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Char Reaction Kinetics in a Transport Gasifier

Jason P. Jacobsen

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CHAR REACTION KINETICS IN A TRASPORT GASIFIER

by

Jason P. Jacobsen

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for the degree of

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This thesis, submitted by Jason P. Jacobsen in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

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ABSTRACT

In the field of energy generation, coal gasification is one of the burgeoning technologies that are becoming an attractive alternative to conventional coal conversion. This study will provide valuable data to aid in optimizing and understanding this type of technology, in particular the char reactions of a transport coal gasifier that utilizes the M. W. Kellogg process. It has been very difficult to develop an accurate model for this process due to the lack of kinetic/equilibrium data of the coal char re-burn reaction and its effects on the gasification process.

Char reaction data on carbon monoxide (CO) and carbon dioxide (CO_2) production as well as kinetic equations were developed as a function of the primary control variables: oxygen-to-carbon ratios, temperature, coal type, and water content. Bench scale tests were preformed using a pressurized fluidized bed reactor (PFBR) to simulate the conditions of a transport gasifier. From these experiments qualitative data on CO and CO_2 production of the coal chars have been generated as a function of temperature, oxygen-to-carbon ratios, and fuel types. Also quantitative tests were preformed using a thermogravimetric analyzer (TGA) to generate kinetic equations as well as analyze the effects of steam injection. Utilizing these two analysis techniques, a better understanding of the gasification process as it relates to the interaction with the coal char re-burn was developed.

CHAPTER 1

INTRODUCTION

The purpose of this chapter is to give a quick overview of the process of gasification, including its advantages, its challenges, and industry trends. Knowledge of this process is essential before an in-depth analysis of the topic proposed in this thesis can be understood.

1.1 Overview of Gasification

As the demand and cost for energy increases and natural gas supplies become depleted. Technologies that utilize plentiful, low cost fuels in an efficient and environmentally friendly manner become increasingly attractive. One of these technologies is a process known as gasification. Gasification is a process that converts any carbon containing material into light gases, condensable vapors, and tars. Solid products may also be formed during gasification in the presence of reactive gases. However most applications involving gasification are primarily concerned with the reaction of solid and/or liquid material to gaseous products. Materials that are chiefly used in gasification include coal, fuel oil, crude oil, petroleum coke, dense gases, or waste materials generated as by-products from other fossil or biomass fuel processing methods [1]. For the purpose of this thesis, gasification will focus solely on coal and petroleum coke as the reactive media.

Because of the natural abundance of coal in the United States the utilization of this resource must be tapped. Gasification can offer a supplemental fuel source for natural gas, propane, and other light combustible gasses. This aids to insure an adequate energy supply by providing high-energy gas products that can be utilized in the energy and industrial sectors. The major product of gasification is referred to as synthesis gas or syngas. Syngas is composed mainly of hydrogen and carbon monoxide. This provides a reliable fuel for energy generation and is often referred to as a substitute natural gas (SNG). Other uses for syngas can include being a reactant gas that can be converted to other chemical products or used as an on-site fuel for power generation.

According to a recent study by the Energy Information Agency (EIA) [2] there are over 160 gasification plants operating in 28 countries throughout the world. These plants have the capacity to produce a substantial amount of syngas that rivals the output of the oil industry in terms of energy capacity. Within the next five years, growth within the gasification industry is expected to increase by nearly 50 percent throughout the world (see Figures 1-1 and 1-2). [2] This will lead to increased production capacity and greater product diversity (see Figure 1-3). Note the shift in focus in the gasification industry to power generation.

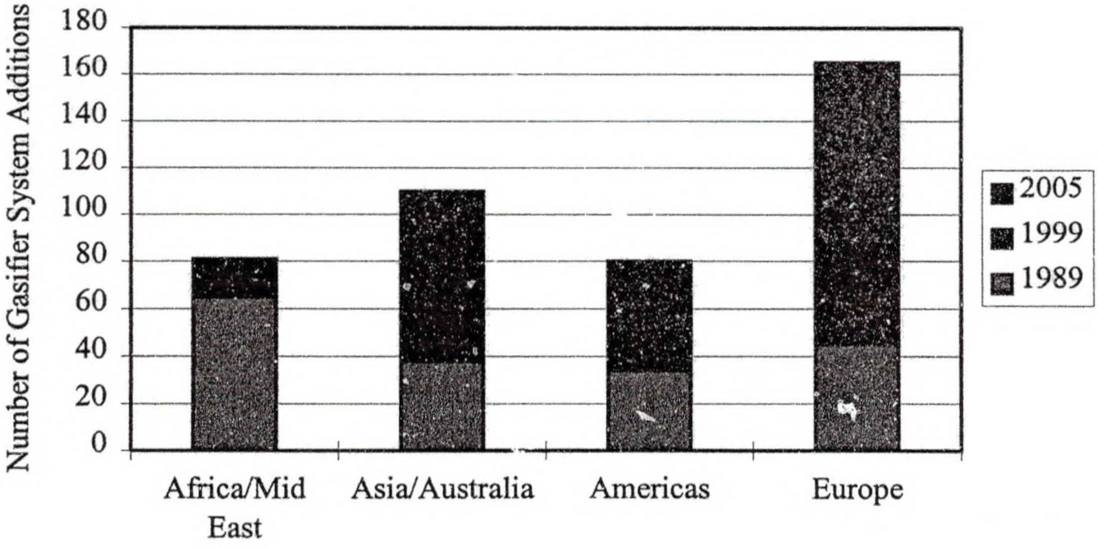


Figure 1-1. Addition of gasifiers by area (EIA, 2000)

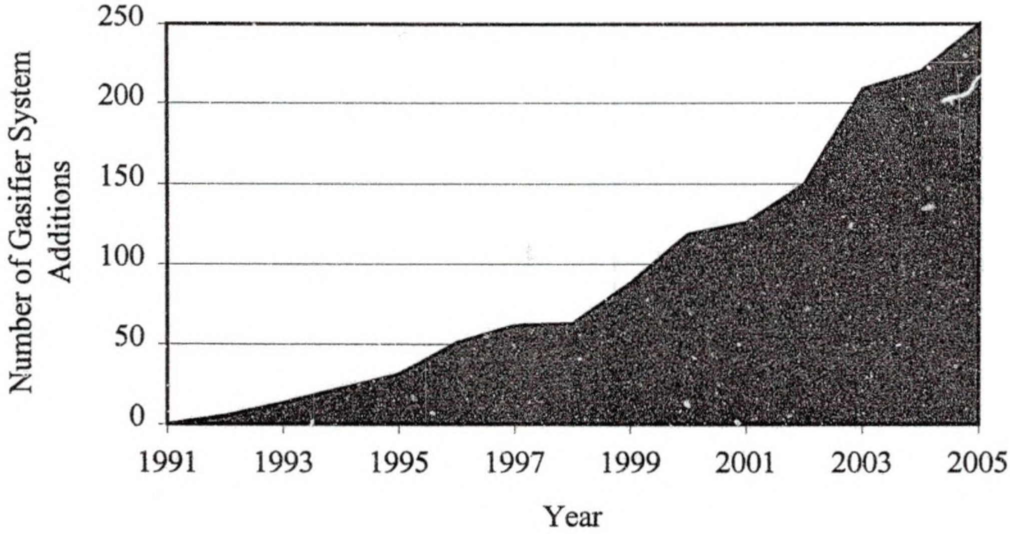


Figure 1-2. Cumulative addition of gasifiers projected to 2005 (EIA, 2000)

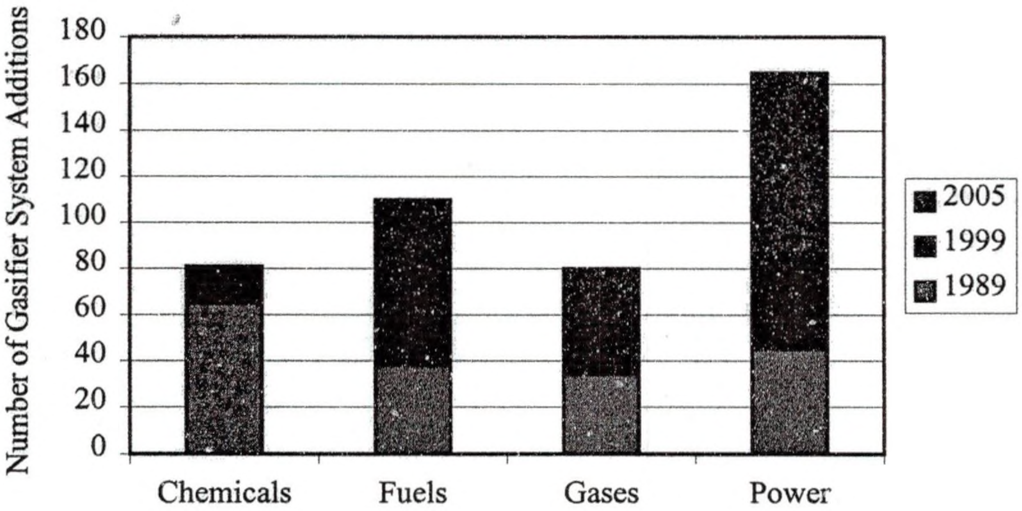


Figure 1-3. Distribution of gasifier products (EIA, 2000)

1.2 Gasification Process

Coal is gasified by destructive distillation. This is accomplished by reacting coal with steam and oxygen at elevated temperature and pressure. In order for coal to gasify oxygen must be fed at sub-stoichometric levels. This insures that the combustion reaction will not dominate (producing primarily carbon dioxide) and high levels of carbon monoxide will be produced. Proper reaction conditions will produce a syngas that can be used as SNG. The syngas formed in most cases will consist of 85% carbon monoxide and hydrogen, with the balance being mainly carbon dioxide and methane along with small quantities of various volatile gases and water vapor [1,3].

1.2.1 Chemistry of Gasification

Gasification is a very complex process. Numerous chemical reactions can take place during the procedure. The main chemical reactions governing the process involve the conversion of organic constituents into product gases. The five most predominate reactions of gasification are the combustion, Boudouard, partial combustion, carbon-steam, and the gas-water shift reactions. These reactions occur in varying combinations and degree depending upon the physical parameters of the gasifier and the reactivity of the coal [4,5].

The combustion reaction is the classic reaction involving the conversion of organic fuels to carbon dioxide and water, as illustrated in Equation 1-1. This reaction takes place when there is sufficient oxygen supply and the reaction does not form carbon monoxide as a by-product.

$$C_XH_Y + \left(\frac{2X+Y}{2}\right)O_2 \xrightarrow{\text{heat}} XCO_2 + YH_2O \qquad \text{Eq. 1-1}$$

This equation can be simplified to be concerned only with the carbon available in the coal. Yielding Equation 1-2.

$$C + O_2 \xrightarrow{\text{heat}} CO_2 \qquad \text{Eq. 1-2}$$

The Boudouard reaction involves the conversion of carbon dioxide to carbon monoxide. This reaction is one of the goals of coal gasification and is accomplished by adding an insufficient supply of oxygen in comparison to the amount of coal fed. This produces one of the desired products of gasification; it is illustrated in Equation 1-3.

$$C + CO_2 \longrightarrow 2CO \qquad \text{Eq. 1-3}$$

The partial combustion reaction, which is essentially the combination of Equations 1-2 and 1-3, is considered an undesirable by-product of combustion. This is not the case in gasification. Like the Boudouard reaction it also requires an insufficient oxygen supply coupled with excess carbon to produce carbon monoxide as the product gas. This reaction is shown in Equation 1-4.

$$2C + O_2 \longrightarrow 2CO \qquad \text{Eq. 1-4}$$

The carbon-steam reaction is one of the most important reactions in the gasification process. It produces the most desirable products. It is shown in Equation 1-5

$$C + H_2O \longleftrightarrow CO + H_2 \qquad \text{Eq. 1-5}$$

The water-gas shift reaction generally takes place following the combustion reactions. This reaction converts the carbon monoxide in the flue gas to carbon dioxide and hydrogen upon the addition of steam, as seen in Equation 1-6

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \text{Eq. 1-6}$$

Another reaction that may occur at very high temperatures and increased pressure is carbon-hydrogenation. This reaction forms methane from hydrogen liberated in the carbon-steam or gas-water shift reactions. The concentration of methane is generally low in gasification and is extent its usually determined by the amount of volatile matter in the coal feed. It is illustrated in Equation 1-7.

$$C + 2H_2 \longleftrightarrow CH_4 \qquad \text{Eq. 1-7}$$

Due to the heterogeneous nature of the coal feed, side reactions also occur involving inorganic constituents. These reactions are often undesirable and can cause numerous problems during operation. This is not always the case however; some gasification processes will concentrate and sell the inorganic material within the raw coal such as trace metals. The inert material created during gasification also has commercial value. Slag, tar, and ash all have value in the construction and contracting industries. These reactions and occurrences, while important in the study of coal conversion systems, were not considered as part of this study.

1.2.2 Formation of Char

The main focus of this thesis is the role coal char has on the gasification process. The study of char reaction kinetics is relatively easy compared to the initial coal feed reactions. This is due to the fact that the composition of the feed gas reacting with the coal char generally known. In most gasification systems and in particular the one studied for this thesis, unreacted char is recycled and reburned then reintroduced into the raw coal feed in a mixing zone. The feed gas reacting with the initial coal feed often contains gases formed by these char reactions. This gas composition can vary depending upon coal rank and physical conditions. This is why studying the effects of coal char are of importance. A better understanding of the char/coal feed interaction in their mixing zone should lead to a more accurate gasification model. This can lead to better reactor designs for new facilities and increased efficiencies of existing plants.

Char is created following the initial heating of the feed coal (coal cracking). Char is often defined as coal with the volatile components and moisture removed. A more conventional definition is that it is simply the residues left following heat treatment of coal [6]. The properties of char are slightly different then the original coal feed. The reactivity is greatly decreased and gasification of char proceeds at a much slower rate. It often requires several passes through the reactor to complete the process. A more detailed description of the char reaction process is given in the subsequent chapters.

1.3 Brief History of Gasification

Coal gasification is not a relatively new or a revolutionary concept in the field of fuel processing or energy generation. The fundamental process itself has been understood for over 150 years. Gasification plants have been in operation in England and other European countries since the 1860s [3, 4]. However gasification offers advantages in its versatility and also its appeal concerning environmental issues, and not until the latter part of the twentieth century has research to improve this process based on thermodynamics, physics, and chemical kinetics been investigated [6].

The firsts gasifiers were designed by K. W. Siemens. They were essentially brick combustion chambers that gravity fed coal along an angled baffle where it was combined with air at the bottom and off gases collected at the top. The gas generated from this early process is known as producer-gas. Producer-gas is a product of incomplete combustion and has a relatively low heat value compared to syngas. It contains approximately 33% carbon monoxide, with the balance as nitrogen and carbon dioxide

[3, 4]. As demand for high-energy gas grew, new gasifiers were constructed to produce what is known as water-gas. The process developed by Gaillard, du Motay, and Lowe in the late ninetieth century injected steam into the gasification process along with air as seen in Equation 1-5. This yielded a gas that, for the most part, was carbon monoxide and hydrogen. The advantage of water-gas was that it contained double the heat content of producer-gas. By the 1920s gasifiers had evolved and became much more efficient. They were able to be run independently without an outside fuel source for steam generation, allowed for ash and slag recovery, were capable of handling a high throughput of gas, and could be operated at pressure. In 1936 the Lurgi gasifier was introduced and produced a high quality syngas for the first time [7, 8, 9, 10]. Continuing improvements being made to gasification equipment led to what is known as second-generation gasifiers. These modern day gasifiers were capable of running at high temperatures and pressures, could handle very high throughputs, introduced catalysts to the process, and produced very high quality syngas which could perform as SNG.

A pilot scale second-generation gasifiers is located at the University of North Dakota's (UND) Energy and Environmental Research Center (EERC). It is a transport gasifier that utilizes the M. W. Kellogg process for gasification. Generating accurate kinetic data that could be used in modeling this gasifier is one of the main objectives of this research. Details about this reactor and its process will be discussed in the following chapters.

CHAPTER 2

BACKGROUND

The purpose of this research was to determine the properties of coal char reactions as they relate to the gasification process; in particular the kinetics of char re-burn in combination with raw coal feed in the mixing zone of a transport reactor. To accomplish this goal two separate sets of experimental data were obtained. Bench scale tests were run on coal chars using a pressurized fluid-bed reactor (PFBR) and adding air to simulate conditions of a full-scale transport gasifier like the Transport Reactor Development Unit (TRDU) located at the EERC. Kinetic data on coal char reactions were also obtained using thermogravimetry.

This chapter gives background information on the operation and process of the TRDU and how it will benefit from the research presented in this thesis. Also information will be presented on thermogravimetry and the bench scale tests of the PFBR.

2.1 The TRDU and Transport Gasification

The TRDU is a pilot scale pressurized circulating fluidized bed staged coal-processing unit. It is capable of operation in both combustion and gasification modes. The latter is the basis for the topic of this thesis. The TRDU makes use of the Kellogg process of operation. This process utilizes the thermal and transportation effects that calcium carbonate ($CaCO_3$) have on transport gasification. The gasification of coal is aided in this process by recirculating $CaCO_3$ with steam at elevated pressure and temperature. The $CaCO_3$ helps in transporting the unreacted char and ash through the reactor while maintaining heat generated by the initial coal cracking. The char/$CaCO_3$ mixture is recycled and re-burned prior to being combined with the raw coal feed. This assists in providing heat to the reactor and converting the more complex hydrocarbons. [4, 11]

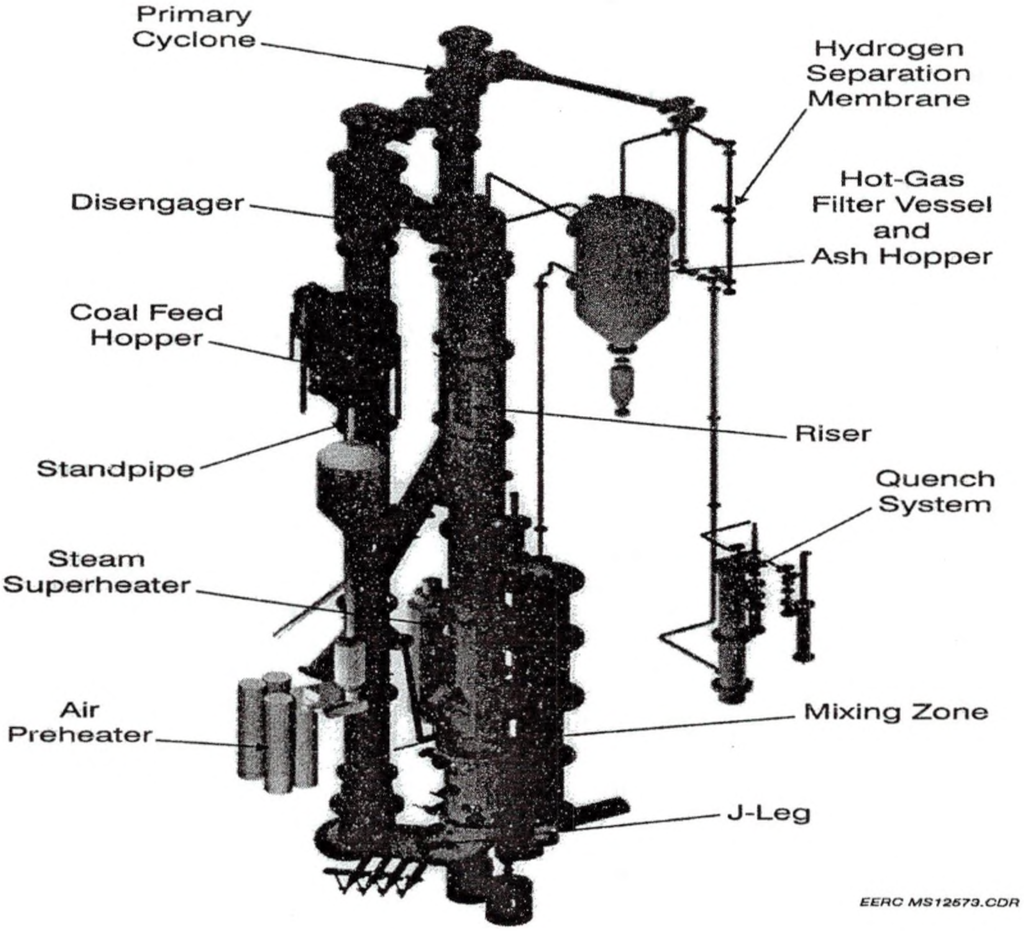


Figure 2-1. Illustration of the TRDU

A schematic of the TRDU is illustrated in Figure 2-1. The initial gasification takes place in the riser. The standpipe contains the ungasified char formed from the initial coal cracking. The riser and standpipe are connected by the J-leg where steam and air are injected in the char flow prior to entering the mixing zone. While the volatile matter and some of the char formed from the original coal feed is gasified rapidly, the gasification of the more refractory char proceeds at a slower rate requiring recirculating through the TRDU. Most of the recirculated char is partially combusted in the bottom of the mixing zone to provide heat necessary for gasification. The design parameters of gasification systems are largely dependent upon the reaction rates of the coal char. Therefore it is of great importance that the kinetics and reactivity of coal chars are studied in order to obtain accurate models for equipment manufacturing.

The reactions pertaining to coal chars are the same as the ones presented in Equations 1-1 thru 1-5; only the char reactions proceed at a slower rate then reactions of the initial raw coal feed. While these reactions pertaining to coal chars have been studied at length, the majority of the experiments conducted to obtain kinetic data have been done using fixed-bed flowing gas systems [6]. The study proposed in this thesis will also include data obtained using a fluidized-bed system. To determine the effects of char re-burn on the overall reaction kinetics of the transport reactor.

Thermogravimetry, a fixed-bed system was used to determine the rates at which three different chars react. The TGA experiments analyzed the effects of varying gas composition, temperature, and steam effects as they relate to char reaction kinetics. The second set of experiments using a fluidized-bed system; the PFBR was used to determine the carbon monoxide/carbon dioxide production rates of two different char types. The combination of these two experimental sets provided a good indication of the properties of the char reactions.

2.2 Thermogravimetry and the TGA

The first sets of experiments utilize thermogravimetry in order to study the reaction rates of the coal chars created during previous TRDU runs at the EERC. The three different types of coal chars studied were Freedom (a lignite from western North Dakota), Illinois #6 (a bituminous from Illinois), and a petroleum coke from Alabama [11].

Thermogravimetry is a type of thermal analysis and involves studying the change in the reacting species mass on a time basis. The type of thermogravimetry used for this research was known as isothermal thermogravimetry. This type of thermal analysis measures the mass change of the reactant at a constant temperature as a function of time. This particular technique is useful in determining rate constants of a reaction, which is what was hoped to be accomplished with this thesis. The basic premise behind this technique is that a small amount of a reacting sample is placed on a balance. The sample pan is then heated to the desired temperature and a fixed gas composition is passed over the sample. Next the percent loss of mass is recorded over a set period of time, where upon implementation of data analysis techniques a rate constant can be determined for that particular set of physical conditions.

Determination of kinetic parameters for char-reburn in a transport gasifier can easily be found using the thermal analysis previously mentioned. This technique has been used in prior experiments [6, 12, 13] in order to assist in the determination of char kinetics. Previous works have shown that in general the carbon-steam reaction, Equation 1-5, of coal chars often is the most dominant reaction at these conditions [14, 5]. This reaction and its potential interaction with other gasses present during char gasification will be the basis of the work to be done using the TGA equipment. It is hoped that general kinetic data involving the carbon-steam reaction of the chars mentioned will provide a good indication of the reaction rates within the TRDU under varying physical conditions.

The generation of kinetic data using isothermal thermogravimetry is relatively straightforward. Weight loss versus time curves are generated using a TGA and are fit to the differential kinetic equation.

$$-\frac{dC}{dt} = kC^n \qquad \text{Eq. 2-1}$$

Where:

$$k = Ae^{-\frac{E}{RT}} \text{ (rate constant)} \qquad \text{Eq. 2-2 (Arrhenius Equation)}$$

T = Temperature

C = Concentration of reactant remaining at temperature T

n = order of reaction

E = Activation energy

A = Pre-exponential factor

R = Universal gas constant

t = time

A detailed description of the process used to determine the rate constants for this thesis are illustrated in the subsequent chapter.

2.3 Fluidized Bed Technology

The second method used to determine the properties of coal char during gasification analyzed the carbon monoxide and carbon dioxide production with varying physical conditions in a fluidized-bed reactor. The goal of these experiments was meant to simulate the conditions of the J-leg and mixing zone in the TRDU to investigate the effects of temperature and oxygen-carbon ratios on the carbon monoxide/carbon dioxide production of the char reaction, best illustrated in Equations 1-2 through 1-4. This was to be accomplished using the EERC's bench scale reactor the PFBR.

Fluidized beds are a relatively complex unit operation. Truly understanding them and there properties is beyond the scope of this thesis. A brief description of this type of system will be presented in this section in order to understand their usefulness and operation.

A fluidized bed reactor such as the PFBR is generated by passing a reacting gas through the bottom of a fixed bed of fine particles. If the velocity of the gas (fluidizing velocity {V_f}) is high enough the particles will become suspended in the flowing gas to where the pressure drop across the bed is equal to the weight of the reacting solids. When this phenomenon occurs the velocity of the gas has reached the minimum fluidization velocity (V_{mf}). This type bed is said to be incipiently fluidized [6]. The relationship between the minimum fluidizing velocity and fluidizing velocity is illustrated in Equation 2-3.

$$V_f = \frac{V_{mf}}{\epsilon_{mf}} \qquad \text{Eq. 2-3}$$

Where ϵ_{mf} is the average void fraction in the bed at V_{mf}.

When the fluidization velocity becomes greater than V_{mf} bubble regions will form creating two separate regions within the bed, the emulsion of solids and bubble voids. The regions around these bubble voids cause a good deal of mixing and insure relatively homogenous physical conditions such as temperature and pressure drop. These bubble voids also insure that there will be a good deal of mass transfer between the solid and gas phase, thus increasing reaction rates.

The use of a fluidized bed in coal gasification is very efficient and has been done previously on numerous occasions [15 - 18]. Fluidized beds offer several advantages in the field of gasification. They insure a good heat transfer rate, a relatively uniform temperature distribution, and as mentioned before a good mass transfer rate. This results in high conversion rates, simplified controlling, and supports a variety of reaction conditions. For large-scale systems this type of technology makes controlling the process relatively easy due to the suspension of fine particles that can act as a flowing system [6].

While the use of fluidized bed reactors have become relatively common in coal conversion systems it should be noted problems might occur. The difficulties are that in order to achieve an efficient fluidized bed, gas velocities must not become too low or high; also the size distribution of solid particles cannot vary greatly. These problems could result in agglomeration, gas back-mixing, gas bypass, and particle carry-through.

The PFBR illustrated in Figure 2-2; was originally designed as a small-scale fluidized bed combustion reactor. Fuel material is fed to a 55-in. tall 3-in. vertical reactor pipe through a variable speed rpm controlled auger. The feed material is then passed over an air and/or air-nitrogen gas combination that is controlled independently to the desired flow rate and can be preheated to a desired temperature. The feed material enters approximately 22-in. above the bottom of the pipe. The reactant gas is injected through the bottom of the pipe where it fluidizes the feed material as it reacts. Temperature is controlled through three ceramic heaters placed along the reacting pipe. The hot cyclone

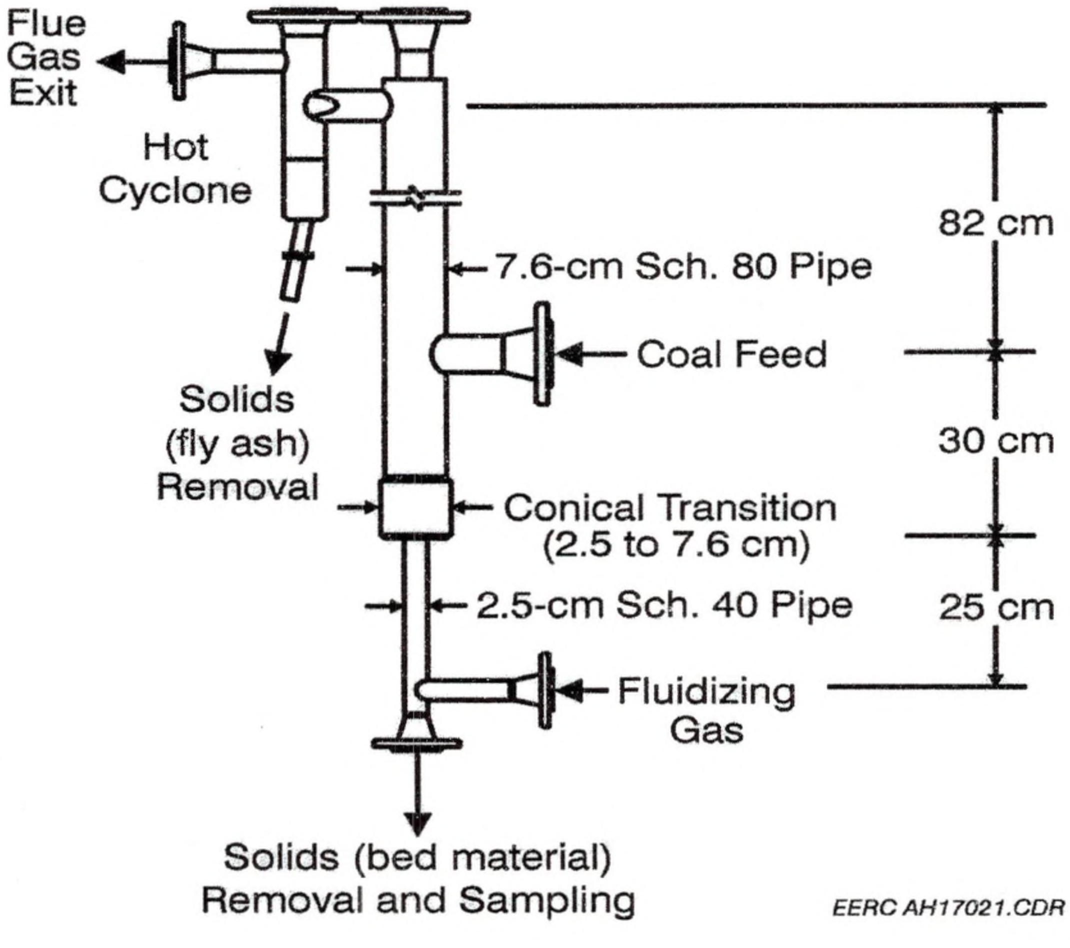


Figure 2-2. Schematic of the EERC's PFBR

removes ash and other fine particulates from the flue gas prior to being sent to gas analyzers.

This system is capable of measuring temperature along the reactor; with 11 thermocouples at varying heights, pressure drop across the reactor, superficial gas velocity, and emissions. All of these parameters can be sent to a computerized data acquisition program for further analysis [19].

A study similar to the one presented for the PFBR was conducted to analyze the properties of a Pittsburgh seam coal [16]. It utilized a bench scale fluidized bed reactor to study exit gases, temperature, pressure, and a variety of reaction parameters. This study was used to determine optimal operating conditions for coal gasification, as was proposed by tests in the PFBR. The results obtained in this study, especially the carbon monoxide-to-carbon dioxide ratios were hoped to parallel the experiments in this thesis. This experiment showed that bench scale fluidized bed reactors are successful in determining operating conditions for the gasification of coal in an air/steam system. However the bench scale experiments in this thesis will deal with char in pure air.

2.3.1 Problems with current PFBR

The PFBR as previously mentioned works very well as a model for combustion systems. However when gasification was required of the system, numerous problems were encountered that were unanticipated. The first problem encountered was that the coal-char feed was too fine for the current auger's gear system. Even at the lowest rpm setting, the char feed was too high to allow time for data collection. This was remedied by replacing the original small auger gear with a larger one. This resulted in char feed rates that could allow for sufficient data collection time. The next problem to be dealt with was the low velocity of the fluidizing gas. While the velocity itself was capable of fluidizing the coal-char, the flue gas was too low of volume to produce much more than 0.5 SCFH to the gas analyzers. This resulted in a possible error in the readings of the analyzers. The original sample pump was replaced, however low flow rates were common with these PFBR tests. The results obtained appeared to be consistent even though flow rates were lower than recommended for the analyzers. It is felt that the readings for oxygen, carbon monoxide, and carbon dioxide gas compositions were still relatively accurate.

Even with the problems previously described of the PFBR some good results were obtained. A detailed description of the process used and the results are described in the subsequent chapter.

CHAPTER 3

EXPERIMENTAL

The data collected as part of this research project was obtained through two separate experimental methods. One, a quantitative set of laboratory experiments, was run to determine the kinetic rate data of the coal-chars previously mentioned. Using the TGA located at the EERC. The other set was done using a bench-scale reactor, the PFBR in order to determine the effects that temperature and oxygen/carbon ratios had on carbon monoxide and carbon dioxide production of the coal-chars. The goal of these sets of experiments was to generate data that could be used to aid in generating more accurate models of the TRDU mixing zone.

This chapter will briefly describe the equipment used, detail the experimental procedure including problems encountered during test runs, and define the test matrices for both experimental procedures. In addition proposed results of the test sequences will be briefly described, this includes modifications made during test sequences due to procedural and equipment problems. Knowledge of the equipment used and the process implemented will aid in comprehending the results obtained and the conclusions drawn presented in the following chapter.

3.1 TGA

The TGA located at the EERC utilizes the principle of thermogravimetry presented in Chapter 2. The purpose of the experiments run using this equipment was to determine kinetic data, in particular the rate constant k, presented in Equation 2-2. The data obtained from the TGA will analyze the effects temperature, steam content, and the carbon dioxide/carbon monoxide split has on the rate of reaction for a specific coal type.

3.1.1 Equipment Description

The EERC's TGA is a Dupont 951 interfaced with a 1090 thermal analyzer control unit and data processor. The TGA contains a highly sensitive electronic balance connected to a 100-mg capacity platinum sample pan that records weight loss of the reacting species. Typical sample sizes usually are in the range of 10 to 40 mg. It contains a furnace capable of operating at temperatures up to 1200 °C (2192 °F) with a maximum heating rate of 100 °C/min [19]. The TGA is illustrated in Figure 3-1.

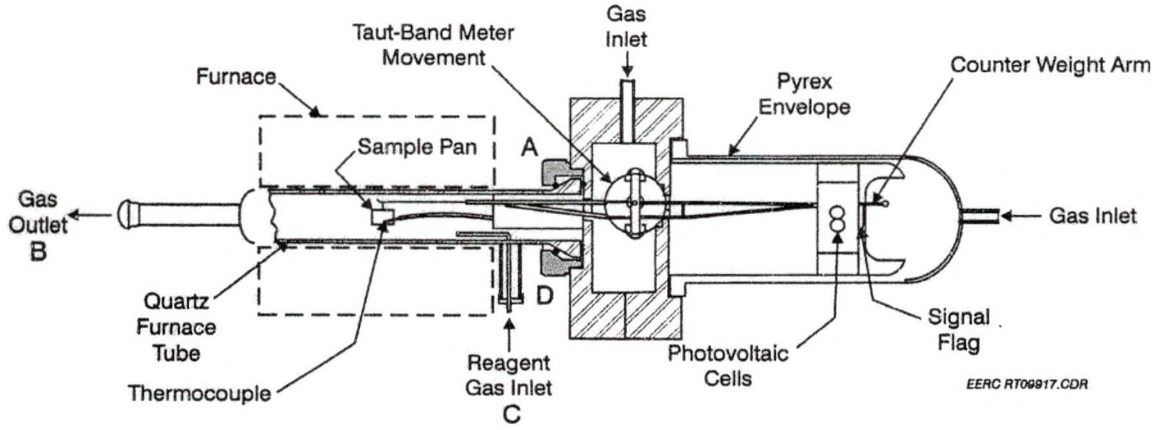


Figure 3-1. Schematic of the Dupont 951 TGA

Operation of the TGA is relatively straightforward. A user defined gas mixture flows over the sample pan, which is suspended by a horizontal quartz beam in the center of the furnace. The temperature of the reacting species located in the sample pan is determined by a chromel-alumel thermocouple located approximately 1-mm above the center of the sample pan. Temperature, time, sample weight loss percentages, and time based weight loss percentages (derivative weight loss) data is electronically collected for further analysis.

3.1.2 TGA test matrix

The three controlled variables in the TGA experimental test matrix were coal-char type, temperature, and gas composition. Experiments were set up in four separate experimental blocks in order to estimate the effects these variables had on the rate constant.

The first variable, char type was determined on the basis that samples with a broad range of reactivity be represented. Petroleum coke, lignite, and bituminous chars were tested to determine the effects of char type on kinetic data. These three fuels were chosen since char samples from previous TRDU runs were readily available. The chars were obtained from sample ports in the J-leg of the TRDU. The J-leg samples contained a char/limestone mixture from the standpipe in the TRDU. Each sample was classified through a 30-mesh Tyler screen removing the fine limestone particles. Next pure carbon char particles were removed from the ash by hand until approximately 500-mg of pure carbon char was obtained. The char particles were then crushed into a fine powder before they were used in the TGA.

The petroleum coke, from the Hunt Oil Refinery in Tuscaloosa, Alabama; was obtained from TRDU run P061 in March 7 – 11, 1999. Lignite, from the Freedom mine in North Dakota; came from TRDU run P065 during February 2000. Bituminous was represented by an Illinois No. 6, obtained from Seam 6 of the Baldwin mine in Baldwin, Illinois; from the P063 run during August 28 – September 2, 1999 [11]. Originally there were seven different coal types that would be tested, however due to lack of funding the test matrix was scaled down to test the three types mentioned.

Temperature, the second variable was determined based on previous TRDU runs with these particular fuels as well as knowledge gained from other runs using the same coal types from different locations and mines. Temperature effects are studied in the first block of experiments in the TGA test matrix. The data collected from this block was used to generate Arrhenius plots that directly relate rates of reaction as a function of temperature for each separate coal type.

The final variable, gas composition, was more difficult to determine since very little previous knowledge or literature was available on these types of experiments. The problem was that in most TGA experiments there is usually only one reacting gas coupled with an inert such as a noble gas or nitrogen that is passed over the sample. The experimental matrix proposed for this research used a gas mixture of five gasses in order to better simulate the conditions of the TRDU during char re-burns. The gas mixture contained nitrogen, steam, carbon dioxide, carbon monoxide, and hydrogen. The goal was to determine the effects of the carbon-steam reaction when other gasses are present. The interactions and reactions proposed in these experiments will be presented in detail in the following chapter.

A reasonably representative gas composition was chosen based on gas compositions from previous TRDU runs [11].

Table 3-1. Experimental Test Matrix for TGA Runs

Block 1-Temperature & Char Type								
				Gas Composition (Weight %)				
Run	Fuel	Coal Type	Temp (°F)	N_2	H_2O	CO	CO_2	H_2
1	Illinois No. 6	Bituminous	1600	55	15	10	10	10
2	Freedom	Lignite	1500	55	15	10	10	10
3	Pet Coke	Petroleum Coke	1750	55	15	10	10	10
4	Illinois No. 6	Bituminous	1850	55	15	10	10	10
5	Freedom	Lignite	1750	55	15	10	10	10
6	Pet Coke	Petroleum Coke	2000	55	15	10	10	10

Block 2-Steam Composition								
				Gas Composition (Weight %)				
Run	Fuel	Coal Type	Temp (°F)	N_2	H_2O	CO	CO_2	H_2
7	Freedom	Lignite	1500	95	5	0	0	0
8	Illinois No. 6	Bituminous	1850	95	5	0	0	0
9	Pet Coke	Petroleum Coke	2000	95	5	0	0	0
10	Freedom	Lignite	1500	85	15	0	0	0
11	Illinois No. 6	Bituminous	1850	85	15	0	0	0
12	Pet Coke	Petroleum Coke	2000	85	15	0	0	0
13	Freedom	Lignite	1500	50	50	0	0	0
14	Illinois No. 6	Bituminous	1850	50	50	0	0	0
15	Pet Coke	Petroleum Coke	2000	50	50	0	0	0

Table 3-1 (cont.)

Block 3-CO/CO_2 (Isolated effects)								
				Gas Composition (Weight %)				
Run	Fuel	Coal Type	Temp (°F)	N_2	H_2O	CO	CO_2	H_2
16	Freedom	Lignite	1500	55	15	20	0	10
17	Illinois No. 6	Bituminous	1850	55	15	20	0	10
18	Freedom	Lignite	1500	55	15	0	20	10
19	Illinois No. 6	Bituminous	1850	55	15	0	20	10

Block 4-CO/CO_2 (Interaction Effects)								
				Gas Composition (Weight %)				
Run	Fuel	Coal Type	Temp (°F)	N_2	H_2O	CO	CO_2	H_2
20	Freedom	Lignite	1500	45	15	20	10	10
21	Illinois No. 6	Bituminous	1850	45	15	20	10	10
22	Freedom	Lignite	1500	60	15	5	10	10
23	Illinois No. 6	Bituminous	1850	60	15	5	10	10

3.1.3 Experimental procedure for TGA runs

Approximately 40 – 50 mg of the char samples previously described were placed in the sample pan. The TGA furnace was heated at a rate of 100 °C/min until the desired temperature was reached. Simultaneously the defined gas mixture was passed over the sample during the heat up and continuous operation. The data collection began as soon as the gas mixture was passed over the sample. The TGA collected data until the gasification of the char was complete. Once it appeared that the gasification reaction(s) had reached the limit, the amount of ash left in the sample was determined by burning off remaining carbon in pure air until weight loss leveled off.

3.1.4 Proposed Results of the TGA Experiments

The TGA experiments previously described were designed to illustrate the effects of temperature, steam content, and carbon dioxide/carbon monoxide ratios had on char reactivity. It was hoped that the four individual experimental blocks would give a distinct correlation between the proposed reaction(s) and the variable(s) studied, as well as give some overlap between experimental blocks for comparison of different reaction system(s).

Block one (from Table 3-1) was designed to show the effect of temperature on the carbon-steam reaction. Temperature ranges were representative temperatures based on maximum and minimum values run on previous TRDU runs described earlier. The data obtained from this block should give a direct relationship between temperature and char reactivity. This will aid in determining the optimum temperature for char-reburn in the TRDU.

Block two (from Table 3-1) shows the effect varying steam composition has on the carbon-steam reaction. This experimental block contains only two gasses, nitrogen and steam, to exclusively study the carbon-steam reaction of the particular char type. Temperatures for this block were determined from the optimum temperature settings obtained during previous TRDU runs. Analysis of this experimental block should give a good indication of char reactivity values based on steam content.

Blocks three and four (from Table 3-1) are designed to illustrate the effects of carbon monoxide and carbon dioxide concentrations on the reactivity of the carbon-steam reaction of two chars. Temperatures were determined by the same method as Block two. Block three analyzes the impact of each gas separately, while Block four has both gasses present. Data analysis of these two experimental blocks should show the effects the gas-water shift (Eq. 1-6), carbon-steam (Eq. 1-5), and Boudouard (Eq. 1-3) reactions have on char reactivity. Post test analysis indicated that all three reactions were occurring, but the design of the experimental matrix did not provide adequate data to determine the extent of these reactions relative to one another therefore, these two experimental blocks will be difficult to interpret. Hence further experiments will be needed in order to accurately describe the system. The results that will be obtained in this research will only show the effects these gasses have on the overall char reactivity and not propose a reaction system. The results and proposed reactions of the TGA experiments will be discussed in the following chapter.

3.2 PFBR

The second type of experiments were performed on the EERC's PFBR. The PFBR as described before is a fluidized bed reactor. These experiments were intended to simulate the conditions of the TRDU during char re-burn to provide an analysis of the products gasses when burned in substoichiometric air. Data obtained from these experiments were proposed to aid in determine the rate of carbon monoxide production from chars from previous TRDU runs.

3.2.1 Equipment description

The major components of the PFBR were described in the previous chapter. It was originally designed to study the properties of a combustion reaction under well-controlled conditions. Most of the system is designed to be controlled electronically through a single computer interface program. This includes nitrogen and air flow rates, PID controlled to a desired set point. Coal feed rate and temperature are the only two variables that require manual control. The system is connected to a computerized data acquisition package that is capable of logging temperature at 11 locations along the reactor, including cyclone and entering fluidizing gas temperatures; bed pressure; emissions; and gas velocity on 30-second intervals. Typical operating conditions are shown in Table 3-2.

Table 3-2. Normal PFBR Operating Conditions

Reactor Diameter	2.875-in. ID
Temperature	1400 – 1700 °F
Pressure	0 – 150 psig
Gas Flow Rate	1 – 30 scfm
Coal Feed Rate	1 – 8 lbs/hr
Velocities	1 – 10 ft/sec
Cyclone Exit Temperature	Max. 1600 °F
Particulate Loading	200 – 9000 ppm

3.2.2 Initial Problems of the PFBR

Upon inspection of the typical operating conditions of the PFBR it should be noted that while this will work well for combustion and other fluidized bed reactions, it is probably not the best for gasification. Temperature ranges needed to be approximately 1500 – 2000 °F, gas flow rates around 0.2 – 2 scfm, and coal feed rates near one pound per hour. The remaining variables presented were not considered since they were not a controlled variable in the work proposed in this thesis for the PFBR. However since no previous work done on the PFBR suggested that these operating conditions were unattainable, exploratory research into the viability of this system as a small-scale gasifier was done.

Since the PFBR was the only suitable piece of equipment that was readily available for this type of research it was determined that this was the best option. The PFBR equipment was designed to match the operating conditions proposed, even though previous experiments had not yet been run at these settings. However the high temperature and low gas flow rates were at the controllable limit and careful consideration had to be taken in order to prevent equipment failure or inaccurate data. After the initial literature investigation of the PFBR equipment, shakedown experiments with petroleum coke char were performed.

3.2.3 Results of the Shakedown Experiments

3.2.3.1 Operating procedure

The first shakedown experiments preformed on the PFBR were performed using the following procedure. Before an experiment was run, equipment was tested to insure correct operation. This included a visual inspection of the equipment to insure no obvious problems were noted. Also the thermocouples were checked to see if they were giving an accurate reading; air flow rates were checked to insure proper operation; the char feed auger was tested; and the computerized data acquisition system was checked to see if it was in working order. The gas analyzers were zeroed with nitrogen and calibrated using a known span gas (16 % CO_2, 45% CO, and 5 % O_2). To begin the test 1000-g of petroleum coke char was placed into the feed hopper. The unit was heated to the desired temperature. Air flow was started once the temperature was reached. Next char feed was started and data collection began. This particular experimental set up was used for six runs.

3.2.3.2 Shakedown Number 1

The first experiment differed from the other five experiments in that a 500-g bed of petroleum coke was added initially to the reactor then 500 additional grams was added continuously at 1.3 pounds per hour approximately 30 minutes after start up. Temperature was set at 1500 °F ± 25 °F nitrogen flow was set at 1.75 scfm and air flow set at 0.75 scfm.

This experiment did not produce any measurable carbon monoxide concentrations.

3.2.3.3 Shakedown Number 2

The second shakedown test was similar to the first except that 1000-g was continually added at the rate of 1.3 lbs/hr instead of the initial 500-g start up. The conditions and the results are the same as in shakedown number one.

3.2.3.4 Shakedown Number 3

The purpose of this experiment was to see if changing the air flow rates affected the production of carbon monoxide. Also a slightly higher temperature was tried, since it was postulated that carbon monoxide production is more favorable at higher temperatures. A quantity of 1000-g of petroleum coke was added at a rate of 1.3 lbs/hr and the temperature was set at 1600 °F ± 25 °F. Nitrogen flow was set at 1.5 scfm and air was added at 0.2, 0.3, and 0.7 scfm changed at 30-minute intervals.

The results of this experiment showed that, for this particular run, changing the air flow rate did not significantly affect the rate of carbon monoxide production.

3.2.3.5 Shakedown Number 4

This shakedown test was run to determine the amount of air that could be added to the coal feed until oxygen breakthrough occurred. This was done to determine the stoichiometric amount of air required for complete combustion. Once this was known it was possible to define a reference point for the system and determine and adjust accordingly.

The same experimental procedure in shakedown Experiments 2 and 3 was used for this run. No nitrogen was added to the system and air was added in increments of 0.2 scfm starting at a rate of 1.3 scfm. Oxygen breakthrough was found at approximately 1.85 scfm. Air flow was then backed off to 1, 0.8, and 0.5 scfm. There was a slight increase in carbon monoxide production at the initial reduction but none was noted for the following decreases.

3.2.3.6 Shakedown Numbers 5 & 6

Once the stoichiometric air flow rate was determined, two additional runs were performed to see if there would be a significant amount of carbon monoxide production in the petroleum coke char. Shakedowns 2 – 4 experimental operating procedure was used for these two runs. Air flow was set at 0.3 and 0.7 scfm for experiments 5 and 6 respectfully.

The results of these two experiments were similar to the ones previously run. No significant carbon monoxide production was shown.

With the results of the first six experiments unable to produce carbon monoxide in quantities that suggested gasification was occurring, the validity of this experimental approach was questioned. Upon investigation of the PFBR and the shakedown experiments it was determined that perhaps a different char would produce better results since the reactivity of petroleum coke is generally low. Also for future runs using the petroleum coke it was found that perhaps significantly higher temperatures were needed, under the presumption that carbon monoxide production is temperature sensitive.

3.2.4 Initial PFBR Experiments with P065 Lignite

A lignite char from the EERC's TRDU run P065 was run through a 30-mesh Tyler screen and prepared for experiments in the PFBR. Due to the change in density of the lignite char only 600-g of test material was needed to produce a similar volume to the petroleum coke char. The experimental procedure was the same as in the petroleum coke shakedown Experiments 2 – 6. The reaction conditions were set at a feed rate of 0.7 lbs/hr, temperature was set at 1550 °F ± 25 °F, and air flow at 0.3 scfm with no nitrogen flow.

The results of this initial experiment produced a nearly 50:50 split of carbon monoxide and carbon dioxide. This showed that gasification conditions could be reached using the PFBR. Therefore an experimental test matrix was created and run.

3.2.5 Test Matrix for PFBR

The test matrix used for the PFBR set of experiments contained two controlled variables, temperature and air flow. The goal of this test matrix was to determine the effects of these variables on the production of carbon monoxide and carbon dioxide in a simulated gasification atmosphere. Two char types were tested in this matrix, P065 lignite and P061 petroleum coke. P063 Illinois No. 6 was not tested due to the lack of char material.

Temperature values were determined from previous TRDU runs and literature values for gasification temperatures for each particular fuel [11]. Air flow rates were determined as follows. The high flow values were one-half of the oxygen breakthrough flow rate of each fuel. Low flow values for lignite were the lowest possible controllable value that could be attained from the PFBR. The low flow value for the petroleum coke char was determined on the basis of density differences between char types times the low flow value of the lignite char as given by Equation 3-1. The experimental test matrix is shown in Tables 3-3 and 3-4.

$$v_{PetroleumCoke} = \frac{\rho_{PetroleumCoke}}{\rho_{Lignite}}(v_{Lignite}) \qquad \text{Eq. 3-1}$$

Table 3-3. PFBR Test Matrix for P065 Lignite Char

Temperature (± 25 °F)	Air Flow Rate (scfm)
1500	0.3
1500	0.5
1750	0.3
1750	0.5

Table 3-4. PFBR Test Matrix for P061 Petroleum Coke Char

Temperature (± 25 °F)	Air Flow Rate (scfm)
1900	0.5
1900	1.1
1850	0.5
1850	1.1

results of these experiments were evaluated in a qualitative, rather than a quantitative manner.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter will present the results obtained from the TGA and PFBR test matrices, as well as a discussion of the results and some of the possible conclusions drawn from the data analysis. Also included in this chapter will be some of the problems that occurred in the PFBR runs and the modifications made to the previously presented test matrix.

4.1 Determination of Kinetic Data from TGA Test Matrices

The test matrices presented in the previous chapter were run as presented. Complete summaries of all TGA experiments are presented in Appendix A.

The reaction process in the TGA took place in three distinct steps de-volatilization, char gasification, and final burn. The de-volatilization took place within the first 9 – 15 minutes of the process during heat up. This is illustrated by the irregular curve seen in the beginning of the reaction noted in Figure 4-1. The second stage, char gasification took place immediately following de-volatilization. This usually took 40 – 200 minutes depending upon the reactivity of the char and reaction conditions. It is noted by the smooth weight loss curve during the majority of the reaction. The final burn takes place at the end of the reaction when gasification has appeared to reach a limit. A sample test sequence is illustrated in Figure 4-1.

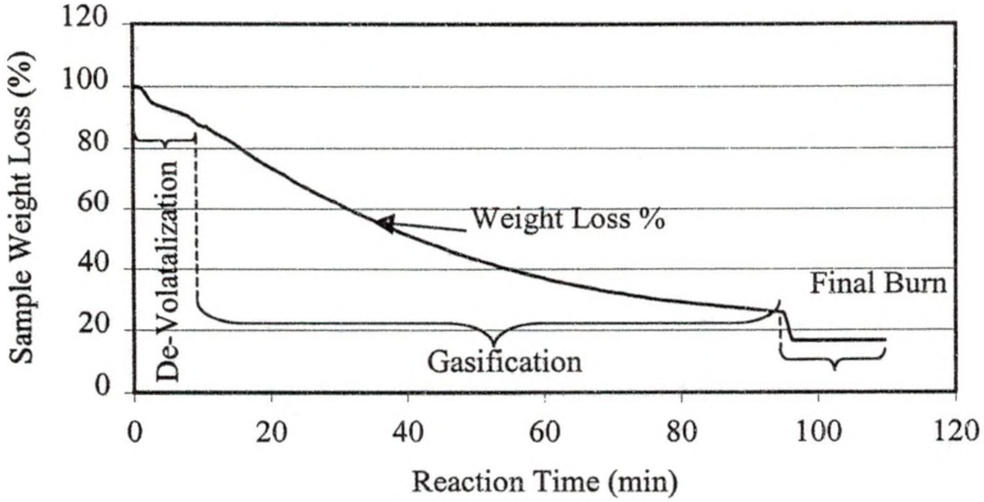


Figure 4-1. Typical Thermogram of a TGA Test Run

The de-volatilization stage removes the strait chain aliphatic, un-branched aromatic, and volatile hydrocarbons from the char. Since the test matrices involve only coal-char this stage is generally small. The initial coal cracking takes place in the TRDU and removes most of the easily gasified compounds. Gasification takes place following de-volatilization and involves the char reactions presented in Equations 1-2 thru 1-7. It usually involves the conversion of more complex hydrocarbons. The final burn is done in pure air to determine the amount of ash material in the char. The data analysis for this thesis was performed on the gasification stage of the reaction. De-volatilization and final burn data are truncated and not included in determining the kinetic data for char gasification.

4.1.1 Initial Calculations

To develop kinetic values from the data collected they first must be converted into a usable form. The TGA records data as a percentage weight loss of the total sample mass. These values must be converted into molar concentrations of pure carbon in order to apply to the equations previously presented (Eq. 2-1 and 2-2). To accomplish this the fractional loss of material is multiplied by the total sample weight at the beginning of the experiment, then the amount of ash remaining in the TGA is subtracted and converted to a normalized molar basis and expressed in terms of fractional conversion. To accomplish this Equation 2-1 is expressed in terms of fractional conversion in accordance to Equation 4-1. This process is illustrated in Equations 4-2 to 4-6.

$$-\frac{dX}{dt} = kX^n \qquad \text{Eq. 4-1}$$

$$M_T(t) = \frac{wt\%(t)}{100} \cdot M_o \qquad \text{Eq. 4-2}$$

$$M_C(t) = M_T(t) - M_{ash} \qquad \text{Eq. 4-3}$$

$$\overline{N}_C(t) = \frac{M_C(t)}{MW_C} \qquad \text{Eq. 4-4}$$

$$N_C(t) = \frac{\overline{N}_C(t)}{\overline{N}_C(0)} \qquad \text{Eq. 4-5}$$

$$X(t) = 1 - N_C(t) \qquad \text{Eq. 4-6}$$

Where:

X = Fraction of carbon reacted (from 0 to 1)

$M_T(t)$ = Mass of total sample at time t (mg)

$wt\%(t)$ = Weight loss percent as recorded by the TGA (%)

M_o = Mass of initial sample (mg)

$M_C(t)$ = Mass of carbon at time t (mg)

M_{ash} = Mass of ash remaining at the end of the experiment (mg)

$\overline{N}_C(t)$ = Number of moles of carbon at time t (millimoles)

$\overline{N}_C(0)$ = Initial moles of carbon present at the beginning of the experiment (millimoles)

$N_C(t)$ = Number of moles of carbon at time t normalized (millimoles)

MW_C = Molecular weight of carbon (mg/millimole)

$C(t)$ = Normalized molar concentration of carbon at time t (millimoles)

$X(t)$ = Normalized molar concentration based on fractional conversion of carbon at time t (millimoles)

For each experiment conducted using the TGA a reaction order (n) and rate constant (k) were calculated from the data collected. To generate these values the natural log of Equation 2-2 was solved symbolically. Then values were obtained from the data collected and a plot was made of the natural log of the concentration derivative versus the natural log of concentration as seen in Equation 4-7.

$$\ln\left(\frac{dX(t)}{dt}\right) = \ln k + n \cdot \ln X(t) \qquad \text{Eq. 4-7}$$

The values for k and n are easily determined by plotting a regression line through the manipulated data. The rate constant is simply the anti-log of the intercept and the reaction order is the slope of the line. A sample regression analysis is shown in Figure 4-2.

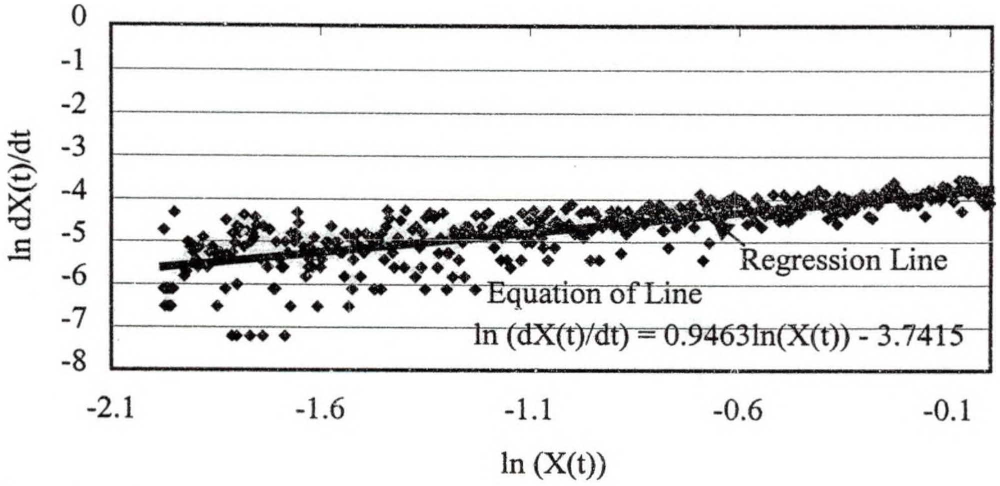


Figure 4-2. Illustration of TGA Regression Analysis (TGA Run #2)

For this particular example the slope of the line generated and the y-intercept are 0.9463 and –3.7415 respectively. With these values the rate constant would be $e^{(-3.7415)}$ or approximately 0.0237 min^{-1} with a reaction order of 0.9463. The same approach presented in this example was used for all TGA experiments to generate the kinetic data. The results are summarized in Table 4-1.

Table 4-1 Summaries of TGA Reaction Data

Block 1						
Run	Fuel Name	Fuel Type	Temp. (°F)	k*	n	n (apparent)
1	Illinois No. 6	Bituminous	1600	0.0045	3.99	4
2	Freedom	Lignite	1500	0.0237	0.95	1
3	Pet Coke	Petroleum Coke	1750	0.0006	-1.16	1
4	Illinois No. 6	Bituminous	1850	0.0283	1.18	1
5	Freedom	Lignite	1750	0.1822	0.87	1
6	Pet Coke	Petroleum Coke	2000	0.0123	1.00	1
Block 2						
7	Freedom	Lignite	1500	0.0174	0.05	0
8	Illinois No. 6	Bituminous	1850	0.0326	0.62	0.5
9	Pet Coke	Petroleum Coke	2000	0.0102	0.68	0.5
10	Freedom	Lignite	1500	0.0238	0.38	0.5
11	Illinois No. 6	Bituminous	1850	0.0351	0.54	0.5
12	Pet Coke	Petroleum Coke	2000	0.0183	0.53	0.5

Table 4-1 (cont.)

Block 2 (cont.)						
Run	Fuel Name	Fuel Type	Temp. (°F)	k*	n	n (apparent)
13	Freedom	Lignite	1500	0.0809	0.72	0.5 or 1
14	Illinois No. 6	Bituminous	1850	0.1027	0.96	1
15	Pet Coke	Petroleum Coke	2000	0.0256	0.50	0.5
Block 3						
16	Freedom	Lignite	1500	0.0029	0.32	0.5
17	Illinois No. 6	Bituminous	1850	0.0113	1.72	1.5 or 2
18	Freedom	Lignite	1500	0.0632	0.77	1
19	Illinois No. 6	Bituminous	1850	0.0382	1.10	1
Block 4						
20	Freedom	Lignite	1500	0.0122	0.79	1
21	Illinois No. 6	Bituminous	1850	0.0284	1.36	1.5 or 1
22	Freedom	Lignite	1500	0.0214	0.90	1
23	Illinois No. 6	Bituminous	1850	0.0341	1.14	1

*Rate constant based on fractional conversion.

4.1.2 Reactions Studied in TGA Test Matrices

4.1.2.1 Block 1

The purpose of the experiments run in Block one of the TGA test matrix was to study the temperature effects of char reactivity and determine activation energies. To accomplish this the Arrhenius Equation (Equation 2-2) was solved using the rate data generated with respect to temperature. A linear regression was performed by taking the natural log of Equation 2-2 forming Equation 4-8.

$$\ln k = \ln A - \frac{E}{RT} \qquad \text{Eq. 4-8}$$

The y-intercept of a plot of the natural log of the rate constant versus reciprocal temperature determined the pre-exponential factor (A); the slope of the line is (E/R). With the pre-exponential factor known Equation 2-2 was solved to determine the activation energy for each experimental run in Block one. The results of the analysis are summarized in Table 4-2 and Figure 4-3

Table 4-2. Summaries of TGA Block 1 Reaction Data

Run	Fuel Name	Fuel Type	Temp (°F)	Temp (°R)	k	A	E (Btu/lb-mol)
1	Illinois No. 6	Bituminous	1600	2060	0.00454	1.01E+05	6.51E+04
2	Freedom	Lignite	1500	1960	0.02372	1.59E+06	4.63E+04
3	Pet Coke	Pet Coke	1750	2210	0.00055	1.05E+10	1.09E+05
4	Illinois No. 6	Bituminous	1850	2310	0.02835	1.01E+05	6.46E+04
5	Freedom	Lignite	1750	2210	0.18223	1.59E+06	4.32E+04
6	Pet Coke	Pet Coke	2000	2460	0.01231	1.05E+10	1.06E+05

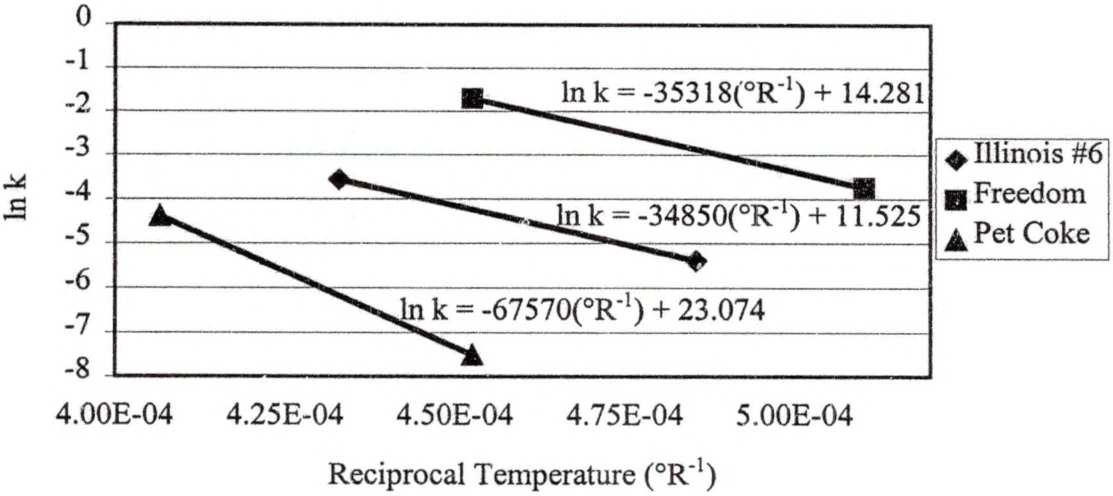


Figure 4-3. Block 1 Temperature Effects Based on Arrhenius Equations

Numerous studies have taken place that support the results obtained in Block one of these TGA experiments [6, 20]. These experiments as well as the ones presented in this research show similar slopes (activation energies) based on similar char types as the ones presented in Figure 4-3. Results from previous studies did not match the reaction conditions of this research exactly since most of the previous work done was analyzed using a less complex reaction gas composition (N_2/inert with H_2O). However the results and findings are very similar to the ones discovered in this research. The general conclusion that can be drawn from this and previous research is that the reactivity of char will increase with elevated temperatures. Differences in reactivity between the chars tested are also obvious with the lignite being the most reactive, and the petroleum coke being the least reactive.

4.1.2.2 Block 2

Block two was designed to study the effects that varying steam concentration has on the rate of the carbon-steam reaction Equation 1-5. This particular block of experiments was designed to isolate the effects of this reaction by performing the test in an atmosphere that contains only steam and nitrogen.

$$C + H_2O \longleftrightarrow CO + H_2 \qquad \text{Eq. 1-5}$$

The generally accepted rate expression used to describe the carbon-steam reaction based on carbon monoxide production is shown in Equation 4-9. [18, 21]

$$\mathrm{Rate}_{CO} = \frac{k_1 P_{H_2O}}{1 + k_2 P^{m}{}_{H_2} + k_3 P_{H_2O}} \qquad \text{Eq. 4-9}$$

Where:

k_1, k_2, k_3, m = Individual kinetic parameters based on the forward and reverse reaction rates of the carbon-steam reaction.

P_{H2O}, P_{H2} = Partial pressure of steam and hydrogen respectively.

The derivation and comprehension of this equation is not necessary to explain the basic principles it represents. The key point to notice when interpreting this equation is to see that as the amount of steam present in the reaction system increases so does the rate. It also shows that the rate of gasification is inhibited by the presence of hydrogen almost exclusively, since k_3 is generally assumed to be negligible. [18]

The analysis of the data generated from these TGA experiments is relatively predictable and coincides with the rate expression presented in Equation 4-8. As expected the experiments with higher steam concentrations gives a larger rate constant. The increase in steam will drive the equilibrium reaction to the right causing a higher yield in products (CO and H_2). The results are summarized in Figure 4-4.

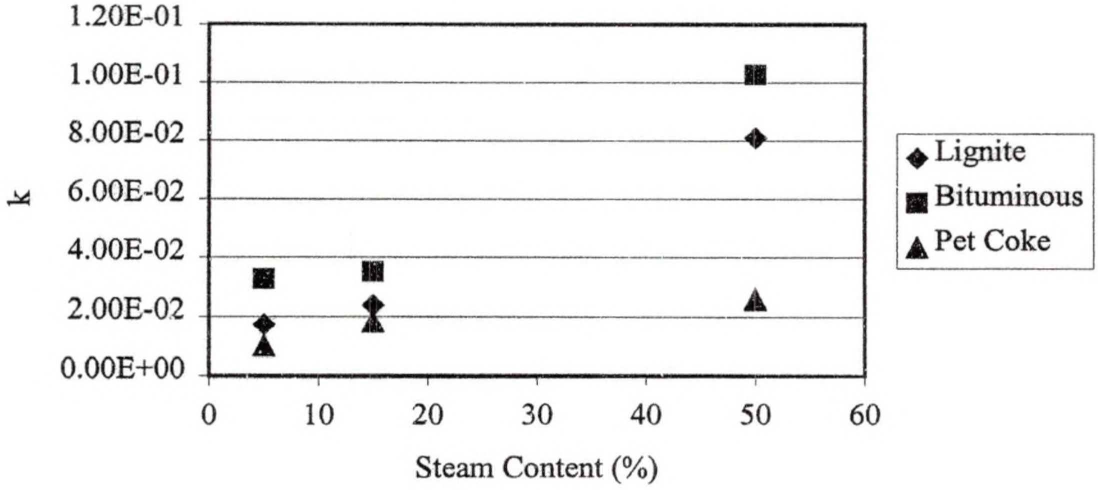


Figure 4-4. Summaries of TGA Block 2 Experiments

The tendency when interpreting the data illustrated in Figure 4-4 is to fit polynomial curves to formulate trends. However the reactivity most likely will not continue this exponential increase, but will tend to level off at steam percentages higher than the ones tested in these experiments. This appears to be the case when looking at the petroleum coke trend. This probably occurs since the number of active carbon sites will eventually reach a maximum in relation to the amount of steam in the system. Previous studies conducted have shown that increasing steam concentrations produce higher rate constants [6, 18, 21] and will most likely reach a maximum value, which is consistent with the findings in TGA Block two. These previous experiments were done primarily to study the effects of hydrogen inhibition on the carbon-steam reaction. While the TGA experiments conducted for this research lowered steam concentrations independently, the previous studies decreased the effect of steam concentrations by increasing the amount of hydrogen fed to the system.

4.1.2.3 Blocks 3 & 4

The final two blocks of experiments performed on the TGA were designed to study the effects that carbon monoxide and carbon dioxide had on the carbon steam reactions as well as look at some of the char reactions involved with these compounds. Block three looked at the individual affects each compound (CO and CO_2) had on the reaction process. This was accomplished by running an experiment with only one of the gases (CO or CO_2) present. Block four experiments contained both gases in varying concentrations. The combination of the data obtained from both Blocks 3 and 4 coupled with data from Block one were used to analyze the effects of carbon monoxide and carbon dioxide on char reactivity in steam.

The analysis of the data for the CO/CO_2 effect was more difficult express than the previous two phenomenons. For this analysis the rate constants are compared as they relate to the carbon monoxide ratio. This ratio is defined as the moles of carbon monoxide divided by the moles of carbon monoxide plus the moles of carbon dioxide on a basis of mole percentages. The results are summarized in Figure 4-5.

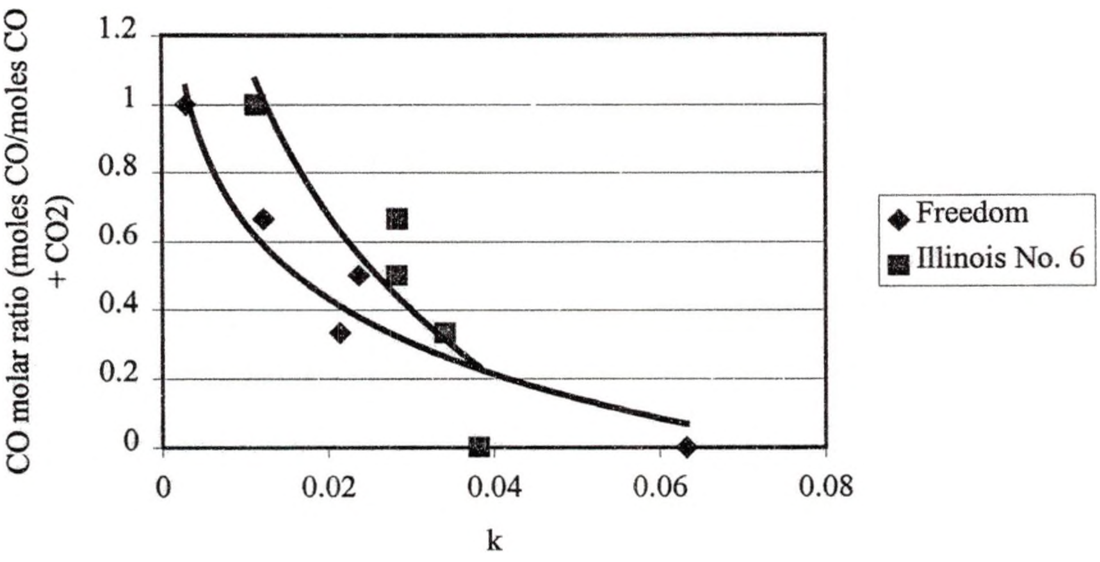


Figure 4-5. Summary of CO/CO_2 Effects of TGA Experiments

The most obvious effect noted from this interpretation of the data is that as the amount of CO increases, the rate constant decreases. This implies that in the presence of CO, the gas-water shift reaction (Eq. 1-6) favors products to the right of the equilibrium. This decreases the amount of steam available for the carbon steam reaction in proportion to the amount of CO present.

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \qquad \text{Eq. 1-6}$$

The Boudouard reaction also plays a role in the changing rate constant. Presented earlier the Boudouard reaction involves the conversion of carbon to carbon monoxide upon the addition of carbon dioxide as seen in Equation 1-3. This is apparent

$$C + CO_2 \longrightarrow 2CO \qquad \text{Eq. 1-3}$$

when data from Block two which contains only steam and nitrogen is compared with data in Block three with carbon dioxide present. In Runs 10 and 11 from the TGA test matrix the composition of the reacting gas contained 15 percent steam and the balance of nitrogen. When the rate data obtained from these two experiments is compared to Runs 18 and 19 which contains 20 percent carbon dioxide along with 15 percent steam; a significant increase in reactivity is noted (see Figure 4-6).

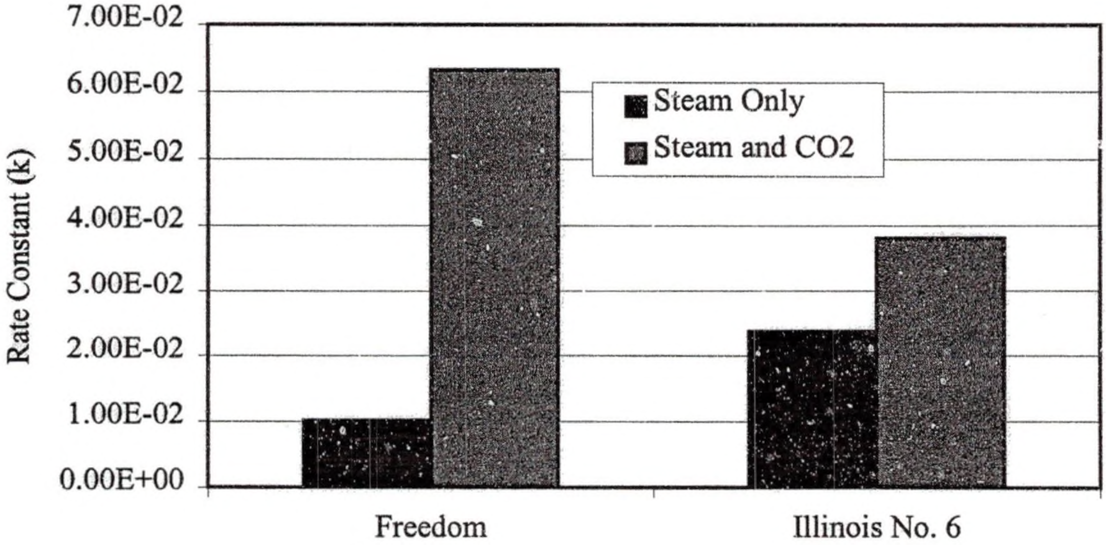


Figure 4-6. Comparison of Char Reactivity in Steam/Steam-CO_2 Gas Systems

The water gas shift reaction shows that carbon monoxide in the system will reduce the amount of steam, however in the presence of carbon dioxide an equal amount of steam is generated. Therefore the total reactant gases (CO_2 and H_2O) are the same.

The decreasing rate constant with increasing carbon monoxide indicates that the char-steam reaction dominates the reaction kinetics more than the Boudouard reaction.

Most studies done that looked at reaction data in this type of system usually show a slight parabolic curve that reaches a minimum value sharply as carbon monoxide concentrations are increased [22, 23, 24]. Results from the lignite testing mimic that trend while the bituminous results appear to be linear. The reason for this deviation is unclear at this point.

A number of different studies have been performed that look at gasification in a carbon monoxide-carbon dioxide system and tend to agree with the results obtained in this thesis [25, 26]. These studies showed that gasification rates with carbon dioxide present tend to proceed slower with increasing carbon monoxide concentrations. The equation generally used to describe this type of system is presented in Equation 4-10 [6].

$$\text{Rate(CO)} = \frac{k_c P_{CO_2}}{1 + K_{c,1} P_{CO} + K_{c,2} P_{CO_2}} \qquad \text{Eq. 4-10}$$

Where:

k_c, $K_{c,1}$,$K_{c,2}$ = Individual kinetic parameters

P_{CO}, P_{CO2} = Partial pressures of carbon monoxide and carbon dioxide respectively

While the derivation and understanding of this equation is beyond the scope of this thesis; the most important observation should be noted that as the amount of carbon monoxide is increased in the reaction system the rate expression would decrease. While Equation 4-10 is not the only rate expression derived that describes gasification in a carbon monoxide carbon dioxide system [26, 27]. However, the relationships formulated in previous studies support the claim that carbon monoxide tends to slow the reactivity.

When compared with Equation 4-10 and previous studies, the results obtained in this research are consistent with these findings.

4.1.3 Summary and Discussion of the TGA Test Matrices

Predictably, the reaction rates for all chars were higher with increased temperature and steam contents. The regression analysis of these first two sets of TGA experiments can be used to aid in the modeling of char characteristics for the TRDU. The carbon monoxide/carbon dioxide effects were dependent upon the amount of each reacting species their effect on the gas-water shift and Boudouard reactions.

The correlations concerning temperature, steam content, and carbon monoxide-carbon dioxide contents made based on the four experimental test blocks were supported by literature on previous experiments at similar reaction conditions. Another comparison that was not explored in previous sections was how char types varied based on reactivity. The trend noted seemed to show that the Illinois No. 6 char tended to exhibit higher reaction orders. The Freedom char exhibited greater reactivity based on the Arrhenius relationship compared to the Illinois No. 6 and petroleum coke chars. This is also supported by previous experiments [5, 6, 28, 29, 30]. As was the case in most of the literature searched the reaction conditions did not exactly match the conditions in this research but did agree with the conclusions drawn.

When comparing previous research with the TGA work done in this thesis few experiments have been done that involve a full mix of gases (N_2, CO, CO_2, H_2O and H_2). Some however have looked at this situation and have developed some models that can be used to compare with the work done in this research. One of the most comprehensive studies was conducted by Johnson that looked at char gasification rates in hydrogen-methane, hydrogen-steam, and carbon monoxide-carbon dioxide-hydrogen-steam-methane systems using thermal analysis. In these experiments a wide variety of bituminous chars were tested under varying temperatures and pressures [31]. The results found in these experiments relevant to this research tend to support the findings of this research. The correlation between high temperatures, increased steam and carbon dioxide concentrations tending to increase reactivity were all findings supported in the work by Johnson and others [6].

The equation that generally is used to describe the kinetics of a gasification system using a full mix of gases is presented in Equation 4-11 [6].

$$\mathrm{Rate} = \frac{k_1 n_t P_{H_2O}\left[1-(k_2 P_{H_2} P_{CO}/P_{H_2O})\right] + k_3 n_t P_{CO_2}\left[1-(k_4 P^2{}_{CO}/P_{CO_2})\right]}{1 + k_5 P_{CO_2} + k_6 P_{CO} + k_7 P_{H_2} + k_8 P_{H_2O}} \qquad \text{Eq. 4-11}$$

Equation 4-10 has been extremely simplified from its original version. The kinetic parameters k_1 through k_8 are complex constants based on the forward and reverse reaction rates of the carbon-steam and Boudouard reactions and their complexes. These constants can vary depending upon the reaction conditions and the char type. The term n_t is the concentration of active carbon sites plus oxygen-carbon complexes. While understanding these terms is beyond the scope of the research presented in this thesis the relationships between the partial pressures of the gas concentrations is of importance. This equation shows that the overall reaction rate is in general, the sum of the carbon-steam (first term in the numerator) and Boudouard (second term in the numerator) reactions. This equation supports the data generated in the TGA experiments conducted in this research in particular the carbon dioxide effects presented earlier that showed that the addition of carbon dioxide to a steam-char gasification system increases the reactivity. Equation 4-11 is not the only relationship that has been developed that describes a char gasification system involving a full gas composition. However most other models generated seem to agree with the relationships presented in Equation 4-11 [32].

The kinetic data generated from these TGA experiments can be used to aid in creating a better model of the TRDU mixing zone. Higher temperatures coupled with increased steam concentration seem to produce optimal char reaction conditions. Also it appears that maximizing the amount of carbon dioxide relative to carbon monoxide will produce the most favorable kinetic conditions in the TRDU mixing zone.

4.2 Bench Scale PFBR Experiments

The previously presented test matrices for the PFBR were not completely run as presented due to unforeseeable difficulties during operation. The matrices presented for the Freedom lignite were run as presented and replicated to give two data sets per experiment. In addition two fully charged bed experiments of the lignite char were run. However problems arose with the petroleum coke experiments and only two tests were run. The complications will be discussed later in this chapter. Complete summaries of the PFBR tests are presented in Appendix B.

4.2.1 Determination of Carbon Monoxide/Carbon Dioxide Production Using the PFBR

4.2.1.1 Assumptions

Since previously generated coal-char was used for these experiments the following assumptions were made in order to better describe the effects. The first assumption made was that the char was free of water vapor and volatiles. The char was assumed to contain only carbon and ash. Second, only the combustion and partial combustion reactions (Equations 1-2 and 1-4) were considered part of the process. The final assumption made was that all oxygen fed to the system was converted to either carbon monoxide, carbon dioxide, or left as unreacted free oxygen.

While these assumptions are not completely true they are valid for the semi-qualitative analysis presented in this section.

4.2.2 Freedom Tests

The tests run on the Freedom lignite produced the most useful data for analysis. Ten total tests, the four original experiments and replicates, plus two fully charged runs were performed using this char type. A typical reaction sequence is illustrated in Figure 4-7.

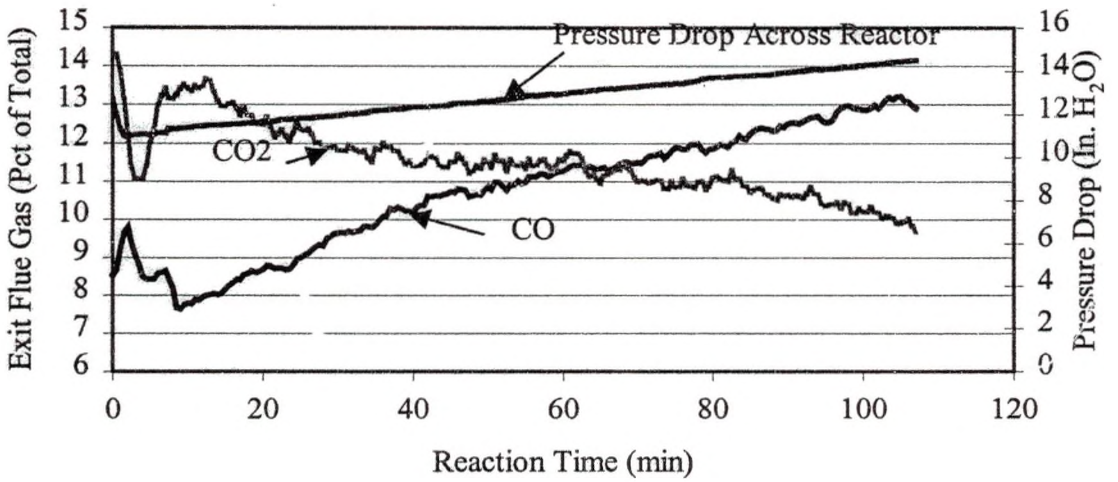


Figure 4-7. Typical Data Obtained from PFRB Experiments (T = 1500 °F & Air Flow = 0.3 SCFM)

Notably, the reaction sequence does not come to a steady state value for any appreciable amount of time. Generally this was the case for nearly all tests with the Freedom char. This phenomenon was not expected when the original test matrix was created. The plan was to obtain steady state values for carbon monoxide and carbon dioxide production upon the addition of air. It was hoped that varying air flow rates and reaction temperatures would produce distinct carbon monoxide-carbon dioxide ratios. From this data it was proposed that these ratios would help in determining temperatures and air flow rates for the J-leg reburn of the TRDU char. Unfortunately this was not the case and more inventive ways of interpreting the data was investigated.

4.2.2.1 Initial Interpretation of the PFBR Experiments

It was determined that the reason a steady state value could not be attained was that the sub-stoichiometric air flow rates produced a build up of carbon in the reactor. As seen in Figure 4-7, the pressure increase in the reactor shows a build up of material in the reactor. Since the rate of air flow was insufficient to convert all incoming carbon to ash and stack gases the material build up within the reactor must contain some amounts of unreacted carbon. Since oxygen was fed at a constant rate this would change the oxygen/carbon ratio during the reaction. From this observation it was determined that the best way to analyze the data generated from the PFBR was to study the effects the oxygen/carbon ratio had on the tests ran. This proved to be an unsuccessful way of interoperating the data. However, this type of analysis showed promise and its failure was probably due to incorrect assumptions and lack of steady state values. While this analysis technique was inconclusive, its results and procedure will be presented in the next section to serve as reference for future research/researchers dealing with this topic.

4.2.2.2 Attempted PFBR Analysis Method of Oxygen-to-Carbon Ratios

The data gathered from the Freedom runs was converted into molar concentrations of carbon, oxygen, carbon dioxide, and carbon monoxide. This was done by doing a material balance of the system over 30-second time intervals. It was assumed that the air feed contained 21 percent oxygen, and was fed at a constant rate defined by the experimental matrix. As stated earlier it was assumed that all oxygen fed to the system was converted into carbon monoxide or carbon dioxide by the combustion or partial combustion reactions. Therefore the composition of the stack gas was assumed to contain only carbon monoxide, carbon dioxide, and nitrogen. The moles of carbon monoxide and carbon dioxide were then calculated by the volume fraction obtained from the gas analyzers at a given time. The molar amount of carbon build-up within the reactor was calculated using the previously determined carbon content of the char and was assumed to be homogeneous and fed at a continuous rate. The moles of carbon in the reactor were calculated as the moles of carbon fed minus the moles of carbon leaving as carbon monoxide and/or carbon dioxide. Since the number of moles of carbon leaving the reactor as carbon monoxide and carbon dioxide was less than the amount fed, there was an accumulation of carbon within the reactor, this lead to a decrease in the molar oxygen-to-carbon ratio within the reactor over time.

To determine whether a correlation exists between carbon monoxide/carbon dioxide production and the oxygen-carbon ratio, a graphical analysis was performed from the previously presented test runs. The data gathered was plotted as molar ratios of carbon monoxide-to-carbon dioxide production versus the oxygen-to-carbon ratio within the reactor. The results of this analysis technique for the experiment shown in Figure 4-7 are illustrated in Figure 4-8.

The overall trend depicted in Figure 4-8 is that carbon accumulates within the reactor decreasing the oxygen-carbon ratio, the production of carbon monoxide is favored and the partial combustion reaction begins to dominate. This was the overall trend noted in nearly all cases of the Freedom experiments.

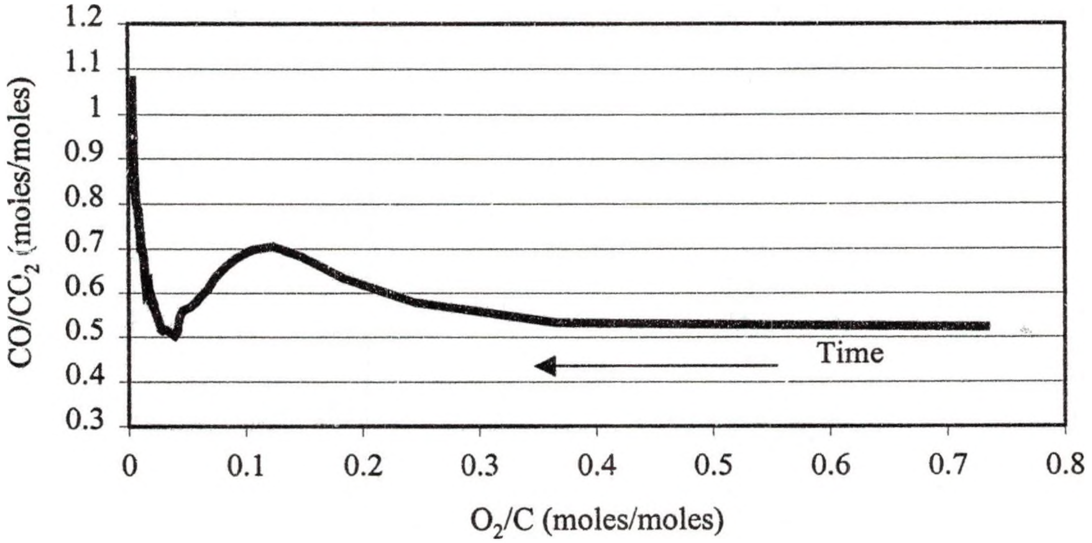


Figure 4-8. Typical Analysis of PFBR Carbon Monoxide/Carbon Dioxide Production Based on Oxygen-to-Carbon Ratios

4.2.3 Petroleum Coke Tests

4.2.3.1 Difficulties in Petroleum Coke Experiments

The test matrix designed for Petroleum Coke in the PFBR was not completed as presented. Two major problems arose during this test sequence: agglomeration and insufficient heat up capacity.

The first problem, agglomeration was not expected and was probably the result of the mixing of the inert materials from the residual Freedom ash coupled with the elevated temperature. Agglomeration deposits within the reactor caused the entire reactor to seize and lose it fluidizing characteristics. The only remedy to this problem was to run an experiment until agglomeration occurred and then manually clean the reactor afterwards.

The other problem was due to inadequate equipment. The heaters on the PFBR were incapable of producing the desired reaction temperatures. These two problems caused a great deal of mechanical and procedural problems, so due to lack of equipment availability and resources only two petroleum coke experiments could be completed.

4.2.3.2 Experiments Run

The two experiments ran on the PFBR with the petroleum coke char are defined in Table 4-3.

Table 4-3. Petroleum Coke PFBR Test Matrix as Ran

Run	Average Temperature (±25 °F)	Air Flow (SCFM)
1	1900	1.1
2	1820	0.5

The choice of this test sequence was entirely due to the limitations of the equipment and time. However, even though only two tests were run the results obtained using the previously mentioned analysis technique were consistent with the Freedom tests and produced some usable data. The analysis of the two petroleum coke experiments is illustrated in Figure 4-9.

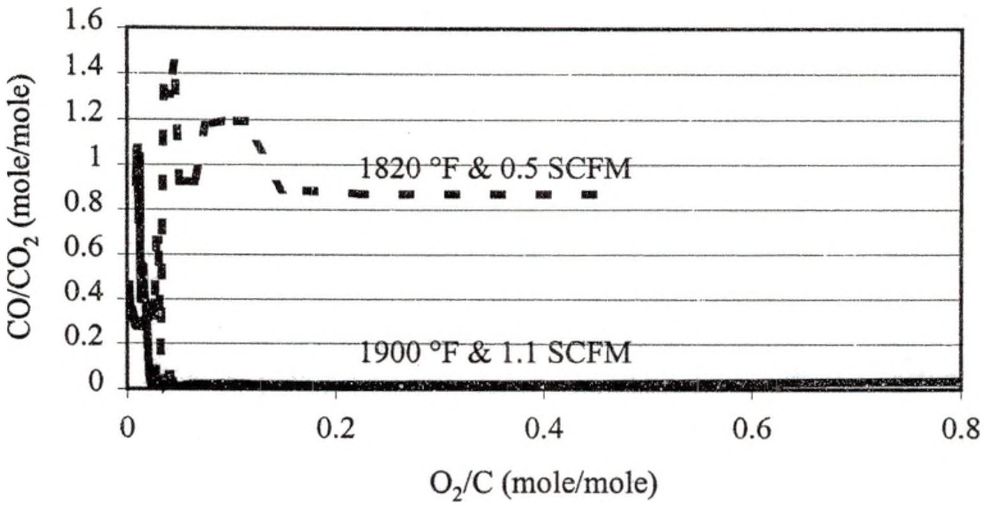


Figure 4-9 Analysis Summary of PFBR Petroleum Coke Experiments

4.2.3.3 A Qualitative Interpretation of the PFBR Tests

Quantitatively the analysis of the data obtained from the PFBR based on carbon monoxide carbon dioxide production rates as they relate to the oxygen-to-carbon ratio is a good way to summarize the experiments analytically. However, a qualitative look at the raw data can also be done to determine if some of the original hypothesis hold true. To accomplish this, the raw carbon monoxide and carbon dioxide percentage data (Figures B-1 to B-12) was analyzed to see if any reliable steady state values of 40 minutes to one hour could be gathered. From these assumed steady state values, molar ratios based on carbon monoxide concentrations were compared with their corresponding temperature and air flow. The results are summarized in Table 4-4 and Figure 4-10.

Table 4-4. Qualitative Summary of the PFBR Experiments.

PFBR Freedom Tests						
Temp (°F)	Air Flow (SCFM)	CO (% at Steady State)	CO_2 (% at Steady State)	CO ratio*	Steady State Acheived	Comment
1750	0.5	7.5	15	0.33	Yes	Reasonable
1750-R	0.5	6	16	0.27	Yes	Questionable
1750	0.3	30	2	0.94	Yes	End Value
1750-R	0.3	27	3	0.90	No	
1500	0.5	9	15	0.38	No	Opposite Trends ?
1500-R	0.5	11	13	0.46	No	
1500	0.3	13	10	0.57	No	
1500-R	0.3	15	12	0.56	Yes	Questionable
Full Bed PFRB Freedom Tests						
1750	0.3	15.5	5	0.76	Yes	1st Hour
1500	0.3	11	8	0.58	Yes	1st Hour
PFBR Petroleum Coke Tests						
1900	1.1	12	10	0.55	Yes	End of test
1820	0.5	6	14	0.30	Yes	Middle

*CO ratio is defined as % CO/(% CO + % CO_2) at steady state

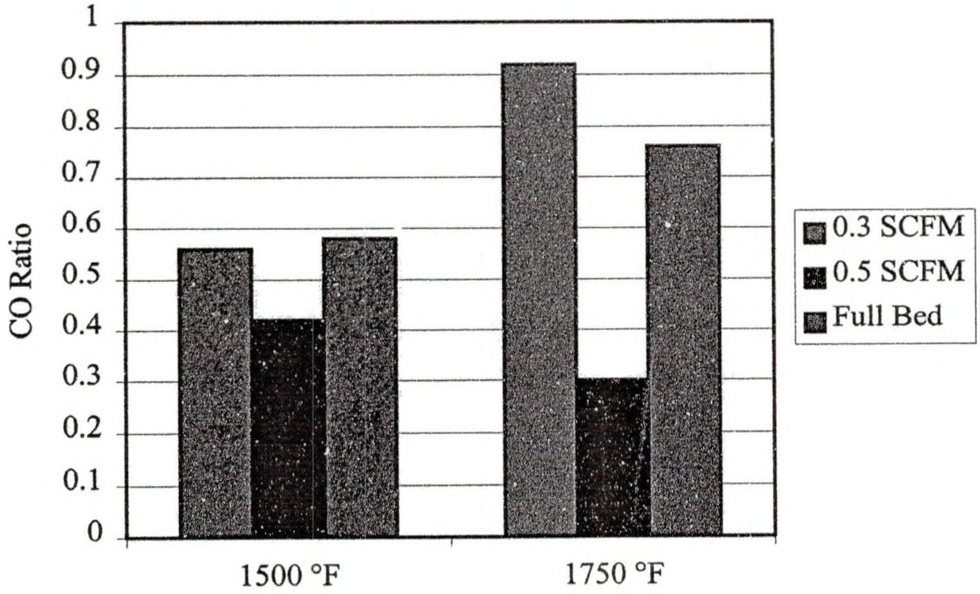


Figure 4-10. Qualitative Summary of PFBR Freedom Experiments

The results obtained from a qualitative look at the PFBR did show that some of the original hypothesis held true, while some did not. The Full bed and 0.3 SCFM test seem to agree with the assumption that higher temperatures produced more carbon monoxide, however the test ran at 0.5 SCFM did not exhibit this same trend. Lower air flow rates seemed to produce higher carbon monoxide ratios as was expected.

The interpretation of this qualitative analysis for the most part reinforced some of the initial predictions. However the inconsistency with the test performed at 0.5 SCFM are of concern. This could be due in part by the inconsistent data at 1500 °F. Therefore no conclusive findings can accurately by presented with this type of analysis.

4.2.4 Summary of PFBR Tests

The general and expected trend noted from the PFBR tests is that as the oxygen to carbon ratio decreased there was a tendency for the incomplete combustion reaction to dominate. This would produce elevated levels of carbon monoxide in the exit flue gas.

The data generated from these experiments will aid in determining carbon monoxide-carbon dioxide ratios for the char reburn as it enters the mixing zone. However the most valuable information gained from the PFBR experiments in this thesis is the information gained on using this equipment for future work. Basically this equipment can serve as a gasifier, but for more accurate data collection further modifications or process improvements should be made. This will insure proper gasification conditions are met and the data collected accurate.

As far as using this data for mixing zone model(s) or equipment settings the results obtained are somewhat inconclusive. Typical oxygen to carbon ratios in the mixing zone range from 0.152 to 0.0084 (mole/mole). The original assumption made when designing these PFBR experiments was to determine the effects temperature and air flow rates have on carbon monoxide and carbon dioxide production. It was hoped that equations could be formulated and general trends determined. However when looking at the data collected from these experiments it is difficult to generalize any patterns or trends, and future experimentation must be done before useable data can be acquired. The analysis of the data collected from the PFBR experiments at typical mixing zone oxygen/carbon ratios is illustrated in Figure 4-11 (F designates Freedom char, F2 designates a replicate).

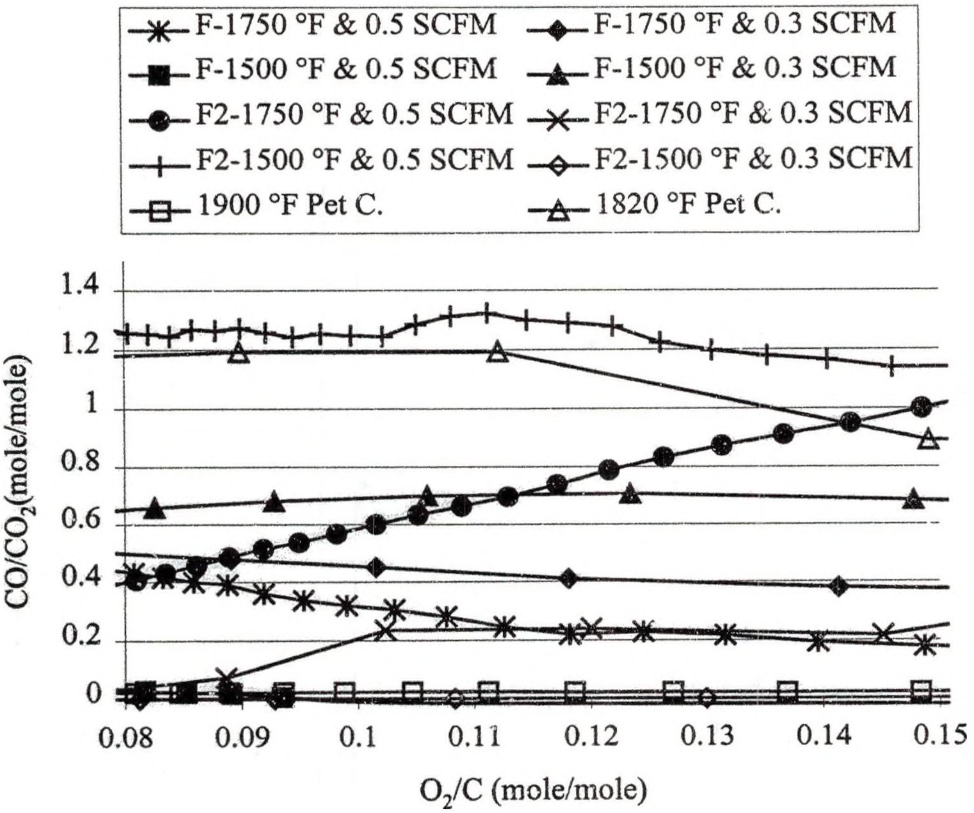


Figure 4-11. Summary of PFBR Data at Typical TRDU Mixing Zone Oxygen-to-Carbon Ratios

4.2.4.1 Failure of the PFBR Analysis Method of Oxygen-to-Carbon Ratios

While the results shown in Figure 4-8 showed promise, overall the results obtained were irreproducible and no conclusive results could be drawn from the data using this analysis technique (as seen in Figure 4-11). No conclusive evidence was found that could relate air flow rates and temperature to carbon monoxide carbon dioxide production of the coal-chars tested using the PFBR. Some possible explanations as to the failure of these experiments could be do to incorrect assumptions, lack of flow to the gas analyzers, inconsistent carbon content of the feed material due to density segregation, lack of steady state values, inaccurate measurements, as well as other numerous issues that are unexplainable at this point.

4.2.4.2 Discussion of PFBR Results

The initial hypothesis for this type of data was to assume that carbon monoxide would be favored at higher temperatures and lower air flow rates. However this was not the case from the data collected in the PFBR for mixing zone oxygen to carbon ratios using the analysis procedure displayed in Figure 4-11. In some cases lower temperatures produced greater amounts of carbon monoxide as well as did higher air flow rates. Also replicated data did not coincide with each other very well. In order to derive any type of conclusions from this type of experiment more data needs to be collected and replicated with accuracy. A small gasification system should be set up that could produce these oxygen-to-carbon ratios for an extended period of time. This could be accomplished by having a continuous drain that would prevent the build-up of carbon over time. Then air flow and temperature could be studied and more accurate effects could be noted. The data collected from the PFBR in this thesis did show that char gasification conditions could be done under these reaction parameters. However the validity of the assumptions used and equipment accuracy must be explored before future experiments with coal-char are tested using the PFBR.

These test runs will serve as a good starting point for more detailed future experiments. This data will better explain and define trends from varying temperature and air flow rates as they relate to carbon monoxide and carbon dioxide ratios from char gasification.

4.3.4 PFBR Experimental Difficulties

The fluctuating and erratic data gathered from the PFBR in this thesis may be due to some of the problems that were encountered during these experiments. While the correction of these problems may produce more accurate results the general trends noted from the original PFBR experiments should hold true. However these issues must be addressed before conclusive results on these bench scale tests are obtained. One of the major problems encountered during these bench scale tests was due to the low air flow rates through the PFBR. This caused a limited amount of flow to the exit gas analyzers. While these analyzers were consistent throughout these experiments the low flow rates may have resulted in inaccurate readings. Also the fine char particles would often clog the sample lines sent to the analyzers resulting in a loss of flow. In order to return flow these lines had to be broke and cleared in order to free the trapped debris. This process would lead to zero percent readings until the analyzer lines were repaired. Another problem that may have occurred was that the carbon content of the char feed might be inconsistent. Carbon analysis of both chars were performed and assumed to consistent throughout the entire experiment. However in the feed hopper there may have been sections were the carbon content of the incoming char may have varied from the original analysis. This would result in oxygen to carbon ratios different than assumed. This might have favored different reactions under these conditions resulting in varying carbon monoxide carbon dioxide production rates. Problems with temperature control also may have effected the results. Since the PFBR heaters are not controlled to handle the heat effects of the reaction process, temperatures would often fluctuate within 25 degrees Fahrenheit. These temperature fluctuations while only slight may have had an effect on the results obtained.

Suggestions for future experiments and remedies to these problems discussed will be presented in the following chapter.

CHAPTER 5

SUMMARY AND CONCLUSIONS

The results presented in this thesis can be generalized into three distinct sections for a succinct synopsis; these include the background and literature information, the TGA experiments, and the bench scale PFBR tests. The significant information gained from these three research methods will be summarized in this chapter. Also some recommendations will be presented for future work on this thesis as well as offer some information on remedies to the problems encountered during experiments run for this research.

5.1 Summary of Literature Review

- Gasification is a successful alternative method to convert carbon-containing material into light gases, condensable vapors, and tars.
- The products generated from gasification can be used as a substitute natural gas. This will aid in generating energy when conventional fuels become scarce. The syngas generated from gasification can replace or supplement fuels such as natural gas, propane, and other light hydrocarbon gases.
- Over the next five years the gasification industry is expected to grow by nearly 50 percent. The general trend in the gasification industry is to shift most of its focus to the field of energy generation.
- Char is generated following the initial cracking of coal. The reactivity of char is generally much lower than that of raw coal and requires recirculating and recycling to a great extent in order to gasify. Studying char reactions and

- reactivity in a gasification system will aid in generating models and designing equipment.
- Thermogravimetry is a successful technique used to determine kinetic data for solid/gas systems. It is capable of operating under a wide range of physical conditions and is easily controlled.
- Fluidized bed technology offers a useful reaction system for coal processing and gasification systems. They assert a good heat transfer rate, a relatively uniform temperature distribution, and an excellent mass transfer rate. This produces high conversions and facilitates control in gasification systems.
- Higher temperatures tend to produce elevated reaction rates with the three chars tested in this research.
- The presence of carbon monoxide tends to inhibit the carbon/char steam reaction, while the presence of carbon dioxide tends to increase the overall reaction rate of the carbon/char steam reaction system.
- An increase in steam within the reactor tends to increase char reaction rate constants.

5.2 Summary of TGA Work

- The EERC's TGA was successful in producing reliable kinetic data of the chars tested.
- The designed TGA test matrix produced the results desired. The use of the four-block test matrix was successful in isolating the effects each variable had on char reactivity. The results obtained from these experimental blocks were consistent with previous experiments and hypothesis.

- The solution to the Arrhenius equation was generated using the data in experimental Block one. From this, activation energies were found and used to relate rate data to temperature for each char type.
- The trend noted from Block one was that an increase in temperature produced higher reactivity.
- Higher steam concentrations produced greater char reactivity. Excess steam tends to drive the carbon-steam reaction (Equation 1-5) equilibrium to the right.
- The carbon monoxide carbon dioxide ratios in TGA experimental Blocks three and four showed that increasing carbon monoxide in the system tended to decrease reactivity. This was probably due to the gas-water shift reaction (Equation 1-6) reducing the total amount of steam in the system and the retardation of the Boudouard reaction (Equation 1-3) noted in Equation 4-8.
- The kinetic data obtained from the TGA experimental matrix can be used to aid in generating models for the EERC's TRDU.
- The difference in reactivity of different char types proved consistent with previous studies. The three chars tested had the following progression (starting with the lowest): petroleum coke, Illinois No. 6, and Freedom.
- Optimal reaction conditions within the mixing zone should be accomplished by maximizing steam concentrations while minimizing the presence of carbon monoxide.

5.3 Summary of PFBR Experiments

- The retrofitted PFBR was capable of producing data that described the complete and incomplete combustion reactions (Equations 1-2 and 1-4 respectively) for Freedom and petroleum coke chars.
- For the PFBR experiments the analysis of the oxygen-to-carbon ratio and the carbon monoxide/carbon dioxide production rates, while inconclusive showed promise in relating those parameters to one and other.
- The general trend discovered from the PFBR test matrix was that as the oxygen-to-carbon ratio decreases, the incomplete combustion reaction tends to dominate producing more carbon monoxide.
- The qualitative analysis showed that in some cases the hypothesis that higher temperatures would increase carbon monoxide production held true. However, no conclusive evidence was found that would support this claim.
- Analysis of the PFBR test data at parameters typically found in the TRDU mixing zone proved erratic and further testing is required.

5.4 Recommendations

5.4.1 TGA Testing

- The results obtained from the TGA test matrix proved to be sufficient for the work of this thesis. Running more data points and replicates should be explored in order to validate the work completed in this research. The new data points could include variable values at higher and lower settings as well as midpoint values. Tests of other char types might be explored to see how they compare to the chars tested in this research.

5.4.2 PFBR Testing

- A good deal more data is required using this particular technique before conclusive results are obtained. The major obstacles encountered during these tests were:

    a) The lack of equipment availability because of prior PFBR commitment at the EERC.

    b) Inadequate equipment.

  A complete maintenance of the EERC's PFBR should be done to insure all equipment is operating properly. Also additional experiments should be done without major time constraints.

- With a properly running PFBR, additional data should be obtained using the techniques presented in this thesis. Data gathered should be replicated until consistent results are obtained.

APPENDIX A

SUMMARIES OF TGA EXPERIMENTS

This section contains summaries graphical summaries of the thermograms generated from the TGA.

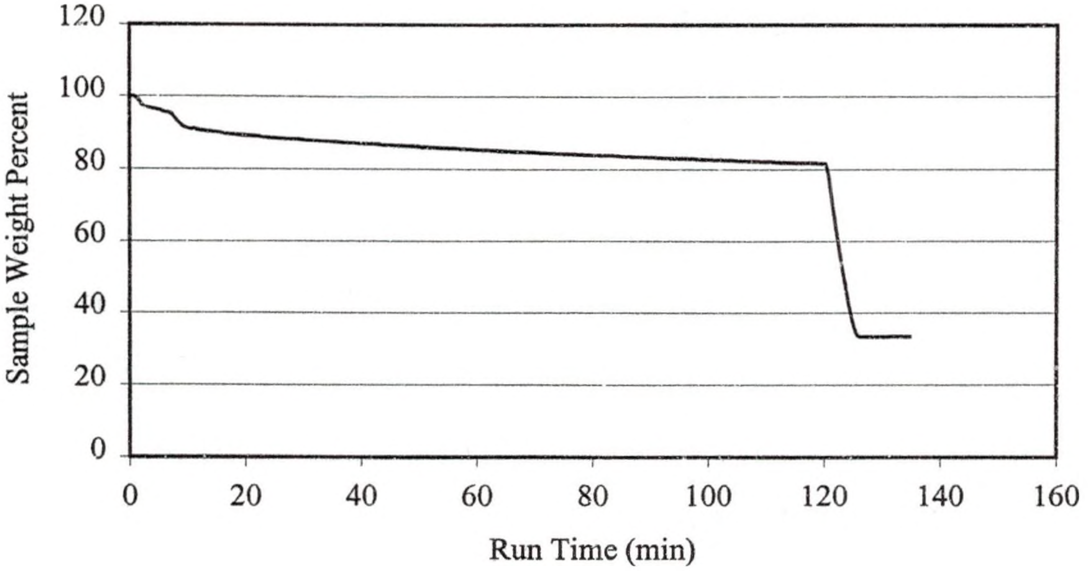


Figure A-1. Raw Data of TGA Run Number 1

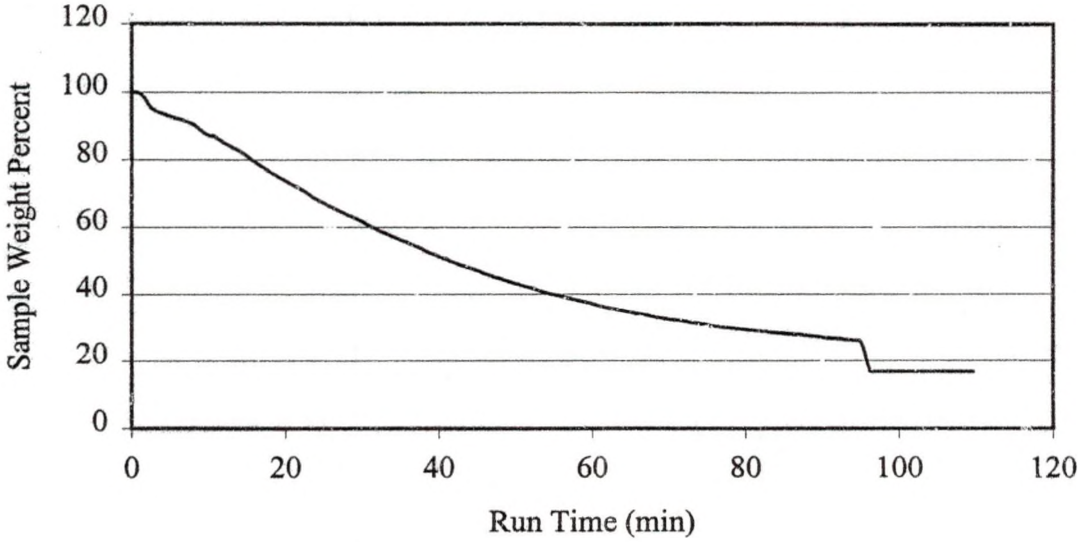


Figure A-2. Raw Data of TGA Run Number 2

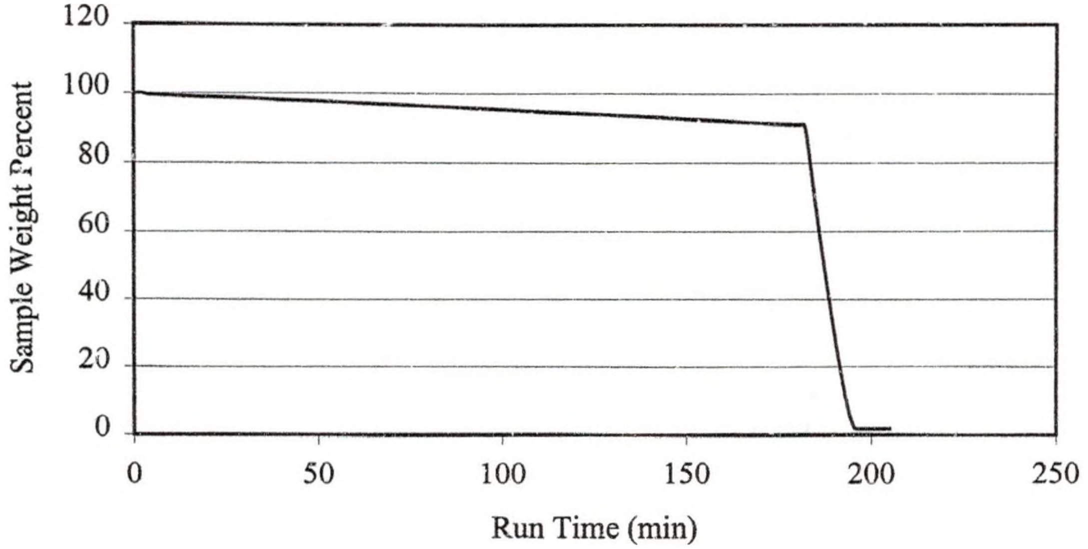


Figure A-3. Raw Data of TGA Run Number 3

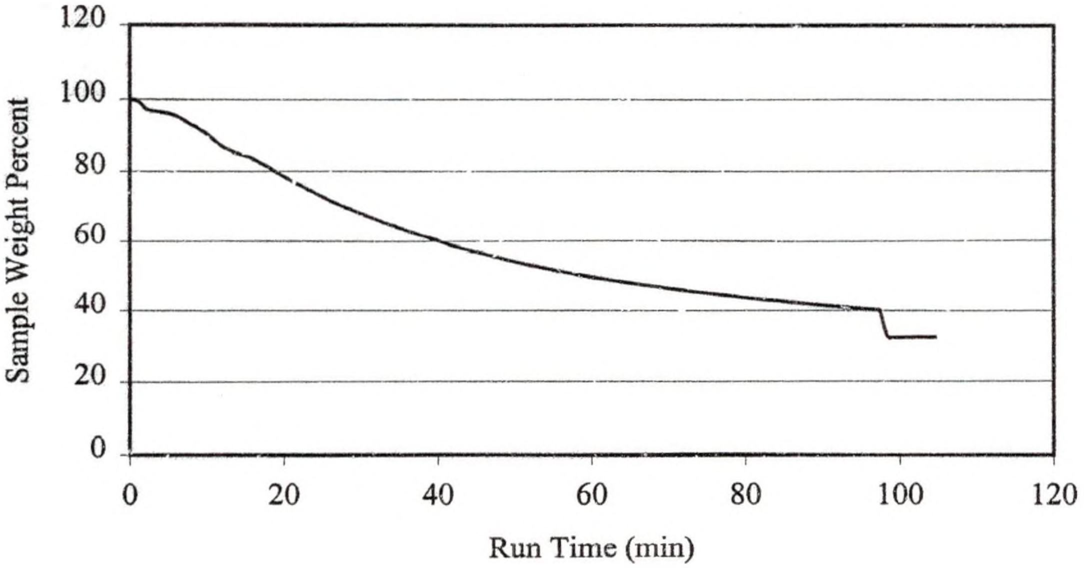


Figure A-4. Raw Data of TGA Run Number 4

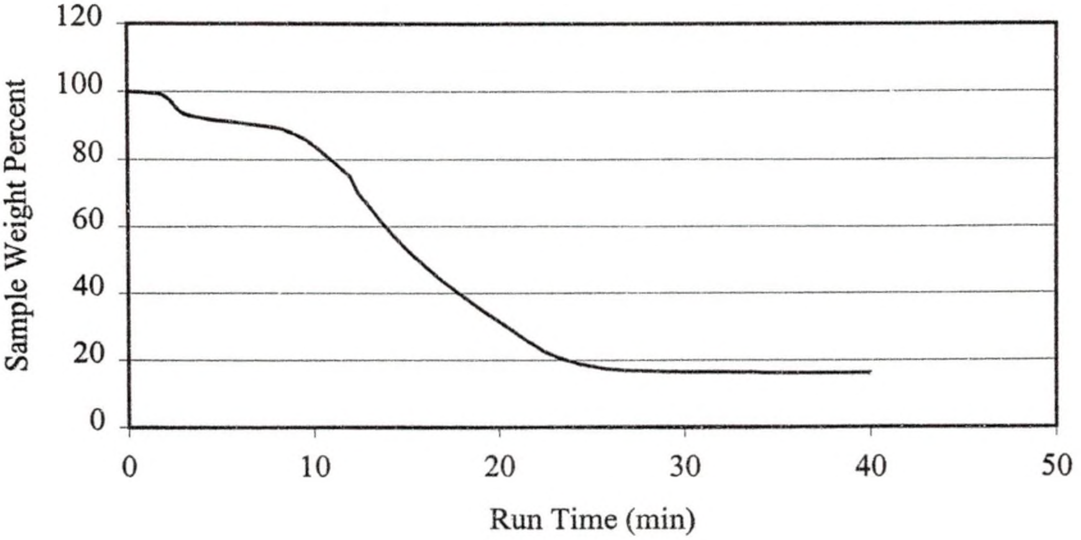


Figure A-5. Raw Data of TGA Run Number 5

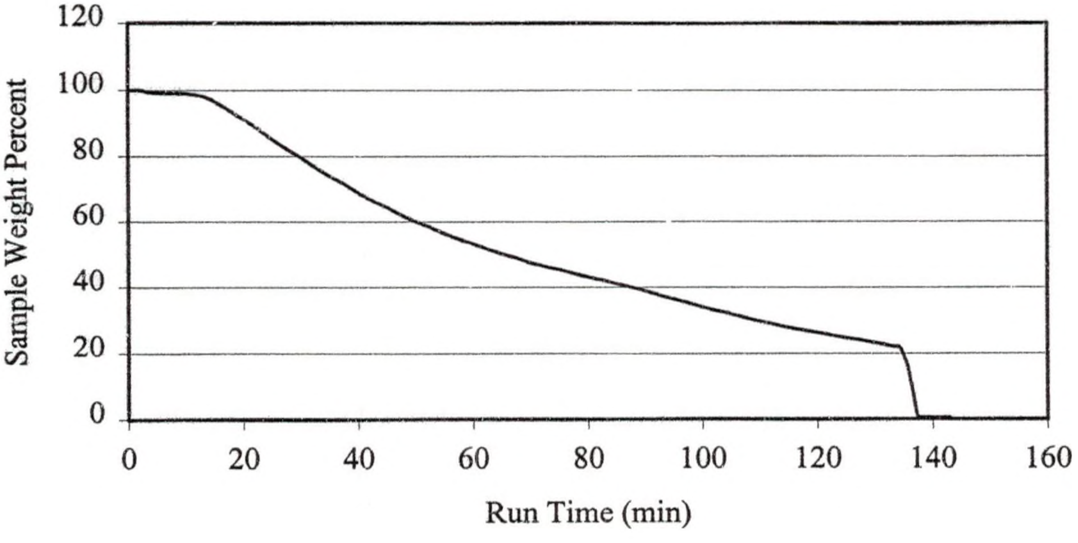


Figure A-6. Raw Data of TGA Run Number 6

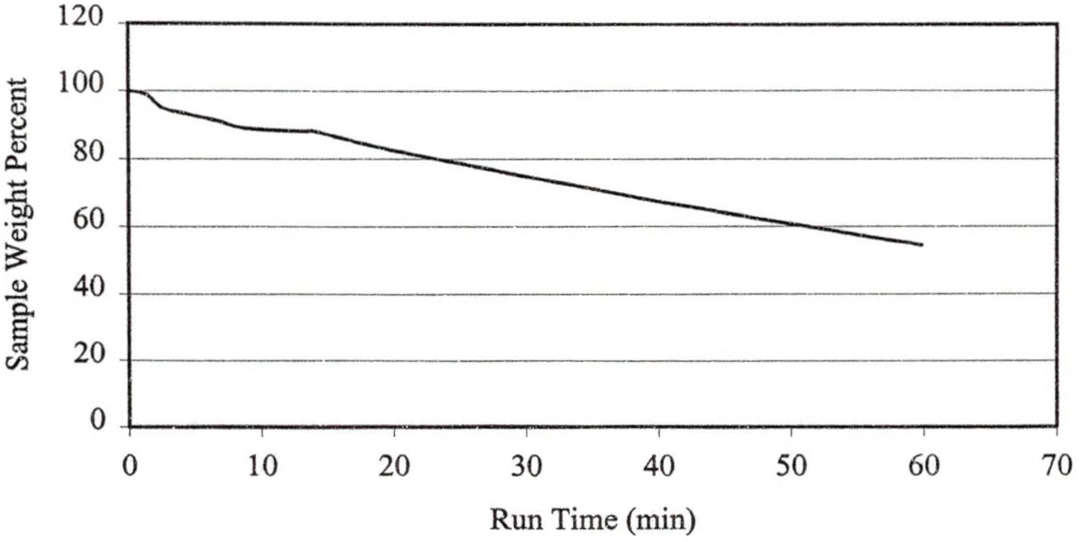


Figure A-7. Raw Data of TGA Run Number 7

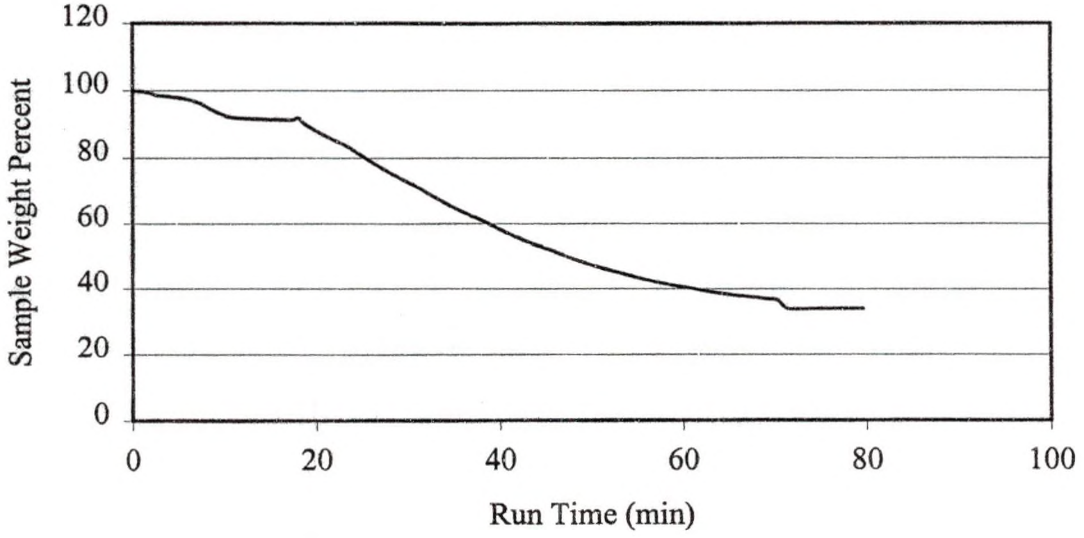


Figure A-8. Raw Data of TGA Run Number 8

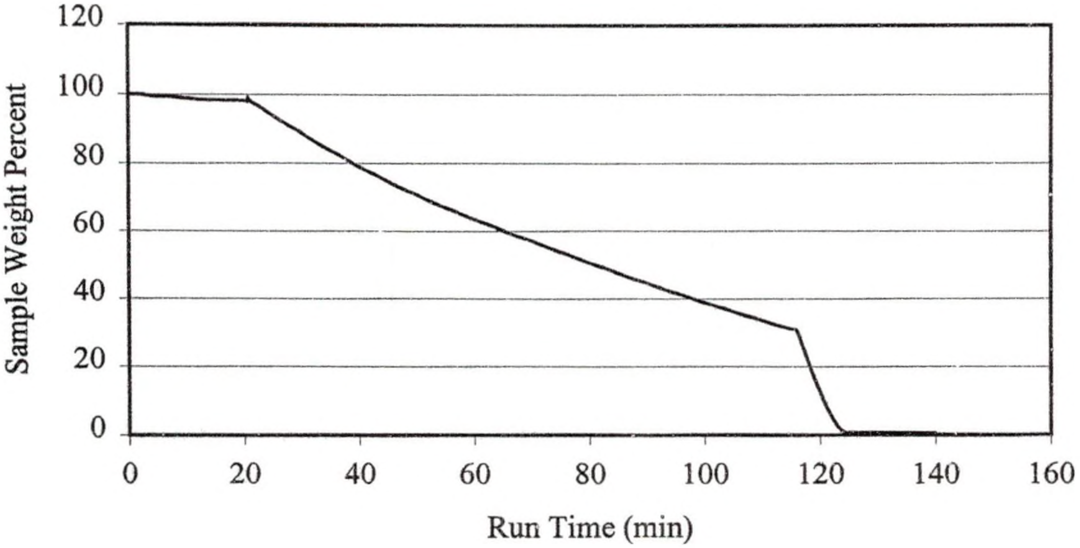
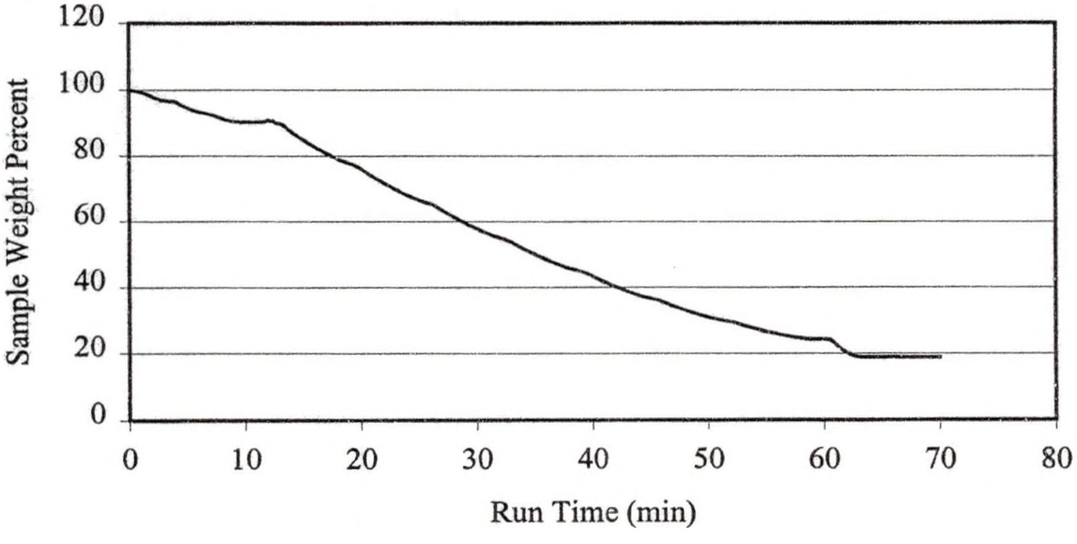


Figure A-9. Raw Data of TGA Run Number 9



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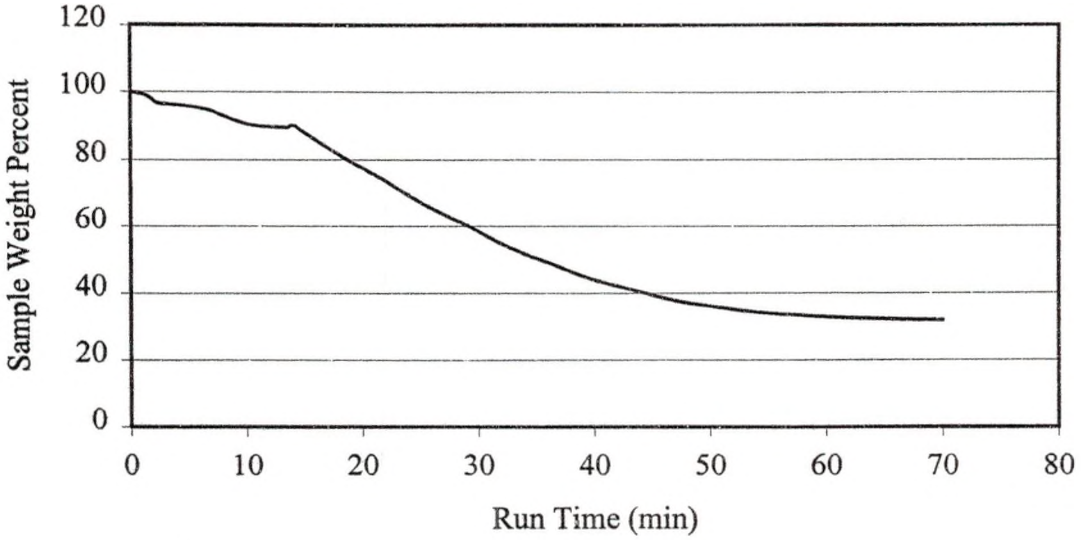

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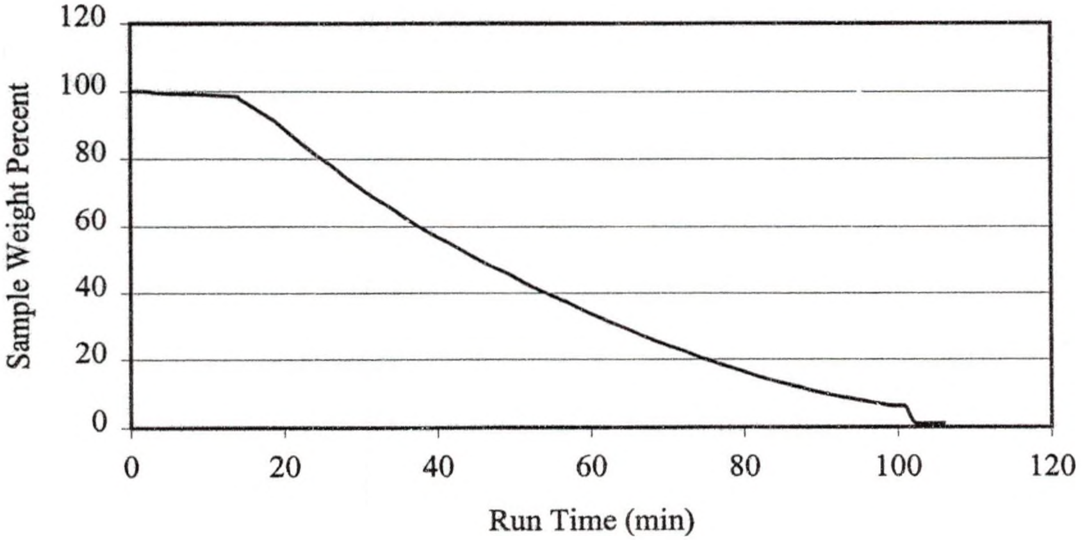

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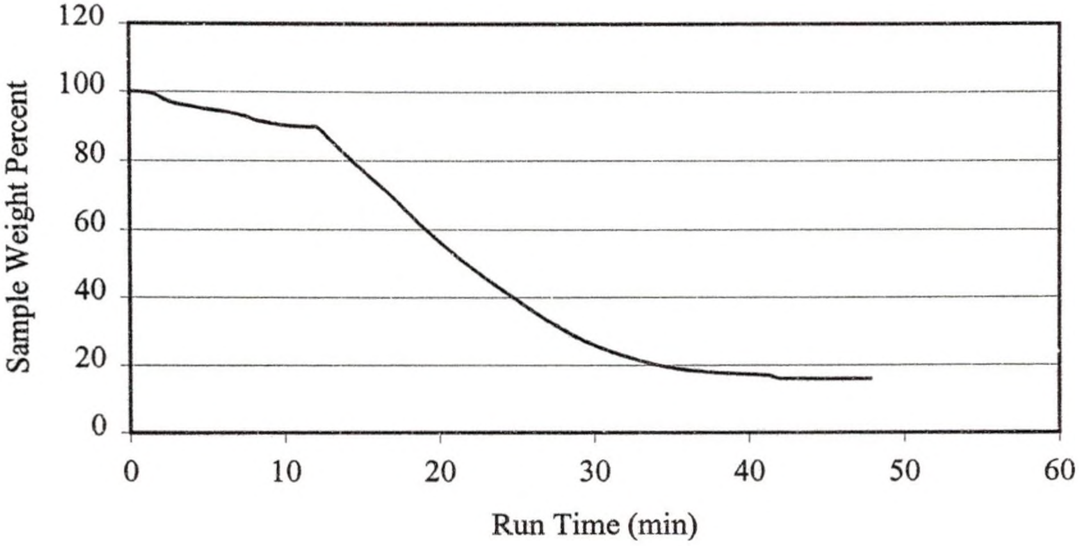

Figure A-13. Raw Data of TGA Run Number 13

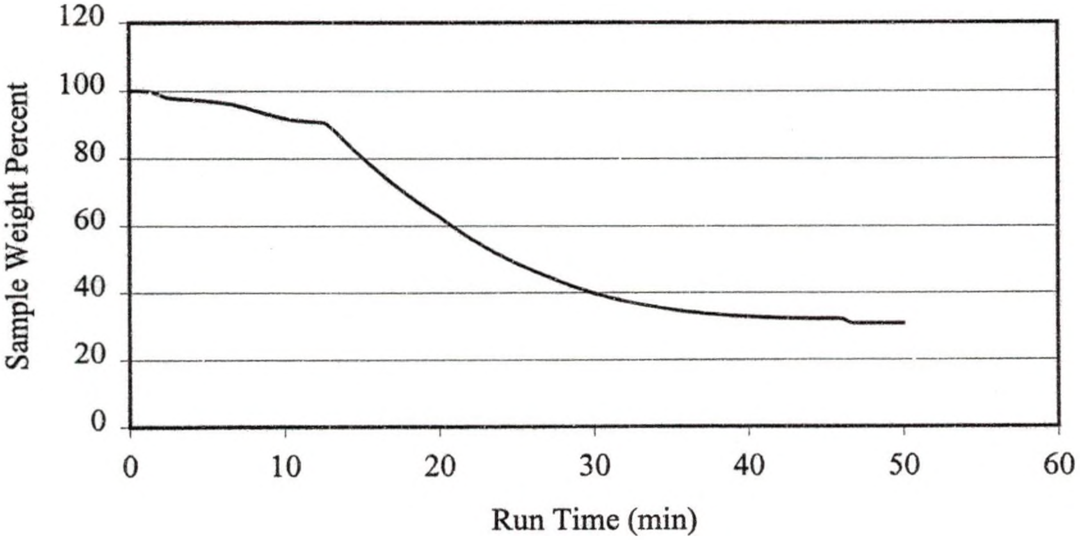

Figure A-14. Raw Data of TGA Run Number 14

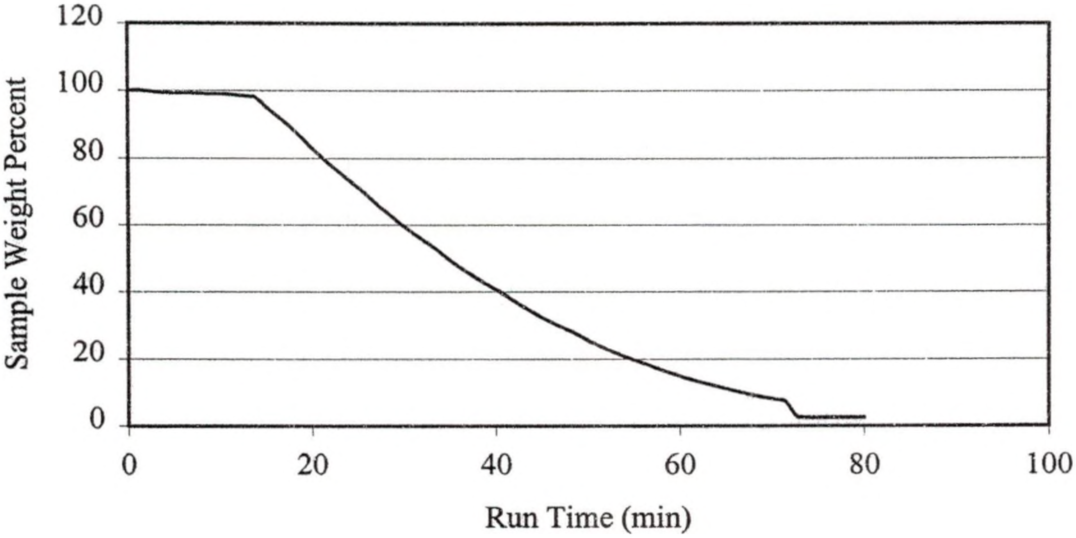

Figure A-15. Raw Data of TGA Run Number 15

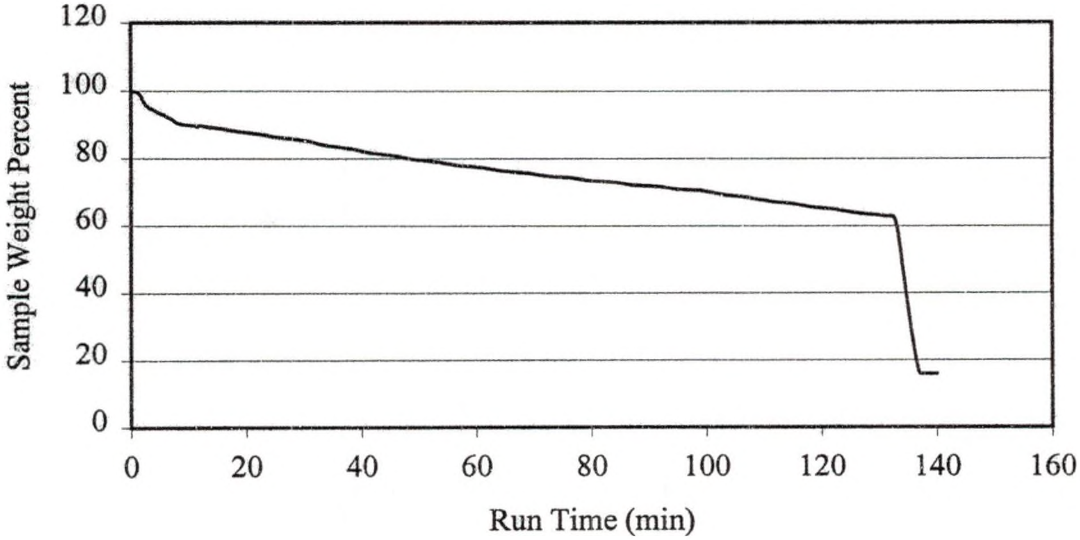

Figure A-16. Raw Data of TGA Run Number 16

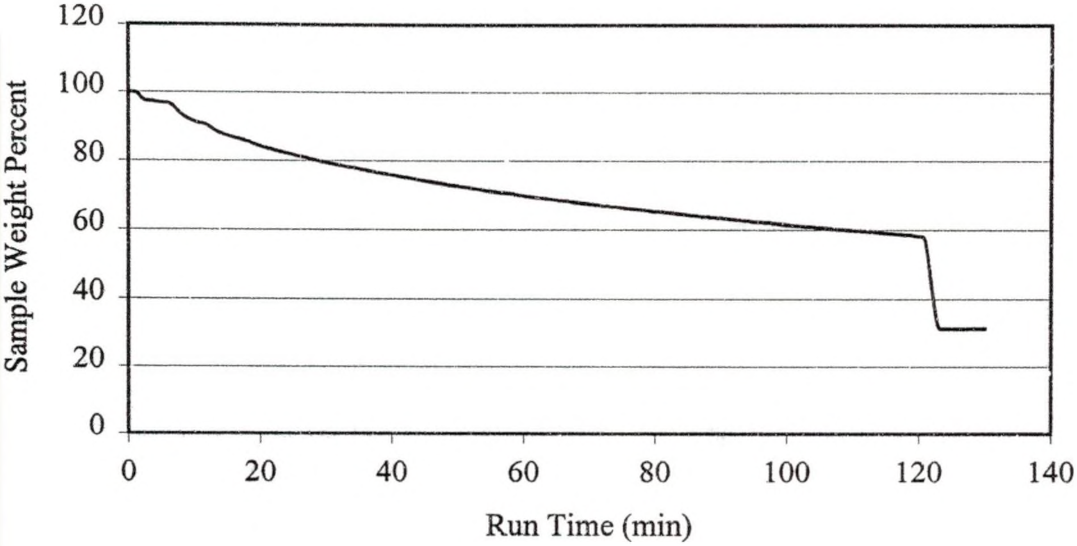

Figure A-17. Raw Data of TGA Run Number 17

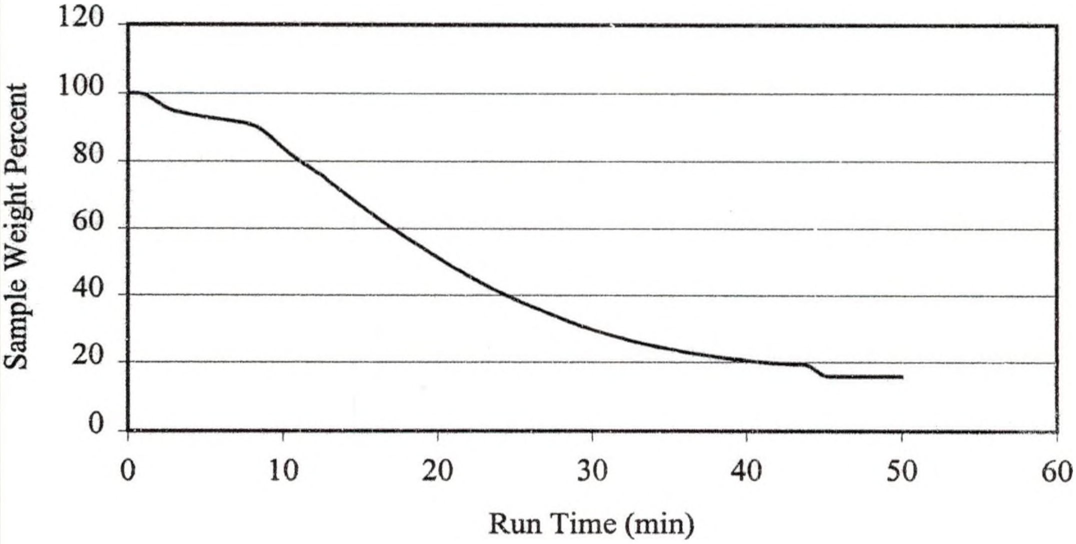

Figure A-18. Raw Data of TGA Run Number 18

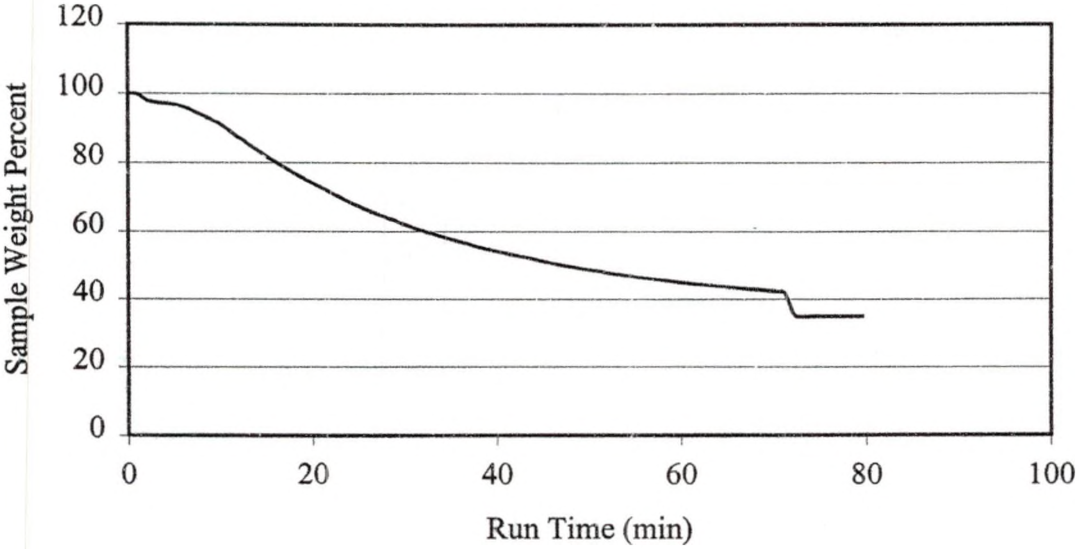

Figure A-19. Raw Data of TGA Run Number 19

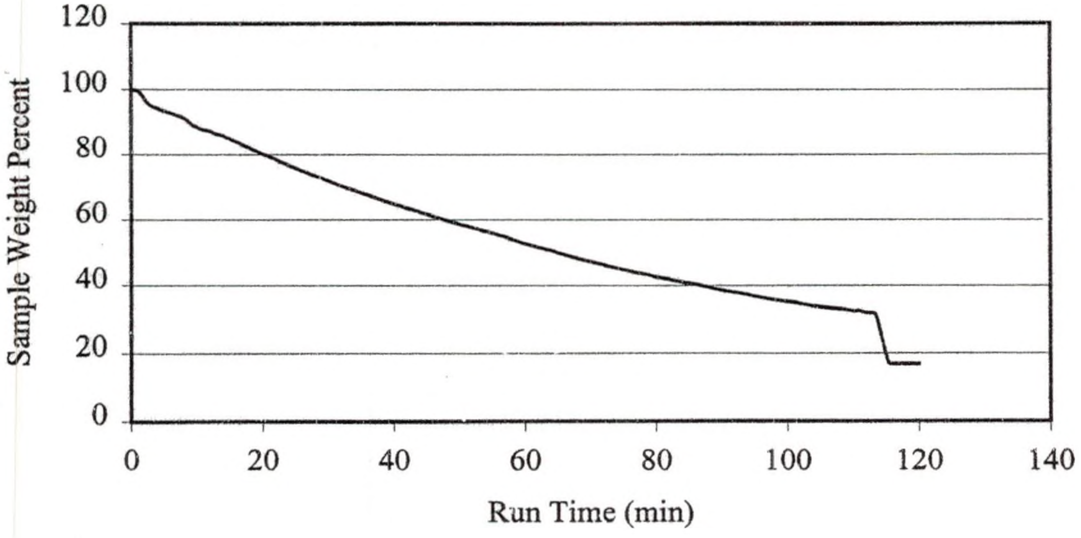

Figure A-20. Raw Data of TGA Run Number 20

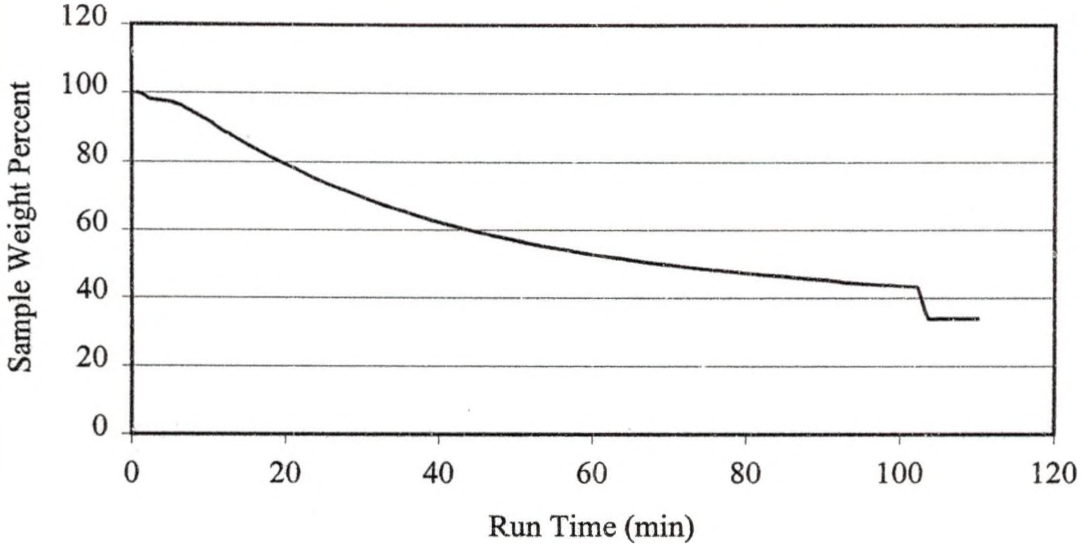

Figure A-21. Raw Data of TGA Run Number 21

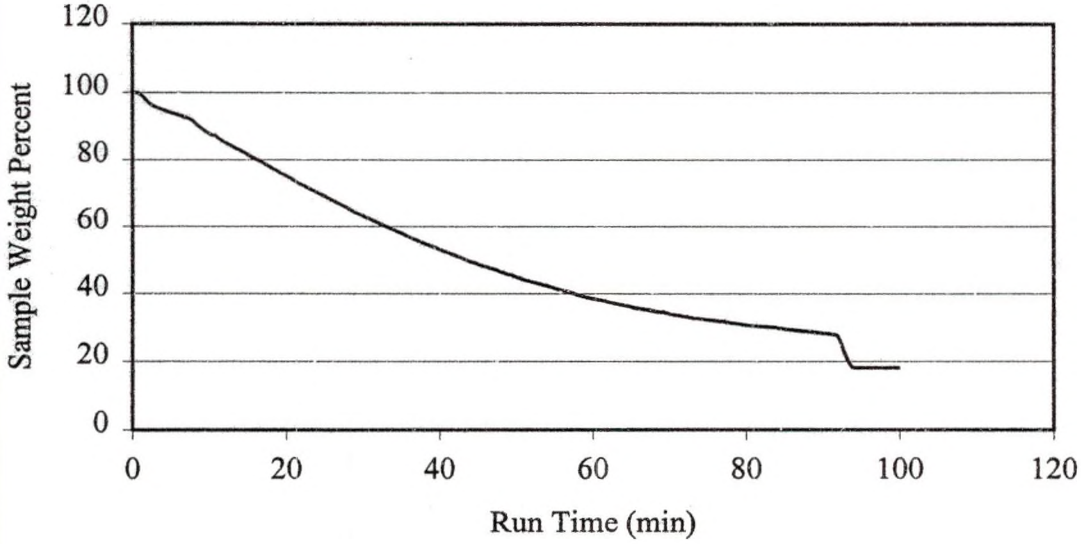

Figure A-22. Raw Data of TGA Run Number 22

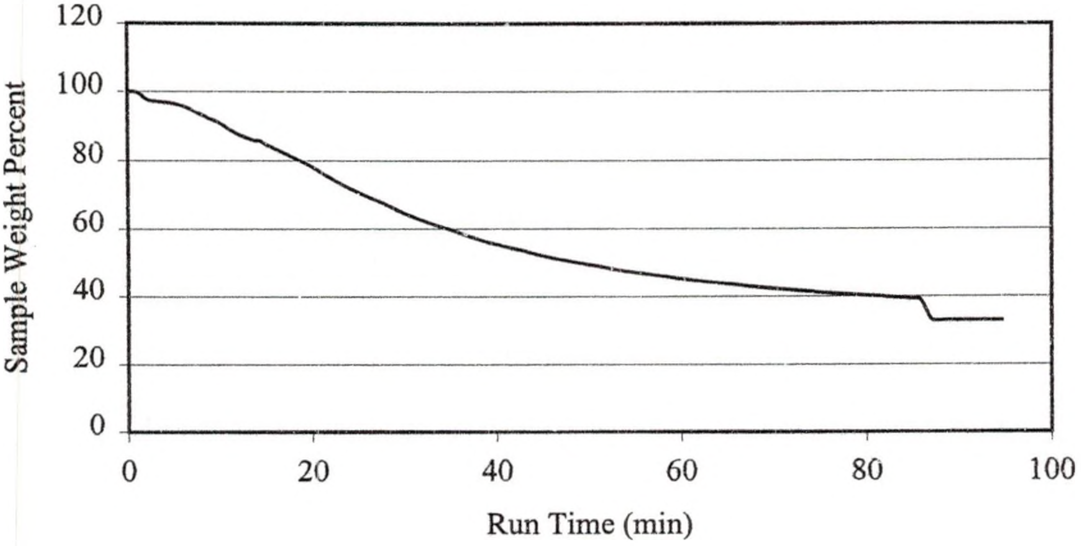

Figure A-23. Raw Data of TGA Run Number 23

APPENDIX B

PFBR DATA SHEETS AND ANALYSES

This section contains graphical representations of the raw data obtained from the PFBR's data acquisition software. Temperatures reported for each run are within ± 25 °F. Notes are given with each illustration as to where agglomeration and loss of flow phenomenon occurred. Also included in this section are illustrations of the carbon monoxide carbon dioxide molar production ratios compared to the oxygen-to-carbon ratios in the PFBR reactor.

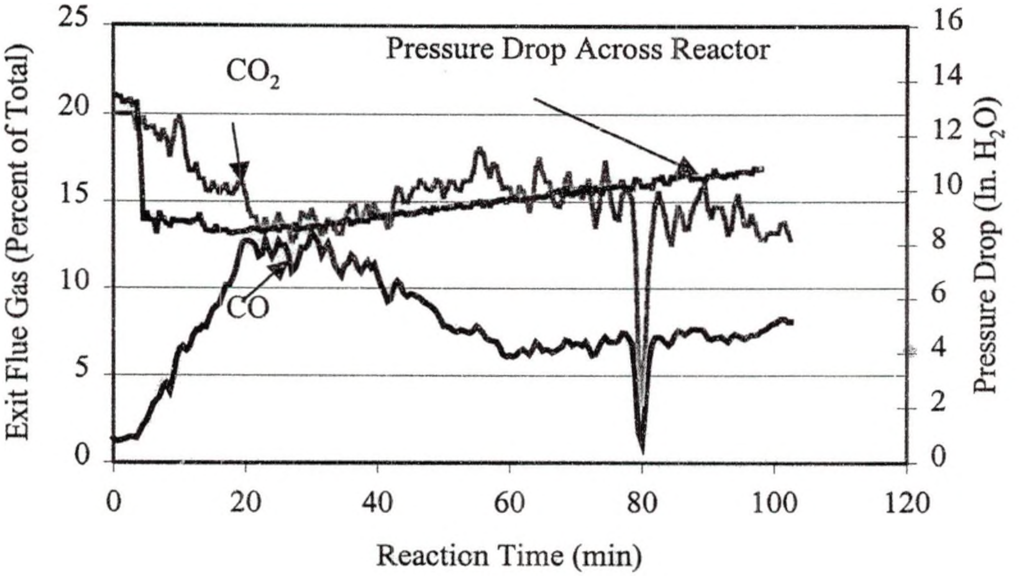

Figure B-1. Raw Data of PFBR Freedom Char Run at 1750 °F & 0.5 SCFM

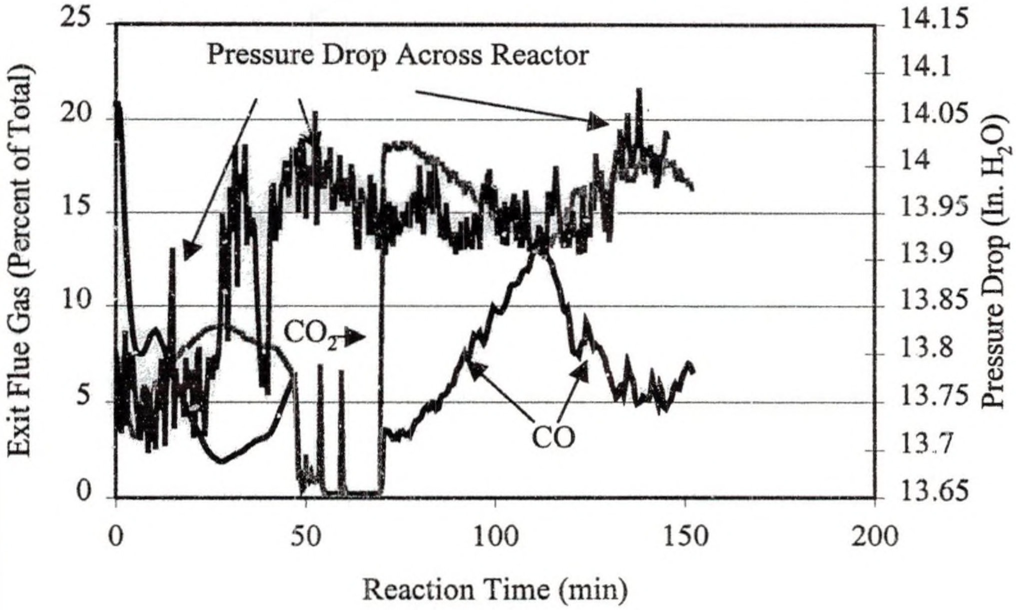

Figure B-2. Raw Data of PFBR Freedom Char Replicate Run at 1750 °F & 0.5 SCFM
Note: Analyzer flow restricted until approximately 70 minutes into the test

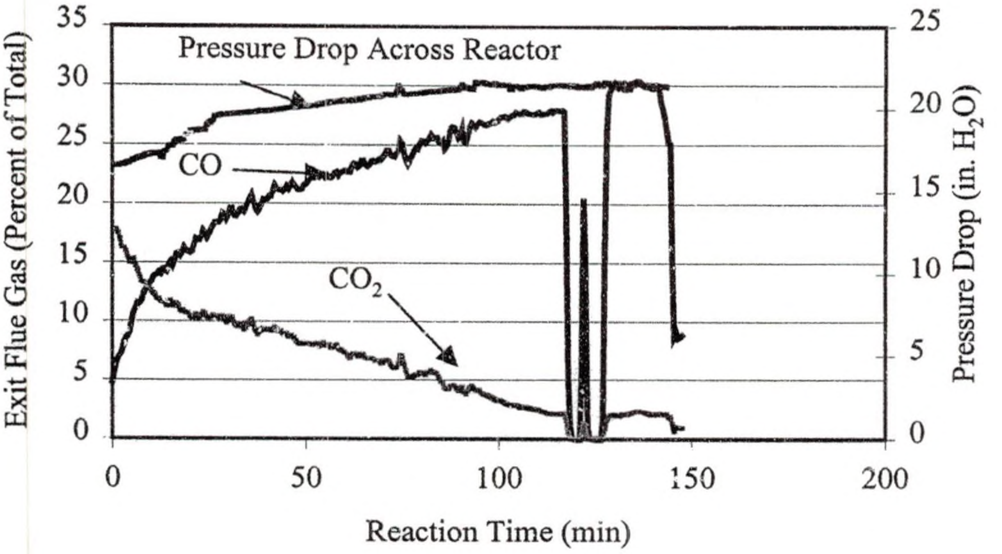

Figure B-3. Raw Data of PFBR Freedom Char Run at 1750 °F & 0.3 SCFM
Note: Analyzer flow restricted until approximately 70 minutes into the test

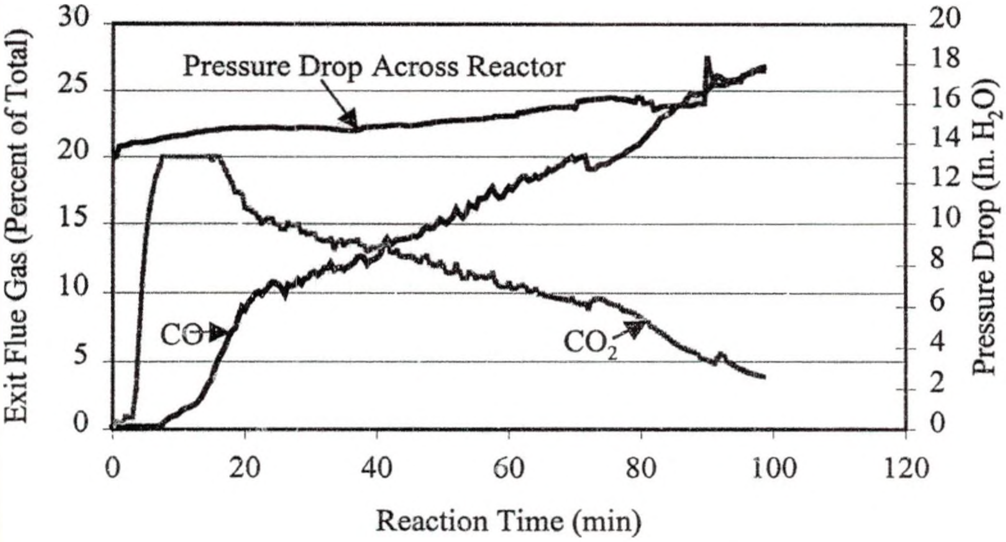

Figure B-4. Raw Data of PFBR Freedom Char Replicate Run at 1750 °F & 0.3 SCFM

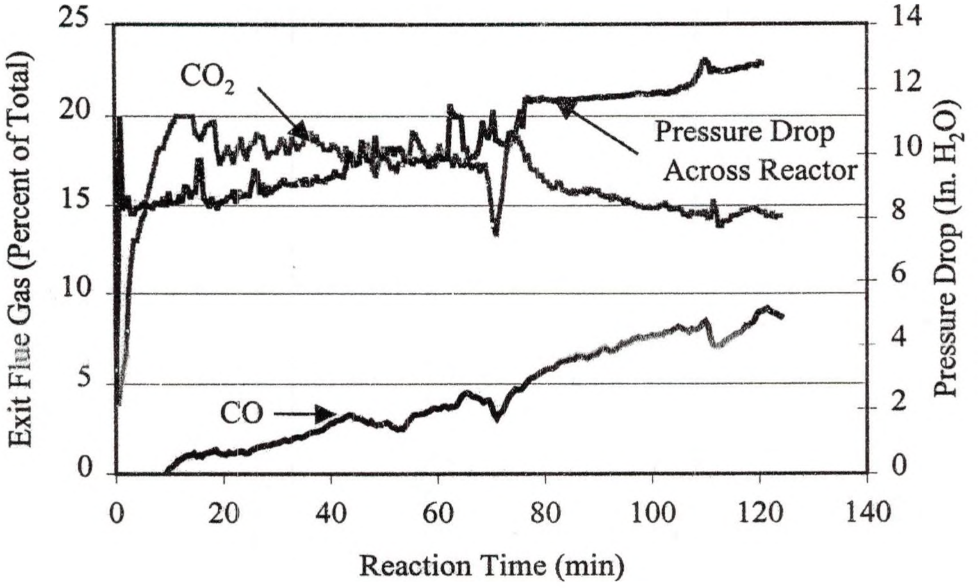

Figure B-5. Raw Data of PFBR Freedom Char Run at 1500 °F & 0.5 SCFM

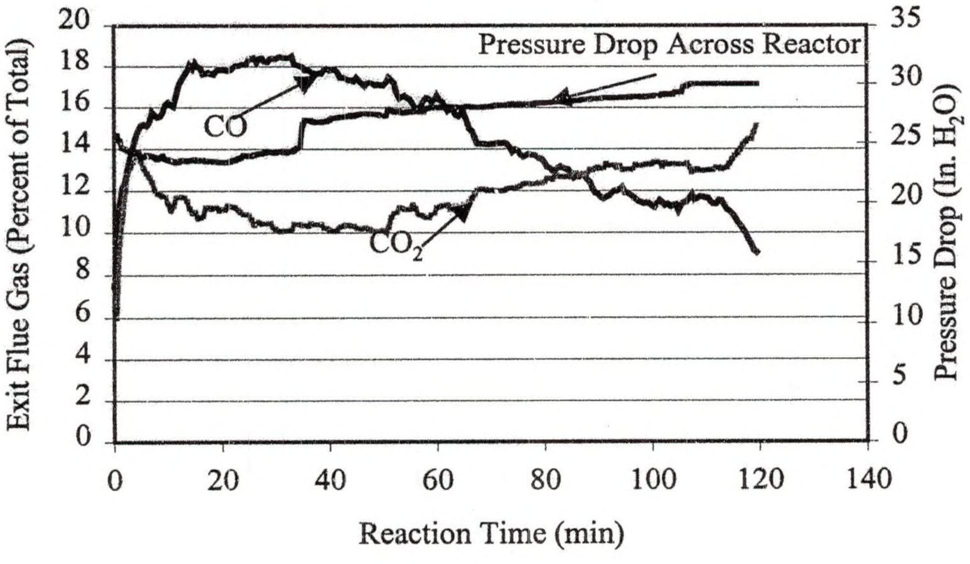

Figure B-6. Raw Data of PFBR Freedom Char Replicate Run at 1500 °F & 0.5 SCFM

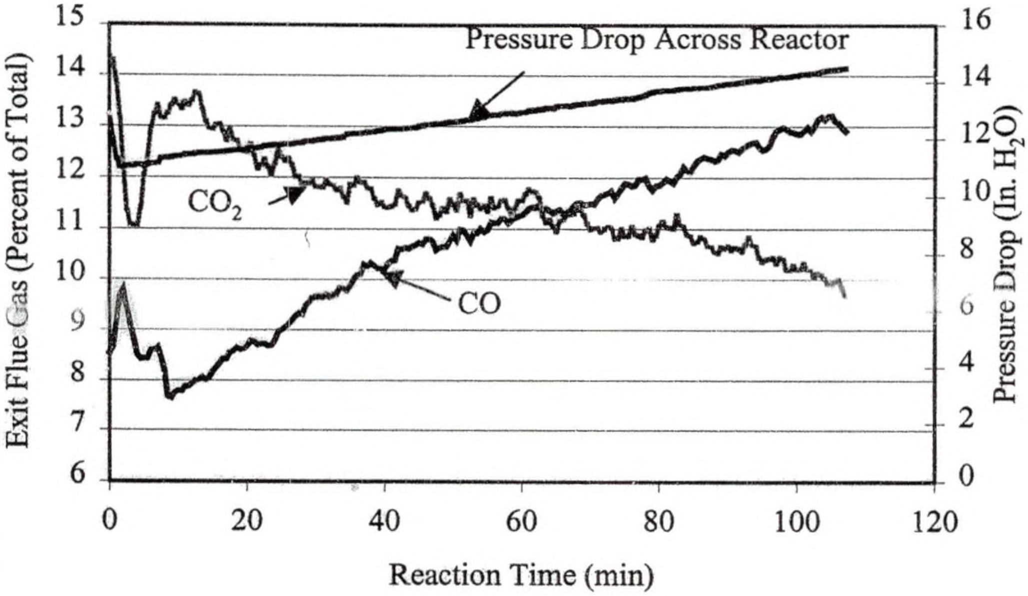

Figure B-7. Raw Data of PFBR Freedom Char Run at 1500 °F & 0.3 SCFM

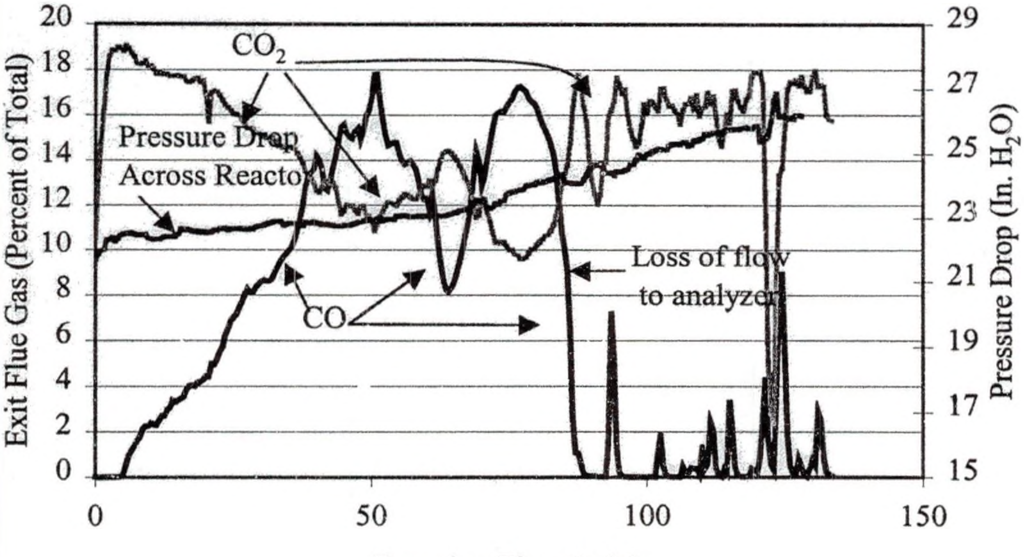

Figure B-8. Raw Data of PFBR Freedom Char Replicate Run at 1500 °F & 0.3 SCFM

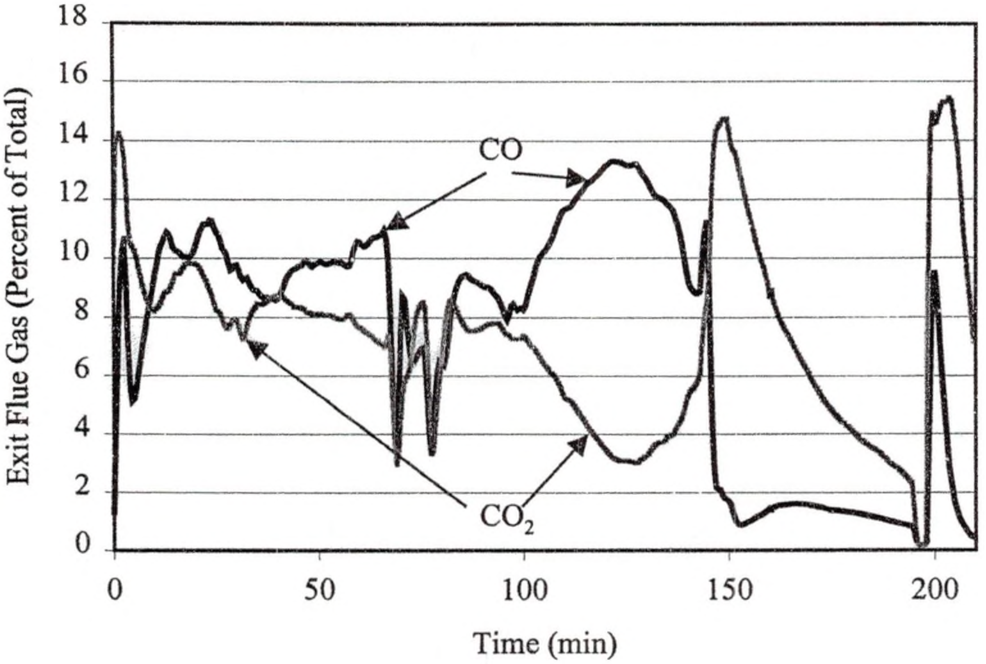

Figure B-9. Full Bed Lignite Char Test at 1500 °F & 0.3 SCFM
Note: Problems occurred during this test with char agglomeration

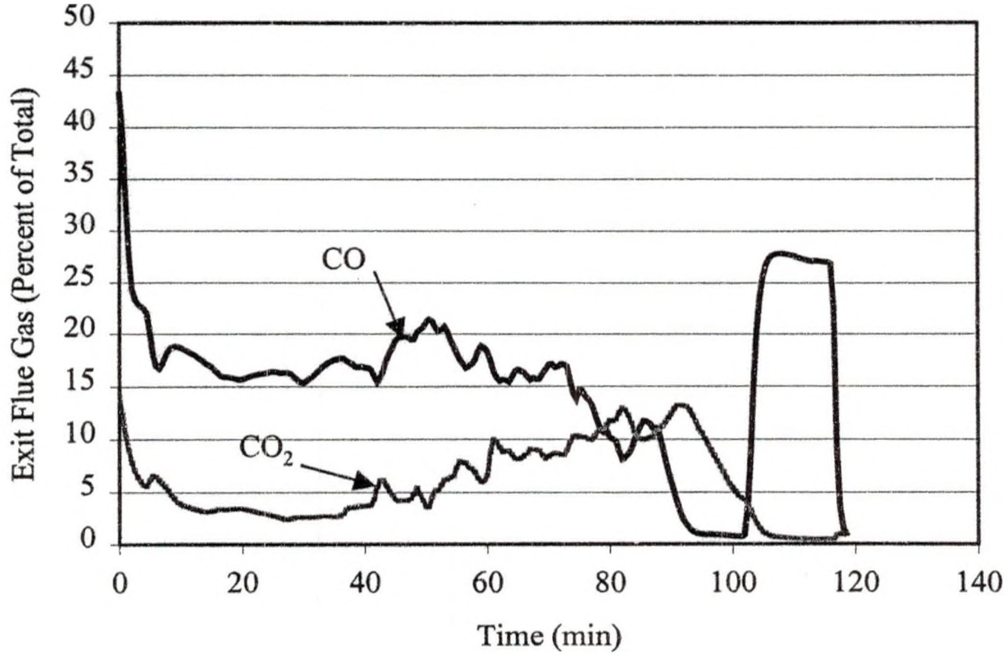

Figure B-10. Full Bed Lignite Char Test at 1750 °F & 0.3 SCFM
Note: Problems occurred during this test with char agglomeration

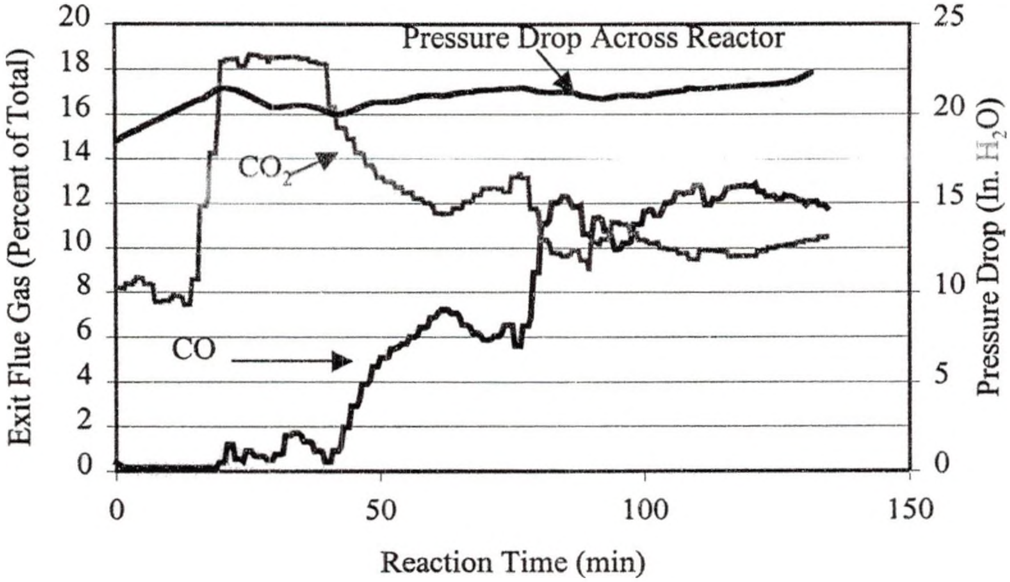

Figure B-11. Raw Data of PFBR Petroleum Coke Char Run at 1900 °F & 1.1 SCFM

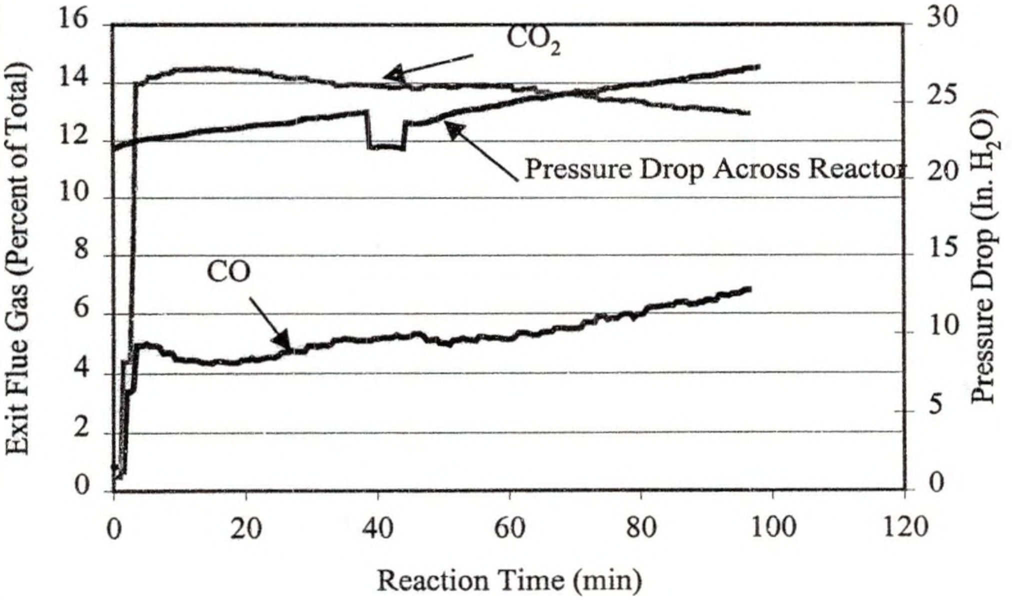

Figure B-12. Raw Data of PFBR Petroleum Coke Char Run at 1820 °F & 0.5 SCFM

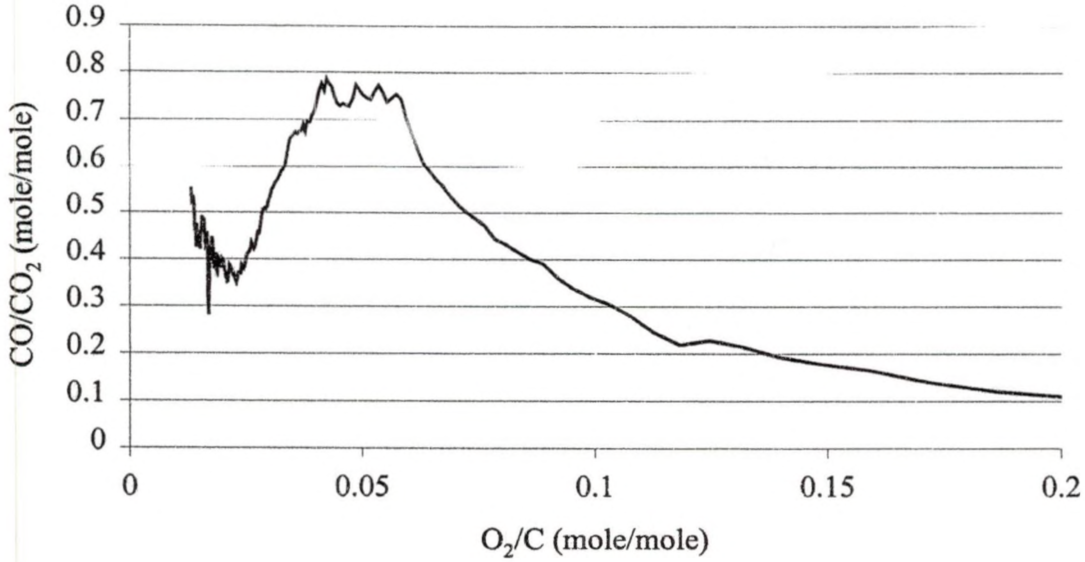

Figure B-12. Oxygen-Carbon Analysis of PFBR Freedom Char Run at 1750 °F & 0.5 SCFM

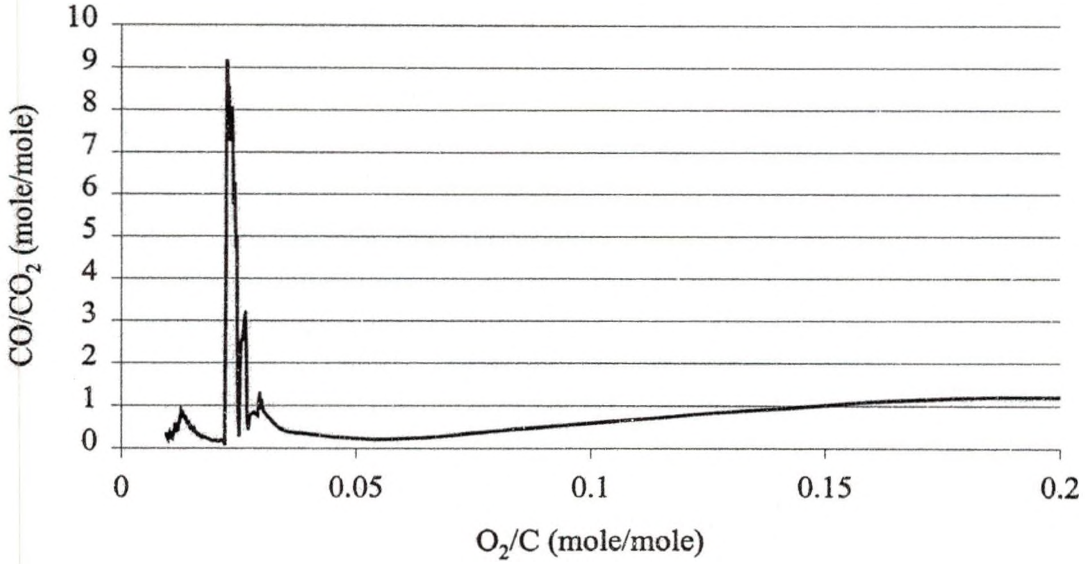

Figure B-13. Oxygen-Carbon Analysis of PFBR Freedom Char Replicate Run at 1750 °F & 0.5 SCFM

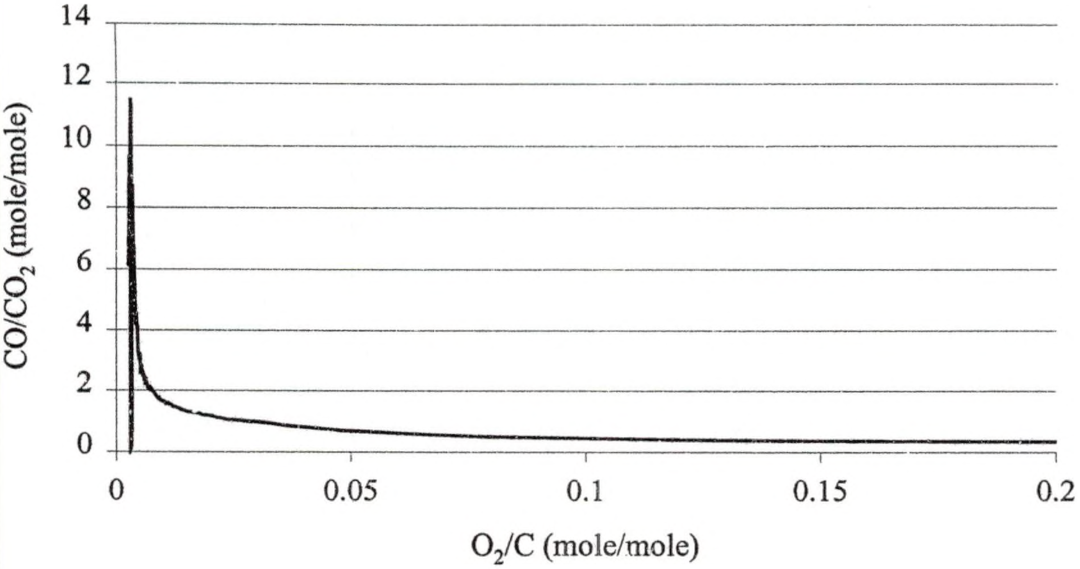

Figure B-13. Oxygen-Carbon Analysis of PFBR Freedom Char Run at 1750 °F & 0.3 SCFM

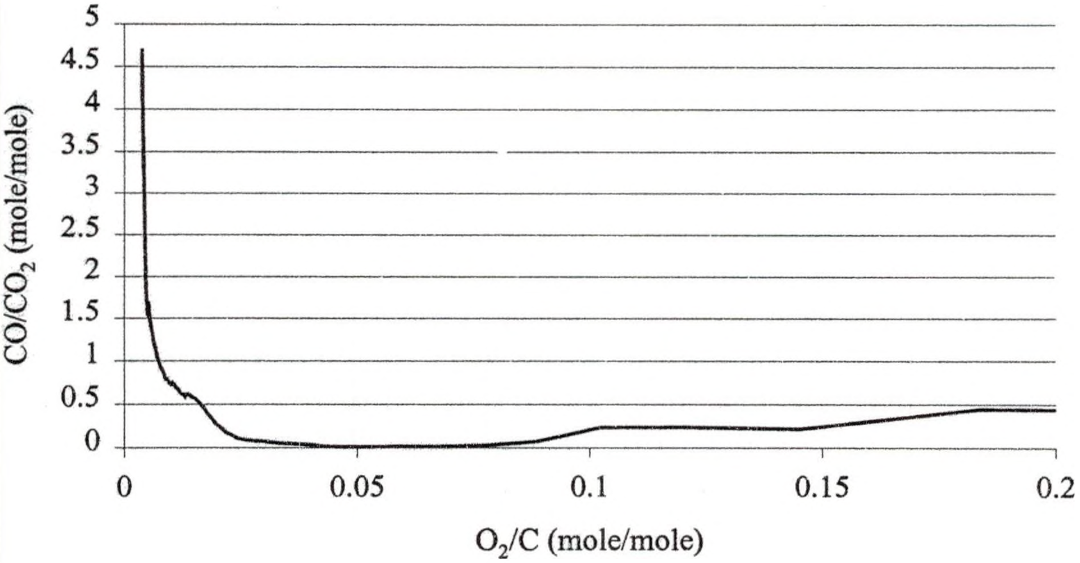

Figure B-14. Oxygen-Carbon Analysis of PFBR Freedom Char Replicate Run at 1750 °F & 0.3 SCFM

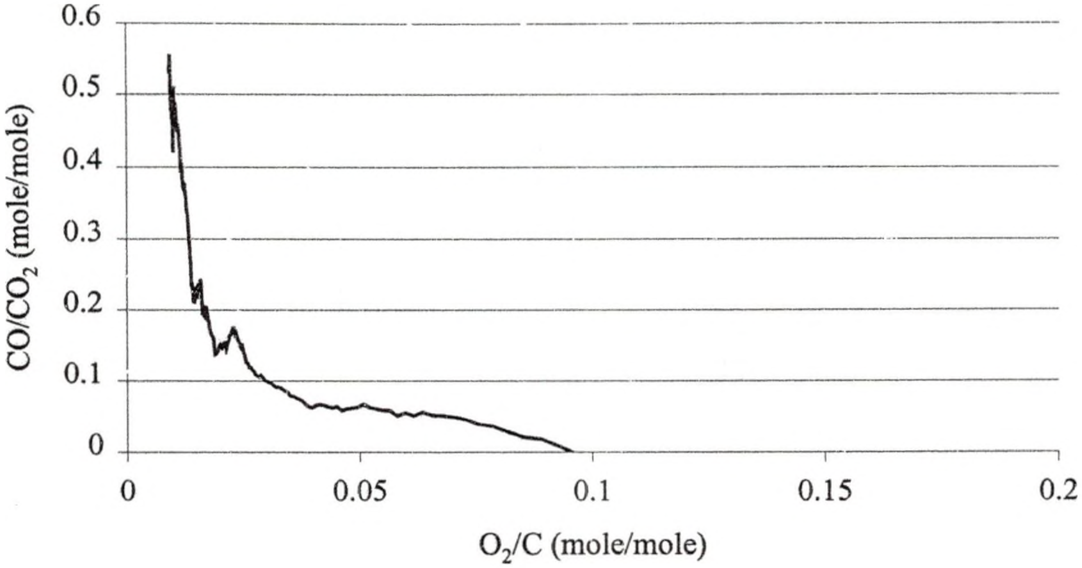

Figure B-15. Oxygen-Carbon Analysis of PFBR Freedom Char Run at 1500 °F & 0.5 SCFM

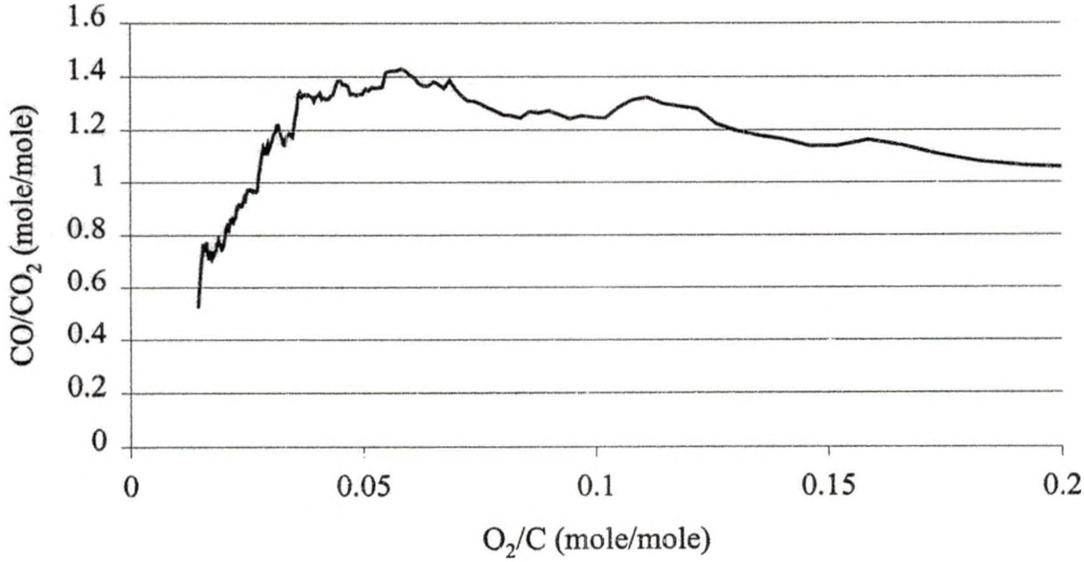

Figure B-16. Oxygen-Carbon Analysis of PFBR Freedom Char Replicate Run at 1500 °F & 0.5 SCFM

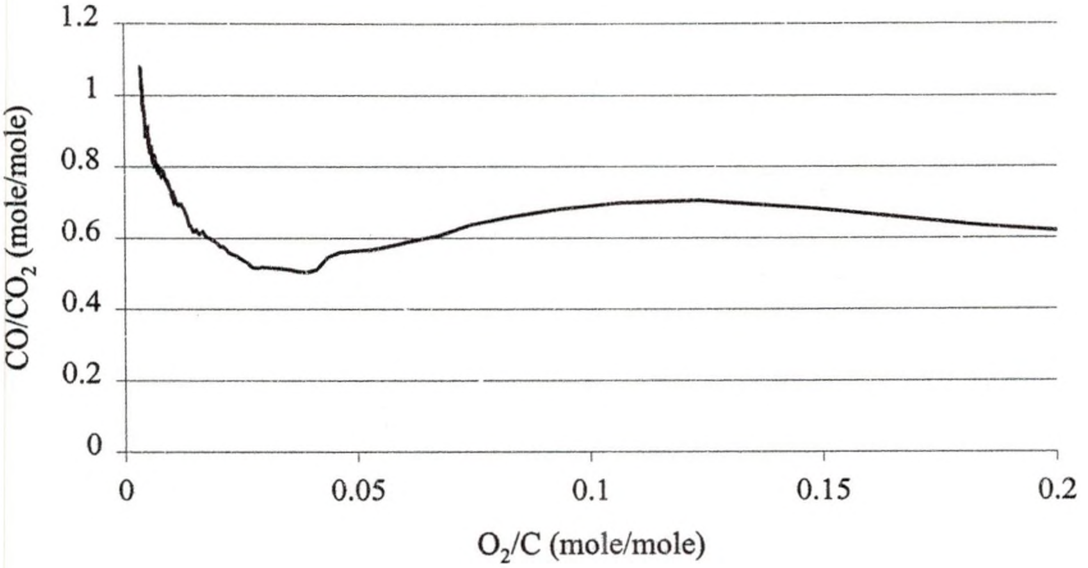

Figure B-17. Oxygen-Carbon Analysis of PFBR Freedom Char Run at 1500 °F & 0.3 SCFM

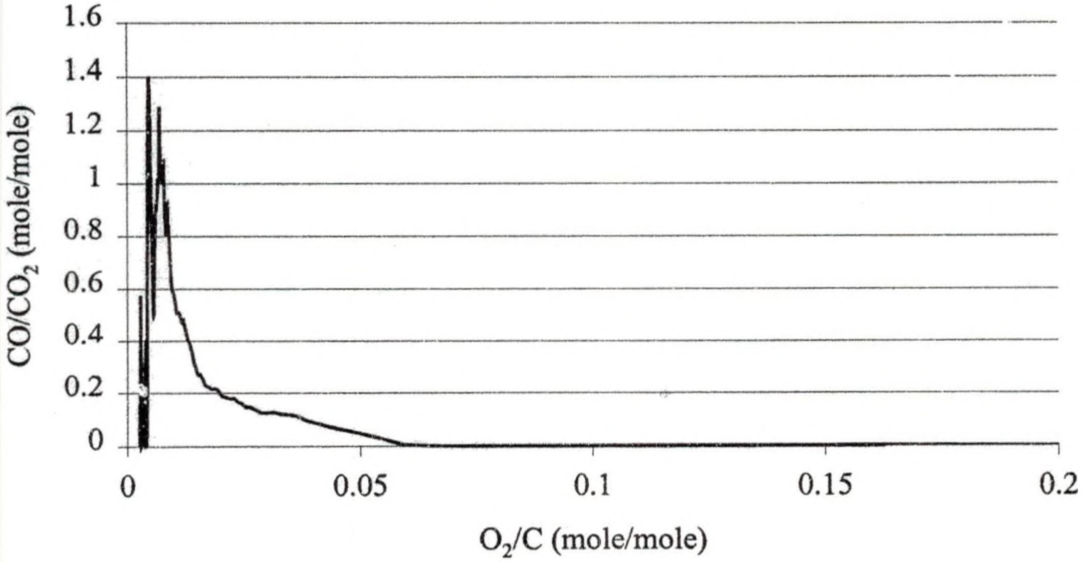

Figure B-18. Oxygen-Carbon Analysis of PFBR Freedom Char Replicate Run at 1500 °F & 0.3 SCFM

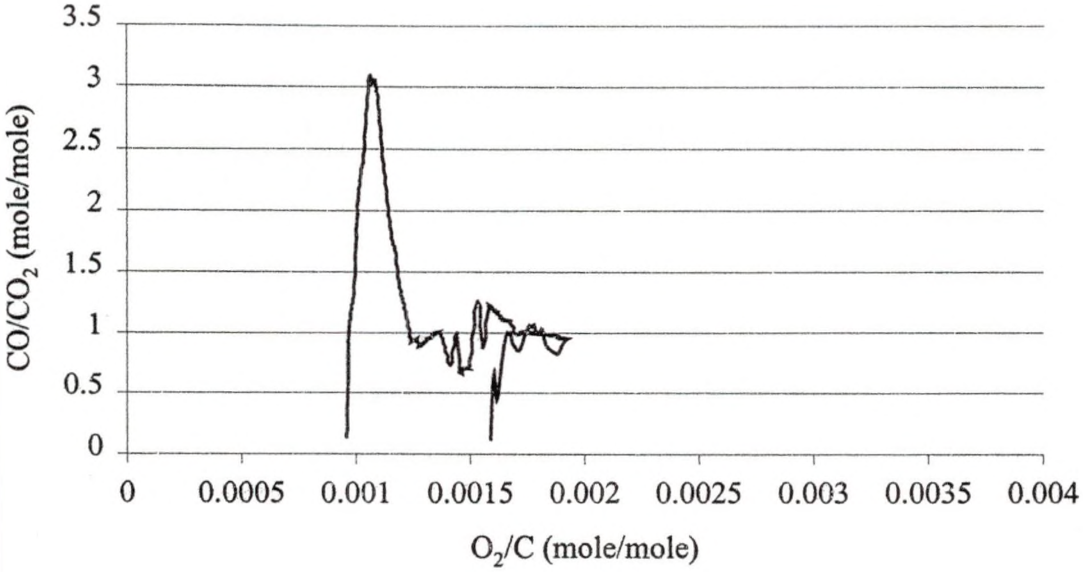

Figure B-19. Oxygen-Carbon Analysis of PFBR Freedom Char Full Bed Run at 1500 °F & 0.3 SCFM*

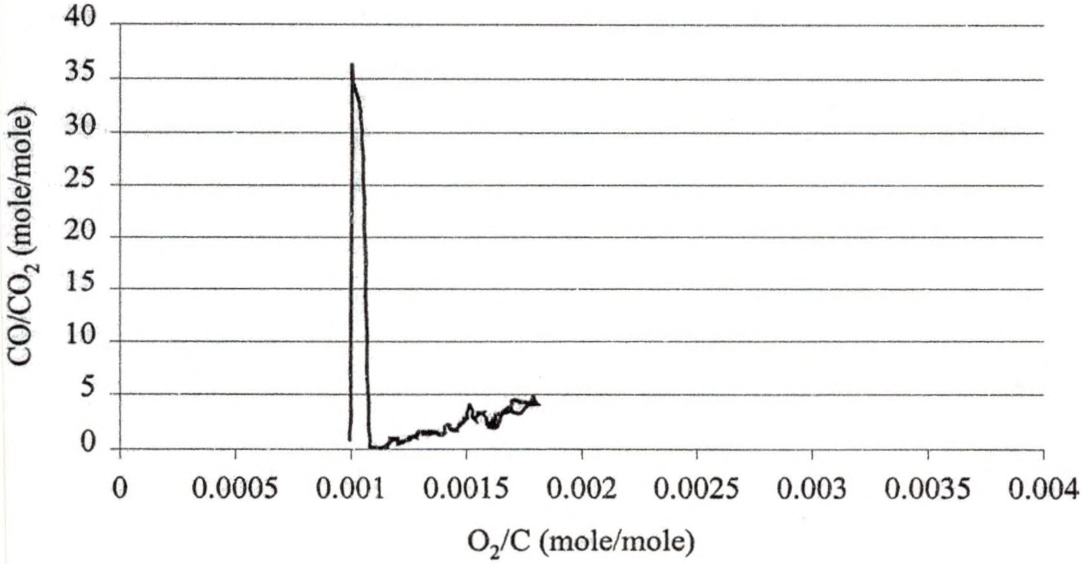

Figure B-20. Oxygen-Carbon Analysis of PFBR Freedom Char Full Bed Run at 1750 °F & 0.3 SCFM*

* Note: The x-axis scale is much lower than the other analysis of the freedom char

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