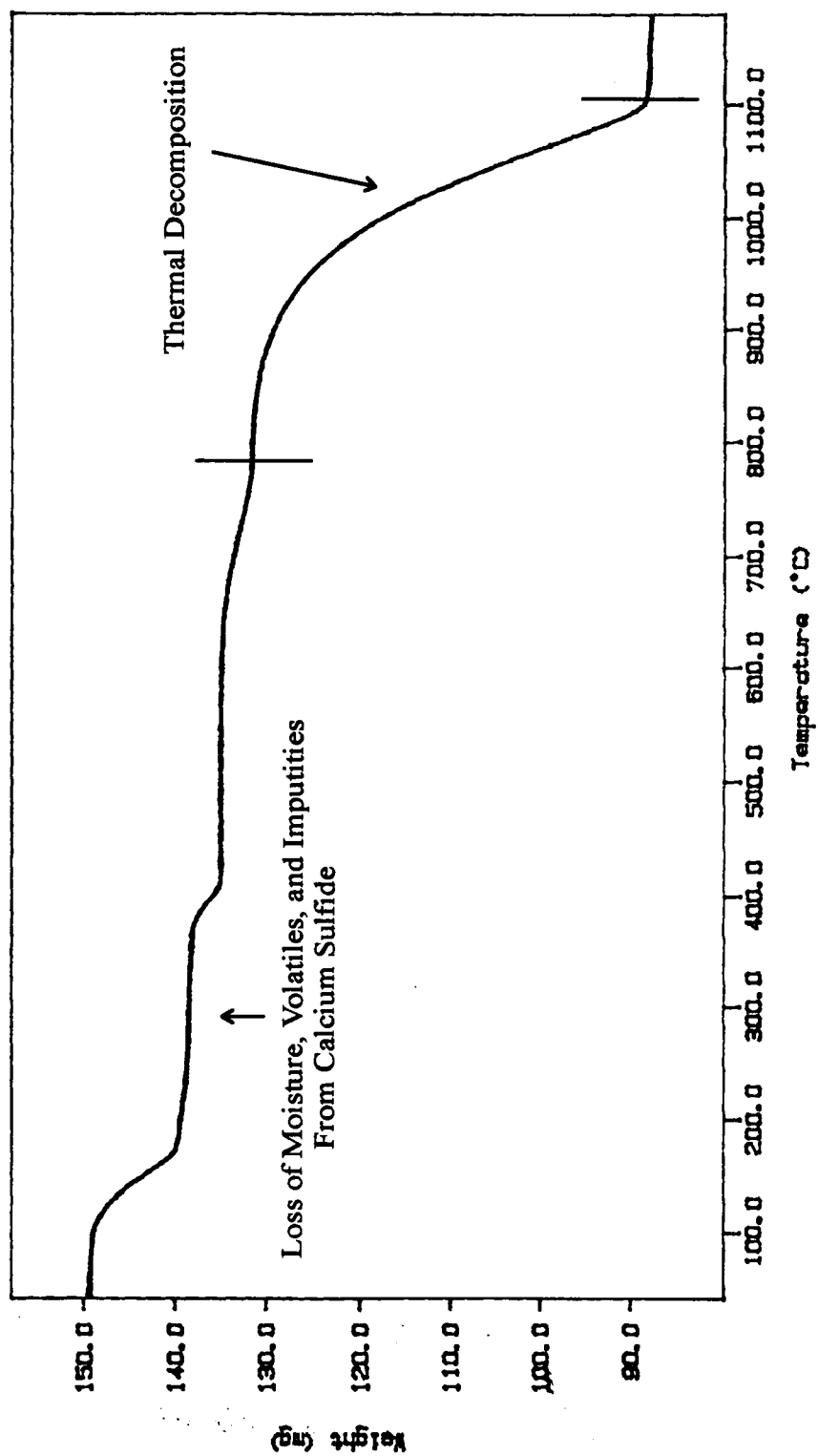


Figure 5.15 Thermogravimetric Analysis of a Mixture of Calcium Sulfide and Calcium Sulfate in Argon

percent of the weight of the original sample. This extent of decomposition is consistent with the previous test of calcium sulfide in argon. From this it is possible to assume that calcium sulfide and calcium sulfate do not react to any measurable extent within a temperature range of 200 °F to 2190 °F, as covered by this TGA test.

A few important observations can be made from the TGA tests. The first of which is that sulfur dioxide will be the primary product from the combustion of calcium sulfide starting at 1800 °F for a pure sample of calcium sulfide, or 1970 °F for the HIPPS char. Below the aforementioned temperatures calcium sulfate will be the favored product from the oxidation of calcium sulfide. The second observation is that carbon dioxide will have a negligible effect on the conversion of calcium sulfide when compared to the effect of thermal decomposition. This observation appears to be true for both pure calcium sulfide and the HIPPS char. The last observation is that the reaction of calcium sulfide and calcium sulfate, shown by equation 3.7:



will not occur to any significant level below approximately 2200 °F, and, therefore will play at most a minor role in the possible production of sulfur dioxide in the HIPPS HITAF.

Results from Bench-Scale Oxidation Studies

With the first group of tests relating to the LECO SC132 completed an attempt was made to verify the proposed kinetics of non-isothermal char combustion, Test 4.1 through 4.3. It was indicated in the literature that the combustion of carbon in excess oxygen would follow a first order rate. To verify the proposed kinetics a plot of the $-\ln(1-X_C)$, where X_C is the conversion of carbon, versus time was made. If the combustion of HIPPS char obeyed first order kinetics then the plot would show a linear trend passing through the origin for each of the data sets. As can be seen from Figure 5.16, this is far from true. Since first order kinetics failed to describe the combustion of HIPPS char in excess air, investigations into other kinetics rate expressions were undertaken. First a zeroth order rate was tested. This seemed to loosely fit a portion of the data, and can be seen in Figure 5.17. A zeroth order reaction is independent of the concentration of the reactants. From the plot of carbon conversion, X_C , versus time it is possible to determine the rate equation for the char combustion data. The kinetic equation has the form:

$$-r_C = -\frac{dC_C}{dt} = \bar{k} \quad (5.2)$$

which when integrated yields:

$$C_{C_0}X_C = \bar{k}t \quad (5.3)$$

where $\bar{k}$ is an average over the temperature range covered in a given test. The $\bar{k}$ or rate

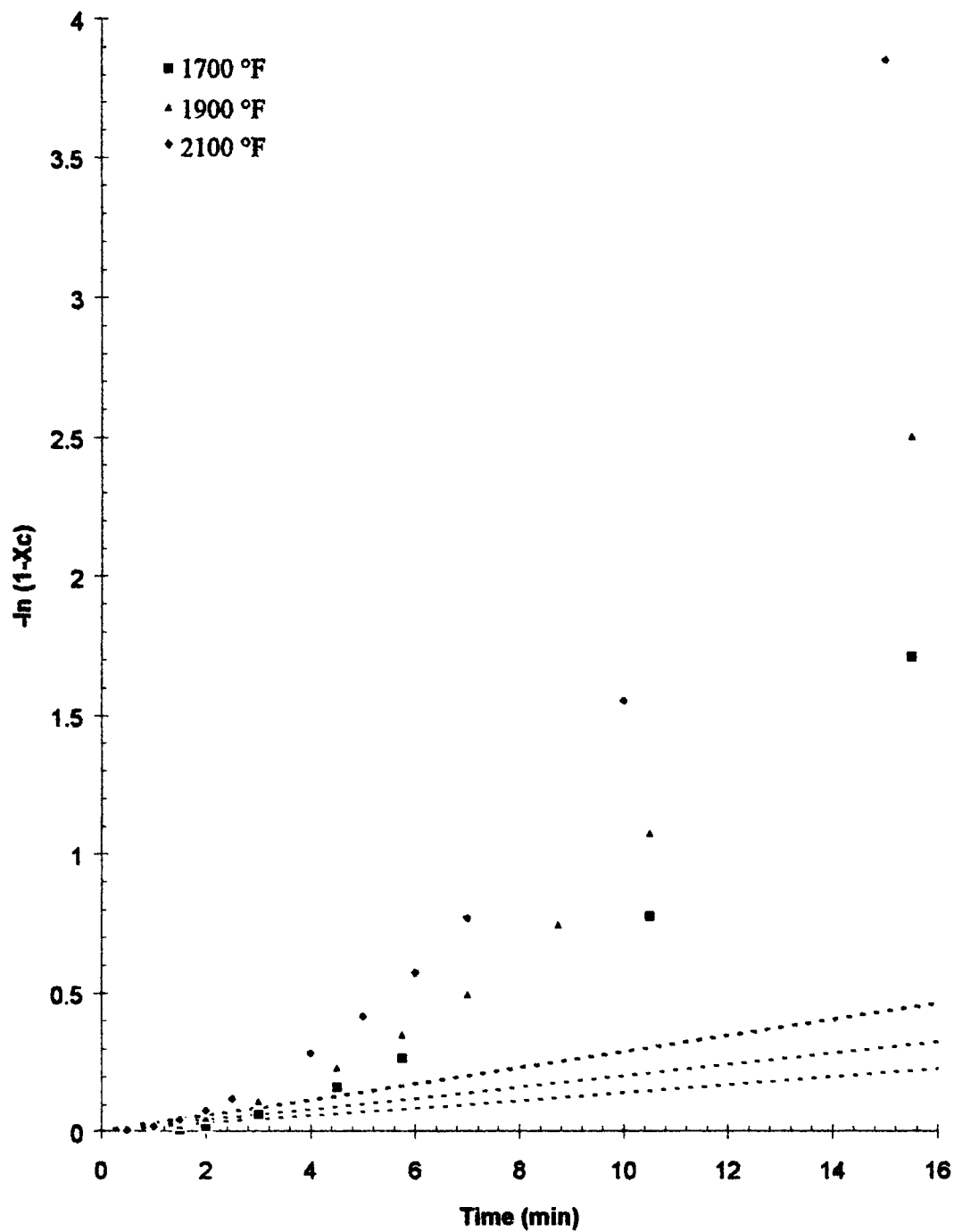


**Figure 5.16 Testing of the First Order Kinetic Model
for the Non-Isothermal Combustion of Char in Excess Air
Tests 4.1, 4.2, and 4.3**

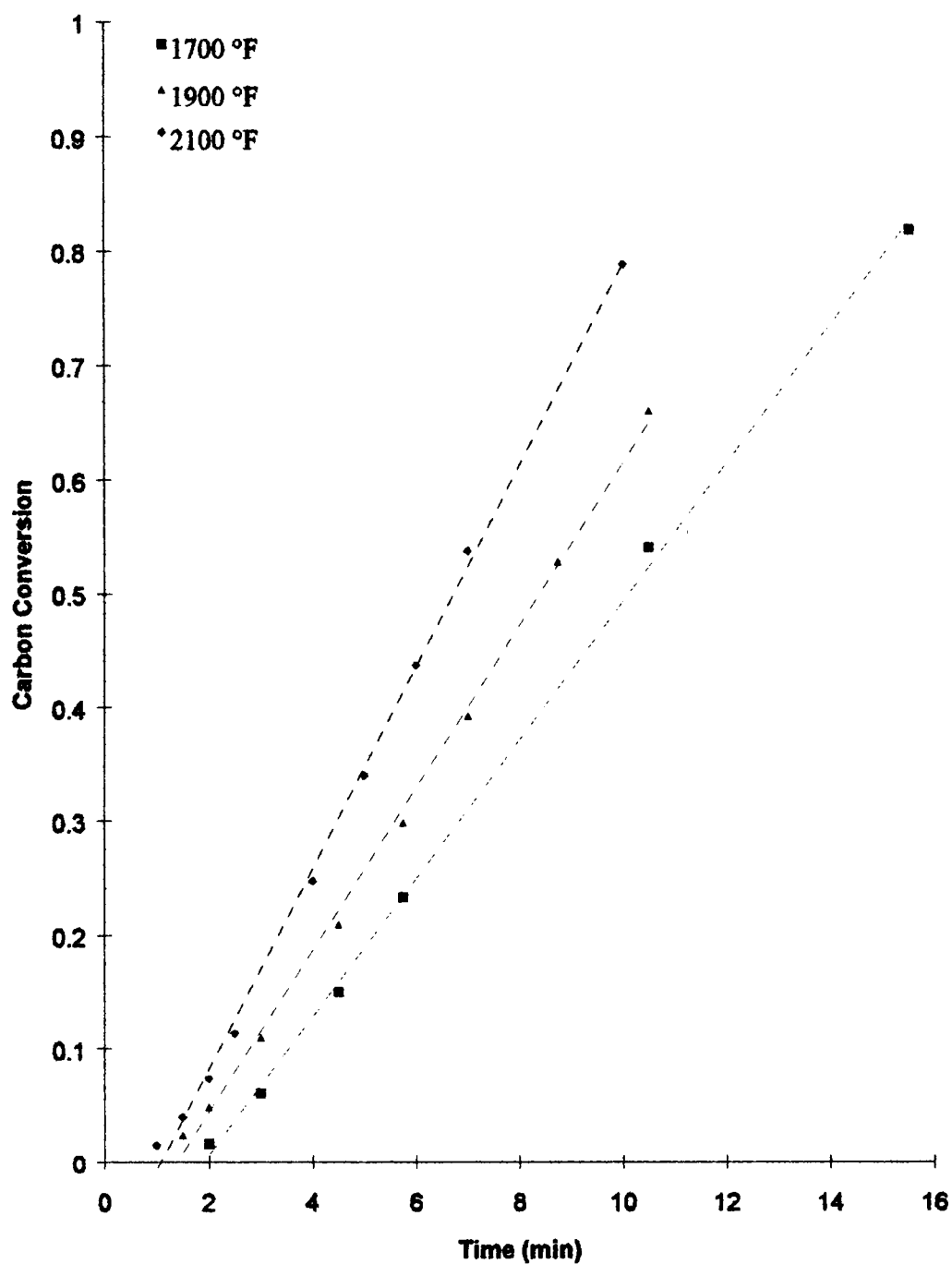


**Figure 5.17 Testing of the Zeroth Order Kinetic Model
for the Non-Isothermal Combustion of Char in Excess Air
Tests 4.1, 4.2, and 4.3**

constant value can be determined for the given data, by multiplying the slope of the line by the initial concentration of carbon. Despite the loose correlation of the zeroth order rate model in the range of X_C of .015 to .80, additional models were investigated to see if a wider X_C range can be covered or not. A plot of the measured X_C versus time was made and can be seen in Figure 5.18. From this plot it was evident that the results displayed a seemingly autocatalytic behavior, low initial rate, high rate in the middle, and finishing with a low rate. A possible explanation of this behavior is that the reaction is not autocatalytic in the classical sense, but could be autothermal. By this it is meant that the exothermic reaction produces localized heat that increases the localized rate of reaction. An autocatalytic reaction in its simplest form has a rate equation of the form:

$$-r_C = -\frac{dC_C}{dt} = \bar{k}C_C(C_{C0} - C_C) \quad (5.4)$$

No suitable rate equation for an autothermal reaction was found in the literature, therefore a modification to the above rate equation was performed to fit the data. To account for the possible influence of the heat released by carbon combustion, the above equation was modified to the following form:

$$-r_C = -\frac{dC_C}{dt} = \bar{k}C_C^\alpha(C_{C0} - C_C) \quad (5.5)$$

Equation 5.5 can be further simplified to relate the change in conversion as time progresses. This simplification results in the following equation:

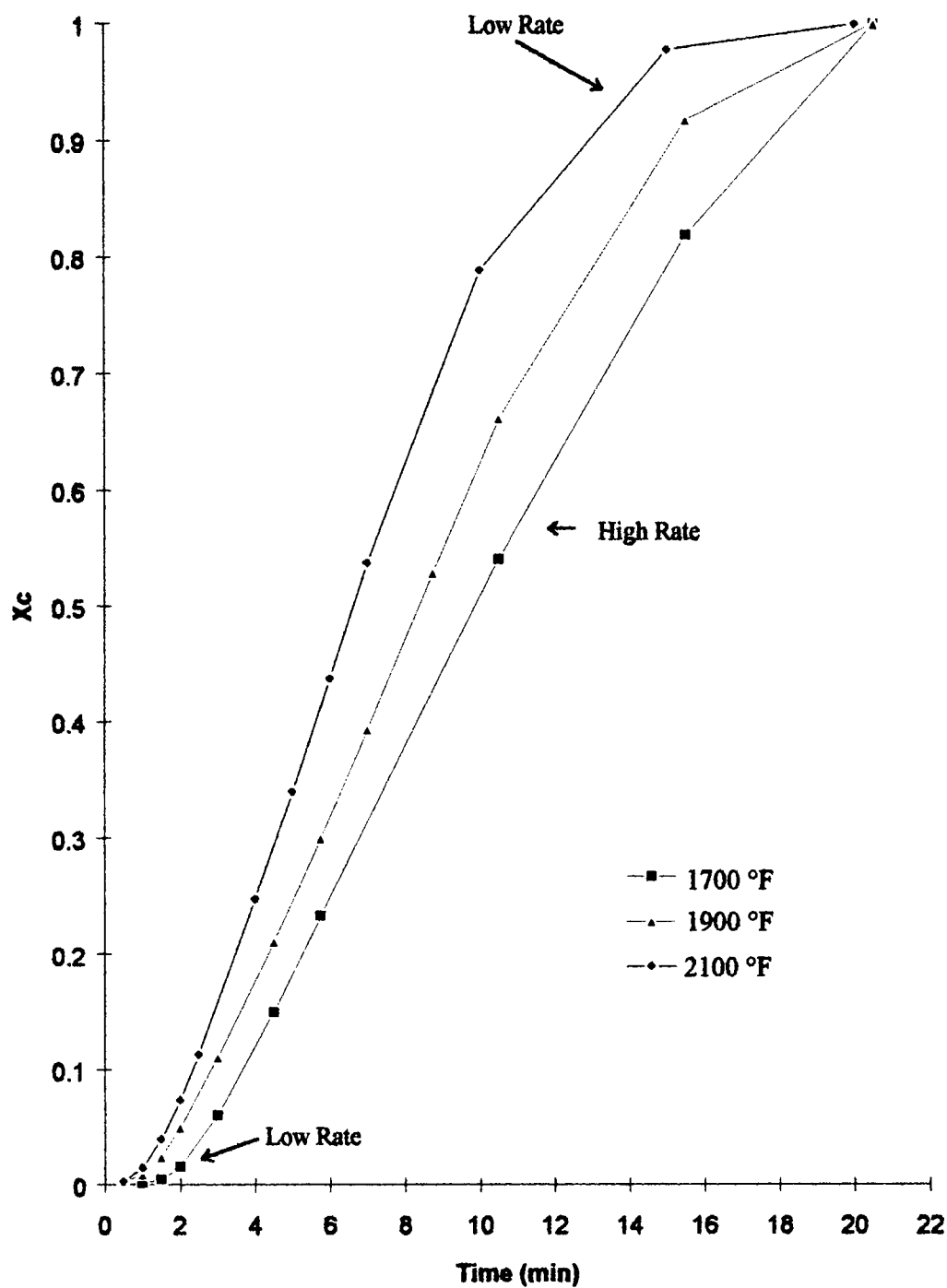


**Figure 5.18 Conversion of Carbon versus Time
for Non-Isothermal Bench-Scale Experiments
Tests 4.1, 4.2, and 4.3**

$$-\frac{dX_C}{dt} = \bar{k}C_{C0}^\alpha X_C^\alpha (1 - X_C) \quad (5.6)$$

which when numerically integrated yields:

$$-\frac{(1 - X_C)X_C^{(1-\alpha)}}{(1-\alpha)(X_C - 1)} \left(\sum_{j=0}^{\infty} \frac{(1-\alpha)}{(2-\alpha)} \frac{X_C^j}{j!} \right) = \bar{k}C_{C0}^\alpha t \quad (5.7)$$

This integration was performed using a power mathematics software package called Mathematica. From this equation it is possible to determine the values of $\bar{k}$ and α . A plot of the left side of the previous equation versus time will, if this is an adequate model, yield a straight line through the origin whose slope is $\bar{k}C_{C0}^\alpha$. The procedure for determining values for $\bar{k}$ and α is as follows:

- [1] Set initial value for α .
- [2] Plot left side of equation 5.7 versus time.
- [3] Determine slope of best fitting straight line for the data passing through the origin. The slope is equal to $\bar{k}C_{C0}^\alpha$.
- [4] Adjust α to increase the accuracy of the approximation.
- [5] Repeat steps [2] through [4] until best value for α is determined.

- [6] Repeat steps [1] through [5] for all available data sets runs.
- [7] Average the various values of α .
- [8] Repeat steps [2] and [3] for each data set.

As can be seen in Figure 5.19, this rate model is valid for describing the non-isothermal combustion of carbon from the HIPPS char. The values for $\bar{k}$ and α as determined for the non-isothermal tests, Tests 4.1, 4.2, and 4.3, are as follows:

$$\alpha = 0.55$$

$$\bar{k}_{1700^{\circ}\text{F}} = .391 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

$$\bar{k}_{1900^{\circ}\text{F}} = .520 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

$$\bar{k}_{1700^{\circ}\text{F}} = .471 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

The following three plots, Figures 5.20, 5.21, and 5.22, show the comparison between the measured and calculated conversions of carbon as a function of time for these three non-isothermal temperature tests, Tests 4.1, 4.2, and 4.3. Within experimental errors these fits follow the trend of the data better than the other rate models investigated and as such is supportive of the proposed autothermal nature of the experiments. Normally an Arrhenius relationship for the rate constants would be determined, but the scatter,

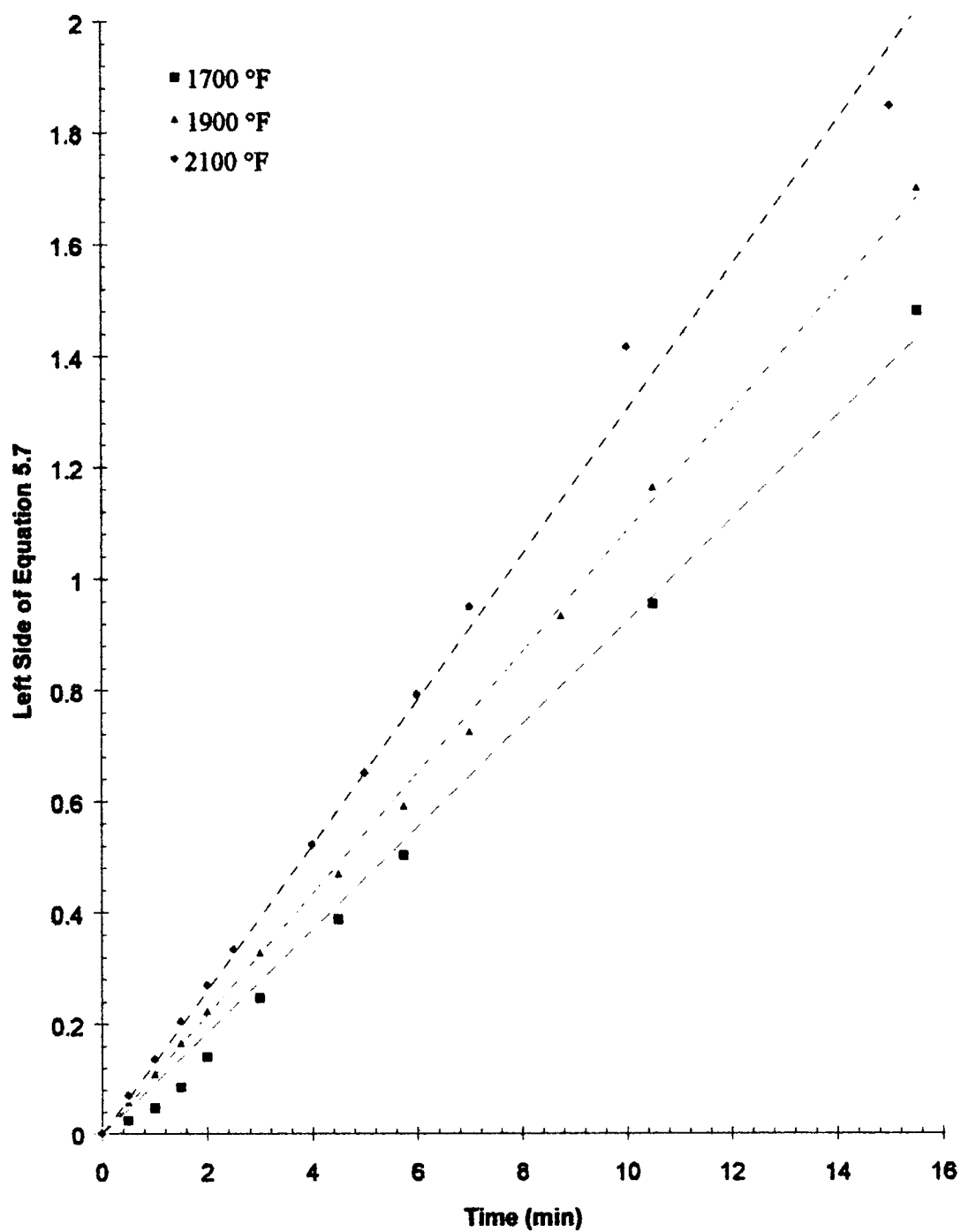


**Figure 5.19 Verification of the Autothermal Kinetic Model
for the Non-Isothermal Combustion of Char in Excess Air
Tests 4.1, 4.2, and 4.3**

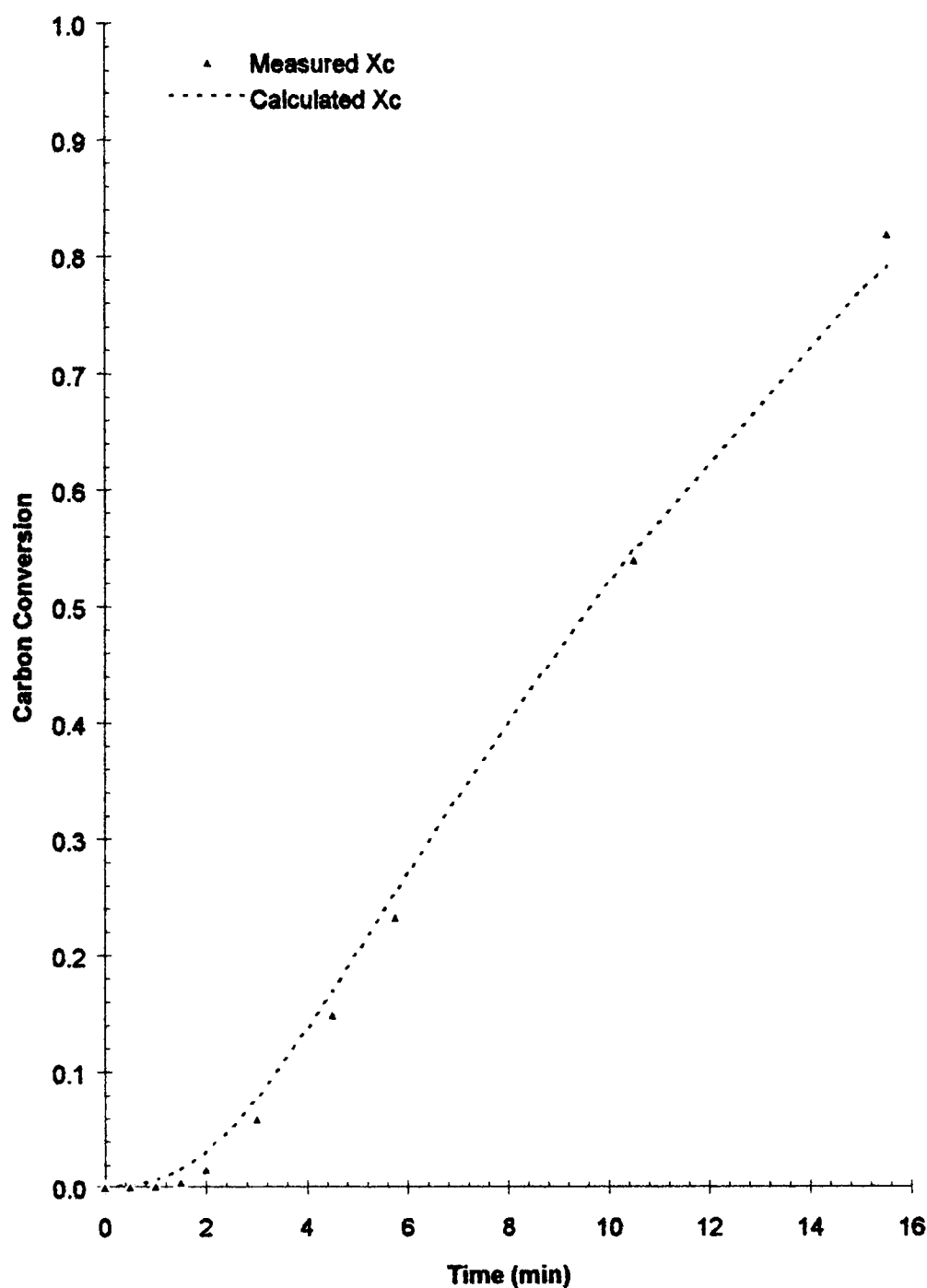


**Figure 5.20 Verification of Autothermal Kinetic Model for the
Non-Isothermal Combustion of HIPPS Char
Starting at 1700 °F**

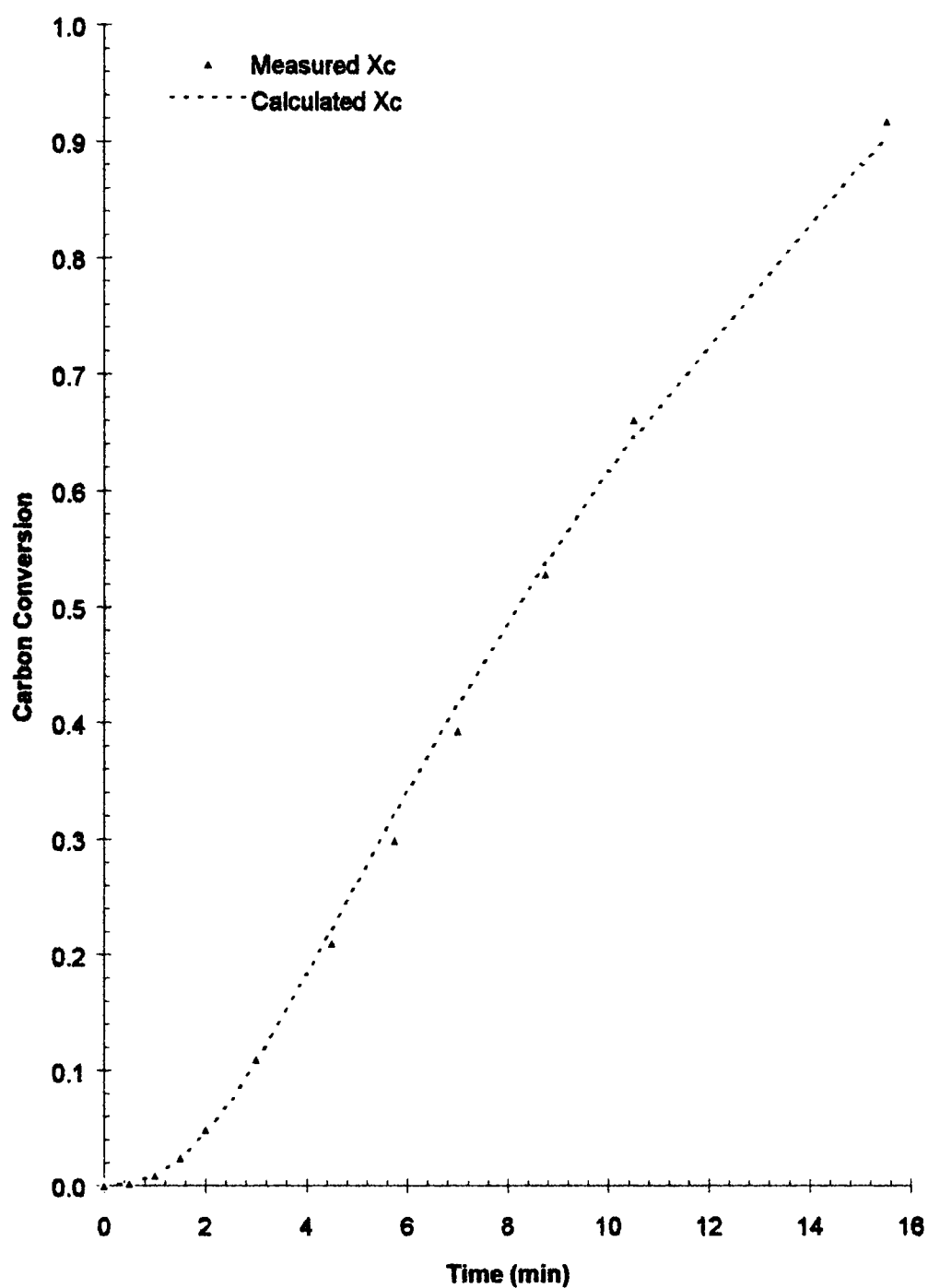


**Figure 5.21 Verification of Autothermal Kinetic Model for the
Non-Isothermal Combustion of HIPPS Char
Starting at 1900 °F**

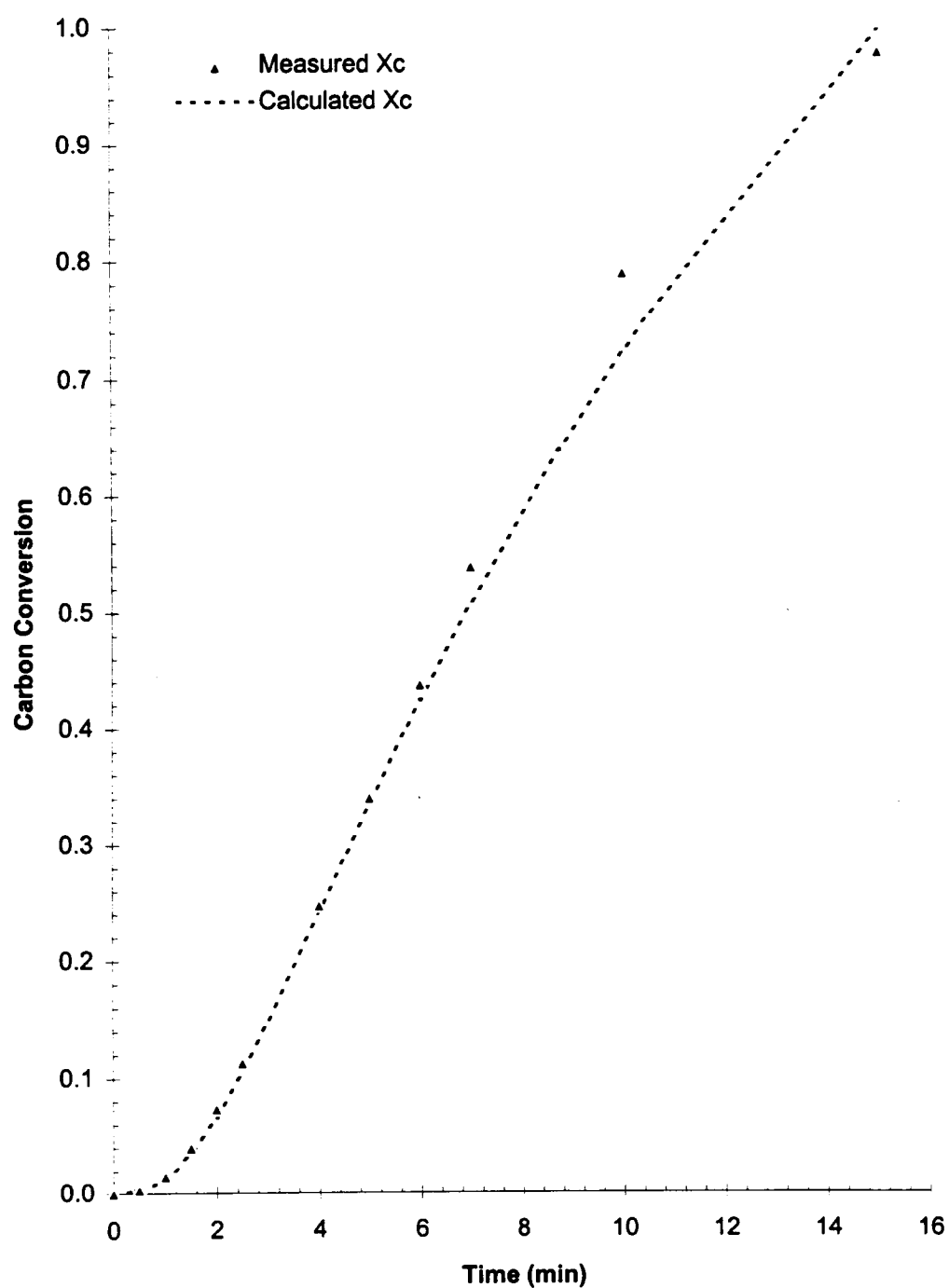


**Figure 5.22 Verification of Autothermal Kinetic Model for the
Non-Isothermal Combustion of HIPPS Char
Starting at 2100 °F**

unknown temperature rise for each test, and limited number of data points make any such attempt a moot point at present.

With the combustion of HIPPS char investigated the next group of experiments, Tests 4.4 through 4.11, were undertaken to study the production of sulfur dioxide from a char combustion reaction. As indicated earlier, Phase 2 consisted of two separate series of experiments. The first part of Phase 2, Tests 4.4 through 4.7, was concerned with non-isothermal reactor conditions, and the second portion of Phase 2, Tests 4.8 through 4.11, was concerned with isothermal conditions. The first set of experiments was designed to measure the levels of sulfur dioxide produced, using the IR detector in the LECO SC132. Four separate runs were undertaken, spanning the temperature range of the HIPPS HITAF, up to the maximum temperature achievable with the available Mellon tube furnace. As with the previous combustion studies the temperature dropped rapidly when the sample probe and sample were inserted into the reactor. The initial temperatures of the four runs were, 1350 °F, 1725 °F, 2035 °F, and 2140 °F. During the first use of the LECO SC132 unit a calibration for the printer/display values was not available, however since the flow rate to the IR detector was now externally controlled in these tests a calibration was performed for various sulfur dioxide levels. The resulting calibration indicated a linear correspondence between the LECO display values and actual sulfur dioxide ppm levels. This calibration is given by the following equation:

$$\text{Sulfur Dioxide (ppm)} = 3.042 \times \text{LECO Reading} \quad (5.8)$$

The results from these tests are given in Figure 5.23 through Figure 5.26. As can be seen from these figures, the production of sulfur dioxide increased markedly as the temperature increased. From this series of plots it is obvious that both the organic sulfur and the calcium sulfide are contributing to the production of sulfur dioxide. This unexpected visual verification of the combustion of calcium sulfide was due to the non-isothermal nature of these tests. The first test, Test 4.4, at 1350 °F was well below the temperatures at which calcium sulfide would combust to form calcium sulfate, as indicated by the TGA tests, primarily Test 3.5. During the next two tests, Test 4.5 at 1725 °F and Test 4.6 at 2035 °F, the temperature dropped below the temperature at which calcium sulfide oxidizes to sulfur dioxide and it is obvious that a second source of sulfur dioxide is contributing to the overall sulfur dioxide. This second source of sulfur dioxide is most probably the organic sulfur species oxidizing as the HIPPS char combusts. It is also obvious that the levels of sulfur dioxide produced were significantly higher at the higher temperature, which was also observed in the original LECO SC132 tests. The last temperature, Test 4.7 at 2140 °F, was well above the typical calcium sulfide oxidation to sulfur dioxide transition temperature and as such it revealed the highest level of sulfur dioxide of any run. From Figure 5.27 it is possible to see that as the temperature increased the peak levels of sulfur dioxide increased, and the time required to reach the first sulfur dioxide peak also decreased to a minimum of about 70 to 75 seconds (See Table 5.6). Similar to Tables 5.3 and 5.4, Table 5.7 shows the important characteristic values common to all four runs. These values serve as a means of

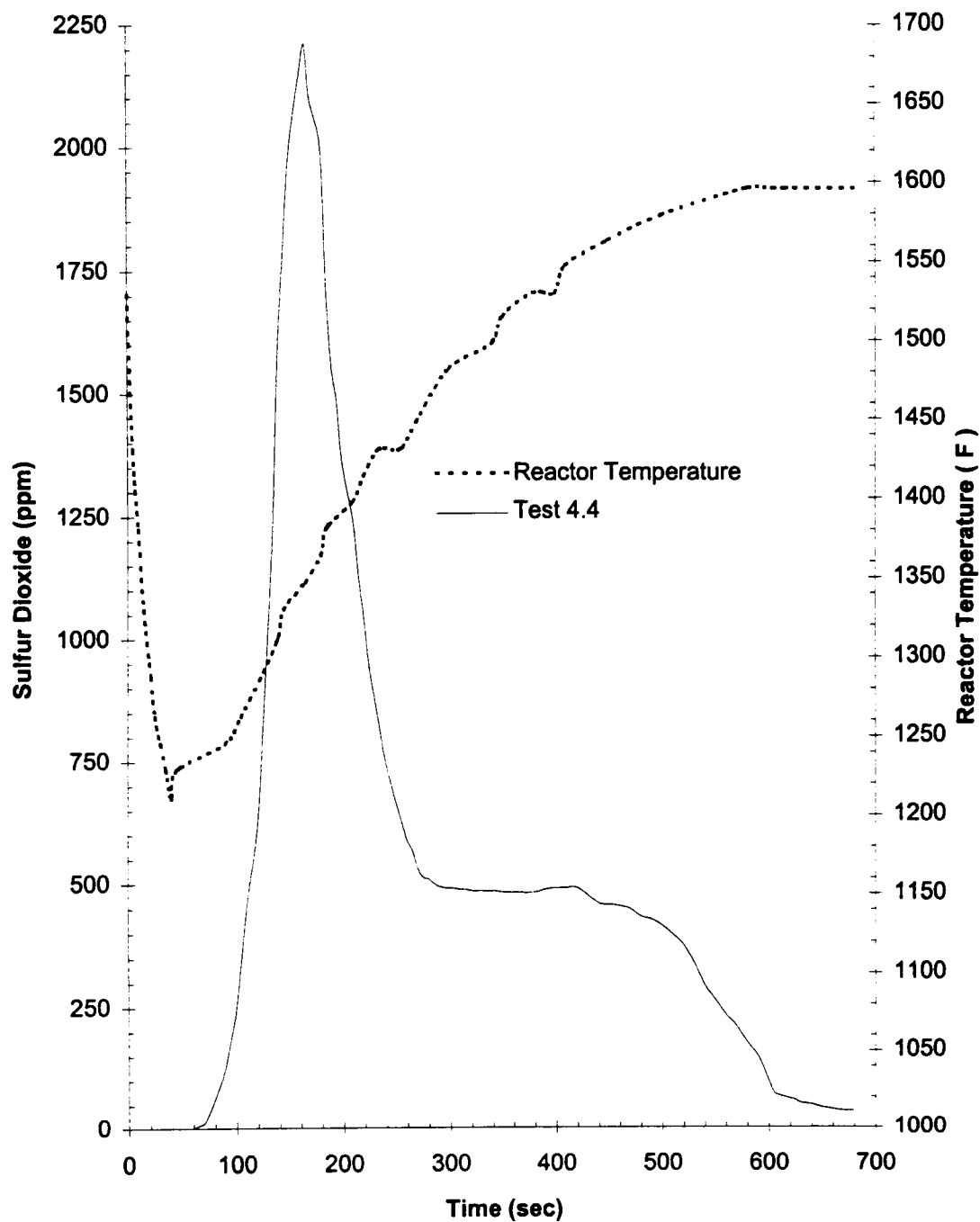


**Figure 5.23 Observed Production of Sulfur Dioxide from
HIPPS Char for Non-Isothermal Test 4.4**

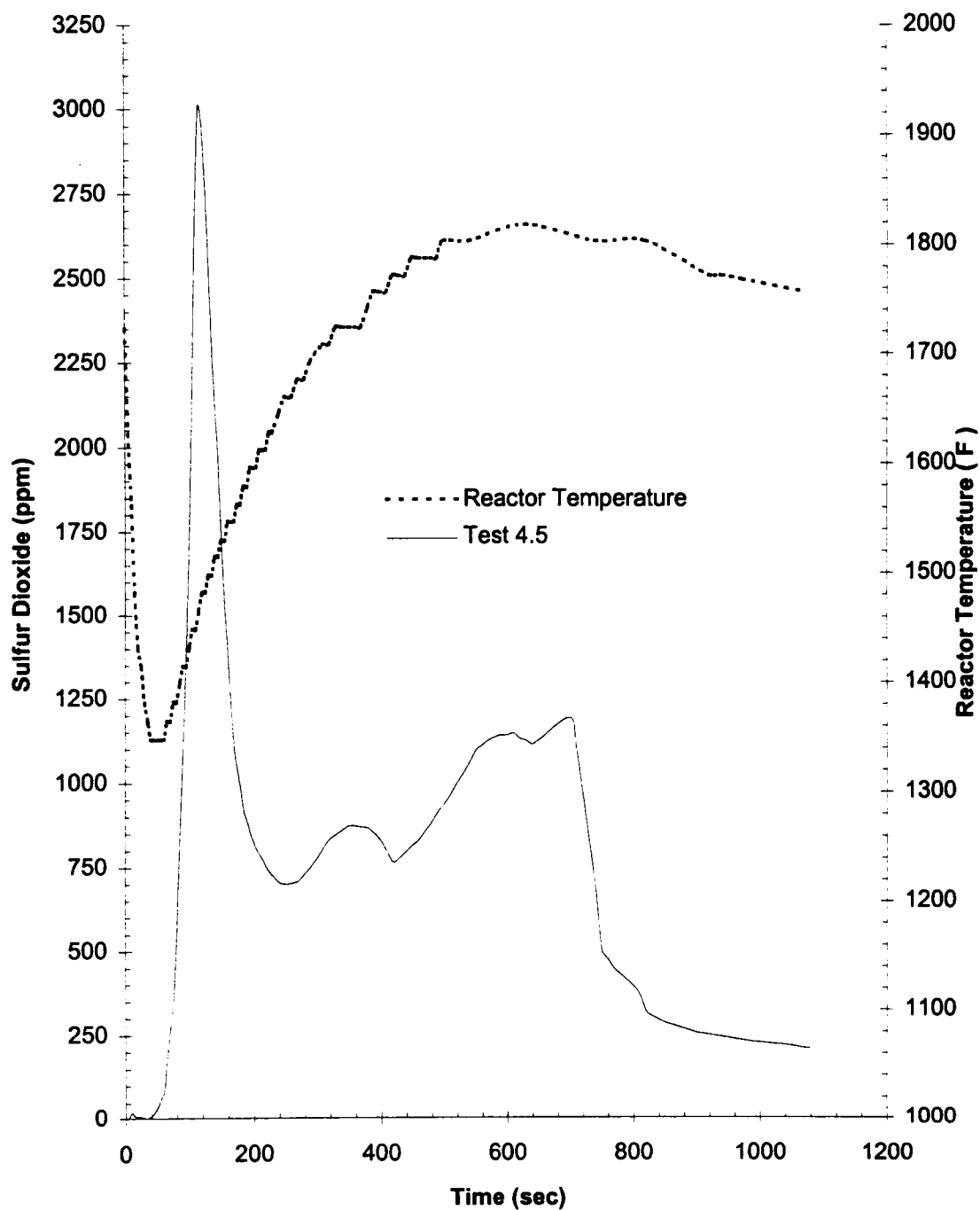


**Figure 5.24 Observed Production of Sulfur Dioxide from
HIPPS Char for Non-Isothermal Test 4.5**

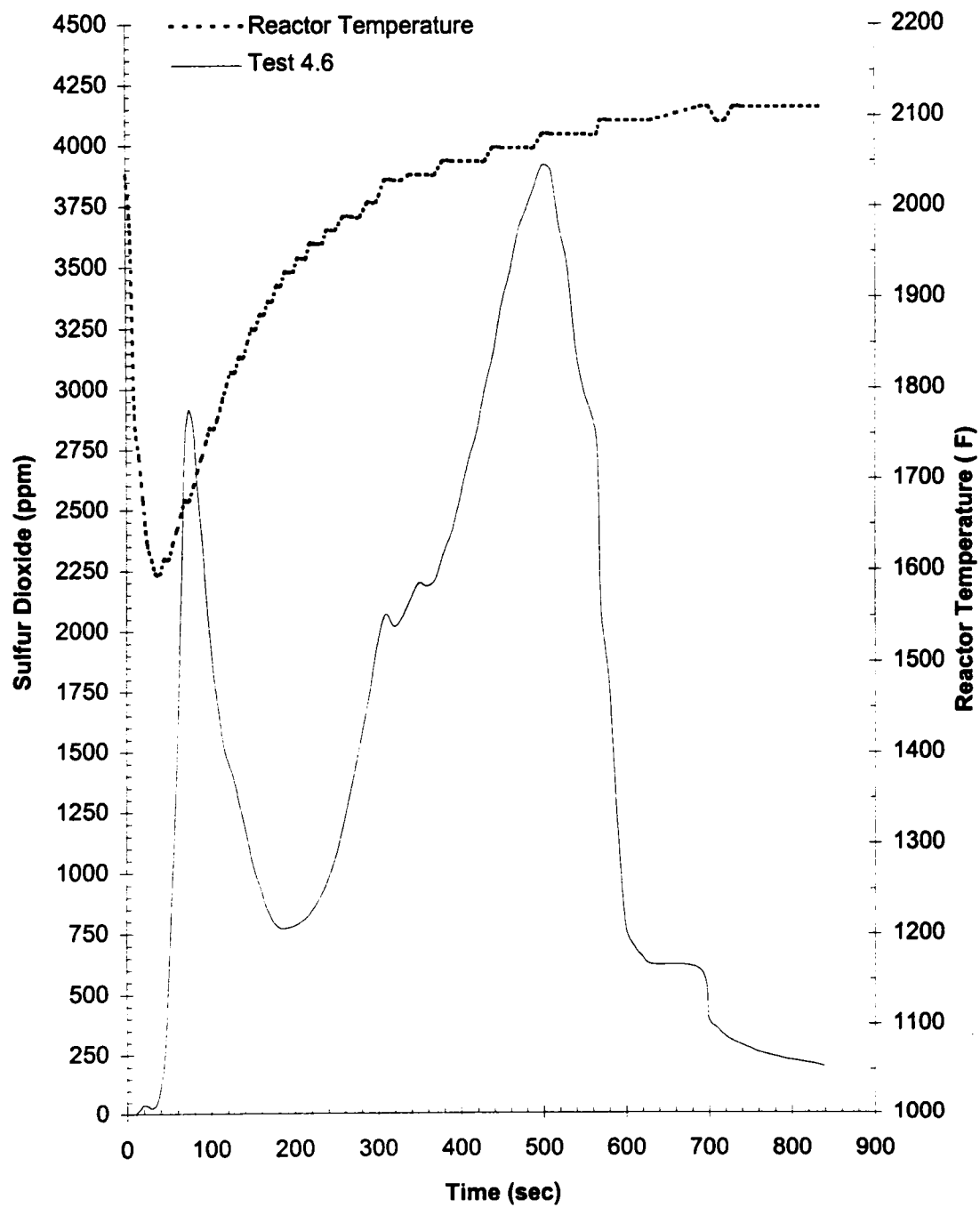


**Figure 5.25 Observed Production of Sulfur Dioxide from
HIPPS Char for Non-Isothermal Test 4.6**

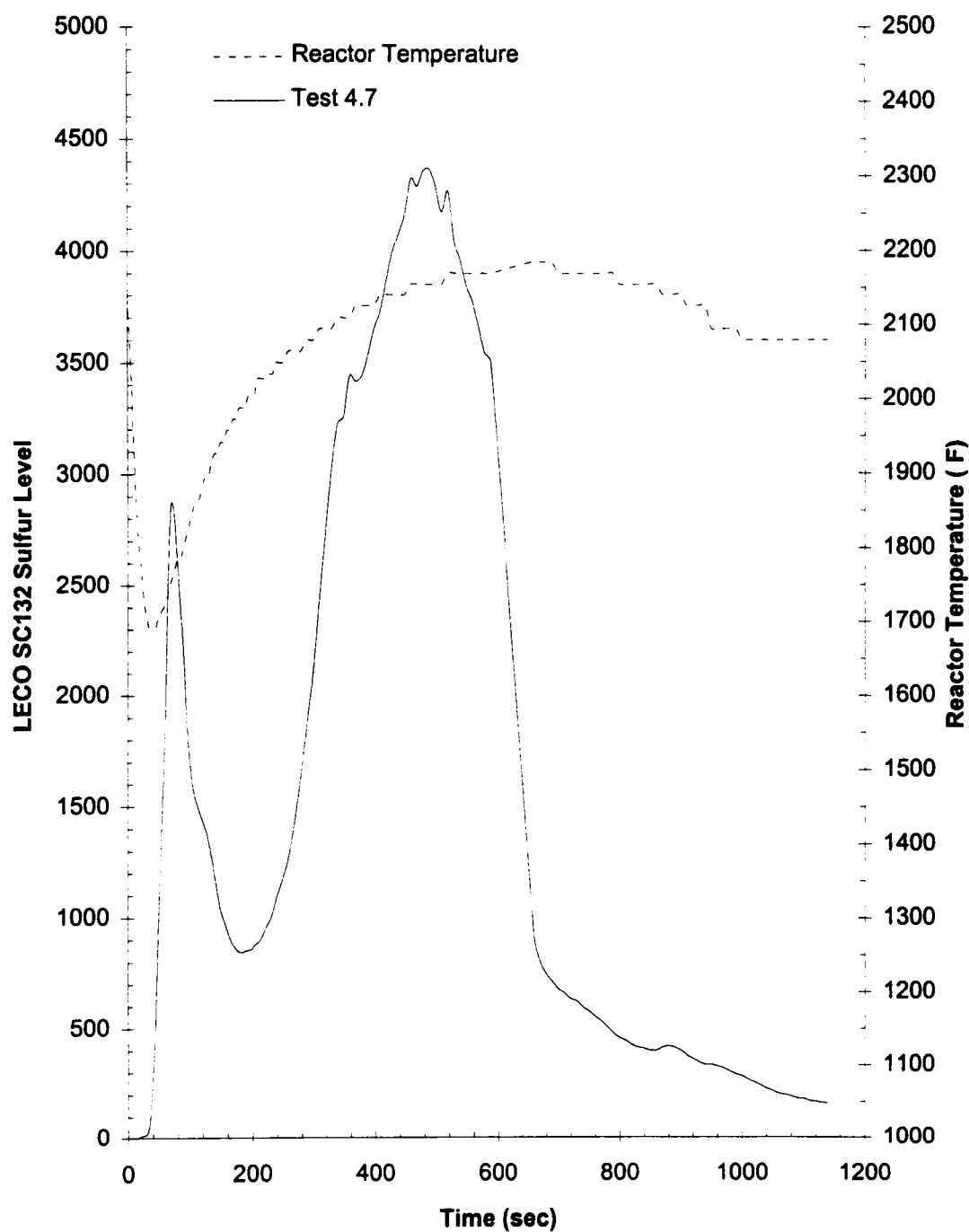
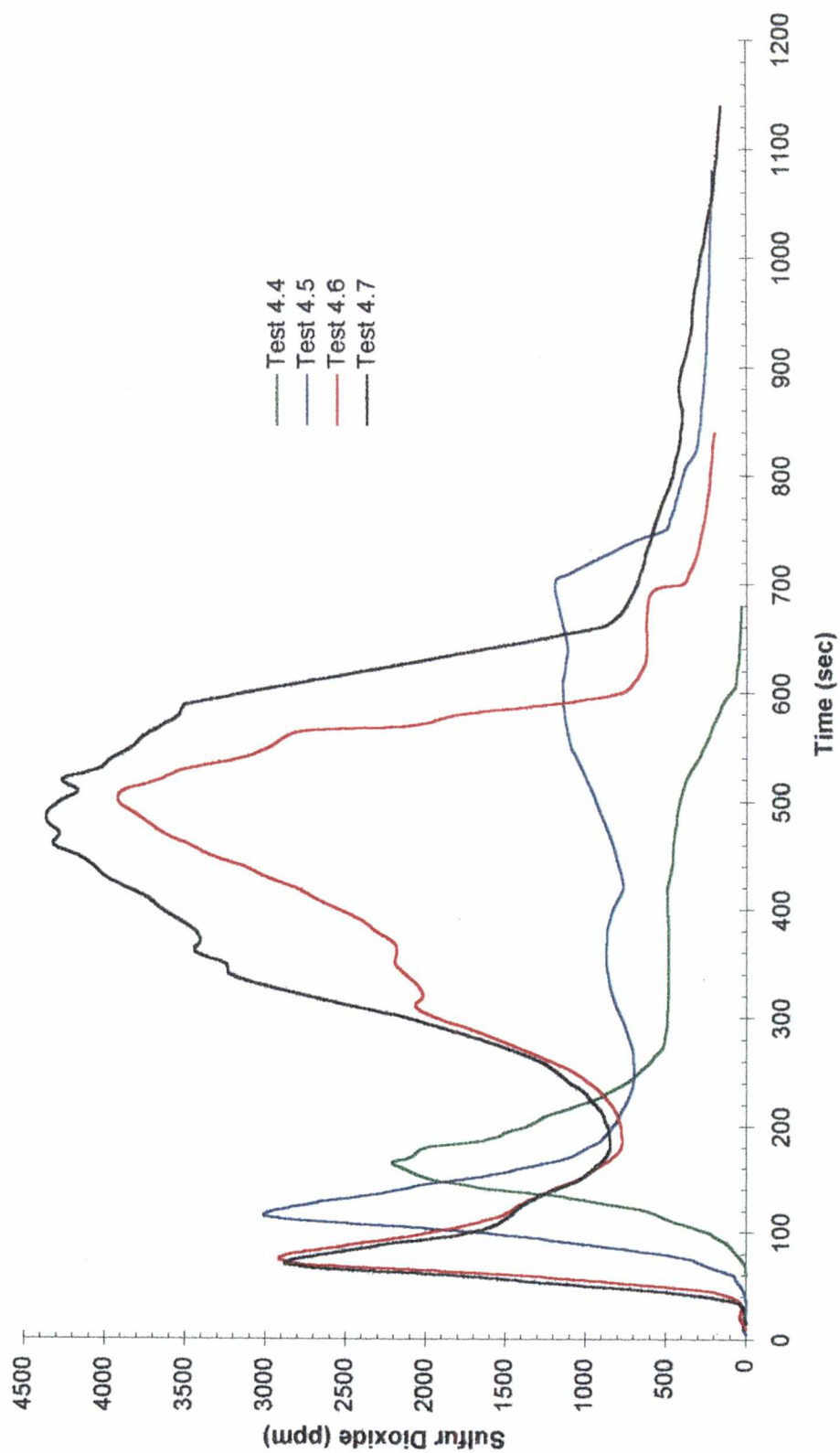


**Figure 5.26 Observed Production of Sulfur Dioxide from
HIPPS Char for Non-Isothermal Test 4.7**



**5.27 Observed Production of Sulfur Dioxide from
HIPPS Char for Tests 4.4 - 4.7**

**Table 5.7 Comparison of Characteristic Values for the
Non-Isothermal Oxidation of HIPPS Char in Air
Tests 4.4 - 4.7**

	Temperature (°F)			
	1350	1725	2035	2140
Initial Time of Measurable Sulfur Dioxide Production (sec)	65	10	15	20
Time of First Peak Sulfur Dioxide Production (sec)	165	115	75	70
Time of Second Peak Sulfur Dioxide Production (sec)	---	700	500	490
Time of Last Measurable Sulfur Dioxide (sec)	680	1080+	840+	1140+
First Peak Value Measured for the Production of Sulfur Dioxide (ppm)	2212	3009	2914	2869
Second Peak Value Measured for the Production of Sulfur Dioxide (ppm)	---	1193	3918	4362

comparison, both between each non isothermal run and the previous LECO SC132 tests. From these results it is obvious that the earlier observations, while at isothermal conditions, still seem to be corroborated by these non isothermal results.

Next, efforts were made to determine overall sulfur conversion levels. The sulfur dioxide evolution data from the IR detector, in parts per million, was used to calculate the overall conversion of the sulfur in the HIPPS char. Once the conversion of sulfur as a function of time was determined the search for an appropriate rate model was undertaken. The first rate model investigated was the first order rate model. A plot of the $-\ln(1 - X_S)$ covering the first eleven minutes of data, for the four runs, can be seen in Figure 5.28. The plot is in terms of the overall conversion of sulfur from both forms in the HIPPS char. The reasoning for only showing this span of time comes from the unfortunate fact that the LECO SC132 unit resets after roughly eleven minutes of operation, and as such resets the cell calibration which even though the flow through the IR detector is shutoff will not return to the same calibration as used prior to the reset. This doesn't mean that the data is of no value, because, as can be seen in the compilation of results in Appendix II, the detector after reset will still show the trend of sulfur dioxide production. However the actual values may or may not be accurate. From this figure it is obvious that the formation of sulfur dioxide from the oxidation of calcium sulfide and organic sulfur species does not follow first order. Next the zeroth order kinetic model was tried. This can be seen in Figure 5.29. As can be seen from the figure, zeroth order kinetics also

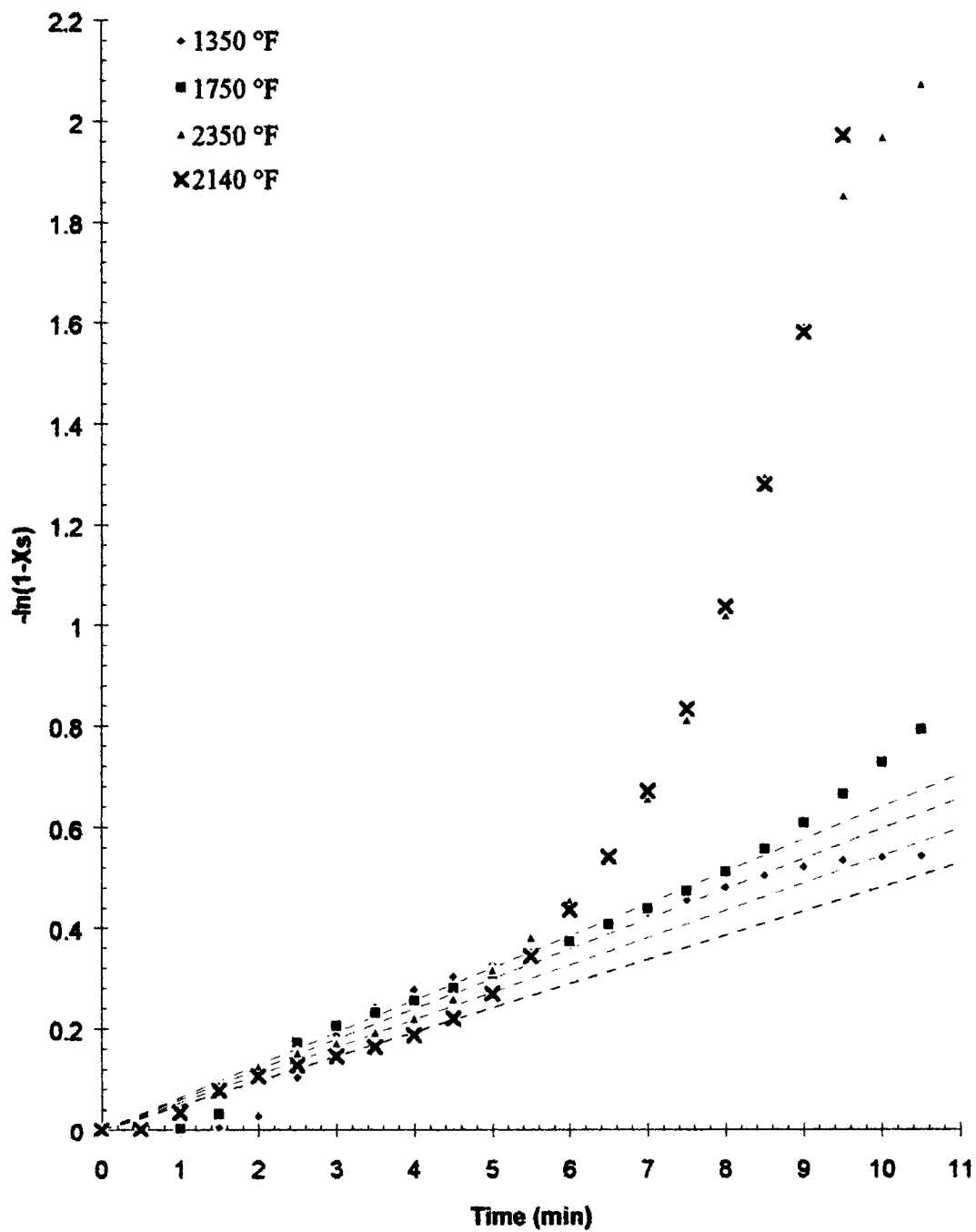


**Figure 5.28 Testing of the First Order Kinetic Model
for the Non-Isothermal Oxidation of Sulfur
in HIPPS Char for Tests 4.4 - 4.7**

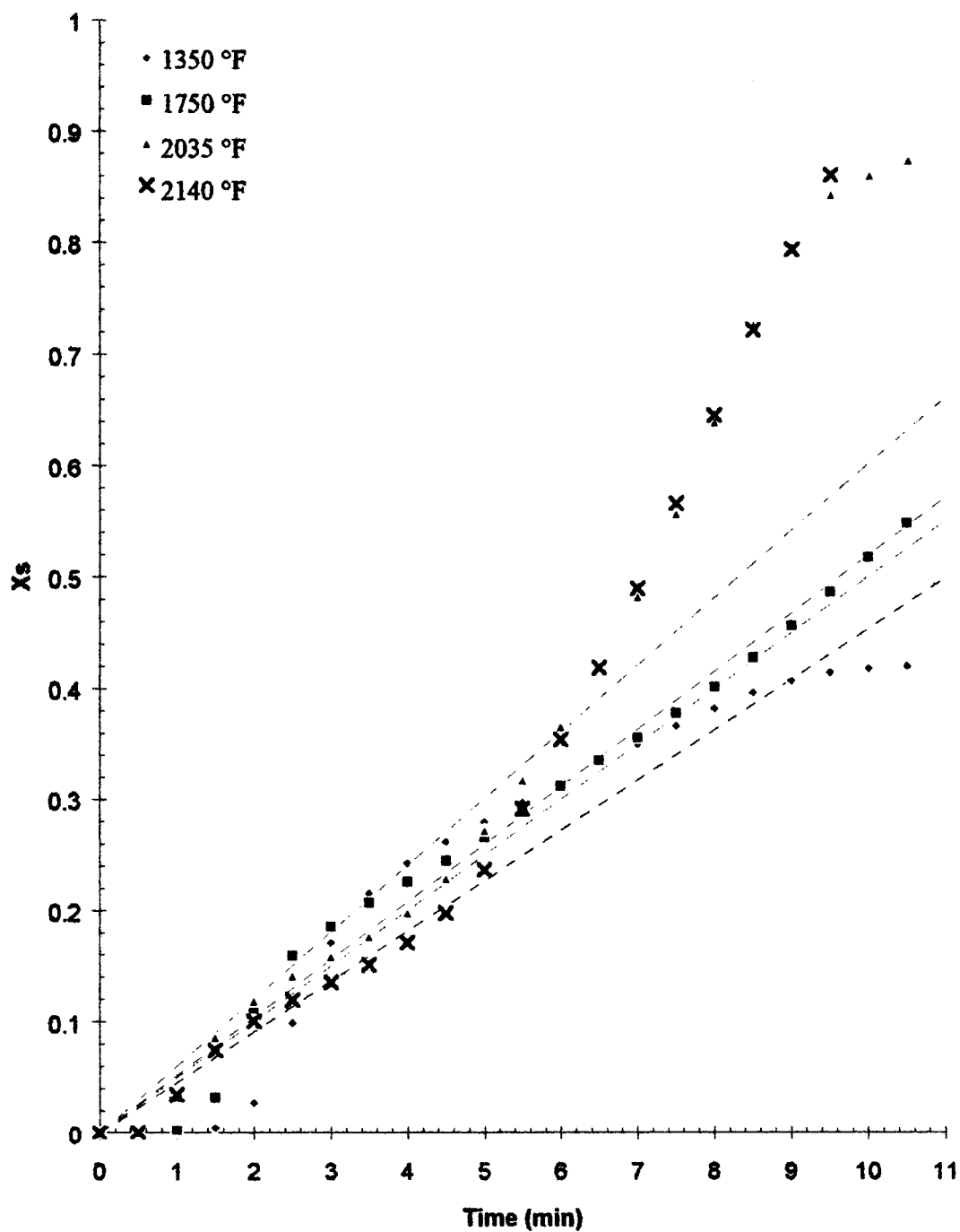


**Figure 5.29 Testing of the Zeroth Order Kinetic Model
 for the Non-Isothermal Oxidation of Sulfur
 in HIPPS Char for Test 4.4 - 4.7**

does not describe the oxidation of sulfur. After considering other kinetic models it was determined that no simple kinetic model would describe this non-isothermal oxidation of sulfur. With this in mind a plot of measured rate of sulfur disappearance versus time, for Test 4.5, 4.6, and 4.7, was prepared to highlight a few observations from these tests. This data can be seen in Figure 5.30. As can be seen from this data the rate goes through a cycle where it initially increases, then after a few minutes decreases. A kinetic explanation of this behavior is not possible at this time. It is possible that something beside the kinetics of combustion is also contributing to the rate of sulfur disappearance, which manifests in the production of sulfur dioxide. It was then proposed that probably some kind of product inhibition effects may be controlling the sulfur dioxide production, by this it is meant that the amounts of sulfur dioxide produced may be restricted by the concentrations of other gases, such as carbon dioxide, present during the combustion process. If this is indeed happening then a plot of the levels, in parts per million, of carbon dioxide and sulfur dioxide versus time should demonstrate this. Figure 5.31 shows the carbon dioxide and sulfur dioxide levels for the test starting at 1750 °F. Figure 5.32 shows similar comparison for the test starting at 2035 °F, Test 4.6. Lastly Figure 5.33 shows similar comparison for the test starting at 2140 °F, Test 4.7. The levels of carbon dioxide were estimated for the above temperatures from the results obtained in the combustion of carbon tests, Test 4.1 through 4.3, at respectively similar initial temperatures. The test, Test 4.4, starting at 1350 °F was not displayed in this fashion as accurate data for carbon dioxide evolution at this temperature was not available. As can

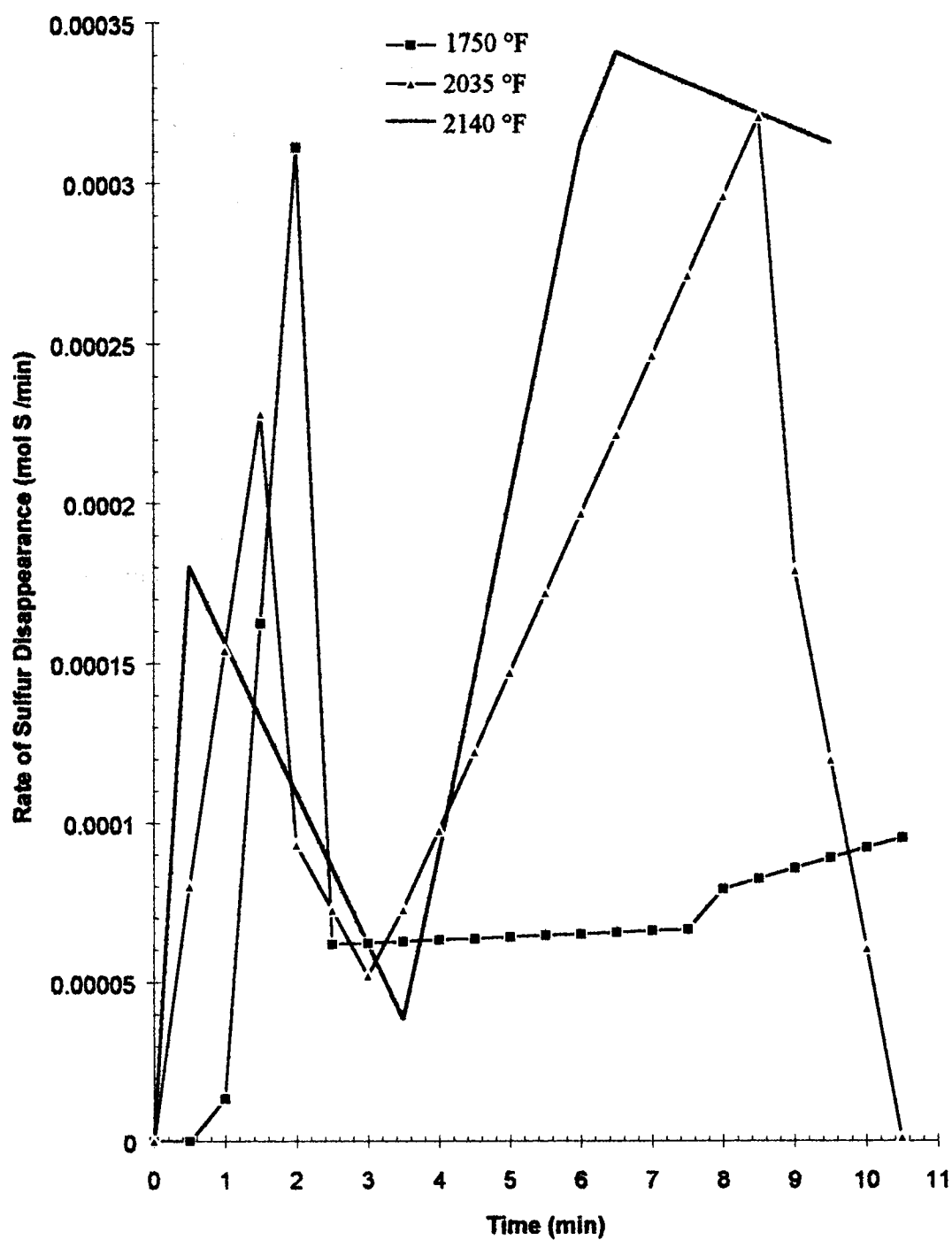


Figure 5.30 Measured Rate of Sulfur Disappearance During the Non-Isothermal Oxidation of Sulfur in HIPPS Char for Tests 4.5 - 4.7

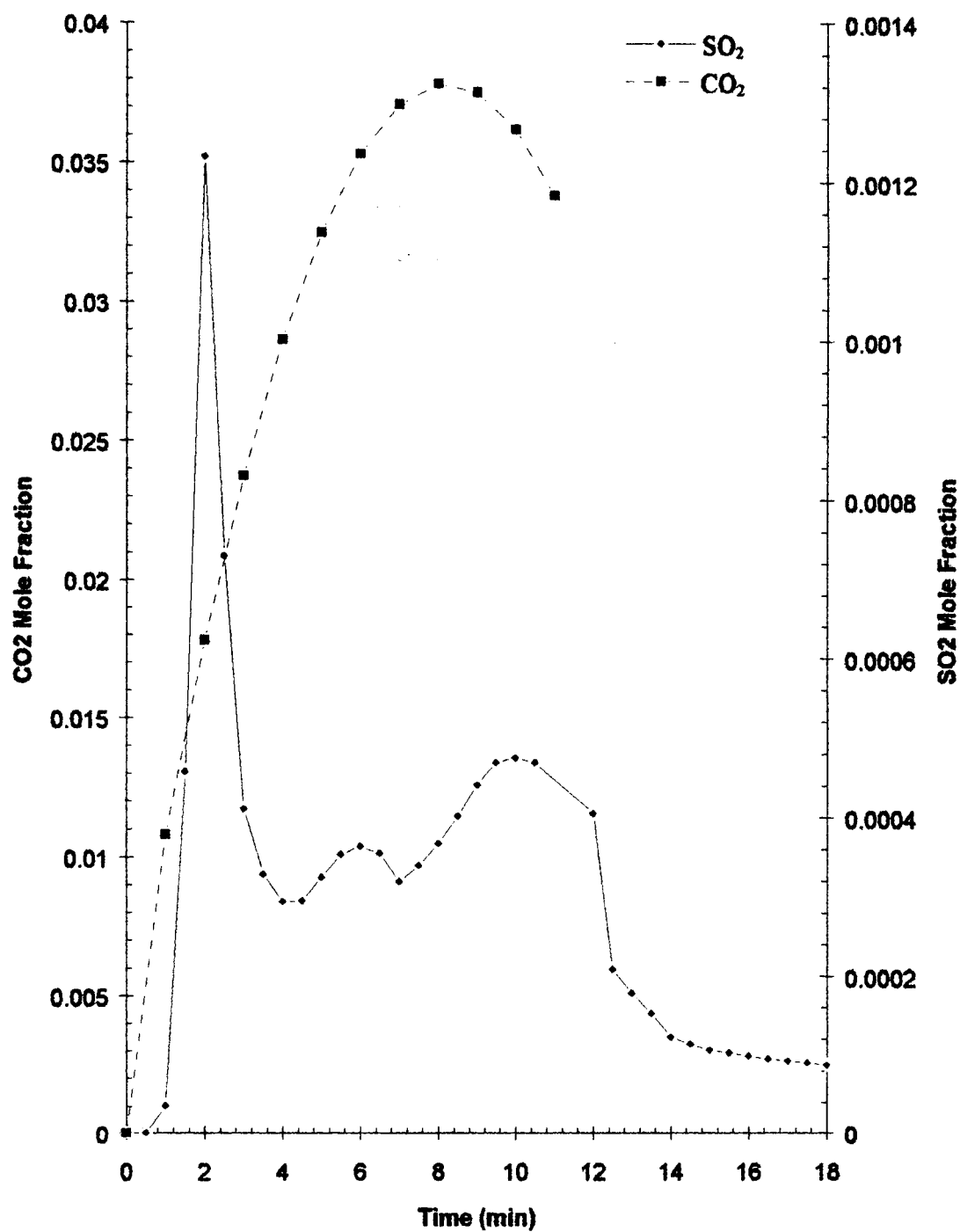


**Figure 5.31 Calculated Carbon Dioxide and Observed Sulfur Dioxide
Evolution from HIPPS Char for a Non-Isothermal
Test Starting at 1750 °F**

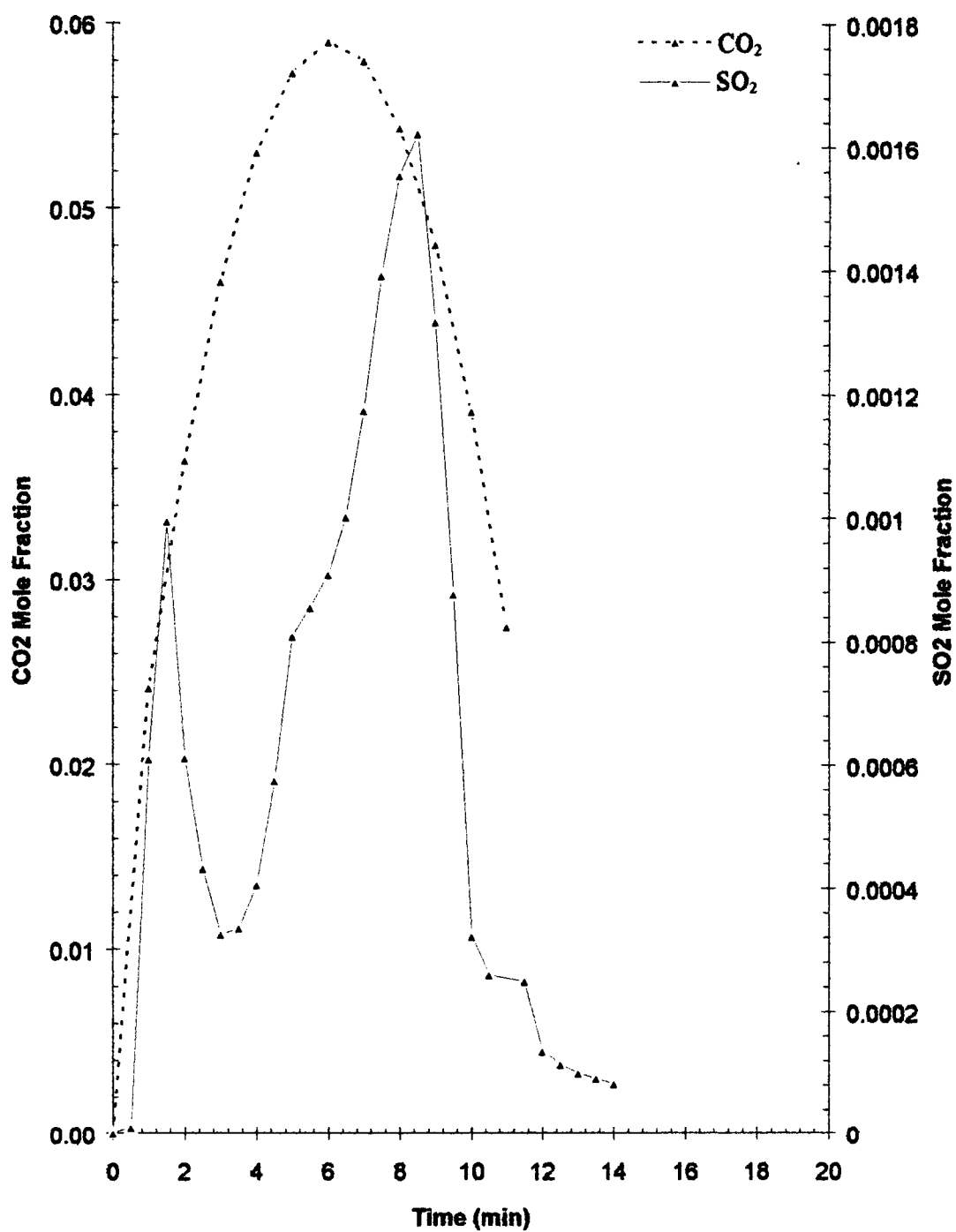


**Figure 5.32 Calculated Carbon Dioxide and Observed Sulfur Dioxide
Evolution from HIPPS Char for a Non-Isothermal
Test Starting at 2035 °F**

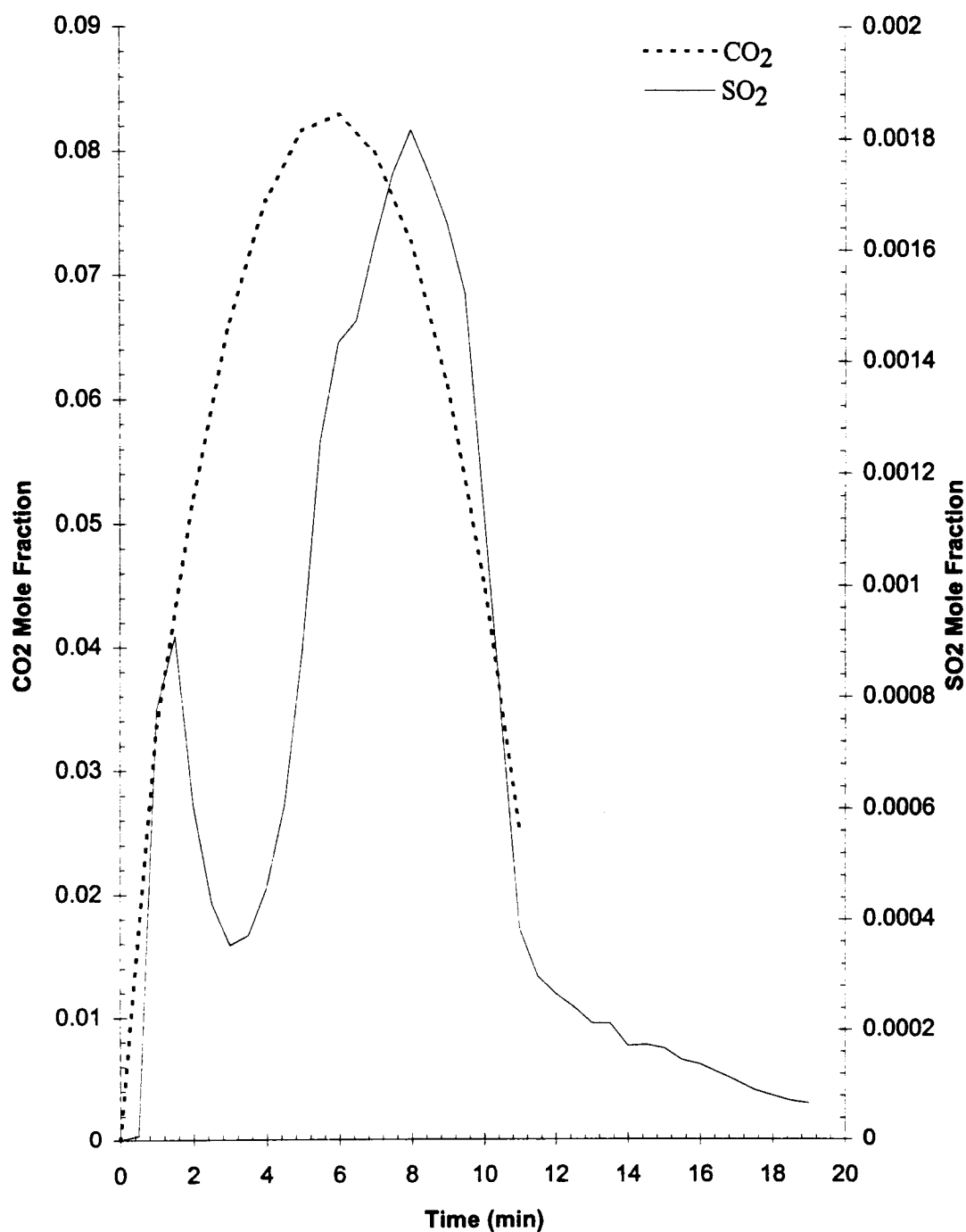


**Figure 5.33 Calculated Carbon Dioxide and Observed Sulfur Dioxide
Evolution from HIPPS Char for a Non-Isothermal
Test Starting at 2140 °F**

be seen from these plots it is difficult to say with any certainty exactly what factors could have caused such results, however a listing of the possible explanations is as follows:

- First and most obvious the non-isothermal nature of these experiments seems to hinder the combustion of the calcium sulfide present in the HIPPS char. This oxidation of calcium sulfide is temperature dependent, requiring a temperature of approximately 1800 °F. These effects can be seen in Figures 5.31 and 5.32.
- Second there appears to be a product inhibition effect visible in the higher temperature tests, where the temperature climbed above 1800 °F fast enough to oxidize the calcium sulfide during the bulk of carbon combustion. This is shown in Figure 5.33. During this test the temperature was above 1800 °F for most of the test and the hindrance in the formation of sulfur dioxide must therefore be resulting from some cause other than temperature.
- Thirdly the autothermal behavior of the carbon combustion, due to the design of the experiment could have affected the combustion of calcium sulfide as seen in these previous figures. As shown in the analysis of the non-isothermal

carbon conversion, an autothermal kinetic model satisfactorily describes the measured combustion of carbon. From this it is evident that localized temperature and therefore localized kinetics may play an important role in both the production of sulfur dioxide and the combustion of carbon. Since it is the combustion of carbon that is the dominant source of the additional heat, the production of sulfur dioxide can be dependent on the combustion of carbon.

As indicated in Chapter III an attempt to determine a function that expressed sulfur conversion as a function of carbon conversion was undertaken. The first step in this was plotting X_s versus X_c for each of the temperature tests. This can be seen in Figure 5.34 for each of the non-isothermal bench-scale tests with starting temperatures of 1750 °F, 2035 °F, and 2140 °F. If a temperature independent correlation was possible then at least a portion of the three curves should overlap, however as is obvious from the plot this was not true. Therefore a temperature independent relationship describing the conversion of sulfur as a function of carbon conversion was not obtainable from the non-isothermal bench-scale tests. It should be noted that as the temperature of the test increases, the conversion of sulfur as a function of carbon conversion decreased consistently. Since the rate of carbon conversion generally increased as the temperature increased, then it is

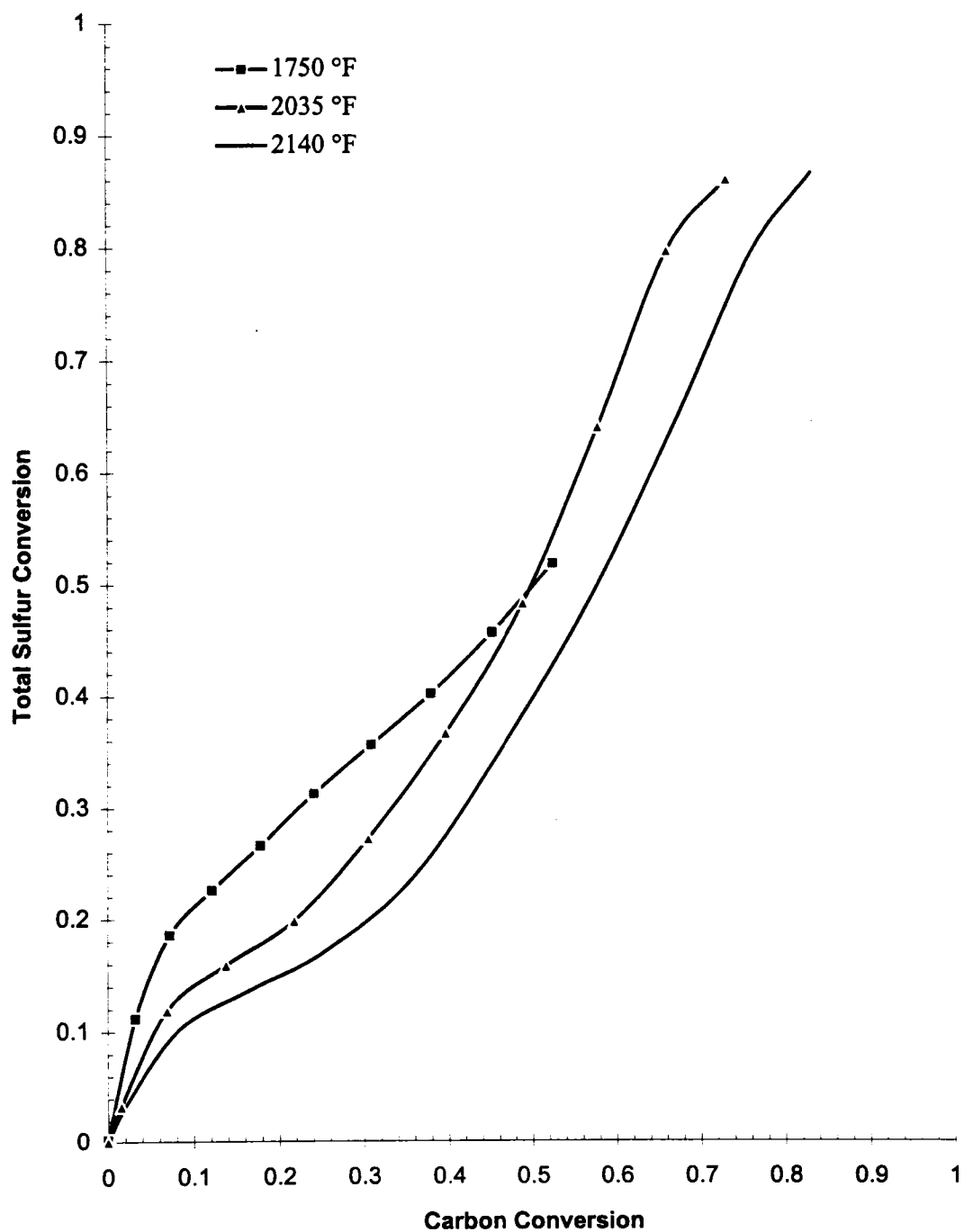


Figure 5.34 Conversion of Sulfur Versus the Conversion of Carbon from the Non-Isothermal Combustion of HIPPS Char

possible that the conversion of sulfur was hindered, not only by the temperature, but also by the conversion of carbon. This means that the rate of production of carbon dioxide affected the rate of sulfur dioxide production by hindering the production initially, then giving way to an increase in the production of sulfur dioxide, as the rate of carbon conversion decreased. This gives support to the possibility that product inhibition effects are controlling more so than kinetics, at least with regards to the production of sulfur dioxide from the sulfur in the HIPPS char. Unfortunately there appears to be no indication that the calcium sulfide is oxidizing to form calcium sulfate, because there is almost a 100 percent conversion of total sulfur, which includes both the organic sulfur and the calcium sulfide, to form sulfur dioxide if the total time of tests is considered.

The next portion of Phase 2, the isothermal tests, was undertaken as indicated in the previous Chapter. These tests, Tests 4.8, 4.9, 4.10, and 4.11, were designed to study the combustion of carbon and the production of sulfur dioxide at the same time. The first data set to be analyzed was the combustion of carbon data. As in the non-isothermal tests, Tests 4.1, 4.2, and 4.3, a first order kinetic model was first attempted, which was indicated by the literature to describe the combustion of carbon particles. Due to the isothermal nature of these tests it was anticipated that the carbon combustion would not be controlled by temperature variations within each test as was the case with the non-isothermal tests. A plot of the $-\ln(1-X_C)$ versus time is shown in Figure 5.35. From this plot it is obvious that the isothermal combustion of carbon is not described adequately by

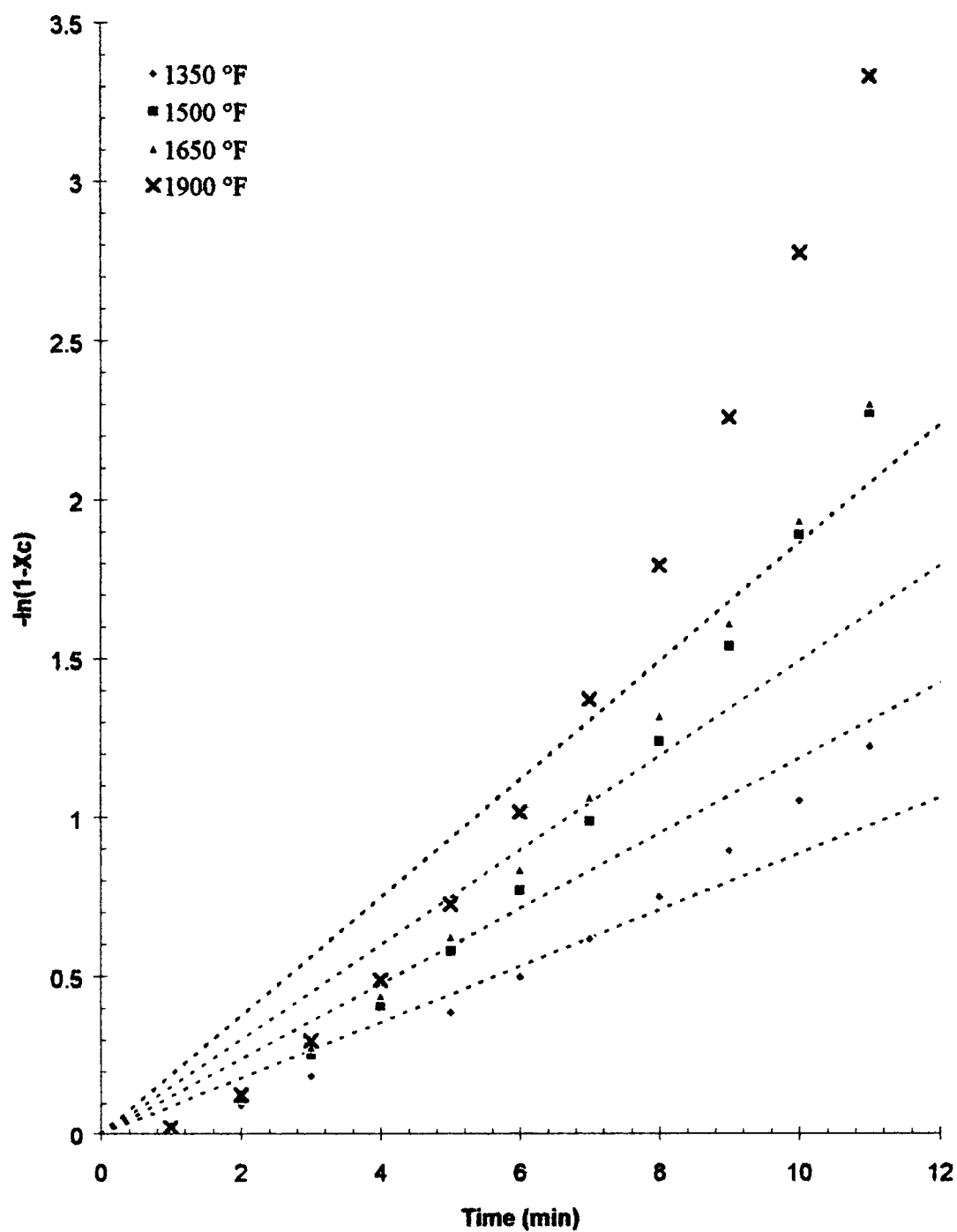


**Figure 5.35 Testing of the First Order Kinetic Model
for the Isothermal Combustion of Char in Excess Air
Tests 4.8 - 4.11**

the first order rate model. Next a zeroth order kinetic model was tested. A plot of the X_C versus time was made and can be seen in Figure 5.36. It is obvious from this plot that the combustion is not described satisfactorily by a zeroth order kinetic model either. It is important to notice the similarity between the non-isothermal results and the isothermal results in that there appears to be a low rate followed by a higher rate which is followed by a lower rate. This was observed and shown earlier in the non-isothermal tests to be best described by an autothermal kinetic model of the form:

$$-r_C = -\frac{dC_C}{dt} = kC_C^\alpha (C_{C0} - C_C) \quad (5.9)$$

Equation 5.9 can be further simplified to relate the change in conversion as time progresses. This simplification results in the following equation:

$$-\frac{dX_C}{dt} = kC_{C0}^\alpha X_C^\alpha (1 - X_C) \quad (5.10)$$

which when numerically integrated yields :

$$-\frac{(1 - X_C)X_C^{(1-\alpha)}}{(1 - \alpha)(X_C - 1)} \left(\sum_{j=0}^{\infty} \frac{(1 - \alpha)}{(2 - \alpha)} \frac{X_C^j}{j!} \right) = kC_{C0}^\alpha t \quad (5.11)$$

From this equation it is possible to determine the values of k and α . A plot of the left side of the previous equation versus time will, if this is an adequate model, yield a

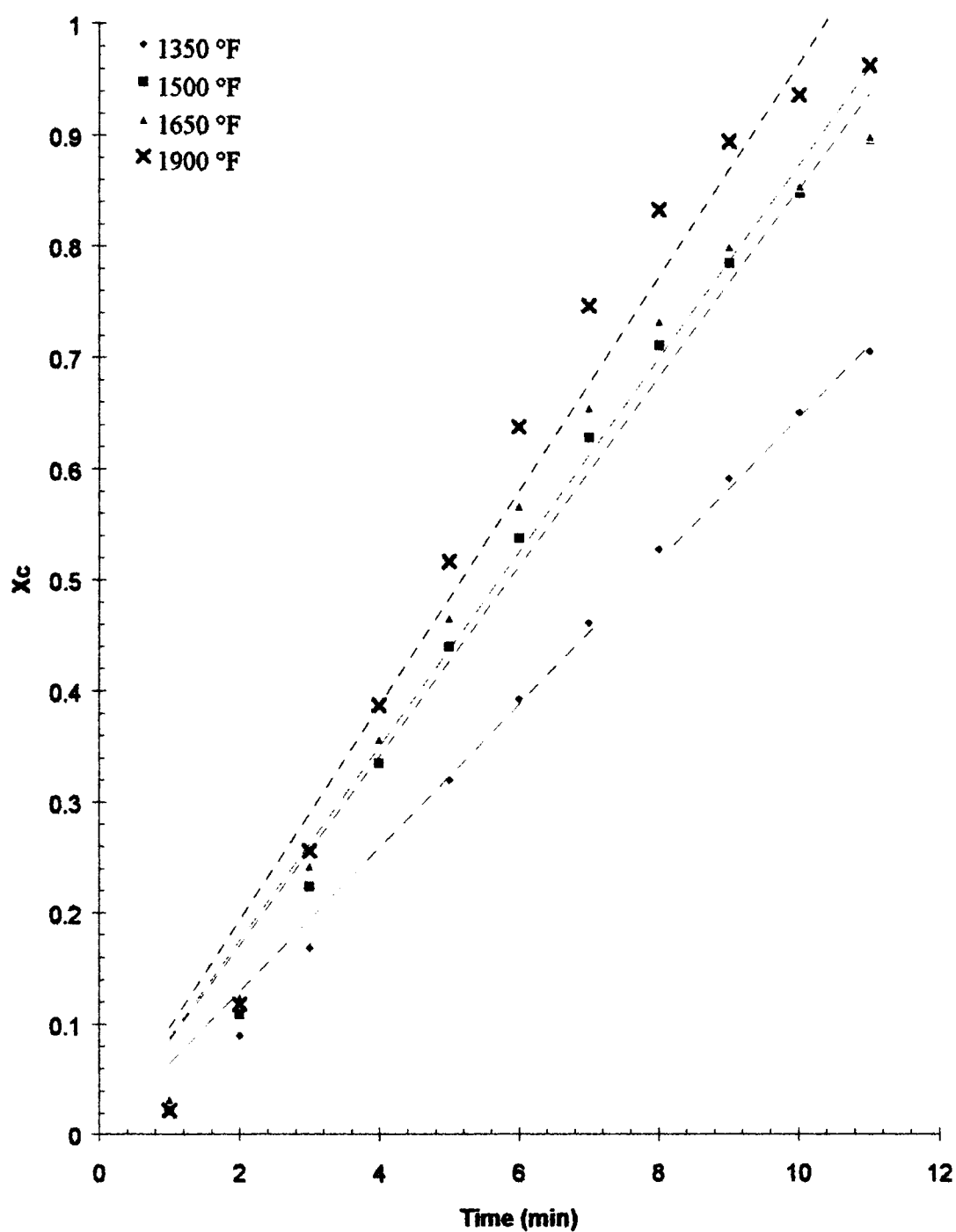


**Figure 5.36 Testing of the Zeroth Order Kinetic Model
for the Isothermal Combustion of Char in Excess Air
Tests 4.8 - 4.11**

straight line through the origin whose slope is kC_{CO}^α . The same method employed in the analysis of the non-isothermal carbon combustion was employed in the analysis of the data from the isothermal carbon combustion experiments. The main difference from the non-isothermal analysis is that the rate constant is not averaged over the temperature range, as the tests were isothermal. As can be seen in Figure 5.37, this rate model is quite satisfactory for describing the isothermal combustion of carbon from the HIPPS char. The values for k and α as determined for the isothermal carbon combustion tests, Tests 4.8, 4.9, 4.10, and 4.11, are as follows:

$$\alpha = 0.55$$

$$\bar{k}_{1350^\circ F} = .477 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

$$\bar{k}_{1500^\circ F} = .600 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

$$\bar{k}_{1650^\circ F} = .705 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

$$\bar{k}_{1900^\circ F} = .811 \frac{1}{(\text{min})(\text{mol C})^{.55}}$$

The following four plots, Figures 5.38, 5.39, 5.40, and 5.41, show the comparison between the calculated and measured conversions of carbon as a function of time for the four isothermal temperature tests, Tests 4.8, 4.9, 4.10, and 4.11. Even with the resolution of values for k even this fit is not an exact fit, however of all attempted models this modification of the autothermal model provided the best fit. With rate constants calculated for each test the Arrhenius relationship between the tests was investigated. A

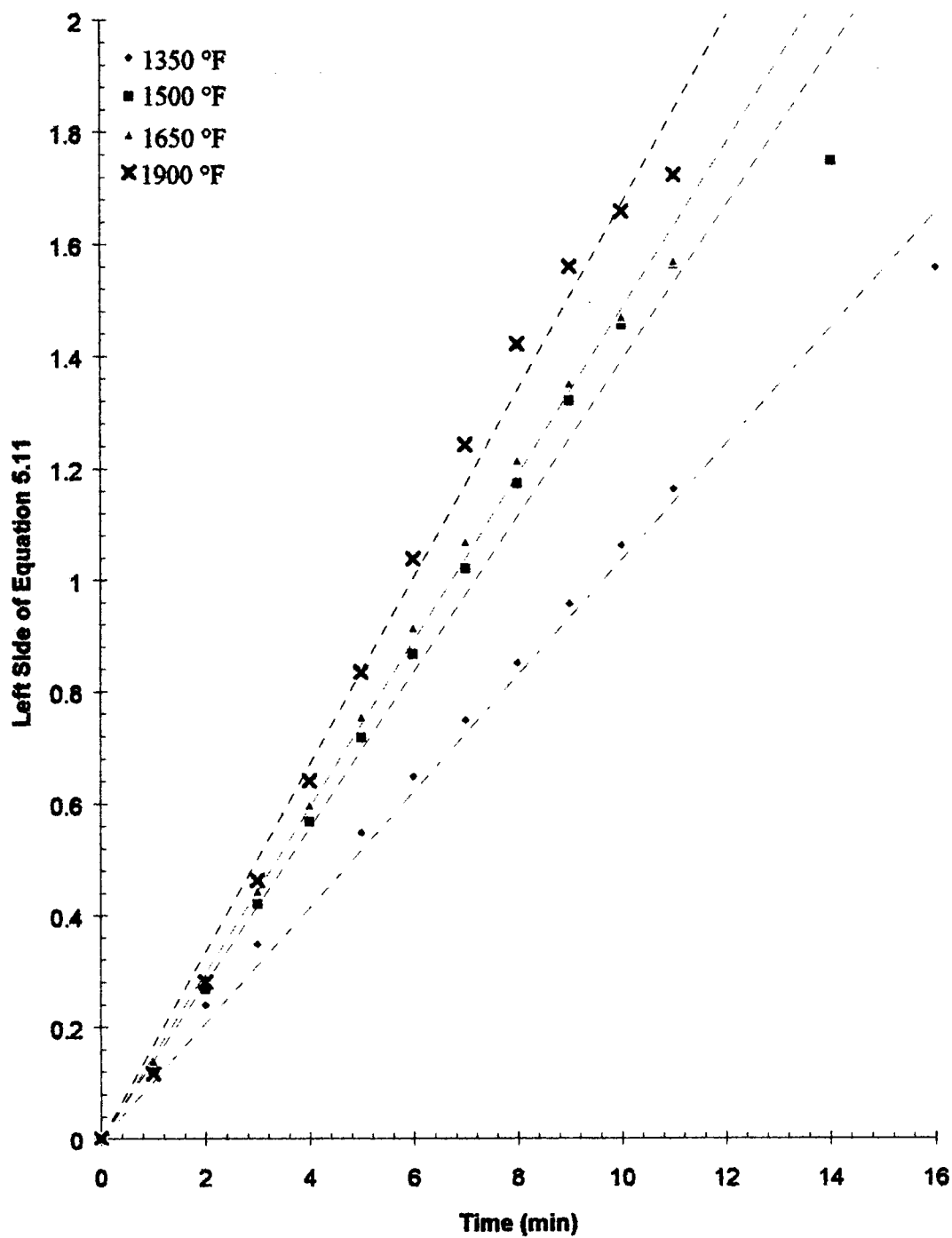


**Figure 5.37 Verification of the Autothermal Kinetic Model
for the Isothermal Combustion of Char in Excess Air
Tests 4.8 - 4.11**

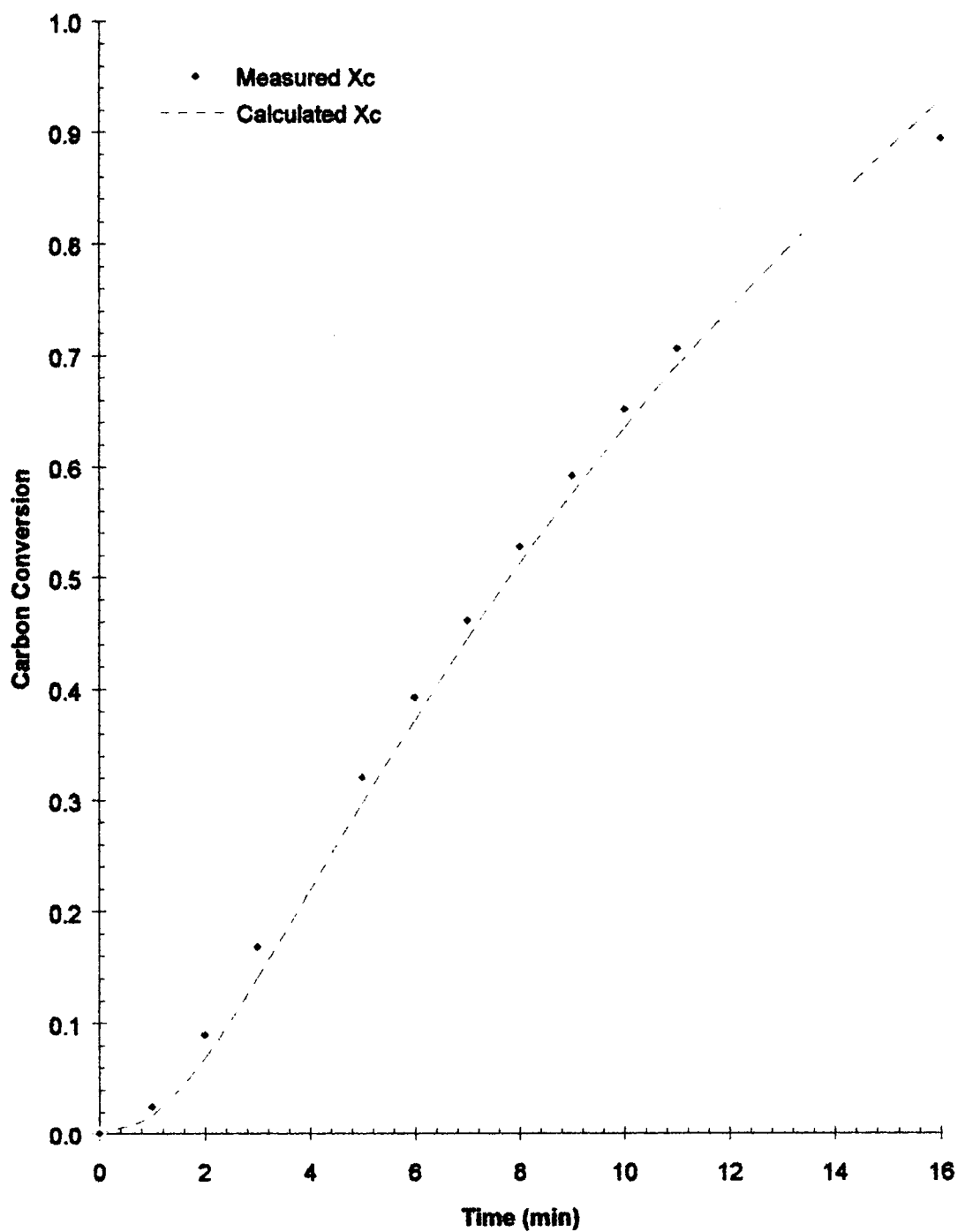


Figure 5.38 Verification of Autothermal Kinetic Model for the Isothermal Combustion of HIPPS Char at 1350 °F

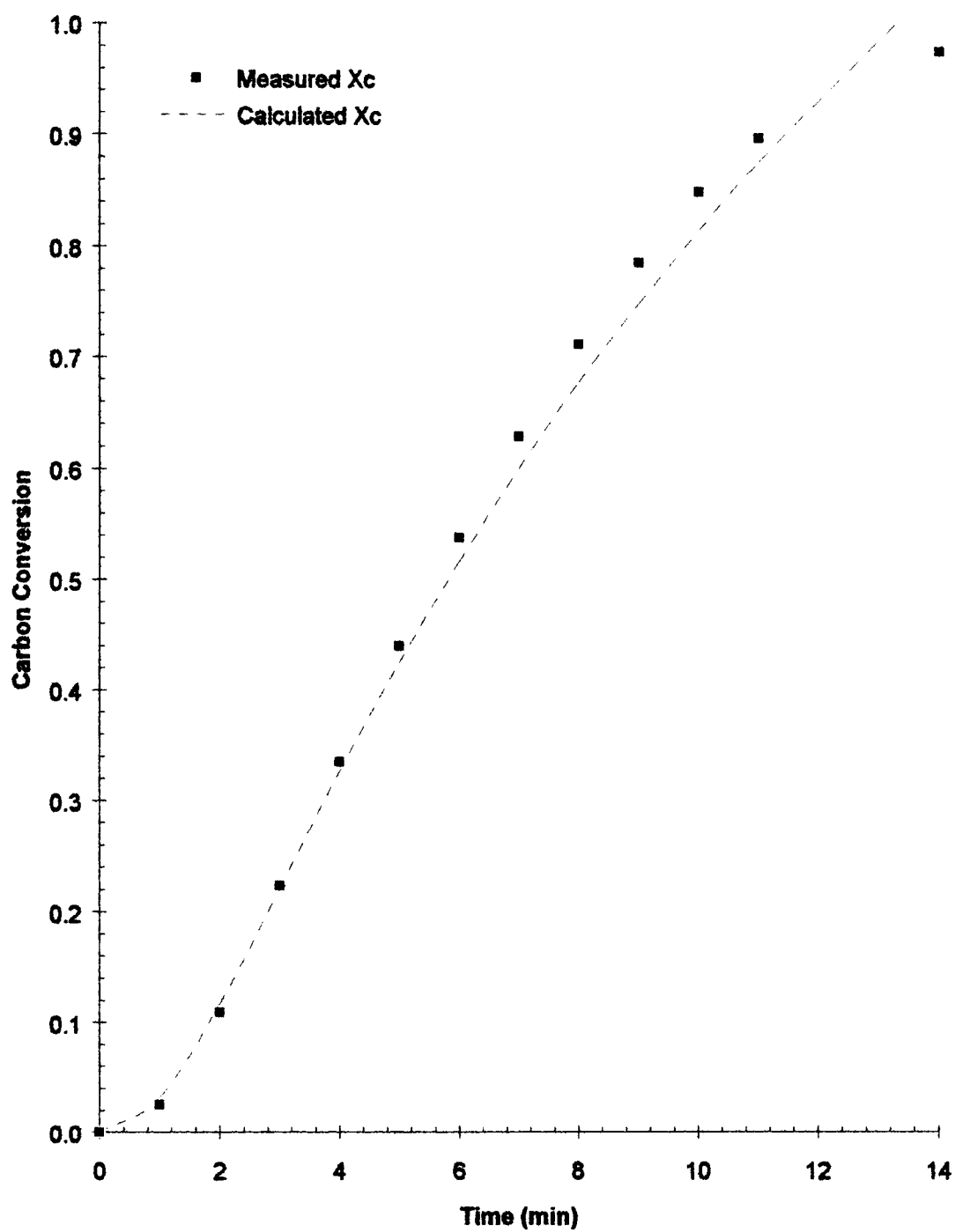


Figure 5.39 Verification of Autothermal Kinetic Model for the Isothermal Combustion of HIPPS Char at 1500 °F

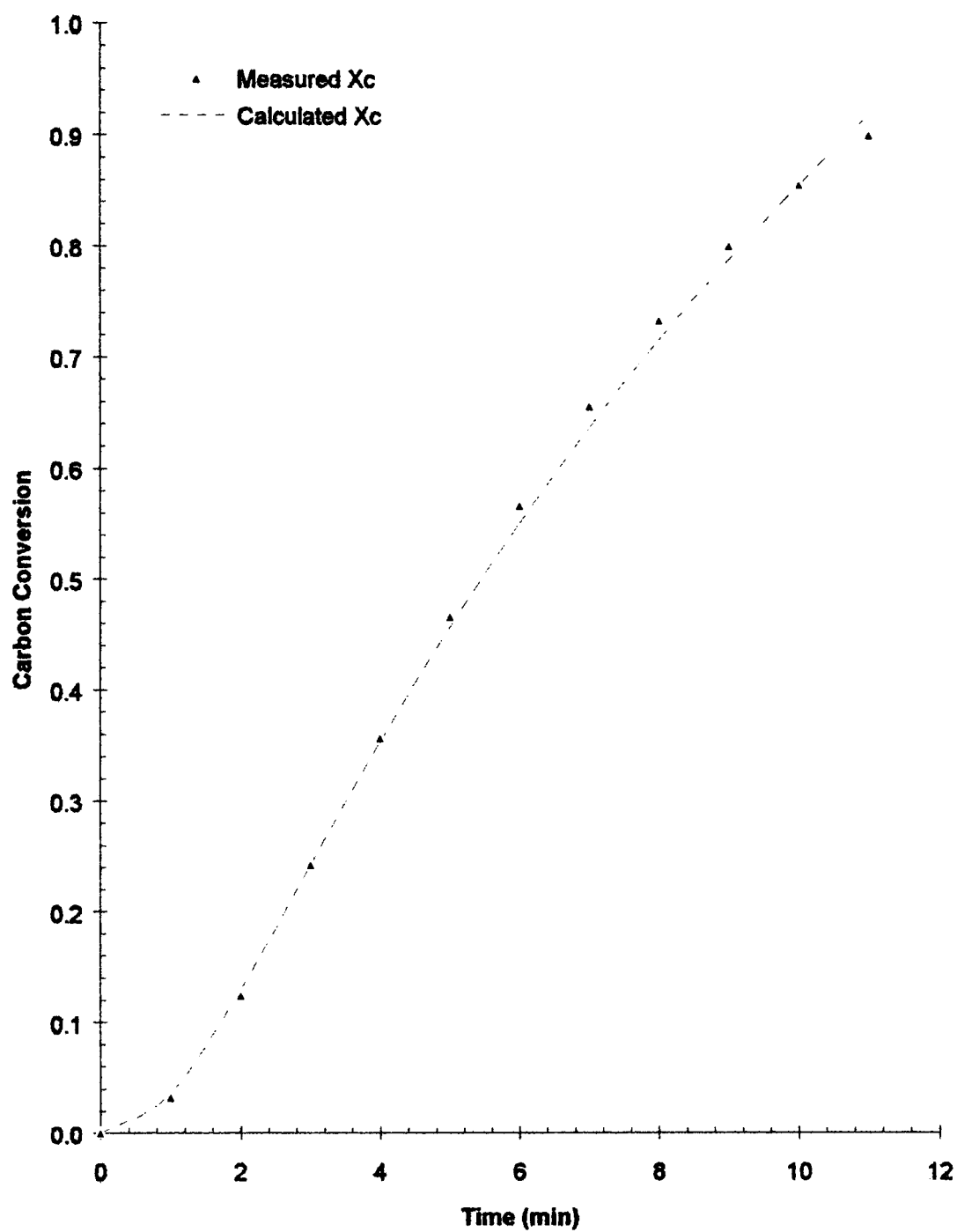


Figure 5.40 Verification of Autothermal Kinetic Model for the Isothermal Combustion of HIPPS Char at 1650 °F

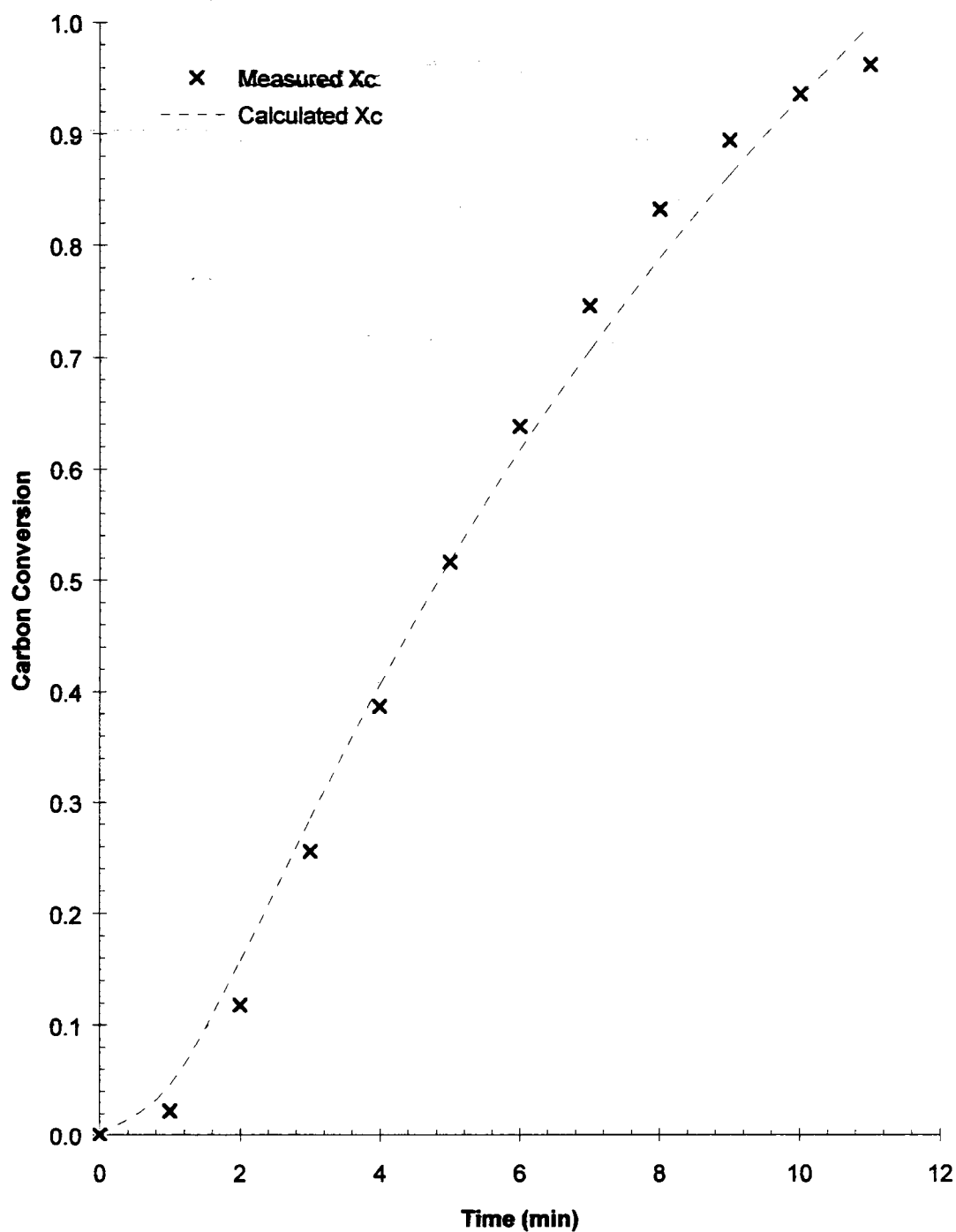


Figure 5.41 Verification of Autothermal Kinetic Model for the Isothermal Combustion of HIPPS Char at 1900 °F

plot, Figure 5.42, of the $\ln k$ versus $1/T$, with temperatures units in Kelvin, shows this relationship. From Figure 5.42, it is possible to determine the energy of activation, E , and the frequency factor, k_0 . The slope of a straight line giving the best fit to all points is known to be $-E/R$ from which the activation energy can be determined. The frequency factor is determined from the y-intercept, which is known to be $\ln k_0$. The activation energy was determined to be $4546.3 \frac{\text{calories}}{\text{mol}}$. The frequency factor determined to be $4.786 \frac{1}{(\text{min})(\text{mol C})^{.55}}$. From this a modified rate equation could be developed utilizing this

Arrhenius relationship for the isothermal test, and is as follows:

$$-r_C = -\frac{dC_C}{dt} = 4.786 e^{-2288/T} C_C^{.55} (C_{CO} - C_C) \quad (5.12)$$

It is interesting to note that the magnitude of the rate constant values for the non-isothermal tests and the rate values for the isothermal tests are the same. From this it is possible to assume that the above frequency factor and activation energy could be applied to a non-isothermal situation as well as the isothermal situation.

With the carbon combustion of HIPPS char investigated the next step was the investigation of the respective sulfur dioxide production. Earlier non-isothermal experiments failed to yield a reasonable kinetic model describing the oxidation of the sulfur species in the HIPPS char, therefore, the first order kinetic model was attempted first. As can be seen in Figure 5.43 the first order kinetic model does not adequately

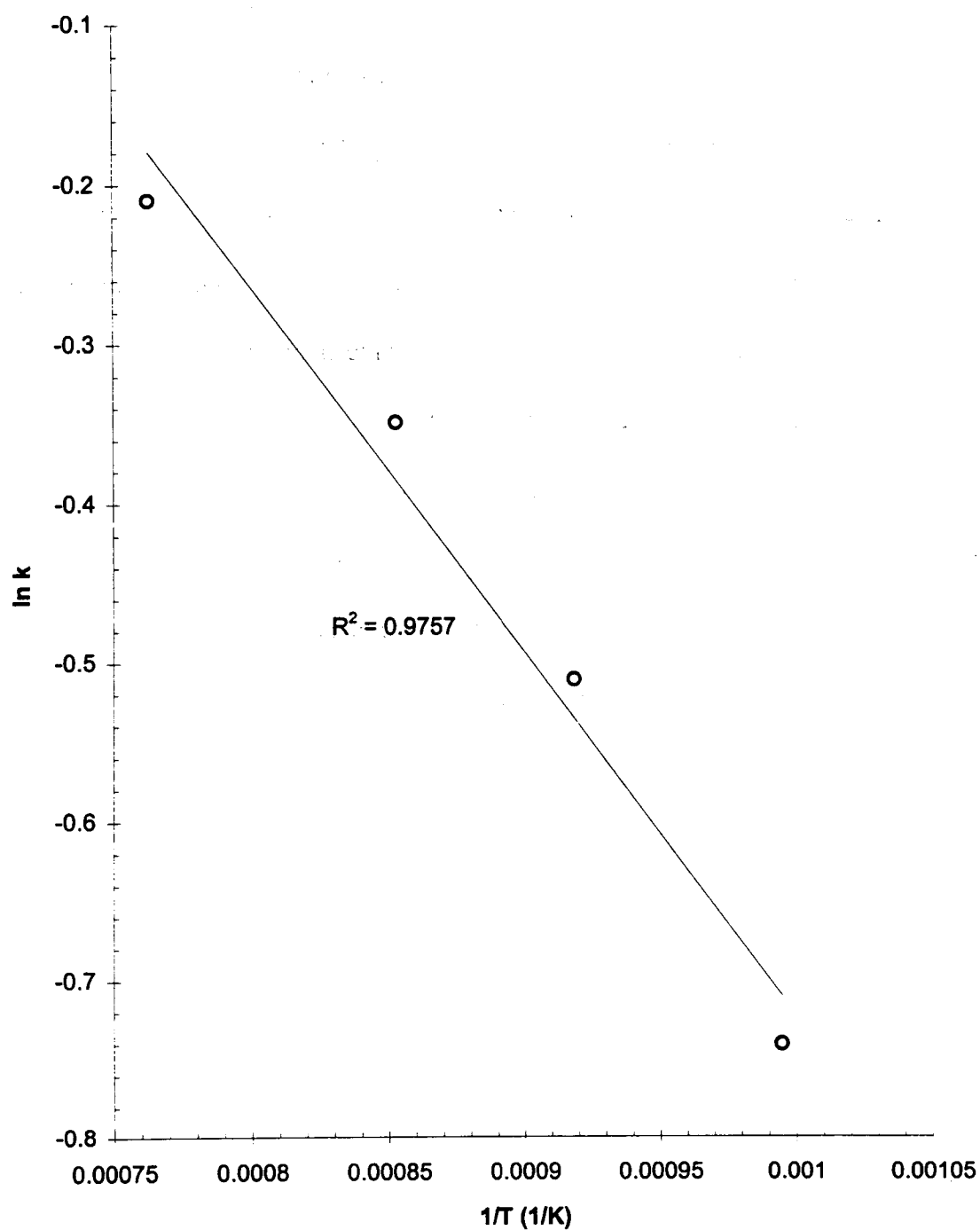


**Figure 5.42 Determination of Arrhenius Relationship for the
Isothermal Combustion of HIPPS Char
Tests 4.8 - 4.11**

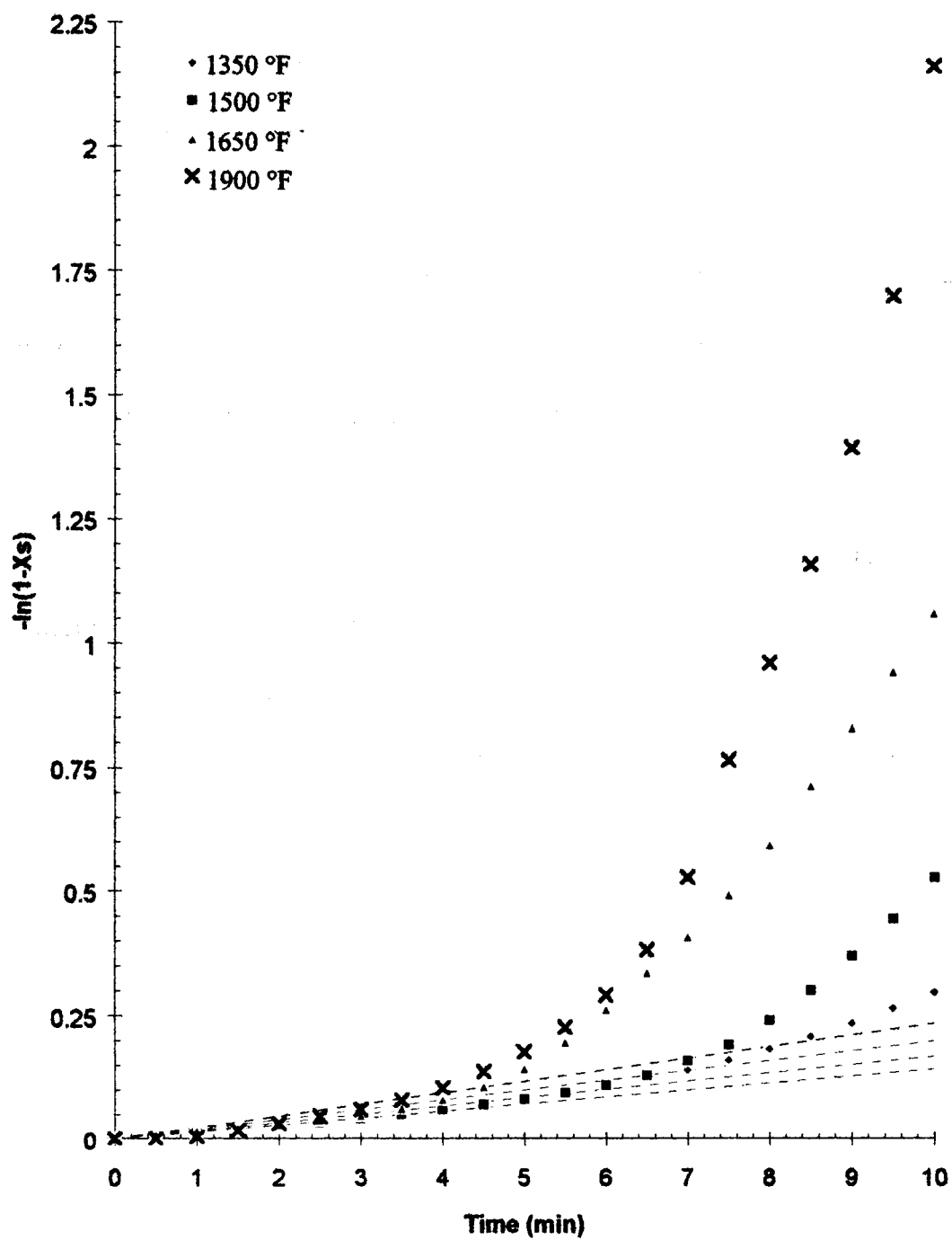


Figure 5.43 Testing of the First Order Kinetic Model for the Isothermal Oxidation of Sulfur from HIPPS Char
Tests 4.8 - 4.11

describe the combustion of sulfur species in the HIPPS char. Next the zeroth order kinetic model was tried. As can be seen in Figure 5.44 the zeroth order kinetic model does not describe the oxidation of HIPPS char sulfur species to form sulfur dioxide either. From the previous investigation into the kinetics of the isothermal combustion of carbon an autothermal kinetic model was determined to describe the behavior of the system, so a similar kinetic model was attempted for the oxidation of sulfur. This model is of the following form:

$$-r_s = -\frac{dC_s}{dt} = kC_s^\alpha (C_{s0} - C_s) \quad (5.13)$$

Equation 5.13 can be further simplified to relate the change in conversion as time progresses. This simplification results in the following equation:

$$-\frac{dX_s}{dt} = kC_{s0}^\alpha X_s^\alpha (1 - X_s) \quad (5.14)$$

which when numerically integrated yields :

$$-\frac{(1 - X_s)X_s^{(1-\alpha)}}{(1 - \alpha)(X_s - 1)} \left(\sum_{j=0}^{\infty} \frac{(1 - \alpha)}{(2 - \alpha)} \frac{X_s^j}{j!} \right) = kC_{s0}^\alpha t \quad (5.15)$$

From this equation it is possible to determine the values of k and α . A plot of the left side of the previous equation versus time will, if this is an adequate model, yield a

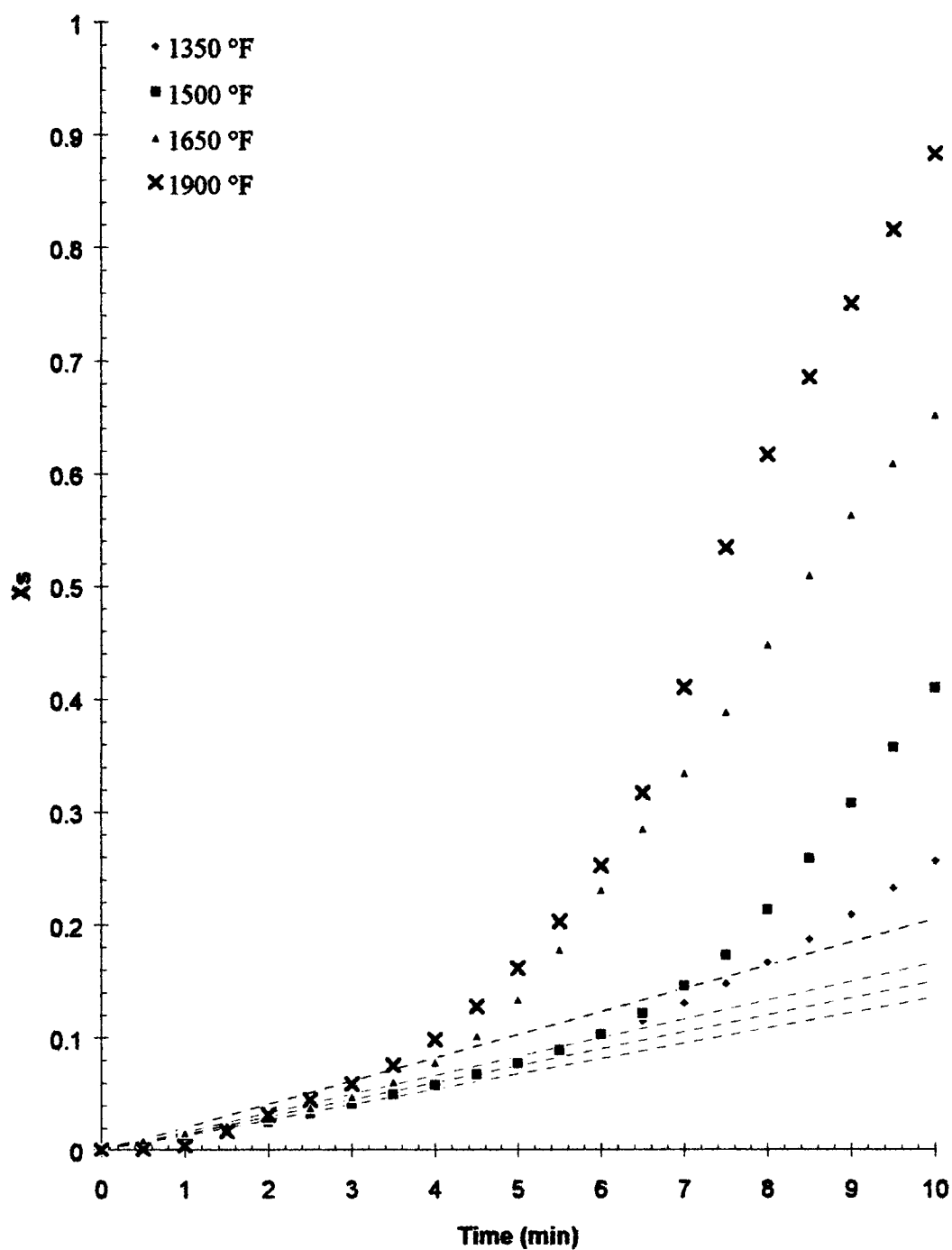


Figure 5.44 Testing of the Zeroth Order Kinetic Model for the Isothermal Oxidation of Sulfur from HIPPS Char
Tests 4.8 - 4.11

straight line through the origin whose slope is $kC_{S_0}^\alpha$. The same method employed in the analysis of the isothermal carbon combustion was employed in the analysis of the data from the isothermal sulfur oxidation experiments. As can be seen in Figure 5.45, this rate model is not valid for describing the isothermal oxidation of sulfur from the HIPPS char. After considering other kinetic models it was determined that no simple kinetic model would describe the isothermal oxidation of sulfur. The isothermal oxidation of sulfur displays a similar behavior to that of the non-isothermal oxidation, and from this a few observations can be made. It is possible, as it was in the non-isothermal tests, that something beside the kinetics of combustion is contributing to the rate of sulfur disappearance, which manifests in the production of sulfur dioxide. It was then proposed that product inhibition effects were controlling, by this it is meant that the levels of sulfur dioxide are restricted by the levels of other gases, primarily carbon dioxide, present during the combustion process. If this is indeed happening then a plot of the levels, in parts per million, of carbon dioxide and sulfur dioxide versus time will demonstrate this. Figures 5.46, 5.47, 5.48, and 5.49 show the mole fractions of both sulfur dioxide and carbon dioxide versus time for the four isothermal temperature tests. From these plots it is also possible to see the hindrance in the formation of sulfur dioxide during HIPPS Char combustion.

It is important to note a few observations with regards to the previous isothermal sulfur dioxide production results.. There are three main possible factors that could be

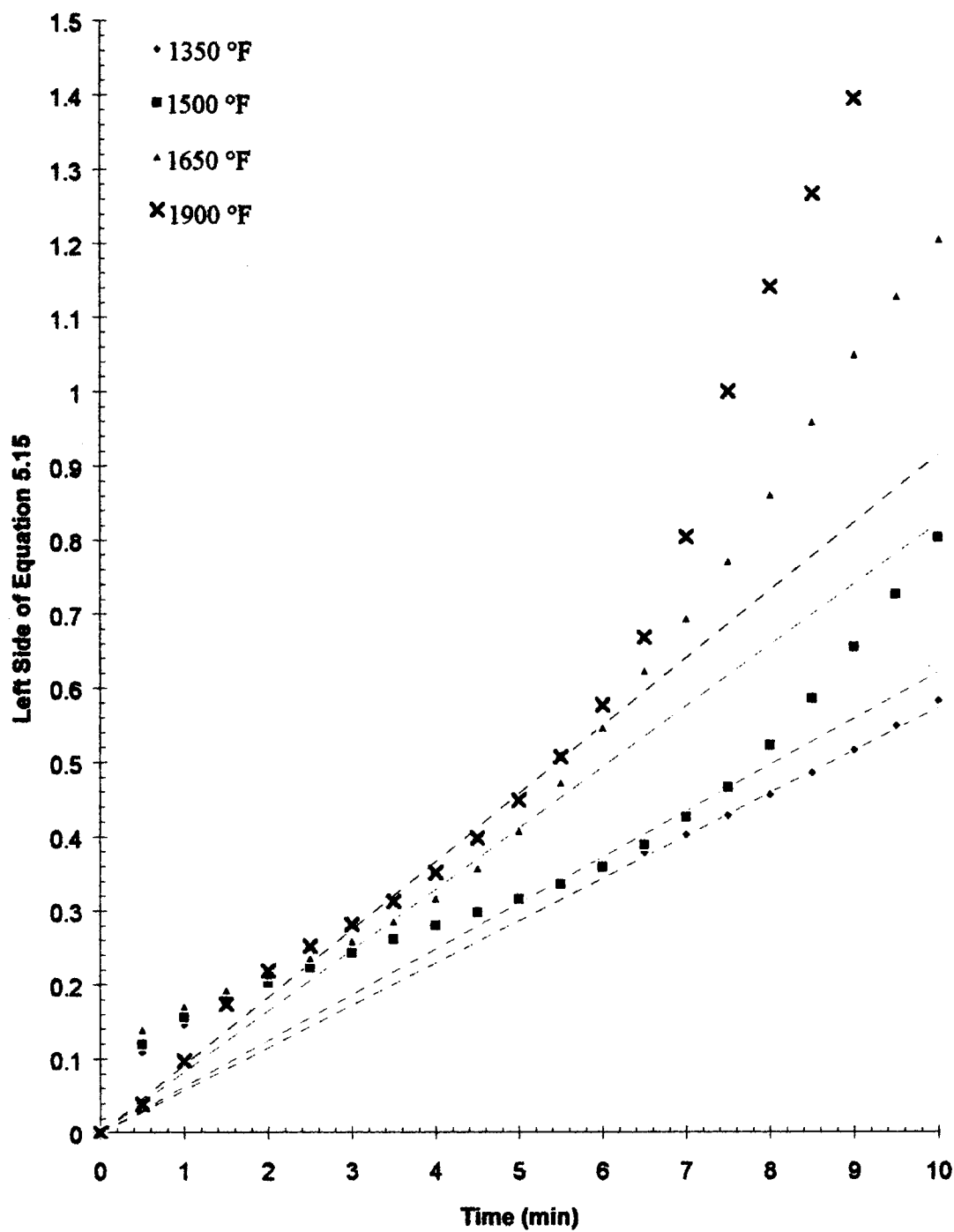


**Figure 5.45 Testing of the Autothermal Kinetic Model for the
Isothermal Oxidation of Sulfur Species in HIPPS Char
Tests 4.8 - 4.11**

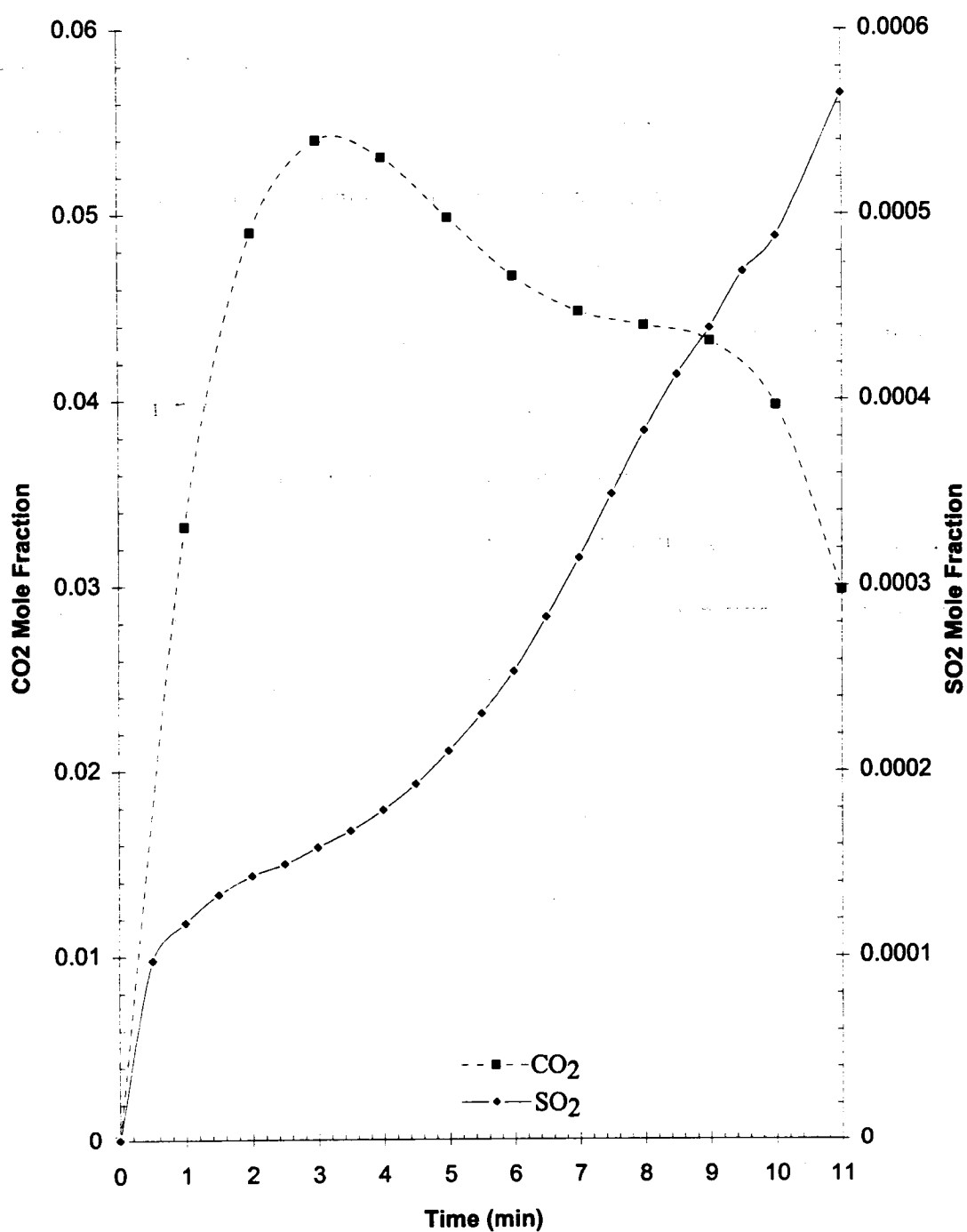


Figure 5.46 Calculated Carbon Dioxide and Measured Sulfur Dioxide Evolution from HIPPS Char for an Isothermal Test at 1350 °F

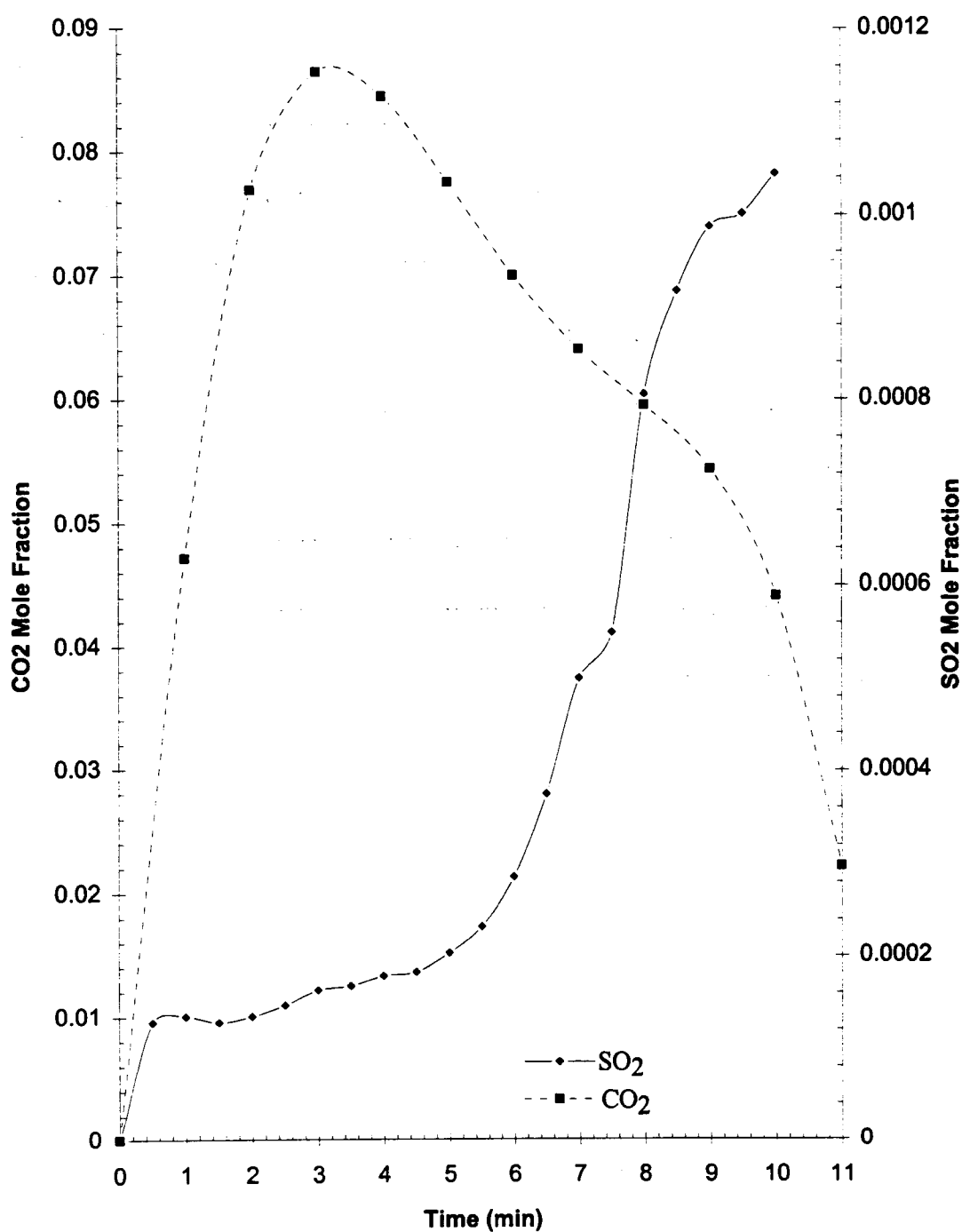


**Figure 5.47 Calculated Carbon Dioxide and Measured Sulfur Dioxide
Evolution from HIPPS Char for an
Isothermal Test at 1500 °F**

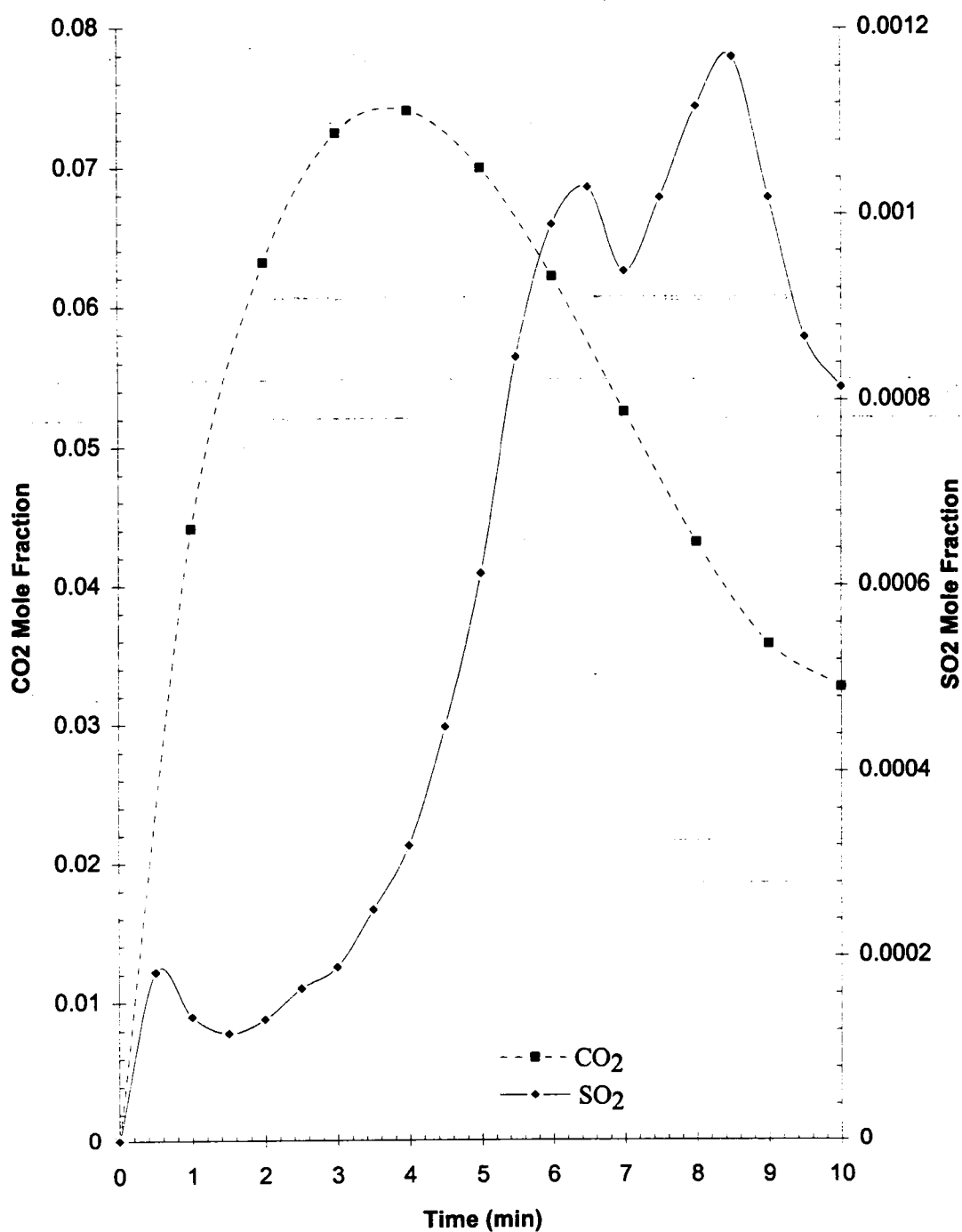


**Figure 5.48 Calculated Carbon Dioxide and Measured Sulfur Dioxide
Evolution from HIPPS Char for an
Isothermal Test at 1650 °F**

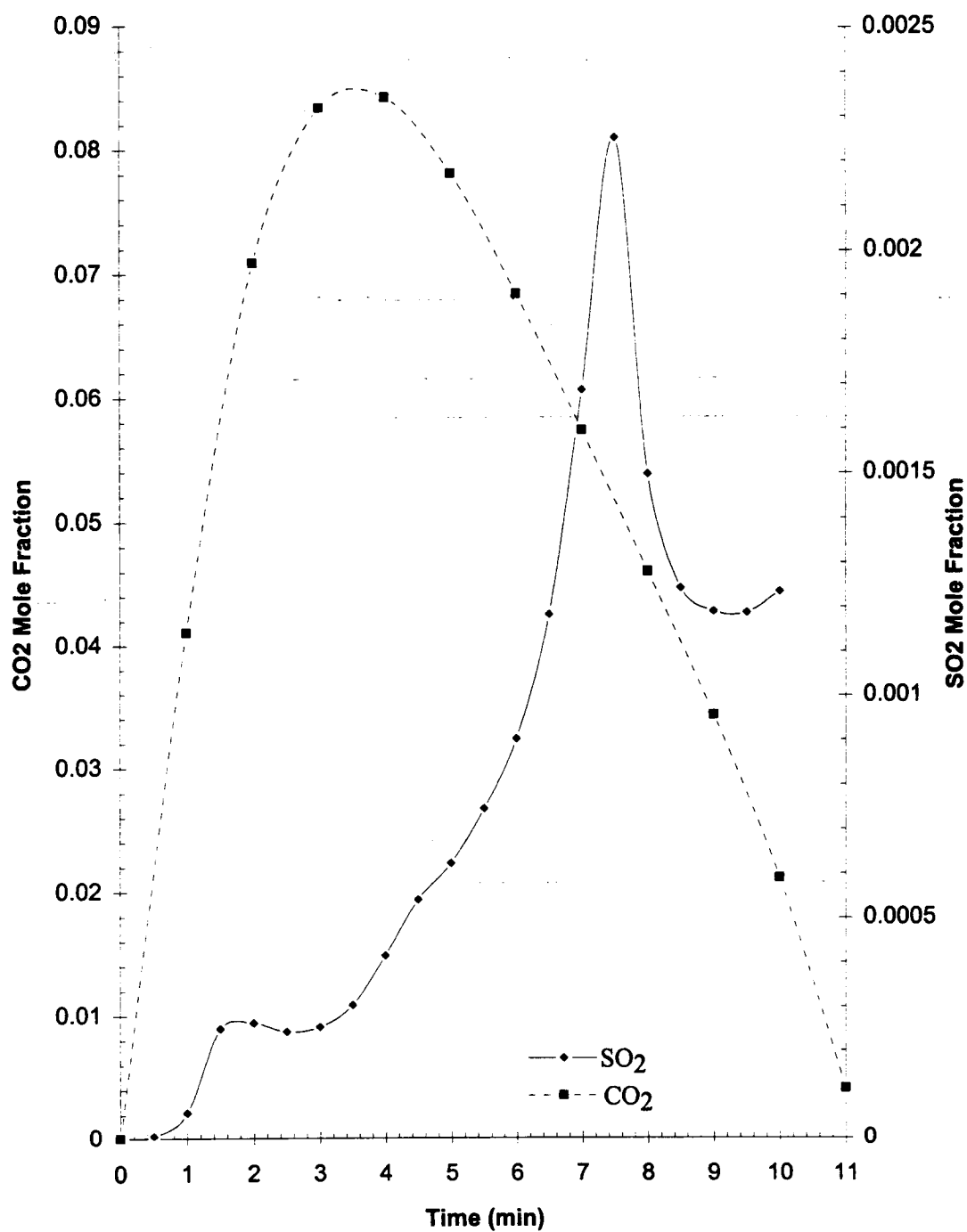


Figure 5.49 Calculated Carbon Dioxide and Measured Sulfur Dioxide Evolution from HIPPS Char for an Isothermal Test at 1900 °F

influencing this oxidation rate. The first is a possible mass transfer limitation. This means that there may be a physical barrier hindering the transport of oxygen to the sulfur containing sites, thereby hindering the levels of sulfur dioxide produced during combustion. The second possible factor is thermodynamic equilibrium effects. This means that after reaching certain levels of specific gaseous components, primarily sulfur dioxide formed from the organic sulfur in the HIPPS char, any additional sulfur dioxide from the oxidation of calcium sulfide is no longer the favored. The last factor, mentioned earlier in the analysis of the non-isothermal sulfur oxidation, is the probable inhibition of sulfur dioxide production by the production of carbon dioxide. Despite the lack of definitive evidence favoring one factor or the other, the previous plots show one important piece of evidence. If the controlling factor was thermodynamic in origin, based on the levels of sulfur dioxide present, then based on equilibrium calculations the total evolution of sulfur would be held to a minimum during the higher temperature test. This is not so, as the X_s for the 1900 °F temperature run was nearly 0.885, which indicated that a large portion of the calcium sulfide was oxidizing to form sulfur dioxide and not calcium sulfate as indicated by the known equilibrium behavior. If the controlling factor had been mass transfer limitations then an effect on the combustion of carbon in the HIPPS char would have been observed also, which was not the case. This information therefore indicates that the most likely limitation to the formation of sulfur dioxide, after temperature, was probably the product inhibition effect caused by carbon monoxide.

It is possible to approximate the levels of calcium sulfate produced in both the non-isothermal and isothermal bench-scale tests with the information gained from the LECO IR detector. Knowing the observed overall conversion of sulfur to be based on the measured levels of sulfur dioxide produced it is possible to estimate the amount of sulfur that oxidized to form calcium sulfate by difference calculation. This relies on one major approximation, which is that the production of sulfur dioxide and calcium sulfate reach a nearly total consumption of the available sulfur over the time of the tests. Table 5.8 shows the measured conversion of sulfur to sulfur dioxide and the estimated conversion to calcium sulfate for the non-isothermal and isothermal bench-scale tests. As can be seen from the table the data seems to follow the general trend that as the temperature increases the levels of calcium sulfate produced decrease to nearly negligible amounts. The general magnitudes observed for both the non-isothermal and isothermal tests appear to be very similar, further this indicates that the dependency on temperature is a serious factor in the production of calcium sulfate and sulfur dioxide.

As indicated in Chapter III, an attempt to determine a relationship between the conversion of sulfur and the conversion of carbon in the HIPPS char was undertaken. As performed in the non-isothermal tests, a plot of measured values of X_S versus calculated values of X_C for each of the isothermal temperature tests was made. If a temperature independent relationship can be determined then it should be obvious from this plot, due to an overlap of the data for the various temperature tests. As can be seen in Figure 5.50, an overlap

Table 5.8 Comparison of the Estimated Conversion of Sulfur to Calcium Sulfate and Sulfur Dioxide During the Non-Isothermal and Isothermal Oxidation of HIPPS Char

Temperature (°F)				
	1350 °F	1725 °F	2035 °F	2140 °F
<i>Non-Isothermal</i>				
Estimated % Conversion to Sulfur Dioxide	42.2	66.9	91.6	99.0
Estimated % Conversion to Calcium Sulfate	57.8	33.1	8.4	1.0
	1350 °F	1500 °F	1650 °F	1900 °F
<i>Isothermal</i>				
Estimated % Conversion to Sulfur Dioxide	49.5	41.1	89.9	90.3
Estimated % Conversion to Calcium Sulfate	50.5	*	10.1	9.7

* Insufficient data for CaSO₄ determination.

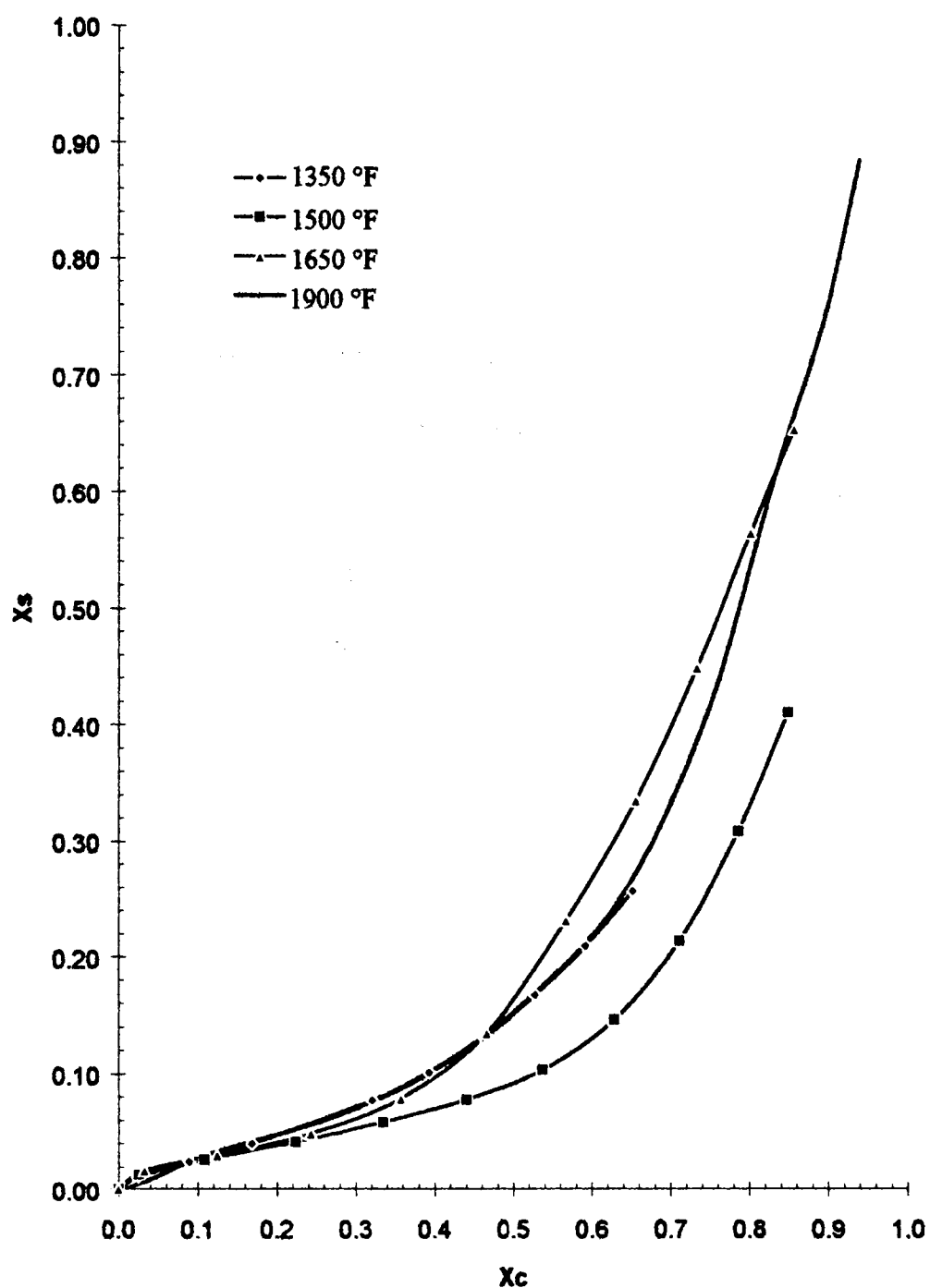


Figure 5.50 Measured Conversion of Sulfur Versus the Observed Conversion of Carbon for the Isothermal Combustion of HIPPS Char Tests 4.8 - 4.11

was observed for the initial conversion of carbon, up to a X_C of approximately 0.175. Even this correlation is minute at best, and since it covers such a slight margin of the carbon and sulfur conversion any relationship derived would be trivial. Therefore, as in the non-isothermal tests, a simple linear analytical relationship between the conversion of carbon and the conversion of sulfur can not be determined by this method. Since a linear relationship is not possible other polynomials of increasing degree were attempted, with the main criteria being that the data would fit within $\pm 10\%$ of the determined function. It was determined that a third order polynomial would fit the results for the 1350 °F, 1650 °F, and the 1900 °F tests. No polynomial investigated would satisfy all the results as the 1500 °F test results deviated greatly from the rest of the results. The third order polynomial developed to correlate the oxidation of sulfur to the combustion of carbon is as follows:

$$X_S = 1.6042 \cdot X_C^3 - 0.9051 \cdot X_C^2 + 0.3476 \cdot X_C \quad (5.16)$$

Figure 5.51 shows this relationship between carbon conversion and sulfur conversion. The dashed lines represents the $\pm 10\%$ range from the calculated values.

The last experiment mentioned in the Chapter III was designed to study the combustion properties of HIPPS char in an entrained flow combustion situation. The goal of these experiments was to determine the effects of entrainment on the production of sulfur dioxide. However during the vertical mounting of the Mellon tube-furnace it was

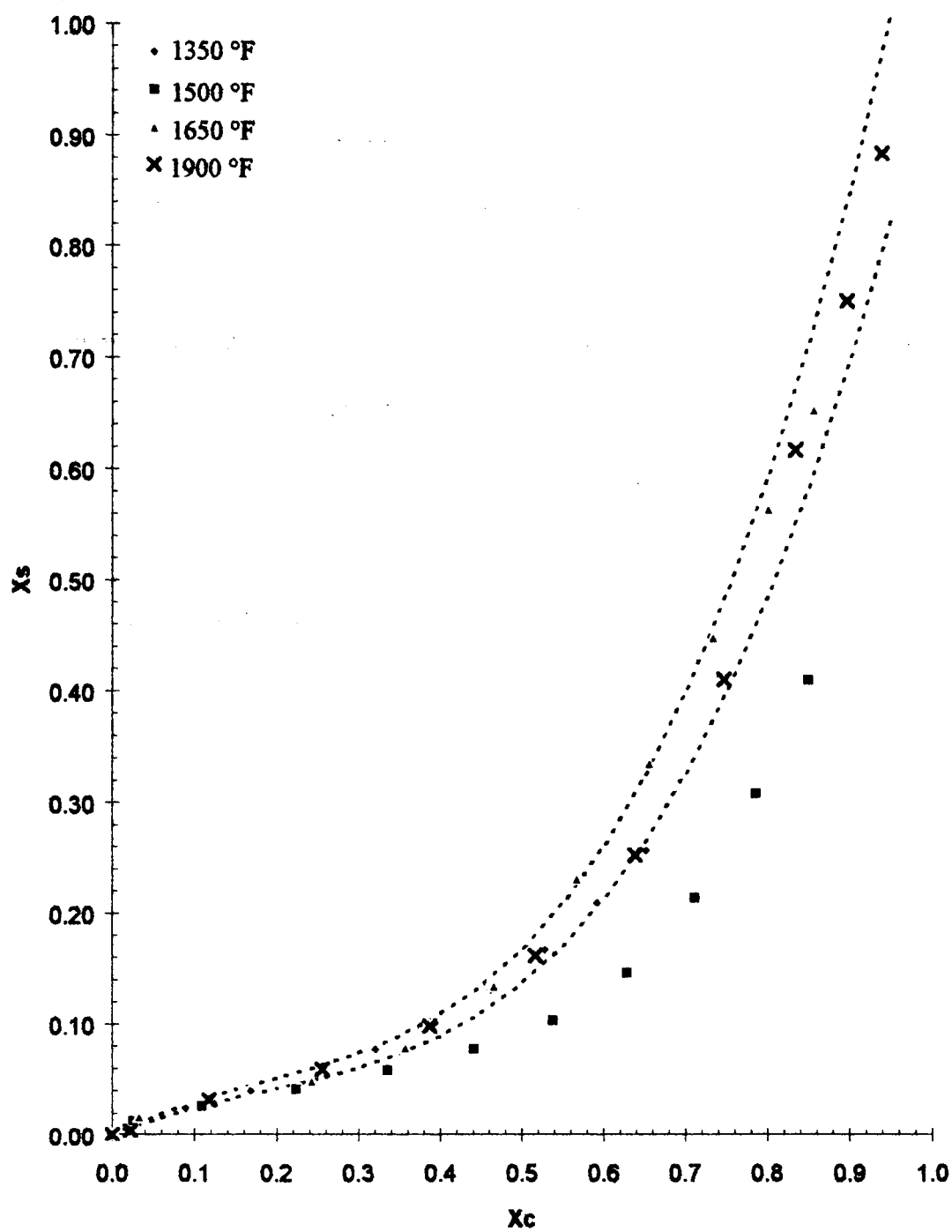


**Figure 5.51 Relationship Between the Conversion of Sulfur to
the Conversion of Carbon
Tests 4.8 - 4.11**

discovered that one of the remaining two heating elements of the furnace had failed. This failure effectively limited the temperature that could be achieved with this furnace to less than 1700 °F. A test at the maximum achievable temperature was performed and the following observations were made:

- Coal conversion of roughly 18 % was observed with an effective temperature of approximately 1700 °F.
- When a steady char flow rate was attained the levels of sulfur dioxide, as measured by the LECO SC132, was found to be roughly constant.
- The feasibility of the entrained char flow experimental concept was verified.

With the failure of the heating element limiting the range of temperatures to below 1700 °F, any further experimentation with this apparatus was terminated.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- From the first tests performed in the LECO SC132, Tests 2.1 through 2.14, it is obvious that calcium sulfide will oxidize to form sulfur dioxide. This oxidation to sulfur dioxide occurs at temperatures greater than 1750 °F. The oxidation of calcium sulfide to form sulfur dioxide at temperatures greater than 1750 °F was further verified in Test 3.4 and 3.5. From Test 3.4 it was observed that the reaction of calcium sulfide with oxygen will produce calcium sulfate primarily below the aforementioned temperature, and sulfur dioxide above it. This transition between oxidation products was also observed in the TGA analysis of the HIPPS char under an air atmosphere, Test 3.5. These results can be seen in Figure 5.13 and 5.14.
- As the temperature of the reaction area increases the level of calcium sulfide oxidizing to form sulfur dioxide also increases. This can be seen in Figures 5.5 through 5.7.
- The level of oxygen present during the combustion of HIPPS char has a direct effect on the ultimate levels of sulfur dioxide produced. It can be seen in Figure 5.8 that as the level of oxygen was decreased from 100 percent to 21 percent the level of sulfur

dioxide produced was found to decrease also. However this does not mean that all the sulfur in the HIPPS char will not oxidize to sulfur dioxide based on a lower level of oxygen, it instead means that the time it takes for the sulfur to oxidize to form sulfur dioxide is increased as the level of oxygen decreases.

- Calcium sulfide appears to thermally decompose at temperatures greater than 1500 °F. This behavior was observed in almost all the TGA tests, with the tests performed in an argon atmosphere, Tests 3.1 and 3.2, however, showing the most dramatic results. Figures 5.9 and 5.10 show the thermal decomposition of both pure calcium sulfide and the calcium sulfide present in the HIPPS char.
- Calcium sulfide will react with carbon dioxide at temperatures greater than 1600 °F, as can be seen in Figure 5.11. However this reactivity does not seem to be great enough to be of any serious concern to the fate of sulfur in the HIPPS HITAF.
- The oxidation of calcium sulfide to form sulfur dioxide at temperatures greater than 1750 °F was further verified in Test 3.4 and 3.5. From Test 3.4 it was observed that the reaction of calcium sulfide with oxygen will produce calcium sulfate primarily below the 1750 °F, and sulfur dioxide above such a temperature. This transition between oxidation products was also observed in the TGA analysis of the HIPPS char under air. These results are shown in Figure 5.13 and 5.14.

- Calcium sulfide and calcium sulfate in a solid: solid mixture will not react with each other below 2200 °F. This was verified in Test 3.6 and can be seen in Figure 5.15. This means that the solid-solid reaction between calcium sulfate and calcium sulfide will play at the most a minor role in the fate of sulfur in a HIPPS HITAF.
- The oxidation of HIPPS char in the non-isothermal bench-scale studies was found not to follow a first order kinetics as initially proposed. A modified autothermal kinetic model was found to adequately describe this non-isothermal combustion. Figures 5.20 through 5.21 show the measured carbon conversion and the carbon conversion calculated from the model versus time for tests 4.1 through 4.3 respectively. An Arrhenius relationship was not possible for the non-isothermal combustion studies due to limited number of the data points.
- The determination of a rate model for the non-isothermal oxidation of calcium sulfide was not possible at this time. Failed first and zeroth order rate models can be see in Figures 5.28 and 5.29. A plot of the rate of sulfur disappearance versus time can be seen in Figure 5.30, and thereof it is obvious that a simple rate model is not possible.
- The level of sulfur conversion to sulfur dioxide appears to be dependent on the temperature of the system as can be seen in Figures 5.23 through 5.26.

- The production of carbon dioxide from the non-isothermal combustion of carbon in the HIPPS char may inhibit the production of sulfur dioxide from the non-isothermal oxidation of calcium sulfide and inorganic sulfur in the HIPPS char. However this inhibition may not affect the rate of sulfur disappearance as much as the temperature of the system does. This product inhibition effect can be seen in Figure 5.33, where the change in the system temperature is no longer a significant factor in the rate of sulfur conversion.
- A modified autothermal kinetic model was found to adequately describe the isothermal combustion of HIPPS char as can be seen in Figures 5.38 through 5.41. An Arrhenius relationship was determined for the isothermal tests and is as follows:

$$-r_C = -\frac{dC_C}{dt} = 4.786 e^{-2288/T} C_C^{.55} (C_{CO} - C_C) \quad (5.12)$$

- The orders of magnitude for the isothermal carbon combustion rate constants and those of the non-isothermal carbon combustion rate constants were found to be the same. From this it is possible that the above energy of activation, E , and the frequency factor, k_o , may satisfy the modified autothermal kinetic model for the non-isothermal tests as well as the isothermal tests.
- The determination of a rate model for the non-isothermal oxidation of calcium sulfide

was not possible at this time. Failed first order, zeroth order, and autothermal rate models can be seen in Figures 5.43, 5.44 and 5.45.

- The product inhibition effect probably caused by carbon dioxide over sulfur dioxide production that was mentioned in the non-isothermal tests was also observed in the isothermal tests. This effect is even more dramatic in the isothermal test due to the fact that a large change in temperature during the test is no longer a factor. As can be seen in Figures 5.46 through 5.49 during the maximum carbon dioxide production the levels of sulfur dioxide are quite suppressed.
- A temperature independent relationship between the isothermal conversion of sulfur and the isothermal conversion of carbon was determined. A linear relationship was not possible however a polynomial of third order was found to satisfy three of the four isothermal tests within an error band of $\pm 10\%$. This polynomial is as follows:

$$X_S = 1.6042 \cdot X_C^3 - 0.9051 \cdot X_C^2 + 0.3476 \cdot X_C \quad (5.16)$$

Discussion of Possible Scenarios

There are two distinct scenarios concerning the fate of sulfur in the HIPPS HITAF. The first is that the calcium sulfide will oxidize to form sulfur dioxide. The second is that the calcium sulfide will not oxidize to form sulfur dioxide. From the literature and

experimentation, it is shown that either outcome is possible, and based on the complex interactions between equilibrium and kinetics it is possible that the real-life scenario may be a combination of these two main scenarios. It is often true in complex chemical processes that the actual behavior of a system falls into a gray area between the various theories concerned with it. This is most likely true within the HIPPS HITAF.

In order to understand the possible fate of sulfur in the HIPPS concept it is beneficial to review the determined factors that influence which scenario will dominate in the HITAF. The factors promoting the first scenario of calcium sulfide oxidation to sulfur dioxide are as follows:

- Kinetics indicate that as the temperature of the system increases the levels of sulfur dioxide produced by calcium sulfide increase.
- The experimentation undertaken during this investigation further indicates that substantial levels of sulfur dioxide can evolve during the combustion of the char.
- Equilibrium calculations indicate that at temperatures greater than 1800 °F the production of sulfur dioxide will be favored.

The factors promoting the second scenario of calcium sulfide not oxidizing to sulfur dioxide are as follows:

- Equilibrium calculations indicate that the production of calcium sulfate will be favored at temperatures lower than 1800 °F.
- Equilibrium theory indicates that the greater the concentration of sulfur dioxide in the air surrounding the sample the greater the production of calcium sulfate will be.
- The available literature also indicates that at larger Ca/C ratios the production of calcium sulfate will increase greatly.

With these factors listed it is now possible to determine which ones are present within the HIPPS HITAF. The first and most powerful factor controlling the levels of sulfur dioxide produced in the HITAF is the very high temperatures at which it is required to operate. With a maximum temperature of 2400 °F it is obvious that simply based on kinetics the decomposition of calcium sulfide is directed toward the formation of sulfur dioxide. In addition to the combustion of calcium sulfide, the observed thermal decomposition of calcium sulfide (See Figures 5.9 and 5.10) will, if occurring in the HITAF, release sulfur that will subsequently react with oxygen in the combustor furnace

to form sulfur dioxide. As the char combusts the levels of sulfur dioxide from organic sulfur increase, which based on the equilibrium data should influence the decomposition of calcium sulfide toward the production of calcium sulfate because of increased sulfur dioxide concentration. Adding to the influence of the equilibrium effects is the entrained particle nature of the HITAF char flow. This means that as the char travels through the HITAF it will be in contact with the same gaseous and condensed materials throughout. As the char combusts it produces gaseous components altering the make-up of the gaseous environment surrounding the char, this in turn alters the levels of sulfur dioxide produced from that observed in the semi-batch experiments. In addition to the effect on the levels of sulfur dioxide produced based on the calcium sulfate-sulfur dioxide equilibrium, the levels of oxygen available to form sulfur dioxide greatly influence the production of sulfur dioxide from calcium sulfide. From equilibrium information it is known that the combustion of carbon is favored above all other reactions considered in this thesis, and as it consumes the available oxygen forming carbon monoxide or carbon dioxide the levels of sulfur dioxide formed from the decomposition of calcium sulfide should decrease. In addition to this the HIPPS HITAF operates with an input gas stream composed of 15 percent oxygen, which is 6 percent, at the least, less oxygen than was used in the testing utilized in this thesis. This lower level of oxygen will, as indicated in the initial LECO SC132 tests, could restrict the rate of sulfur dioxide production, although to what degree it is difficult to say, partly due to the fact that the HITAF has a lot of oxygen in excess of the amounts required for the desired level of carbon combustion. Based on the above factors it is evident that sulfur dioxide will be produced

by the oxidation of calcium sulfide in the HIPPS HITAF, however the levels of sulfur dioxide produced may not be as high as those observed in the bench-scale tests presented in this thesis.

Effects on Foster Wheeler's HIPPS Concept

From the information covered in this thesis it is sure that the HIPPS concept will require some further refinement in order to reach the goals put forward in the Department of Energy's Combustion 2000 initiative. The HITAF combustor functions at such a high temperature that the production of sulfur dioxide from the oxidation of calcium sulfide is virtually guaranteed. In addition to this at the desired levels of char combustion, near 100 percent, the organic sulfur, approximately 2 percent of the initial char weight, will be released to form sulfur dioxide also. It is possible that with the non-calcium sulfide derived sulfur dioxide present that the production of calcium sulfate instead of sulfur dioxide will increase, however this has not been verified in this thesis. Regardless of its origin, sulfur dioxide will be produced in the HIPPS HITAF, and most likely will exceed the desired levels of sulfur dioxide emissions as listed in Chapter One. For this reason it is imperative that a energy efficient and cost effective desulfurization technique be incorporated into the HIPPS concept. In addition to this it might be of value to further investigate suitable physical separation techniques to remove the calcium sulfide from the pyrolyzer char prior to its combustion in the HITAF.

Recommendation for Further Work

Despite the evidence provided in this thesis showing that the most of the calcium sulfide present in the HIPPS char will oxidize to form sulfur dioxide, complete certainty can only be realized upon construction and operation of the pilot plant based on the HIPPS concept. Using the information derived during this investigation it is possible to design and formulate one such final series of experiments to supply sufficient support to influence the possible required corrections to the current HIPPS design. The main source of uncertainty at present lies in the failure of the planned entrained particle flow apparatus. The failure that forced the abandonment of Phase 3 of the experiments was completely physical in nature. The lack of a sufficiently stable and constant char delivery system seriously hampered this portion of the investigation. When combined with the unfortunate degradation in performance of the Mellen tube furnace, which basically limited the temperature range to less than 1800 °F, the entrained particle experiments in this thesis could not simulate sufficiently the HIPPS HITAF conditions and therefore couldn't predict the fate of sulfur in the HIPPS HITAF. In order to satisfy the remaining questions regarding the fate of sulfur the following experiment or one very similar would be quite useful.

An entrained particle flow experiment, similar in design to the Phase 3 bench-scale experiment undertaken in this thesis is recommended. Instead of the vibratory char delivery system a screw fed delivery system would establish a constant and controlled

char flow into the HITAF simulation reactor. A high temperature metal alloy or ceramic tube would also prevent the scaling and degradation of the reactor tube that was observed in the stainless steel tube used in the Phase 3 experiments. Lastly a furnace of sufficient heating power and length would be required to reach the char conversion levels greater than the approximately 18 percent by weight observed in the Phase 3 experiments. A proposed schematic for this apparatus is shown in Figure 6.1. Once constructed this apparatus, when used in conjunction with an online gas analyzer for accurate determination of carbon dioxide, carbon monoxide, sulfur dioxide, and oxygen levels, could be used to completely verify or disprove the predictions put forward in this thesis. Additional testing can then be performed with this apparatus to determine if and what level of oxygen can be used that would limit the levels of sulfur dioxide produced while still allowing for complete char conversion.

With the information gained from these proposed experiments and the information presented by this investigation it will be possible to satisfactorily predict and prove the fate of sulfur in the HIPPS HITAF. Once this information has been determined then it can be used to develop and implement an adequate and efficient desulfurization or separation technique that will help to satisfy the goals put forth by the Combustion 2000 initiative. If this follow-up experiment is not undertaken then based on the results from this investigation the HIPPS concept in its present design is in danger of not reaching the desired goals for sulfur dioxide-emissions. Despite the uncertainty remaining regarding the ultimate levels of sulfur dioxide produced, the evidence presented in this thesis

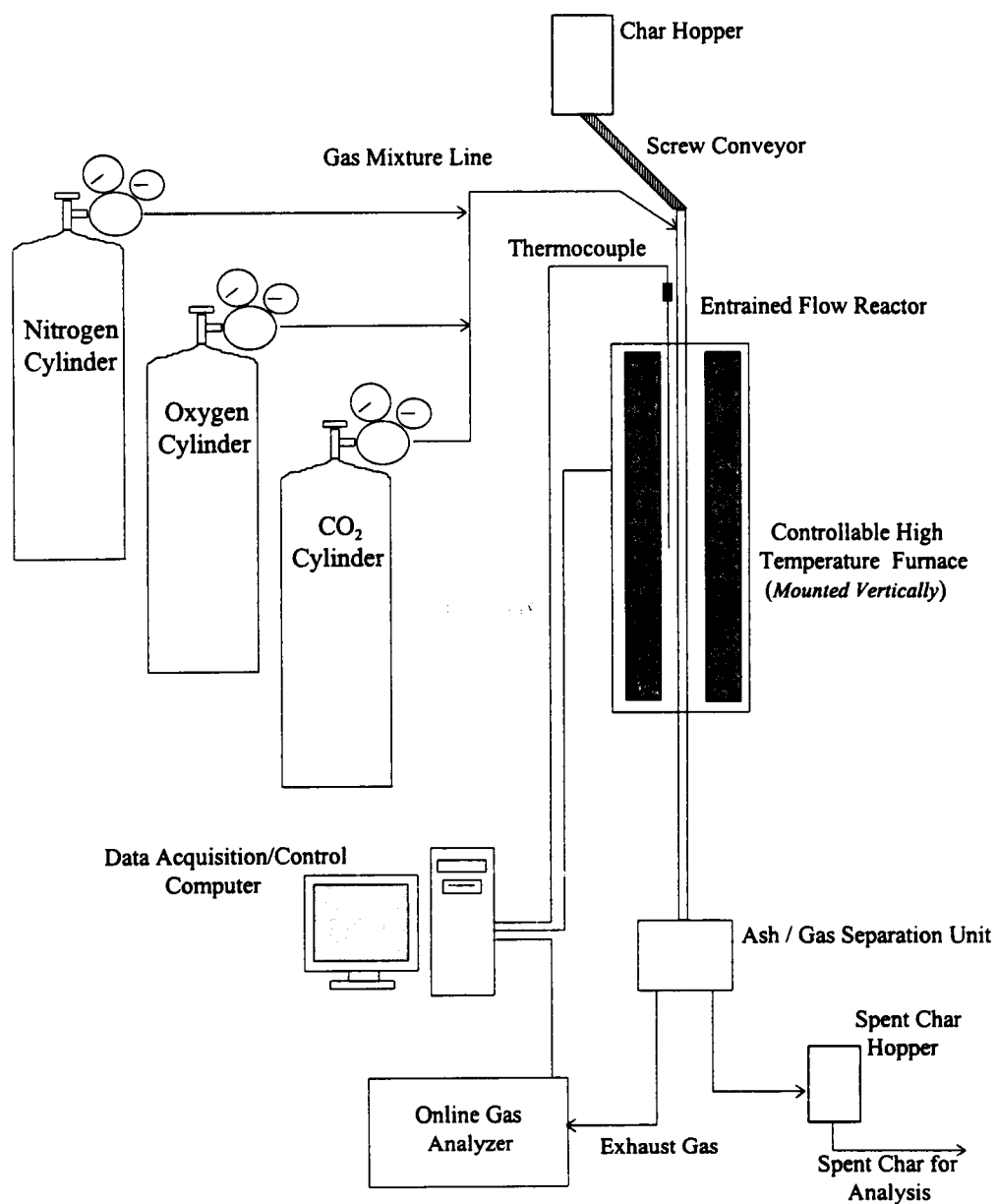


Figure 6.1 Schematic for Proposed Entrained Char Combustion Experiment

heavily favors the basic hypothesis presented in the beginning of this investigation, that sulfur dioxide production will exceed the desired levels and thereby invalidate the HIPPS concept in its present design state.

Suggested Sulfur Dioxide Removal Methods

A wide array of desulfurization techniques exists, however many are very costly and would require extensive development and testing. The addition of a desulfurization unit after the HITAF will also decrease the overall efficiency of the HIPPS concept. To this end there are a few methods that would be of definite interest to the success of the HIPPS concept.

The first and most logical method would be to return the pyrolyzer unit to its original design specifications. This means return the pyrolyzer to having a limestone/sorbent bed within which the coal is pyrolyzed. The current pyrolyzer utilizes a sand bed into which the coal and sorbent are pyrolyzed. The main advantage the original design is that the separation of calcium sulfide from the char by a physical method would be simple and easily performed. From the analysis of the HIPPS char produced under current design HIPPS char it was evident that not all of the sorbent added to the system reacted to form calcium sulfide. When this is considered it is obvious that the original pyrolyzer design was better than the current design. It would be better, both with regards to design and to overall system efficiency, to reinvestigate this method of desulfurization.

The second method would be to take advantage of the particular thermal behavior of the calcium sulfide-oxygen reaction. This would best be performed by a two stage combustor, where the first stage would combust the char at temperatures less than 1750 °F, which is the temperature at where sulfur dioxide replaces calcium sulfate as the favored product of the oxidation of calcium sulfide. The main benefit of this method lies in the formation of calcium sulfate in the first stage. The literature indicates that calcium sulfate is a very stable compound, not prone to decomposition and the formation of sulfur dioxide. A negative side to this alternative would be in the uncertainty as to its affect on the overall efficiency of the HIPPS concept. Additionally this alternative would require a major redesign of the HITAF portion of the HIPPS concept.

The another method would be to use flue gas desulfurization (FGD). There are many proven methods available to perform this task. As indicated in Figure 2.1, a FGD unit was designed into the system, however its purpose was to remove the sulfur dioxide produced by the organic sulfur and any remaining sulfur that was not removed earlier. This FGD unit, as currently designed, is not large enough to remove the sulfur dioxide produced from both the organic sulfur and the calcium sulfide in the HITAF, and as such would require redesign. An additional negative factor to the use of a large FGD is that it would invalidate the design parameters put forth in the HIPPS concept, which was to remove as much sulfur possible prior to the combustion of the HIPPS char in the HITAF.

Lastly, an alternative to the FGD would be to inject finely ground lime/limestone slurry into the HITAF at a point where the subsequent loss of temperature would not drastically affect the efficiency of the HIPPS concept. A logical location for this would be downstream of the heat transfer locations provided to heat the air and steam used in electric power generation stages. The main disadvantages to this proposed method is the limited information available about its technical feasibility, and the simple uncertainty with regards to its desulfurization potential.

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APPENDICES

APPENDIX I

NASA Chemical Equilibrium and Applications Program

Input and Output

Inputs to HITAF for temperature range 1400 - 1650 °F

```
! HIPPS High Temperature Advanced Furnace Calculations
!
! Temperature range is 1400 to 2400 degrees F
! Pressure is atmospheric
!
! Compositions from December 1997 Technical Progress Report

! Calculating every 50 degrees F

prob case=HIPPS_HITAF tp t,f=1400.,1450.,1500.,1550.,1600.,1650,
p,psi=14.696.

reac

! Char input

name C wt=800.175 t,f=80.0
name S wt=23.835 t,f=80.0

! Sorbent input

name CaS wt=46.2 t,f=80.0
name CaO wt=107.8 t,f=80.0

! Vitiated Air

name N2 wt=17173.445 t,f=800.0
name O2 wt=3281.55 t,f=800.0
name CO2 wt=1050.096 t,f=800.0

! Coal input (Spring 97 data)

name Coal C 6.140528 H 4.772109 N .092099 S .085746 O .405715
wt=117 h,cal=-22936. t,f=80.0

outp calories short

end
```

Outputs from HITAF for temperature range 1400 - 1650 °F

NASA-LEWIS CHEMICAL EQUILIBRIUM PROGRAM CEA, OCT. 21 1996
 BY BONNIE MCBRIDE AND SANFORD GORDON
 REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED

TEMPERATURE AND PRESSURE

CASE = HIPPS_HITAF

	REACTANT	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	TEMP K
NAME	C	0.0354058	171298.932	299.817
NAME	S	0.0010546	66209.239	299.817
NAME	CaS	0.0020442	29555.072	299.817
NAME	CaO	0.0047699	10513.182	299.817
NAME	N2	0.7598836	2851.556	699.817
NAME	O2	0.1452007	2986.161	699.817
NAME	CO2	0.0464642	- 89809.494	699.817
NAME	Coal	0.0051770	- 22936.000	299.817

O/F= 0.00000 %FUEL= 0.000000 R, EQ.RATIO= 0.806084 PHI, EQ.RATIO= 0.000000

THERMODYNAMIC PROPERTIES

P, ATM	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
T, K	1033.15	1060.93	1088.71	1116.48	1144.26	1172.04
RHO, G/CC	3.6136-4	3.5139-4	3.4242-4	3.3390-4	3.2580-4	3.1808-4
H, CAL/G	-258.01	-248.18	-240.24	-232.25	-224.23	-216.17
U, CAL/G	-325.03	-317.10	-310.96	-304.78	-298.56	-292.31
G, CAL/G	-2197.90	-2250.19	-2302.71	-2355.43	-2408.35	-2461.47
S, CAL/(G)(K)	1.8776	1.8870	1.8944	1.9017	1.9088	1.9157
M, (1/n)	30.635	30.591	30.591	30.591	30.591	30.591
MW, MOL WT	30.529	30.485	30.485	30.485	30.485	30.485
(dLV/dLP)t	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000	-1.00000
(dLV/dLT)p	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Cp, CAL/(G)(K)	0.2842	0.2854	0.2868	0.2881	0.2894	0.2907
GAMMA _s	1.2958	1.2947	1.2928	1.2911	1.2894	1.2878
SON VEL, M/SEC	602.8	611.0	618.5	625.9	633.3	640.5

MOLE FRACTIONS

*CO2	0.13168	0.13293	0.13293	0.13293	0.13293	0.13293
H2O	0.00423	0.00423	0.00423	0.00423	0.00423	0.00423
*NO	0.00002	0.00002	0.00003	0.00004	0.00005	0.00006
*N2	0.82819	0.82700	0.82700	0.82699	0.82699	0.82698
*O2	0.03242	0.03237	0.03236	0.03236	0.03235	0.03235
CaCO3(caL)	0.00144	0.00000	0.00000	0.00000	0.00000	0.00000
CaO(s)	0.00000	0.00144	0.00144	0.00144	0.00144	0.00144
CaSO4(s)	0.00202	0.00202	0.00202	0.00202	0.00202	0.00202

* THERMODYNAMIC PROPERTIES FITTED TO 20000.K

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

Inputs to HITAF for temperature range 1700 - 1950 °F

```
! HIPPS High Temperature Advanced Furnace Calculations
!
! Temperature range is 1400 to 2400 degrees F
! Pressure is atmospheric
!
! Compositions from December 1997 Technical Progress Report

! Calculating every 50 degrees F

prob case=HIPPS_HITAF tp t,f=1700.,1750.,1800.,1850.,1900.,1950,
    p,psi=14.696.

reac

! Char input

name C wt=800.175 t,f=80.0
name S wt=23.835 t,f=80.0

! Sorbent input

name CaS wt=46.2 t,f=80.0
name CaO wt=107.8 t,f=80.0

! Vitiated Air

name N2 wt=17173.445 t,f=800.0
name O2 wt=3281.55 t,f=800.0
name CO2 wt=1050.096 t,f=800.0

! Coal input (Spring 97 data)

name Coal C 6.140528 H 4.772109 N .092099 S .085746 O .405715
    wt=117 h,cal=-22936. t,f=80.0

outp calories short

end
```

Outputs from HITAF for temperature range 1700 - 1950 °F

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 BY BONNIE MCBRIDE AND SANFORD GORDON
 REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED

TEMPERATURE AND PRESSURE

CASE = HIPPS_HITAF

	REACTANT	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	TEMP K
NAME	C	0.0354058	171298.932	299.817
NAME	S	0.0010546	66209.239	299.817
NAME	CaS	0.0020442	29555.072	299.817
NAME	CaO	0.0047699	10513.182	299.817
NAME	N2	0.7598836	2851.556	699.817
NAME	O2	0.1452007	2986.161	699.817
NAME	CO2	0.0464642	-89809.494	699.817
NAME	Coal	0.0051770	-22936.000	299.817

O/F= 0.00000 %FUEL= 0.000000 R, EQ. RATIO= 0.806084 PHI, EQ. RATIO= 0.000000

THERMODYNAMIC PROPERTIES

P, ATM	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
T, K	1199.82	1227.59	1255.37	1283.15	1310.93	1338.71
RHO, G/CC	3.1071-4	3.0368-4	2.9696-4	2.9053-4	2.8437-4	2.7847-4
H, CAL/G	-208.08	-199.95	-191.79	-183.59	-175.35	-167.05
U, CAL/G	-286.02	-279.70	-273.34	-266.95	-260.51	-254.01
G, CAL/G	-2514.78	-2568.28	-2621.96	-2675.82	-2729.86	-2784.08
S, CAL/(G)(K)	1.9225	1.9292	1.9358	1.9423	1.9486	1.9549
M, (1/n)	30.591	30.591	30.591	30.591	30.591	30.590
MW, MOL WT	30.485	30.485	30.485	30.485	30.485	30.484
(dLV/dLP)t	-1.00000	-1.00000	-1.00000	-1.00001	-1.00002	-1.00005
(dLV/dLT)p	1.0000	1.0000	1.0001	1.0002	1.0006	1.0014
Cp, CAL/(G)(K)	0.2920	0.2932	0.2945	0.2959	0.2977	0.3003
GAMMA _s	1.2862	1.2846	1.2831	1.2815	1.2796	1.2770
SON VEL, M/SEC	647.6	654.7	661.7	668.5	675.2	681.7

MOLE FRACTIONS

*CO2	0.13293	0.13293	0.13293	0.13293	0.13292	0.13292
H2O	0.00423	0.00423	0.00423	0.00423	0.00423	0.00423
*NO	0.00008	0.00010	0.00012	0.00014	0.00017	0.00020
*N2	0.82697	0.82696	0.82695	0.82694	0.82691	0.82688
*O2	0.03234	0.03233	0.03232	0.03231	0.03230	0.03229
SO2	0.00000	0.00000	0.00000	0.00000	0.00001	0.00002
CaO(s)	0.00144	0.00144	0.00144	0.00144	0.00145	0.00146
CaSO4(s)	0.00202	0.00202	0.00202	0.00201	0.00201	0.00200

* THERMODYNAMIC PROPERTIES FITTED TO 20000.K

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

Inputs to HITAF for temperature range 2000 - 2250 °F

```
! HIPPS High Temperature Advanced Furnace Calculations
!
! Temperature range is 1400 to 2400 degrees F
! Pressure is atmospheric
!
! Compositions from December 1997 Technical Progress Report

! Calculating every 50 degrees F

prob case=HIPPS_HITAF tp t,f=2000.,2050.,2100.,2150.,2200.,2250,
    p,psi=14.696.

reac

! Char input

name C wt=800.175 t,f=80.0
name S wt=23.835 t,f=80.0

! Sorbent input

name CaS wt=46.2 t,f=80.0
name CaO wt=107.8 t,f=80.0

! Vitiated Air

name N2 wt=17173.445 t,f=800.0
name O2 wt=3281.55 t,f=800.0
name CO2 wt=1050.096 t,f=800.0

! Coal input (Spring 97 data)

name Coal C 6.140528 H 4.772109 N .092099 S .085746 O .405715
    wt=117 h,cal=-22936. t,f=80.0

outp calories short

end
```

Outputs from HITAF for temperature range 2000 - 2250 °F

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 BY BONNIE MCBRIDE AND SANFORD GORDON
 REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED

TEMPERATURE AND PRESSURE

CASE = HIPPS_HITAF

	REACTANT	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	TEMP K
NAME	C	0.0354058	171298.932	299.817
NAME	S	0.0010546	66209.239	299.817
NAME	CaS	0.0020442	29555.072	299.817
NAME	CaO	0.0047699	10513.182	299.817
NAME	N2	0.7598836	2851.556	699.817
NAME	O2	0.1452007	2986.161	699.817
NAME	CO2	0.0464642	-89809.494	699.817
NAME	Coal	0.0051770	-22936.000	299.817

O/F= 0.00000 %FUEL= 0.000000 R, EQ.RATIO= 0.806084 PHI, EQ.RATIO= 0.000000

THERMODYNAMIC PROPERTIES

P, ATM	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
T, K	1366.48	1394.26	1422.04	1449.82	1477.59	1505.37
RHO, G/CC	2.7279-4	2.6733-4	2.6205-4	2.5692-4	2.5187-4	2.4690-4
H, CAL/G	-158.65	-150.10	-141.24	-131.82	-121.35	-109.79
U, CAL/G	-247.43	-240.68	-233.65	-226.08	-217.50	-207.88
G, CAL/G	-2838.47	-2893.03	-2947.76	-3002.68	-3057.78	-3113.09
S, CAL/(G)(K)	1.9611	1.9673	1.9736	1.9802	1.9873	1.9951
M, (1/n)	30.588	30.585	30.579	30.565	30.539	30.498
MW, MOL WT	30.483	30.480	30.473	30.460	30.433	30.393
(dLV/dLP)t	-1.00012	-1.00027	-1.00059	-1.00125	-1.00254	-1.00001
(dLV/dLT)p	1.0033	1.0073	1.0155	1.0318	1.0632	1.0001
Cp, CAL/(G)(K)	0.3046	0.3123	0.3269	0.3542	0.4044	0.3025
GAMMAS	1.2733	1.2671	1.2569	1.2410	1.2186	1.2746
SON VEL, M/SEC	687.7	693.0	697.1	699.6	700.2	723.2

MOLE FRACTIONS

*CO2	0.13292	0.13290	0.13287	0.13281	0.13270	0.13252
H2O	0.00422	0.00422	0.00422	0.00422	0.00422	0.00421
*NO	0.00024	0.00028	0.00033	0.00038	0.00044	0.00051
*N2	0.82683	0.82672	0.82652	0.82613	0.82538	0.82426
*OH	0.00000	0.00000	0.00000	0.00001	0.00001	0.00001
*O2	0.03228	0.03229	0.03233	0.03243	0.03266	0.03302
SO2	0.00005	0.00012	0.00026	0.00055	0.00113	0.00200
SO3	0.00000	0.00000	0.00000	0.00000	0.00001	0.00001
CaO(s)	0.00149	0.00156	0.00170	0.00199	0.00257	0.00345
CaSO4(s)	0.00196	0.00190	0.00175	0.00146	0.00088	0.00000

* THERMODYNAMIC PROPERTIES FITTED TO 20000.K

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

Inputs to HITAF for temperature range 2300 - 2500 °F

```
! HIPPS High Temperature Advanced Furnace Calculations
!
! Temperature range is 1400 to 2400 degrees F
! Pressure is atmospheric
!
! Compositions from December 1997 Technical Progress Report

! Calculating every 50 degrees F

prob case=HIPPS_HITAF tp t,f=2300.,2350.,2400.,2450.,2500.,
p,psi=14.696.

reac

! Char input

name C wt=800.175 t,f=80.0
name S wt=23.835 t,f=80.0

! Sorbent input

name CaS wt=46.2 t,f=80.0
name CaO wt=107.8 t,f=80.0

! Vitiated Air

name N2 wt=17173.445 t,f=800.0
name O2 wt=3281.55 t,f=800.0
name CO2 wt=1050.096 t,f=800.0

! Coal input (Spring 97 data)

name Coal C 6.140528 H 4.772109 N .092099 S .085746 O .405715
wt=117 h,cal=-22936. t,f=80.0

outp calories short

end
```

Outputs from HITAF for temperature range 2300 - 2500 °F

NASA-LEWIS CHEMICAL EQUILIBRIUM PROGRAM CEA, OCT. 21 1996
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 REFS: NASA RP-1311, PART I, 1994 AND NASA RP-1311, PART II, 1996

THERMODYNAMIC EQUILIBRIUM PROPERTIES AT ASSIGNED TEMPERATURE AND PRESSURE

CASE = HIPPS_HITAF

	REACTANT	WT FRACTION (SEE NOTE)	ENERGY CAL/MOL	TEMP K
NAME	C	0.0354058	171298.932	299.817
NAME	S	0.0010546	66209.239	299.817
NAME	CaS	0.0020442	29555.072	299.817
NAME	CaO	0.0047699	10513.182	299.817
NAME	N2	0.7598836	2851.556	699.817
NAME	O2	0.1452007	2986.161	699.817
NAME	CO2	0.0464642	-89809.494	699.817
NAME	Coal	0.0051770	-22936.000	299.817

O/F= 0.00000 %FUEL= 0.000000 R, EQ.RATIO= 0.806084 PHI, EQ.RATIO= 0.000000

THERMODYNAMIC PROPERTIES

P, ATM	1.0000	1.0000	1.0000	1.0000	1.0000
T, K	1533.15	1560.93	1588.71	1616.48	1644.26
RHO, G/CC	2.4242-4	2.3811-4	2.3394-4	2.2992-4	2.2604-4
H, CAL/G	-101.38	-92.931	-84.458	-75.957	-67.427
U, CAL/G	-201.27	-194.64	-187.98	-181.29	-174.57
G, CAL/G	-3168.59	-3224.24	-3280.03	-3335.98	-3392.07
S, CAL/(G)(K)	2.0006	2.0061	2.0114	2.0167	2.0220
M, (1/n)	30.498	30.498	30.498	30.498	30.498
MW, MOL WT	30.393	30.393	30.393	30.393	30.393
(dLV/dLP)t	-1.00001	-1.00001	-1.00001	-1.00001	-1.00001
(dLV/dLT)p	1.0002	1.0002	1.0003	1.0003	1.0004
Cp, CAL/(G)(K)	0.3035	0.3045	0.3055	0.3066	0.3076
GAMMAS	1.2735	1.2724	1.2713	1.2701	1.2690
SON VEL, M/SEC	729.6	735.8	742.0	748.2	754.2

MOLE FRACTIONS

*CO	0.00001	0.00001	0.00001	0.00002	0.00003
*CO2	0.13252	0.13252	0.13251	0.13251	0.13250
H2O	0.00421	0.00421	0.00420	0.00420	0.00420
*NO	0.00058	0.00066	0.00075	0.00084	0.00094
*N2	0.82422	0.82418	0.82414	0.82408	0.82403
*OH	0.00001	0.00002	0.00002	0.00003	0.00003
*O2	0.03299	0.03295	0.03291	0.03286	0.03281
SO2	0.00200	0.00200	0.00200	0.00200	0.00201
SO3	0.00001	0.00001	0.00001	0.00001	0.00001
CaO(s)	0.00345	0.00345	0.00345	0.00345	0.00345

* THERMODYNAMIC PROPERTIES FITTED TO 20000.K

NOTE. WEIGHT FRACTION OF FUEL IN TOTAL FUELS AND OF OXIDANT IN TOTAL OXIDANTS

APPENDIX II

Experimental Data

**Table A2.1 Results from LECO SC132 Analysis
of Calcium Sulfide Oxidation under Pure Oxygen**

Tests 2.1, 2.2, 2.3, and 2.4

Time(sec)	Temperature (F)			
	1000	1500	2000	2500
0	0	0	0	0
5	0		0	253
6		2		
10	0	14	20	389
15	0	40	216	349
20	1	76	208	37
25	5	81	240	26
30	12	50	121	22
35	35	18	48	31
40	264	9	26	72
45	170	8	17	36
50	141	5	9	24
55	86	4	5	12
60	26	3		13
65	4			25
70				6000
75				6000
80				5345
85				727
90				554
95				381
100				453
105				526
110				600
115				756
120				713
125				541
130				203
135				133
140				119
145				118
150				118
155				119
160				125
165				132
170				141
175				152

Table A2.1 (continued)

Time(sec)	Temperature (F)			
	<i>1000</i>	<i>1500</i>	<i>2000</i>	<i>2500</i>
180				166
185				184
190				206
195				225
200				255
205				286
210				320
215				359
220				394
225				426
230				457
235				487
240				509
245				545
250				556
255				562
260				571
265				576
270				571
275				563
300				523
330				447
360				356
390				275
420				225
450				185
480				136
510				106
540				84
570				66
600				61

**Table A2.2 Results from LECO SC132 Analysis
of Commercial Char Combustion under Pure Oxygen
Tests 2.5, 2.6, and 2.7**

Time(sec)	Temperature (F)		
	1500	2000	2500
0	0	0	0
5	1	20	44
10	5	94	245
15	4	98	178
20	6	99	169
25	8	93	158
30	11	90	141
35	13	84	142
40	724	1309	2506
45	853	1334	1342
50	654	919	816
55	489		603
60	253	475	481
65	101	385	436
70	42	306	143
75	33	189	62
80	28		57
85	24	63	56
90	40		58
95	20	36	62
100	17	30	71
105	15	25	82
110	13	21	94
115	12	19	97
120	11	15	95
125		14	89
130	9	13	80
135			71
140			61
145			52
150			42
155			33
160			24
165			18
170			13
175			11

**Table A2.3 Results from LECO SC132 Analysis
of HIPP Char Combustion under Pure Oxygen
Tests 2.8, 2.9, and 2.10**

Time(sec)	Temperature (F)		
	1500	2000	2500
0	0	0	0
5	1	20	44
10	5	94	245
15	4	98	178
20	6	99	169
25	8	93	158
30	11	90	141
35	13	84	142
40	724	1309	2506
45	853	1334	1342
50	654	919	816
55	489		603
60	253	475	481
65	101	385	436
70	42	306	143
75	33	189	62
80	28		57
85	24	63	56
90	40		58
95	20	36	62
100	17	30	71
105	15	25	82
110	13	21	94
115	12	19	97
120	11	15	95
125		14	89
130	9	13	80
135			71
140			61
145			52
150			42
155			33
160			24
165			18
170			13
175			11

**Table A2.4 Results from LECO SC132 Analysis
of HIPP Char Combustion under Air
Tests 2.11, 2.12, 2.13, and 2.14**

Time(sec)	Temperature (F)			
	1800	2000	2200	2400
0	0	0	0	0
5	0	0	0	4
6			3	
7		1		
9	3			
10	43	57	125	202
15	57		96	164
20	64	67	93	159
25	73	66	94	156
30	82	69	96	150
35	344	71	103	138
40	347	347	460	494
45	296	362	440	544
50	263	339	372	607
55	235		308	563
60	207	240	276	543
65	183	212	261	470
70	164	194	240	453
75	151	183	220	447
80	142	170	204	442
85	136	159	220	454
90	128	148	204	488
95	119	141	201	532
100	111	137	202	579
105	102	130	191	471
110	95	120	159	362
115	90	114	102	346
120	85	102	78	353
125	82	84	63	316
130	79	61	32	295
135	77	42	23	270
140	74	26	22	110
145	70	19	21	62
150	67	15	21	44
155	62	13		32
160	56	12	22	24
165	45	10		17

Table A2.4 (continued)

Time(sec)	Temperature (F)			
	<i>1800</i>	<i>2000</i>	<i>2200</i>	<i>2400</i>
170	38		22	14
175	32		23	11
180	27		23	8
185	22		23	7
190	16		23	6
195	9		23	5
200	4			5
205	4			4
210				4

**Table A2.5 Results from Non-Isothermal Bench-Scale
Combustion Studies - Exhaust Gas Compositions
Tests 4.1, 4.2, and 4.3**

Non-Isothermal Test Starting at 1700 F

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
0.50	1381	0.83031	0.16829	0.00024	0.00117
1.00	1347	0.83133	0.16436	0.00106	0.00325
1.50	1414	0.83244	0.14964	0.00631	0.01161
2.00	1482	0.82722	0.11884	0.02003	0.03390
3.00	1563	0.82557	0.09279	0.01449	0.06715
4.50	1787	0.82114	0.07658	0.00859	0.09369
5.75		0.82384	0.07242	0.00410	0.09964
10.50	1803	0.82679	0.07760	0.00040	0.09521
15.50	1756	0.83114	0.09254	0.00044	0.07588
20.50	1692	0.83253	0.13260	0.00053	0.03433

Non-Isothermal Test Starting at 1900 F

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
0.50	1942	0.82636	0.16184	0.00405	0.00775
1.00	1482	0.82514	0.14426	0.01238	0.01823
1.50	1465	0.83056	0.10905	0.01405	0.04633
2.00	1547	0.83100	0.08715	0.00469	0.07716
3.00	1628	0.82344	0.08191	0.00292	0.09173
4.50	1708	0.82373	0.07634	0.00050	0.09943
5.75	1865	0.82892	0.06410	0.00000	0.10699
7.00	1895	0.82965	0.05948	0.00000	0.11087
8.75	1927	0.82789	0.05782	0.00000	0.11430
10.50	1958	0.82622	0.06887	0.00000	0.10491
15.50	1942	0.83635	0.11899	0.00000	0.04466
20.50	1895	0.83977	0.15759	0.00000	0.00264

Non-Isothermal Test Starting at 2100 F

Table A2.5 (continued)

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
0.50	1644	0.83637	0.14726	0.00496	0.01141
1.00	1692	0.83528	0.11638	0.00623	0.04211
1.50	1818	0.83853	0.07896	0.00116	0.08135
2.00	1912	0.82962	0.07343	0.00055	0.09640
2.50	1988	0.81734	0.06859	0.00039	0.11368
4.00	2079	0.82885	0.04633	0.00006	0.12477
5.00	2109	0.82983	0.04880	0.00003	0.12134
6.00	2140	0.82733	0.03589	0.00002	0.13676
7.00	2156	0.83005	0.03889	0.00000	0.13106
10.00	2169	0.83810	0.06969	0.00001	0.09220
15.00	2229	0.84570	0.14554	0.00000	0.00875
20.00	2184	0.84897	0.14850	0.00000	0.00253

**Table A2.6 Results from Non-Isothermal Bench-Scale
Combustion Studies - Carbon Conversion Data
Tests 4.1, 4.2, and 4.3**

Time(min)	Starting Temperature (F)		
	1700	1900	2100
0.50	0.000228	0.002031	0.003074
1.00	0.001154	0.009329	0.015226
1.50	0.004759	0.024989	0.039795
2.00	0.016416	0.049469	0.073492
2.50			0.113115
3.00	0.060403	0.110225	
4.00			0.247683
4.50	0.149916	0.210696	
5.00			0.340139
5.75	0.233481	0.299739	
6.00			0.437088
7.00		0.393468	0.537675
8.75		0.529113	
10.00			0.789222
10.50	0.540703	0.661155	
15.00			0.97881
15.50	0.819622	0.918588	
20.00			1
20.50	1	1	

**Table A2.7 Results from Non-Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data**

Test 4.4

Time	Temp.	SO2	Time	Temp.	SO2
(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
0	1530	0.0	185	1381	1721.8
5	1431	0.0	190		1560.6
10	1381	0.0	195		1481.5
15	1330	0.0	200		1359.8
20	1296	0.0	210	1398	1241.2
25	1262	0.0	215		1134.7
30	1245	0.0	220	1414	1043.4
35	1228	0.0	225		943.1
40	1210	0.0	230		876.1
45	1228	0.0	235	1431	812.2
50		0.0	240		748.4
55		0.0	245		705.8
60		0.0	250		663.2
65		6.1	255	1431	626.7
70		12.2	260		590.2
75		36.5	265		568.9
80		63.9	270	1448	532.4
85		94.3	275		514.1
90	1245	130.8	280		511.1
95		188.6	285		501.9
100		249.5	290		495.9
105	1262	346.8	295		492.8
110		459.4	300	1482	492.8
120		620.6	310		489.8
125		803.1	315		489.8
130	1296	1006.9	320		486.7
135		1229.0	340	1498	486.7
140	1313	1597.1	350	1515	483.7
145	1330	1788.8	360		483.7
150		1983.4	380	1530	483.7
160		2144.7	390		489.8
165	1347	2211.6	400	1530	492.8
170		2099.0	410	1547	492.8
180	1364	1998.7	420		492.8

Time	Temp.	SO2	Time	Temp.	SO2
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Table A2.7 (continued)

(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
440		462.4	580	1596	176.4
450	1563	459.4	590		149.1
460		456.3	600		97.3
470		450.2	605	1596	73.0
480		435.0	610		66.9
490		428.9	615		63.9
500	1579	416.8	620		60.8
510		398.5	625		57.8
520		377.2	630		51.7
530		340.7	640		48.7
540		295.1	650		42.6
550		264.7	660		39.5
560		234.2	670		36.5
570		209.9	680	1596	36.5

**Table A2.8 Results from Non-Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data**

Test 4.5

Time	Temp.	SO2	Time	Temp.	SO2
(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
0	1724	0.0	170	1547	1107.3
5	1628	0.0	175	1563	1040.4
10	1563	18.3	180	1563	985.6
15	1482	6.1	185	1579	918.7
20	1431	6.1	190	1579	885.3
25	1414	3.0	195	1596	851.8
30	1381	0.0	200	1596	827.5
35	1364	0.0	205	1596	803.1
40	1347	6.1	210	1612	787.9
45	1347	18.3	215	1612	772.7
50	1347	36.5	220	1612	751.4
55	1347	63.9	225	1628	736.2
60	1347	85.2	230	1628	724.0
65	1364	185.6	240	1644	705.8
70	1364	273.8	250	1660	699.7
75	1381	359.0	260	1660	702.7
80	1381	547.6	270	1676	708.8
85	1398	830.5	280	1676	730.1
90	1414	1098.2	290	1692	751.4
95	1414	1362.9	300		778.8
100	1431	1703.6	310	1708	809.2
105	1448	2135.6	320	1708	833.5
110	1448	2683.1	330	1724	848.7
115	1465	3008.6	340	1724	860.9
120	1482	2956.9	350	1724	873.1
125	1482	2792.6	360	1724	873.1
130	1498	2594.9	370	1724	870.0
135	1498	2348.5	380	1740	867.0
140	1515	2147.7	390	1756	851.8
145	1515	1995.6	400	1756	830.5
150	1530	1752.2	410	1756	797.0
155	1530	1542.3	420	1771	766.6
160	1547	1399.4	430	1771	778.8
165	1547	1235.1	440	1771	797.0

Time	Temp.	SO2	Time	Temp.	SO2
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Table A2.8 (continued)

(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
450	1787	815.3	780		428.9
460	1787	830.5	800		395.5
470	1787	857.9	810		368.1
480	1787	882.2	820	1803	319.4
490	1787	912.6	830		304.2
500	1803	937.0	840		295.1
510		964.3	850		286.0
520		997.8	860		279.9
530		1025.2	880		267.7
540	1803	1058.7	890		261.6
550		1095.2	900		255.5
560		1110.4	920	1771	249.5
570		1125.6	940	1771	243.4
580		1134.7	980		231.2
590		1140.8	990		228.2
600		1140.8	1010		225.1
610		1146.9	1020		222.1
620		1131.7	1040		219.0
630	1818	1125.6	1050		216.0
640		1113.4	1060		212.9
650		1125.6	1070	1756	209.9
700		1192.5	1080		209.9
710		1101.2			
720		973.5			
740	1803	690.6			
750		501.9			
760		474.6			
770		447.2			

**Table A2.9 Results from Non-Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data**

Test 4.6

Time	Temp.	SO2		Time	Temp.	SO2
(sec)	(degrees F)	(ppm)		(sec)	(degrees F)	(ppm)
0	2034	0.0		175	1895	797.0
5	1973	0.0		180	1912	778.8
10	1771	0.0		185	1912	769.7
15	1724	18.3		190	1927	772.7
20	1676	39.5		195	1927	775.7
25	1628	33.5		200	1927	781.8
30	1612	24.3		205	1942	790.9
35	1596	42.6		210	1942	803.1
40	1596	109.5		215	1942	818.3
45	1612	243.4		220	1958	839.6
50	1612	596.3		225	1958	867.0
55	1628	1000.9		230	1958	897.4
60	1644	1463.3		235	1958	930.9
65	1660	2111.2		240	1973	973.5
70	1676	2789.6		250	1973	1076.9
75	1676	2914.3		260	1988	1219.9
80	1692	2838.3		270	1988	1378.1
85	1708	2585.8		280	1988	1548.4
90	1724	2388.0		290	2004	1727.9
95	1740	2141.6		300	2004	1940.9
100	1756	1959.1		310	2028	2065.6
105	1756	1785.7		320	2028	2016.9
115	1787	1533.2		330	2028	2053.4
120	1803	1466.3		340	2034	2126.4
125	1818	1417.6		350	2034	2193.4
130	1818	1353.7		360	2034	2181.2
135	1834	1268.6		370	2034	2208.6
140	1834	1195.5		380	2049	2315.0
145	1850	1119.5		390	2049	2403.3
150	1865	1034.3		400	2049	2543.2
155	1865	979.6		410	2049	2698.3
160	1881	930.9		420	2049	2817.0
165	1881	873.1		430	2049	2999.5
170	1895	830.5		440	2064	3139.4

Time	Temp.	SO2	Time	Temp.	SO2
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Table A2.9 (continued)

(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
450	2064	3340.2	630	2094	623.6
460	2064	3471.0	690	2109	599.3
470	2064	3635.3	700	2109	395.5
480	2064	3729.6	710	2094	359.0
490	2064	3823.9	720	2094	325.5
500	2079	3918.2	730	2109	304.2
510	2079	3893.9	740	2109	289.0
520	2079	3665.7	750	2109	273.8
530	2079	3498.4	760	2109	258.6
540	2079	3163.8	770	2109	249.5
550	2079	2981.3	780	2109	240.3
565	2079	2780.5	790	2109	231.2
570	2094	2105.1	800	2109	225.1
580	2094	1785.7	810	2109	219.0
590	2094	1186.4	820	2109	212.9
600	2094	772.7	830	2109	206.9
610	2094	696.6	840	2109	197.7
620	2094	654.1			

**Table A2.10 Results from Non-Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data**

Test 4.7

Time	Temp.	SO2	Time	Temp.	SO2
(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
0	2140	0.0	175	1973	857.9
5	2049	0.0	180	1988	845.7
10	1942	0.0	185	1988	845.7
15	1834	0.0	190	1988	851.8
20	1787	6.1	195	2004	854.8
25	1740	12.2	200	2004	860.9
30	1708	18.3	205	2004	879.2
35	1692	73.0	210	2028	888.3
40	1692	273.8	215	2028	909.6
45	1692	584.1	220	2028	937.0
50	1708	1025.2	225	2034	970.4
60	1724	1861.8	230	2034	997.8
65	1740	2540.2	235	2034	1037.4
70	1756	2868.7	240	2049	1095.2
75	1771	2807.9	250	2049	1177.3
80	1787	2610.1	260	2064	1283.8
85	1787	2394.1	270	2064	1454.1
90	1803	2181.2	280	2064	1654.9
95	1818	1889.1	290	2079	1880.0
100	1834	1706.6	300	2079	2120.3
105	1850	1588.0	310	2094	2436.7
110	1865	1524.1	320	2094	2731.8
115	1865	1475.4	330	2094	3011.7
120	1881	1442.0	340	2109	3221.6
125	1895	1399.4	350	2109	3252.0
130	1895	1338.5	360	2109	3437.6
135	1912	1271.6	370	2125	3410.2
140	1927	1183.4	380	2125	3437.6
145	1927	1098.2	390	2125	3531.9
150	1942	1028.2	400	2125	3647.5
155	1942	985.6	410	2140	3729.6
160	1958	943.1	420	2140	3866.5
165	1958	903.5	430	2140	3997.3
170	1973	876.1	440	2140	4070.3

Time	Temp.	SO2	Time	Temp.	SO2
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Table A2.10 (continued)

(sec)	(degrees F)	(ppm)	(sec)	(degrees F)	(ppm)
450	2140	4164.6	850	2154	398.5
460	2154	4319.8	860	2154	398.5
470	2154	4286.3	870	2140	413.7
480	2154	4356.3	880	2140	412.8
490	2154	4362.4	890	2140	413.7
500	2154	4286.3	900	2140	398.5
510	2154	4170.7	910	2125	377.2
520	2169	4265.0	920	2125	362.0
530	2169	4043.0	930	2125	346.8
540	2169	3957.8	940	2125	334.6
550	2169	3836.1	950	2094	334.6
560	2169	3766.1	960	2094	328.5
570	2169	3650.5	970	2094	319.4
580	2169	3534.9	980	2094	304.2
590	2169	3492.3	990	2094	292.0
660	2184	915.7	1000	2079	282.9
670	2184	803.1	1010	2079	267.7
680	2184	748.4	1020	2079	255.5
690	2184	711.9	1030	2079	243.4
700	2169	678.4	1040	2079	228.2
710	2169	660.1	1050	2079	216.0
720	2169	635.8	1060	2079	203.8
730	2169	623.6	1070	2079	197.7
740	2169	596.3	1080	2079	191.7
750	2169	578.0	1090	2079	182.5
760	2169	553.7	1100	2079	179.5
770	2169	532.4	1110	2079	170.4
780	2169	508.0	1120	2079	167.3
790	2169	477.6	1130	2079	161.2
800	2154	456.3	1140	2079	158.2
810	2154	444.1			
820	2154	425.9			
830	2154	413.7			
840	2154	407.6			

**Table A2.11 Results from Isothermal Bench-Scale
Combustion Studies - Exhaust Gas Compositions**

Tests 4.8, 4.9, 4.10, and 4.11

Isothermal Test at 1350 F

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
1.00	1347	0.82064	0.13402	0.0	0.04534
2.00	1347	0.80977	0.11799	0.0	0.07224
3.00	1347	0.82444	0.10423	0.0	0.07133
5.00	1347	0.82646	0.10654	0.0	0.06700
6.00	1347	0.82760	0.10767	0.0	0.06473
7.00	1347	0.83481	0.10527	0.0	0.05992
8.00	1347	0.83069	0.10871	0.0	0.06060
9.00	1347	0.83504	0.10881	0.0	0.05615
10.00	1347	0.83455	0.11324	0.0	0.05221
11.00	1347	0.82749	0.12511	0.0	0.04740
16.00	1347	0.83574	0.14306	0.0	0.02121
25.00	1347	0.82650	0.17350	0.0	0.0

Isothermal Test at 1500 F

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
1.00	1482	0.79330	0.16362	0.0	0.04308
2.00	1482	0.78970	0.11253	0.0	0.09777
3.00	1482	0.81804	0.08540	0.0	0.09656
4.00	1482	0.82176	0.08596	0.0	0.09228
5.00	1482	0.82226	0.09264	0.0	0.08510
6.00	1482	0.82104	0.09913	0.0	0.07983
7.00	1482	0.82489	0.10153	0.0	0.07358
8.00	1498	0.82831	0.10478	0.0	0.06692
9.00	1498	0.83022	0.11136	0.0	0.05842
10.00	1498	0.83096	0.11997	0.0	0.04906
11.00	1498	0.79599	0.17127	0.0	0.03274
15.00	1498	0.81724	0.18276	0.0	0.00000

Isothermal Test at 1650 F

Table A2.11 (continued)

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
1.00	1660	0.80398	0.14849	0.0	0.04752
2.00	1676	0.81633	0.09780	0.0	0.08587
3.00	1676	0.82687	0.08711	0.0	0.08602
4.00	1676	0.83356	0.08614	0.0	0.08031
5.00	1676	0.83064	0.09199	0.0	0.07738
6.00	1660	0.83189	0.09875	0.0	0.06936
7.00	1660	0.83896	0.10127	0.0	0.05977
8.00	1660	0.84129	0.10590	0.0	0.05281
9.00	1660	0.84554	0.10915	0.0	0.04531
10.00	1660	0.84651	0.11899	0.0	0.03450
11.00	1660	0.84691	0.12299	0.0	0.03009
15.50	1644	0.84674	0.15119	0.0	0.00208

Isothermal Test at 1900 F

Time	Temperature	Nitrogen	Oxygen	Carbon Monoxide	Carbon Dioxide
(min)	(degrees F)	mol fraction			
1.00	1895	0.85671	0.10450	0.00244	0.03635
2.00	1912	0.83996	0.03370	0.00218	0.12417
3.00	1912	0.85247	0.03470	0.00132	0.11152
4.00	1912	0.84667	0.03911	0.00070	0.11352
5.00	1912	0.84511	0.04512	0.0	0.10977
6.00	1912	0.84457	0.05463	0.0	0.10080
7.00	1895	0.84585	0.06731	0.0	0.08684
8.00	1895	0.85656	0.07996	0.0	0.06347
9.00	1895	0.85424	0.10194	0.0	0.04382
10.00	1895	0.85285	0.11790	0.0	0.02925
11.00	1881	0.85955	0.12366	0.0	0.01679
14.50	1865	0.85192	0.14726	0.0	0.00082

**Table A2.12 Results from Isothermal Bench-Scale
Combustion Studies - Carbon Conversion Data
Tests 4.8, 4.9, 4.10, and 4.11**

Time(min)	System Temperature (F)			
	1350	1500	1650	1900
1.00	0.024931	0.025467	0.032717	0.022415
2.00	0.089582	0.10873	0.124552	0.117832
3.00	0.168524	0.223606	0.242892	0.25603
4.00		0.335238	0.3574	0.387222
5.00	0.320655	0.440095	0.465958	0.516645
6.00	0.393091	0.537592	0.566978	0.63831
7.00	0.461632	0.628278	0.655877	0.746726
8.00	0.527901	0.711331	0.733383	0.833578
9.00	0.592096	0.785426	0.800931	0.895572
10.00	0.651678	0.848966	0.855876	0.937794
11.00	0.706449	0.897322	0.900345	0.964394
14.00		0.974732		
16.00	0.895062			

**Table A2.13 Results from Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data**

Test 4.8

Time (min)	Temp. (degrees F)	SO2 (ppm)		Time (min)	Temp. (degrees F)	SO2 (ppm)
0	1330	0.0		12		1092.1
0.5		234.2		12.5		1028.2
1	1347	282.9		13		952.2
1.5		319.4		13.5		812.2
2	1347	343.8		14	1330	724.0
2.5		359.0		14.5		699.7
3	1347	380.3		15		693.6
3.5		401.6		16		699.7
4	1347	428.9		17		693.6
4.5		462.4		20		593.2
5	1347	505.0		21.5		343.8
5.5		553.7		22		252.5
6	1347	608.4		23		82.1
6.5		678.4		23.5		63.9
7	1347	754.4		24		57.8
7.5		836.6		24.5		45.6
8	1347	918.7		25		42.6
8.5		991.7		24		57.8
9	1330	1052.6		24.5		45.6
9.5		1125.6		25		42.6
10	1330	1171.2				
11	1330	1356.8				
11.5		1213.8				

**Table A2.14 Results from Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data
Test 4.9**

Time	Temp.	SO2		Time	Temp.	SO2
(min)	(degrees F)	(ppm)		(min)	(degrees F)	(ppm)
0	1465	0.0		5.5		555.3
0.5		305.3		6	1482	684.2
1	1482	321.1		6.5		897.4
1.5		305.3		7		1197.4
2	1482	321.1		7.5		1315.8
2.5		350.0		8	1498	1931.6
3	1482	389.5		8.5		2200.0
3.5	1482	400.0		9	1498	2368.4
4	1482	426.3		9.5		2402.7
4.5	1482	436.8		10	1498	2505.3
5	1482	486.8				

**Table A2.15 Results from Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data
Test 4.10**

Time (min)	Temp. (degrees F)	SO2 (ppm)		Time (min)	Temp. (degrees F)	SO2 (ppm)
0	1660	0.0				
0.5		438.1				
1	1676	322.5				
1.5		279.9				
2	1676	316.4				
2.5	1676	395.5				
3	1676	450.2				
3.5	1676	599.3				
4	1676	766.6				
4.5		1073.9				
5	1676	1469.3				
5.5		2029.1				
6	1676	2372.8				
6.5		2470.2				
7	1660	2251.2				
7.5		2442.8				
8	1660	2680.1				
8.5	1660	2807.9				
9	1660	2442.8				
9.5		2080.8				
10	1660	1953.0				

**Table A2.16 Results from Isothermal Bench-Scale
Combustion Studies - Sulfur Dioxide Production Data
Test 4.11**

Time (min)	Temp. (degrees F)	SO2 (ppm)		Time (min)	Temp. (degrees F)	SO2 (ppm)
0	1881	0.0				
0.5		12.2				
1	1895	143.0				
1.5		596.3				
2	1912	626.7				
2.5		581.0				
3	1912	605.4				
3.5		724.0				
4	1912	991.7				
4.5		1292.9				
5	1912	1490.6				
5.5		1785.7				
6	1912	2159.9				
6.5		2835.2				
7	1895	4043.0				
7.5		5405.8				
8	1895	3589.7				
8.5		2981.3				
9	1895	2853.5				
9.5		2847.4				
10	1895	2963.0				

VITA

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