DOE/PC/92530--T/1

Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report for the Period
January 1, 1995 - March 31, 1995

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk

Iowa State University
Ames, IA 50011

Work Performed Under Grant
No. DE-FG22-92PC92530

Date Transmitted: April 1995

Prepared for: U.S. Department of Energy
Pittsburgh Energy Technology Center
Pittsburgh, PA

Project Monitor: Wu Lan

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
JSDOE/PETC
95 MAY -3 AM 9:49
U.S. DEPT. OF ASSISTANCE DIV.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

W

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report

January 1, 1995 - March 31, 1995

Robert C. Brown, M. Robert Dawson, and Jerod L. Smeenk

Iowa State University, Ames IA 50011

Abstract

Experiments performed support the hypothesis that a reducing atmosphere during fluidized bed coal combustion contributes to the formation of agglomerates. Reducing conditions are imposed by controlling the amount of combustion air supplied to the combustor, 50% of theoretical in these experiments. These localized reducing conditions may arise from either poor lateral bed mixing or oxygen-starved conditions due to the coal feed locations.

Deviations from steady-state operating conditions in bed pressure drop may be used to detect agglomerate formation. Interpretation of the bed pressure drop was made more straightforward by employing a moving average difference method. During steady-state operation, the difference between the moving point averages should be close to zero, within ± 0.03 inches of water. Instability within the combustor, experienced once agglomerates begin to form, can be recognized as larger deviations from zero, on the magnitude of ± 0.15 inches of water.

Bed Material Agglomeration During Fluidized Bed Combustion

Technical Progress Report
January 1, 1995 - March 31, 1995

Objective

The purpose of this project is to determine the physical and chemical reactions which lead to the undesired agglomeration of bed material during fluidized bed combustion of coal and to relate these reactions to specific causes.

Progress

The work this quarter is presented as the Masters Thesis of Jerod Smeenck titled "The agglomeration of bed material during fluidized bed coal combustion."

Future Work

Work planned for the next quarter includes testing of fuels with differing amounts of silica and iron. In addition "model" fuels will be tested which will be carbon with controlled amounts of clays and pyrites. These tests will allow a more direct evaluation of the interactions of iron compounds with aluminosilicates.

The agglomeration of bed material during fluidized bed coal combustion

by

Jerod Lee Smeenk

**A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE**

**Department: Mechanical Engineering
Major: Mechanical Engineering**

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

**Iowa State University
Ames, Iowa**

1995

TABLE OF CONTENTS

LIST OF FIGURES	iii
LIST OF TABLES	v
ACKNOWLEDGMENTS	vi
CHAPTER 1 INTRODUCTION	1
CHAPTER 2 BACKGROUND	3
2.1 Effect of temperature	3
2.2 Effect of fuel ash composition	6
2.3 Effect of atmosphere	7
CHAPTER 3 EXPERIMENTAL APPARATUS	10
3.1 Fluidized Bed Combustor	10
3.2 Flue gas sampling and analysis equipment	15
3.3 Data monitoring and recording equipment	17
CHAPTER 4 EXPERIMENTAL PROCEDURE	18
4.1 Experimental setup	18
4.2 Experimental startup, steady-state operating conditions, and termination	18
CHAPTER 5 RESULTS AND DISCUSSION	22
5.1 Oxidizing conditions with sand as bed material	22
5.2 Reducing conditions with sand as bed material	26
5.3 Reducing conditions and methane plume with sand as bed material	29
5.4 Oxidizing conditions with limestone as bed material	33
5.5 Reducing conditions and methane plume with limestone as bed material	37
5.6 Reducing conditions with limestone as bed material	42
5.7 Discussion	46
CHAPTER 6 CONCLUSIONS	51
REFERENCES	54

LIST OF FIGURES

Figure 3.1	Laboratory-scale fluidized bed combustor schematic	11
Figure 3.2	Laboratory-scale fluidized bed combustor	12
Figure 5.1	Combustor temperatures for equivalence ratio of 1.10	24
Figure 5.2	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 1.10	25
Figure 5.3	Exhaust gas composition for equivalence ratio of 1.10	25
Figure 5.4	Combustor temperatures for equivalence ratio of 0.50	27
Figure 5.5	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50	28
Figure 5.6	Exhaust gas composition for equivalence ratio of 0.50	28
Figure 5.7	Combustor temperatures for equivalence ratio of 0.50	30
Figure 5.8	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50	31
Figure 5.9	Exhaust gas composition for equivalence ratio of 0.50	31
Figure 5.10	Agglomerate formed under reducing conditions with sand as the bed material	33
Figure 5.11	Combustor temperatures for equivalence ratio of 1.20	35
Figure 5.12	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 1.20	35
Figure 5.13	Exhaust gas composition for equivalence ratio of 1.20	36
Figure 5.14	Exhaust gas composition for equivalence ratio of 1.20	36

Figure 5.15	Combustor temperatures for equivalence ratio of 0.50	38
Figure 5.16	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50	38
Figure 5.17	Exhaust gas composition for equivalence ratio of 0.50	39
Figure 5.18	Exhaust gas composition for equivalence ratio of 0.50	39
Figure 5.19	Agglomerate formed under reducing conditions with limestone as the bed material	41
Figure 5.20	Combustor temperatures for equivalence ratio of 0.50	43
Figure 5.21	Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50	43
Figure 5.22	Exhaust gas composition for equivalence ratio of 0.50	44
Figure 5.23	Exhaust gas composition for equivalence ratio of 0.50	44

LIST OF TABLES

Table 3.1	Thermocouple probe locations within the fluidized bed combustor	14
Table 4.1	Bulk composition of sieved sand	20
Table 4.2	Bulk composition of sieved limestone	20
Table 4.3	Proximate and ultimate analyses of Illinois #6 coal	21
Table 4.4	Proximate and ultimate analyses of Pittsburgh #8 coal	21
Table 5.1	Listing of experiments using laboratory-scale fluidized bed combustor	23

ACKNOWLEDGMENTS

I would like to thank Dr. Robert Brown and Dr. M. Robert Dawson for offering me the opportunity to work on this research project. Their guidance and support have been a benefit to me through this experience. I thank Dr. H. N. Shapiro and Dr. T. D. Wheelock for serving on my graduate committee. I also thank Amy Gensch for her help during several experiments. The financial support for this research provided by the U.S. Department of Energy, Pittsburgh Energy Technology Center, grant number DE-FG22-92PC92530, is gratefully acknowledged.

CHAPTER 1

INTRODUCTION

The fluidized bed combustor has become a widely accepted technology to produce steam for process heat and electricity generation by burning coal and other low-grade fuels in an environmentally acceptable manner. The advantages of using a fluidized bed combustor over other conventional methods of combustion include the capability of burning high-sulfur fuels, better heat transfer characteristics, and lower operating temperatures [1-3]. Lower operating temperatures of fluidized bed combustors decrease NO_x emissions. The ability to burn high-sulfur fuels is achieved by adding sorbents to the bed during combustion, thus decreasing the need for scrubbers.

The bed material usually consists of an inert solid (e.g., sand) or a sorbent (e.g., limestone or dolomite) which is “fluidized” by an air stream at the bottom of the combustor. Fluidization occurs when the upward force of the air overcomes the gravitational force acting on the bed material. Problems can occur when bed material begins to cohere or “agglomerate”, forming larger particles. The hydrodynamics and heat transfer rates of the fluidized bed also change as particle size changes. Additionally, a loss of fluidization may occur, necessitating combustor shutdown, if the size of the agglomerated particles becomes too large. Untimely combustor shutdown results in loss of operating time, loss of revenue, and additional wear on combustor materials due to thermal cycling.

An occurrence similar to that described above took place within a circulating-fluidized bed combustor located at the Physical Plant of Iowa State University [27]. The circulating fluidized bed combustor produces 170,000 pounds of steam per hour. The steam is used for electricity production, process heat, and cooling for the university. The primary air fans, which fluidize the circulating bed and supply 70% of the combustion air, fell to 75% of normal capacity during day operation. No capacity limitations occurred during low loads at night. Upon shut down of the combustor and inspection of the bed material, several agglomerates were found which were large enough in size to cause the combustor malfunction. Bed temperature prior to combustor shutdown was typical of fluidized bed combustion and no temperature excursion took place. However, preceding the combustor malfunction, coal was fed into the boiler only through the loop seal. The influx of coal at one location produced a fuel-rich region where the loop seal entered the combustor [4]. Dawson et al. [4] suggested that agglomeration of bed particles was the result of reactions involving aluminosilicate and iron oxide particles, catalyzed by localized reducing environments within the combustor.

The goal of this research is to determine the physical conditions and chemical reactions which initiate and contribute to the formation of agglomerates and to relate these reactions to specific causes. Although many mechanisms have been posed, this research tested the hypothesis that localized reducing conditions facilitate bed material agglomeration, even when bed temperatures remain below typical ash fusion temperatures. It is also a goal of this research to determine a method to detect agglomerates and monitor their growth. This information may be utilized by boiler operators to assist them in preventing untimely shutdowns due to agglomeration.

CHAPTER 2

BACKGROUND

Agglomeration of bed material is a process by which particles collide and adhere to form a larger particle, which may inhibit combustor performance. It has been observed that the surfaces of bed particles either become “sticky” or are coated with a layer of “sticky” material [2, 5-10]. Other particles then become “glued” to the sticky surfaces to form a larger, consolidated mass of particles. The cause of bed material agglomeration is not well understood, although several mechanisms based on analytical and experimental observation do exist.

Factors that influence agglomerate formation include temperature [7, 11-12, 18], fuel ash composition [2, 4-6, 8-9, 13-18], and atmosphere [4-5, 9, 15-16], with fuel ash composition receiving the most attention. Agglomeration has been connected to physical circumstances and chemical reactions. These circumstances and reactions may occur at typical fluidized bed combustor operating temperatures, which are lower than ash fusion temperatures [5-8, 17].

2.1 Effect of temperature

Fluidized bed combustors normally operate between 1500 and 1700 °F (825 and 925 °C). Ash softening temperatures range from 2200 to 2650 °F (1200 to 1450 °C). Temperatures at which the ash becomes a liquid range from 2550 to 2725 °F (1400 to 1500 °C) [9, 11, 18, 24]. These temperatures were determined within an oxidizing environment. The softening

and liquid temperatures of the ash can drop by as much as 500 °F (260 °C) in a reducing environment. A reducing environment may lower the eutectic point of mineral matter in coal. However, if temperatures rise above normal operating temperatures, either locally or globally within the combustor, agglomeration is imminent due to ash sintering. Ash sintering is referred to as the agglomeration of bed particles under heat without melting [9]. The extent of bed mixing has a direct effect on the occurrence of local hot spots within the fluidized bed combustor.

Basu and Sarka [11] determined that, above the initial sintering temperature, defluidization may occur even though the fluidization velocity is greater than the minimum fluidization velocity. A linear relationship was found to exist between bed temperature and fluidization velocity for which sintering and defluidization of the bed material would take place. The temperature at which sintering took place increased with increasing fluidization velocity. The correlation between fluidization velocity and bed mixing implies decreased sintering potential with well-mixed beds. The sintering temperature increased with coal ash particle diameter. This result led Basu and Sarka to suggest that agglomeration is a surface phenomenon. However, the study analyzed a small range of particle diameters and neglected any chemical reactions which may have occurred with the coal ash.

Ekinici et al. [12] used temperature profiles to map fluidization patterns along the vertical axis of a fluidized bed combustor. While combusting lignites, the bed temperature decreased near the distributor plate with a simultaneous temperature increase in the upper region of the bed. Ekinici et al. termed this effect “segregation-defluidization.” The effect is caused by density and size differences between the lignite and the bed material. Segregation occurs

when particles of different density or size separate during fluidization forming regions concentrated with similar particles. For example, size and density differences between the lignite and bed material led to a high fraction of the lignite particles combusting in the upper portion of the bed. The result of this segregation was a temperature increase in the upper portion of the bed with a subsequent temperature decrease in the bottom portion of the bed. As the lower portion of the bed cools, it is possible for a layer of lignite ash or other bed particles to accumulate at the distributor plate, thus increasing the bed temperature differential and segregation tendency.

Ekinici and Yardim [22] suggested that temperature measurements may also be used to monitor the formation of agglomerates. They observed that prior to the formation of agglomerates the temperature begins to drop near the distributor plate, which is indicative of segregation. When agglomerates were formed in their experiments the temperature near the distributor plate dropped quickly with a corresponding temperature increase in the upper regions of the bed.

The segregation-defluidization effect experienced by Ekinici et al. [12] led them to conclude that agglomeration will occur if the heat transfer out of the bed is less than the heat generated by combustion. Basu and Sarka [11] reported a similar defluidization effect due to sintering. This effect becomes more likely as the temperature differential across the bed increases due to poor mixing of the bed material. Ekinici et al. [12] as well as Basu and Sarka [11] suggested that the pressure drop across the bed may be used to monitor the formation of agglomerates. As agglomerates form, the bed may segregate and defluidize, causing a decrease in the pressure drop. Recommendations by Ekinici et al. [12] for inhibiting the

segregation-defluidization effect and subsequent agglomeration include increasing the fuel particle size, increasing the fluidization velocity, increasing the length of static and dynamic bed heights, decreasing the ash content, decreasing the density of the bed material, and decreasing the bed particle size.

2.2 Effect of fuel ash composition

The solids within the fluidized bed combustor may consist of fuel particles, sulfur sorbents such as limestone or dolomite, or an inert material such as sand. A small percentage, one to five percent, of the bed material enters as fuel [20]. For the study presented in this thesis, the fuel was coal.

Coal is composed of carbon, mineral matter (ash), and a small percentage of various inorganic elements. Most of the mineral matter found in many types of coal are clay or shale impurities [18]. The majority of the carbon will burn within a fluidized bed combustor. However, the mineral matter may reside within the bed and undergo chemical reactions and physical changes leading to agglomeration. The various inorganic elements, including alkalis, may also play a role in the formation of agglomerates. Consequently, agglomerates may form even when bed temperatures remain below ash fusion temperatures. Recognizing the role played by coal ash, Atakul and Ekinici [21] modified their segregation-defluidization hypothesis. They acknowledged that agglomeration may occur below the sintering temperature and is controlled by the ash properties, especially when the bed is experiencing segregation and defluidization of ash particles. They did not specify which ash properties are important and did not change their experiments to test different ash properties.

The presence of alkali elements within the fuel has been linked to deposition and agglomeration [6, 23]. The elements of importance are sodium (Na) and potassium (K). These elements must be volatile to have any detrimental effect. Sodium and potassium may occur in several different forms within coal. Sodium, for example, may be deposited on coal particle surfaces as a salt (NaCl) or may be organically bound in the coal structure. Sodium and potassium in either of these forms readily volatilize under temperatures experienced during the combustion of coal [23]. However, such elements are not volatile if associated with silicate mineral matter. The alkali elements which volatilize may condense on cooler surfaces within the combustor and form deposits. Agglomerates may form if alkali elements condense on bed particles.

Sodium and potassium may lower the eutectic point in a sulfate matrix. Agglomeration is proposed to take place when two particles coated with a sodium or potassium sulfate-rich material cohere due to sulfate-to-sulfate sintering [6]. As volatilized sodium and potassium elements condense on cooler surfaces, they may react with calcium sulfate forming a sticky substance which acts as a glue for bonding bed particles together.

2.3 Effect of atmosphere

Agglomeration probably occurs due to a combination of effects taking place concurrently. Although extremely high temperatures will agglomerate bed material, typical coal ash fusion temperatures are much higher than normal fluidized bed combustor operating temperatures. Alkali elements within the coal cause agglomeration. However, agglomeration has occurred without the presence of such elements. In many instances, the sintering temperature of

minerals found within the ash can be lowered when subjected to reducing conditions. Such conditions are common in combustors that have staged combustion. Alternatively, volatile combustion may consume the majority of the available oxygen near coal feed locations, robbing the char of oxygen required for combustion.

The agglomeration of bed material at the Iowa State University Power Plant is an example of multiple effects taking place concurrently. Analyses of the agglomerated material revealed that particles of calcium sulfate (CaSO_4) were coated with and bonded to a material comprised of iron, aluminum, and silicon. It was suggested that iron in the form of FeO and/or FeS may have acted as a binding agent and flux for the aluminosilicate ash [4]. This observation, along with the fact that coal was being fed into the boiler at only one location, indicates the iron aluminosilicates coated the bed particles and acted as bonding material. Also, a lack of sodium and potassium in the deposit indicates the agglomeration did not occur due to the presence of alkalis.

Other researchers have recognized the connection between lower melting temperatures and reducing conditions [2, 15-16]. Lower softening temperatures may be the result of a chemical reaction involving two mineral particles catalyzed by reducing conditions. A viscous phase forms on the particle's surface as a consequence of the reaction. This mechanism which results in the formation of a viscous phase is referred to as a fluxing reaction [16]. In cases where fluxing has occurred, e.g., the Iowa State Power Plant, interaction between bed material and particles that have a sticky surface leads to agglomeration and possible loss of fluidization.

A laboratory-scale bubbling fluidized bed combustor that simulates conditions found in commercial combustors was used to investigate the affect of reducing conditions on the agglomerating tendency of bed material. Similarities between the dense phase of a circulating-fluidized bed combustor and a bubbling fluidized bed combustor allow results obtained in the laboratory scale fluidized bed combustor to be applied to circulating-fluidized bed combustors. This correlation can be made because it is hypothesized that agglomerate formation occurs in the dense phase of the circulating fluidized bed combustor.

CHAPTER 3

EXPERIMENTAL APPARATUS

3.1 Fluidized Bed Combustor

A schematic of the laboratory-scale fluidized bed combustor is shown in Figure 3.1. A photograph of the laboratory-scale fluidized bed combustor is shown in Figure 3.2. The laboratory-scale combustor used in these experiments measures 8 inches in diameter (circular cross-section) and 6 feet in height. Fluidization and combustion gases enter the combustor through a distributor plate via the plenum. The operator controls the air flow by adjusting a 1/2-inch globe-needle valve. The flow rate is measured as a pressure drop across an orifice plate located prior to the valve. The pressure drop is measured by a 0 to 5 volts, 0 to 10 inches of water, Schaevitz pressure transducer, Model P3061-10 WD. This transducer has an error of ± 0.05 inches of water. The analog signal produced by the transducer is converted to a digital signal and transformed to a flow rate via the data acquisition program.

Natural gas and nitrogen are mixed with the combustion air prior to the plenum to ensure good mixing of the gases. Natural gas is used to preheat the combustor and nitrogen is used as a supplemental fluidization gas to maintain constant superficial velocities among experiments. Natural gas flow is measured and controlled manually with a Cole Parmer FM 044-40C flow meter. Nitrogen flow is measured and controlled manually with a King Instrument flow meter. All gas flow meters and pressure transducers were calibrated using a wet-flow meter built by The American Meter Company.

Figure 3.1 Laboratory-scale fluidized bed combustor schematic.

Figure 3.2 Laboratory-scale fluidized bed combustor.

Three-eighths inch marbles partially fill the plenum. The marbles act to disperse the fluidization gas to ensure uniform gas flow through the distributor plate. The distributor plate, constructed from 1/2-inch stainless steel plate, contains 250, 3/32-inch evenly spaced holes. An 80 x 80 U.S. mesh stainless steel screen spot welded to the distributor plate prevents flame propagation and prohibits bed material from falling into the plenum.

The stainless steel inner wall of the combustion chamber, which measures 10 inches in diameter and 2 feet in height, is lined with a nominal 1 inch thick layer of Kaocast RFT castable refractory. A water jacket, which encircles the stainless steel liner, removes excess heat from the combustor. The outer wall of the water jacket is constructed of mild steel. Water enters the jacket at the bottom and exits at the top of the combustion zone. The water flow is measured and controlled manually with a Dwyer RMC series flow meter. Several ports are located in the combustion zone. Two, 1 inch ports allow six type K thermocouples to be located within the bed. In addition, three ports located 2, 4, and 6 inches above the distributor plate enable three more thermocouples to be placed in the bed for a total of nine thermocouples within the bed. The type K ungrounded sheath thermocouples measure bed temperature. A list of the thermocouple probe locations is displayed in Table 3.1. The analog output of the thermocouple probe is converted to a digital signal which is read by a personal computer. The data acquisition program converts this signal into a temperature and displays it on the computer screen. An error of $\pm 0.75\%$ is associated with the type K thermocouples.

Three 3/8-inch ports are located 2, 4, and 6 inches above the distributor plate. The bottom two ports measure a pressure differential across the bed while the top port enables a

Table 3.1 Thermocouple probe locations within the fluidized bed combustor.

<u>Thermocouple probe #</u>	<u>Inches above distributor plate</u>	<u>Inches away from combustor wall</u>	<u>Probe location</u>
1	1	4	Combustion Zone
2	1	1	Combustion Zone
3	1.5	2	Combustion Zone
4	2	4	Combustion Zone
5	3	2	Combustion Zone
6	4	4	Combustion Zone
7	4	1	Combustion Zone
8	5	2	Combustion Zone
9	5.5	1	Combustion Zone
10	24	4	Freeboard

1/4-inch stainless steel tube to be inserted into the bed. This stainless steel tube is used to produce a plume of natural gas. The pressure taps are constructed of 3/8-inch stainless steel tubing with 80 x 80 U.S. stainless steel mesh spot welded to the end to prevent bed material from entering and plugging the taps. The pressure drop across the bottom two taps is measured using a 0 to 5 inches of water, 0 to 5 volts direct current, differential pressure transducer model number T20-05D5 from MODUS Instruments, Inc. The error in the differential pressure transducer is ± 0.05 inches of water. High frequency electrical noise is removed from the pressure transducer output using a fourth-order low-pass filter. The analog output is then converted to a digital output which is read by the computer. The data

acquisition program then converts this signal into a pressure drop and displays it on the computer screen.

A 4 foot long, uninsulated freeboard constructed of mild steel is fastened above the combustor. The freeboard also has a circular cross-section which measures 10 inches in diameter. Four ports at the bottom of the freeboard are used for a thermocouple probe, two electrode sparkers, and the coal feeder nozzle. The type K thermocouple probe measures the temperature of the exhaust gases exiting the combustion chamber. The two electrodes extend into the combustion chamber a short distance above the bed surface where they continuously ignite the air / natural gas mixture. Coal is fed into the combustor using an AccuRate Dry Material Feeder, model 602, equipped with a 3/4-inch diameter, full pitch helix.

Exhaust gases and small particles exit the combustor through a port located at the top of the freeboard. Particulates entrained in the exhaust are removed by a high-efficiency Stairmand cyclone constructed of mild steel designed to capture 90% of all particles greater than 10 μm . The particles are collected in a mason jar connected to the bottom of the cyclone. After passing through the cyclone, the exhaust gases are removed from the laboratory via an exhaust fan, which vents the gases to the atmosphere.

3.2 Exhaust gas sampling and analysis equipment

Exhaust gases are sampled by a 3/8-inch diameter probe located in the exhaust pipe. The gas sample is piped to a tar trap via 3/8-inch stainless steel tubing. The stainless steel tubing is heated to 400 °F (200 °C) to prevent condensation of water vapor, corrosive acids, and tars. The gases pass through a tar trap to remove traces of hydrocarbon tars sometimes present in

the sample due to incomplete combustion. The trap consists of a fiberglass filter in glassware immersed in an ice bath. After passing through the tar trap, the sample is reheated to 300°F (150 °C) to ensure no condensation of the sample or possible formation of corrosive acids due to condensation. Any particulates remaining in the sample line are removed by a Balston type 30/12 particulate filter, which also is heated to prevent condensation. An acid-mist filter is used to remove any corrosive vapor in the sample. A Perma-Pure heatless dryer, model PD-625-24-AFS, removes water vapor from the gas sample before it passes through a vacuum pump followed by a manifold system which distributes the sample to the gas analyzers. The vacuum pump is a Thomas Industries model 2107CA14.

Five gas analyzers are used to provide continuous measurement of exhaust gas composition, including O₂, CO₂, CO, SO₂, and NO_x. Two Beckmann model 820 non-dispersive infrared spectrometers are used to measure CO and CO₂ concentration with a calibrated peak value of 0.8% for CO and 15.0% for CO₂. The measurement errors for CO and CO₂ are 0.012% and 0.2%, respectively. A Beckmann model 755 oxygen analyzer monitors O₂ concentration with a calibrated peak value of 8.15% (molar basis) with an error of ±0.25% (molar basis). Two Horiba model VIA-500 and VIA-300 non-dispersive infrared spectrometers are used to measure SO₂ and NO_x concentrations with calibrated peak values of 1500 parts per million (ppm) and 795 ppm with errors of 20 and 10 ppm, respectively. The output from each gas analyzer is converted to a digital signal and converted by the data acquisition program into the desired output for each gas.

3.3 Data monitoring and recording equipment

The combustor operating parameters are monitored, displayed, and recorded using a Hewlett Packard 386 SX 16 MHz personal computer. The computer utilizes a MetraByte DAS-8 interface board, Part Number 24810, to retrieve data from various bed monitoring equipment including bed temperature, bed pressure drop, air flow rate, and exhaust gas composition. Current data is displayed on the computer screen using a data acquisition program written in Quick Basic. The data is recorded to a file at 5 second intervals.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Experimental setup

Each experiment used 3.75 liters of either sand or limestone for the bed material. The sand came from Hallet's quarry located near Boone, Iowa and the limestone came from Martin Marietta's quarry located near Ames, Iowa. Both the sand and limestone were sieved to a top size of 20 U.S. mesh (0.0328 inches) and a bottom size of 30 U.S. mesh (0.0232 inches). Tables 4.1 and 4.2 show the bulk composition on a weight basis for sand and limestone. Two types of coal were used: Illinois #6 and Pittsburgh #8. The coal was sieved to a bottom size of 8 U.S. mesh (0.093 inches) with a nominal top size of 3/8-inch (0.375 inches). The sized coal was then divided into equal aliquots. Tables 4.3 and 4.4 show the proximate and ultimate analysis for Illinois #6 and Pittsburgh #8 coals.

4.2 Experimental startup, steady-state operating conditions, and termination

Methane is used to preheat the bed to at least 1300 °F (700 °C) at which point coal is fed into the combustor. The coal feed rate is increased and the methane flow rate decreased simultaneously until the bed is burning only coal. Excess air is used during preheat to ensure a minimum of 2% oxygen in the exhaust gas. After the transition from methane to coal is complete, the air flow rate, nitrogen flow rate, and coal feed rate are all adjusted to achieve the desired equivalence ratio, fluidization gas flow rate, and bed operating temperature. The

equivalence ratio in this study is defined as the air to fuel ratio. Therefore an equivalence ratio of 1.20 is analogous to 120% theoretical air or 20% excess air.

Equivalence ratios ranged from 0.50 to 1.20. The fluidization gas flow rate was usually 13.5 standard cubic feet per minute (scfm) which corresponds to a superficial velocity of 2.51 feet per second (0.76 meters per second) at 1600 °F (870 °C). Nitrogen, an inert gas, supplemented the air to maintain a constant superficial gas flow rate from test to test. Nominal bed temperatures ranged from 1500-1700 °F (815-925 °C). For some experiments conducted under reducing conditions, a methane plume was utilized to produce a localized reducing condition in the bed. The plume allows extreme reducing conditions to be achieved at a well-defined location in the bed. This localized reducing zone may initiate reactions which only take place under highly reducing conditions, similar to those found near coal feed points in industrial-scale combustors.

Tests were terminated for several reasons. First, if the bed temperature rose above 1700 °F (925 °C) the experiment was terminated to prevent melting of bed material. Second, if the bed became defluidized due to agglomeration or ash build-up, the experiment was terminated. Ash build-up occurred during coal combustion because no overflow pipe is included in the combustion zone. Third, the experiment was terminated if the coal feeder hopper emptied. Upon termination of the experiment the coal feed was secured, the nitrogen and cooling water flow rates increased, and the air flow decreased to maintain the test end oxygen concentration throughout the termination period. Nitrogen was used to cool the bed

to room temperature. Upon removal the bed would be weighed to determine bulk density, which could then be compared with the pretest bed bulk density.

Table 4.1 Bulk composition of sieved sand.

<u>Component</u>	<u>Weight Percent</u>	<u>Component</u>	<u>Weight Percent</u>
SiO ₂	69.50	SO ₃	0.14
Al ₂ O ₃	7.46	TiO ₂	0.10
CaO	7.35	SrO	0.09
MgO	2.32	P ₂ O ₅	0.06
Na ₂ O	2.08	BaO	0.04
K ₂ O	1.38	MnO	0.02
Fe ₂ O ₃	1.02	LOI	7.63

Table 4.2 Bulk composition of sieved limestone.

<u>Component</u>	<u>Weight Percent</u>	<u>Component</u>	<u>Weight Percent</u>
SiO ₂	2.10	SO ₃	0.97
Al ₂ O ₃	1.04	TiO ₂	0.05
CaO	96.82	SrO	0.09
MgO	2.00	P ₂ O ₅	0.10
Na ₂ O	0.19	BaO	0.04
K ₂ O	0.02	MnO	0.01
Fe ₂ O ₃	0.41	LOI	7.63

Table 4.3 Proximate and ultimate analyses of Illinois #6 coal.

	<u>As Received</u>	<u>Dry</u>
Moisture (%)	4.8	0.0
Ash (%)	26.5	27.9
Volatile (%)	32.1	33.7
Fixed Carbon (%)	36.6	38.4
Carbon (%)	54.40	57.10
Hydrogen (%)	4.00	3.64
Nitrogen (%)	0.94	0.99
Total Sulfur (%)	4.88	5.12
Ash (%)	26.53	27.85
Oxygen (difference) (%)	9.25	5.30

Table 4.4 Proximate and ultimate analyses of Pittsburgh #8 coal.

	<u>As Received</u>	<u>Dry</u>
Moisture (%)	1.2	0.0
Ash (%)	27.5	27.9
Volatile (%)	34.8	35.2
Fixed Carbon (%)	36.5	36.9
Carbon (%)	59.90	60.65
Hydrogen (%)	4.36	4.27
Nitrogen (%)	0.97	0.98
Total Sulfur (%)	4.93	4.99
Ash (%)	27.51	27.86
Oxygen (difference, %)	2.33	1.25

CHAPTER 5

RESULTS AND DISCUSSION

Experiments were performed to determine the effect of reducing atmospheres on agglomerate formation during fluidized bed coal combustion. Variables tested include equivalence ratio, bed material composition, and the presence of a methane plume in the bed. Analyses of agglomerates formed in fluidized bed combustors [4] and previous experiments performed in the laboratory-scale fluidized bed combustor [28] suggest equivalence ratios less than unity may promote the formation of agglomerates. A methane plume was used to achieve extreme reducing conditions in a well-defined location of the bed. Sand was utilized as a bed material because it is an inert material. Therefore, reactions leading to agglomeration will only be influenced by coal composition and equivalence ratio. Experiments performed using limestone as the bed material may include additional reactions involving calcium compounds, which may lead to agglomeration. The laboratory-scale fluidized bed combustor was utilized to test these variables. A listing of the experiments is shown in Table 5.1.

5.1 Oxidizing conditions with sand as bed material

This experiment was performed under oxidizing conditions using approximately the same amount of excess air as industrial-scale boilers. The experiment is a baseline case to be compared with tests performed under reducing conditions. A minimum equivalence ratio of 1.10, or 110% theoretical air, was maintained throughout the experiment. Air was the only

Table 5.1 Listing of experiments using laboratory-scale fluidized bed combustor

Equivalence Ratio	Bed Material	Flow Rate (scfm)	Methane Plume?	Agglomerates Formed?	Temperature Excursion?
0.50	Sand	13.5	No	No	No
0.50*	Sand	13.5	Yes	Yes	No
1.10*	Sand	13.5	No	No	No
0.50*	Sand	13.5	No	No	No
0.70	Sand	13.5	No	No	No
0.60	Sand	9.5	No	No	No
0.60	Sand	9.5	No	No	No
1.10	Sand	10.5	No	No	No
0.50*	Limestone	13.5	No	Yes	No
0.50	Limestone	13.5	Yes	Yes	Yes
0.50	Limestone	13.5	No	Yes	Yes
0.50	Limestone	13.5	No	Yes	Yes
0.50	Limestone	13.5	Yes	Yes	Yes
0.50*	Limestone	13.5	Yes	Yes	No
0.70	Limestone	13.5	Yes	No	No
0.60	Limestone	13.5	No	Yes	No
1.20	Limestone	9.5	No	No	No
1.20*	Limestone	13.5	No	No	No

* - results of experiment displayed and discussed below

constituent of the fluidization gas. The fluidization gas flow rate was set at a value of 13.5 scfm which corresponds to a superficial fluidization velocity of 2.51 feet per second (0.76 meters per second) at a bed temperature of 1600 °F (870 °C). Pittsburgh #8 coal was used as the fuel. Figures 5.1 through 5.3 display the data obtained during this experiment. The data include bed temperatures, bed pressure drop, and exhaust gas composition.

Bed temperatures ranged from 1500 °F to 1650 °F (815 to 900 °C) throughout the experiment. At time $\approx$ 155 minutes the temperature at thermocouple probe #2 began to decrease. Subsequent temperature decreases occurred at thermocouple probe #1 (time $\approx$ 220 minutes), thermocouple probe #3 (time $\approx$ 245 minutes), and thermocouple probe #4 (time $\approx$ 260 minutes). The decrease in temperature at each probe location is due to large ash particles defluidizing.

Figure 5.1 Combustor temperatures for equivalence ratio of 1.10 (110% theoretical air). (a) thermocouple probe #10, (b) thermocouple probe #2, (c) thermocouple probe #1, (d) thermocouple probe #3, (e) thermocouple probe #4.

Figure 5.2 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 1.10 (110% theoretical air).

Figure 5.3 Exhaust gas composition for equivalence ratio of 1.10 (110% theoretical air).

The magnitude of the bed pressure drop remained at a constant value of 2.25 inches of water for the majority of the experiment. The magnitude of the bed pressure drop began to decrease at time ≈ 220 minutes at a rate of 0.52 inches of water per hour. The decrease was probably the result of defluidization of the bed material although thermocouple probe #4, which is at the same height as the bottom pressure tap, didn't begin decreasing in temperature until time ≈ 260 minutes.

The carbon dioxide concentration averaged 14% for the majority of the experiment. The oxygen concentration varies with time making it difficult to determine an average value. In any event, excess oxygen is present as evidenced by the minimum oxygen concentration of 3% during coal combustion. A low carbon monoxide concentration existed throughout the experiment. In contrast sulfur dioxide emissions were higher than the calibrated peak value of 1500 ppm.

5.2 Reducing conditions with sand as bed material

This experiment was performed under reducing conditions. It is hypothesized that these conditions are similar to those which may occur in industrial size boilers. An equivalence ratio of 0.50, or 50% theoretical air, was achieved and then maintained throughout the remainder of the experiment. A lower equivalence ratio was not used because the combustor becomes increasingly difficult to control at lower ratios. Air and nitrogen combined to achieve a fluidization gas flow rate of 13.5 scfm. Pittsburgh #8 coal was used as the fuel. Figures 5.4 through 5.6 display the data obtained during this experiment. The data include bed temperatures, bed pressure drop, and exhaust gas composition.

The bed temperature climbed slowly throughout the majority of the test from a value of 1575 °F (860 °C) at time $\approx$ 50 minutes to a maximum value of 1700 °F (925 °C) at time $\approx$ 132 minutes. At time $\approx$ 50 minutes the temperature at thermocouple probe #2 began to decrease due to defluidization. Subsequent temperature decreases occurred at thermocouple probe #1 (time $\approx$ 98 minutes), thermocouple probe #4 (time $\approx$ 112 minutes), and thermocouple probe #3 (time $\approx$ 115 minutes). The decrease in temperature at each probe location is due to large ash particles defluidizing.

The bed pressure drop decreased in magnitude between the time the combustor began operating on coal (time $\approx$ 17 minutes) to time $\approx$ 72 minutes. At 72 minutes the magnitude of the bed pressure drop stabilized at a value of 1.95 inches of water. The magnitude of the bed

Figure 5.4 Combustor temperatures for equivalence ratio of 0.50 (50% theoretical air). (a) thermocouple probe #10, (b) thermocouple probe #2, (c) thermocouple probe #1, (d) thermocouple probe #3, (e) thermocouple probe #4.

Figure 5.5 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.6 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

pressure drop remained at this value despite the fact thermocouple probe #4, located at the same height as the bottom pressure tap, began decreasing in temperature, indicative of large ash particle defluidization.

The carbon dioxide concentration averaged 12.5% for the majority of the experiment after the desired condition of 50% theoretical air was achieved. The step changes in the carbon dioxide concentration near the end of the experiment are the result of adjustments in the air and nitrogen flow rates. The oxygen concentration remained at 0% for the portion of the experiment when reducing conditions were present. The carbon monoxide and sulfur dioxide concentrations were higher than the calibrated peak values of the respective monitors.

The experiment ended because the bed temperature at several thermocouple probe locations was reaching the maximum allowable value of 1700 °F (925 °C). Upon removal of the bed material no agglomerates were retrieved. One explanation for the lack of agglomerates may be that the equivalence ratio was not low enough to initiate the reactions necessary for agglomerate formation.

5.3 Reducing conditions and methane plume with sand as bed material

This experiment was performed under reducing conditions. It is hypothesized that these conditions are similar to those which may occur in industrial size boilers. An equivalence ratio of 0.50, or 50% theoretical air, was achieved and then maintained throughout the remainder of the experiment. Additionally, a methane plume was induced to create a well-defined zone in the bed that would experience extreme reducing conditions. It is hypothesized that such extreme reducing conditions may occur near coal feed points in industrial scale boilers. It was

also thought that the extreme reducing conditions were needed to form agglomerates because no agglomerates were formed in the experiment conducted at an equivalence ratio of 0.50 (discussed in Section 5.2). Air and nitrogen combined to achieve a fluidization gas flow rate of 13.5 scfm. Pittsburgh #8 coal was used as the fuel. Figures 5.7 through 5.9 display the data obtained during this experiment. The data include bed temperatures, bed pressure drop, and exhaust gas composition.

An average bed temperature of 1600 °F (870 °C) was experienced during the majority of the experiment. At time $\approx$ 65 minutes the temperature at thermocouple probe #2 began to decrease due to defluidization. Subsequent temperature decreases occurred at thermocouple probe #1 (time $\approx$ 110 minutes), thermocouple probe #3 (time $\approx$ 133 minutes), and

Figure 5.7 Combustor temperatures for equivalence ratio of 0.50 (50% theoretical air). (a) thermocouple probe #10, (b) thermocouple probe #2, (c) thermocouple probe #1, (d) thermocouple probe #3, (e) thermocouple probe #4.

Figure 5.8 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.9 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

thermocouple probe #4 (time $\approx$ 133 minutes). The decrease in temperature at each probe location is due to large ash particles defluidizing.

The bed pressure drop decreased in magnitude between the time the combustor began operating on coal to the time methane flow was initiated. At that point the magnitude of the bed pressure drop stabilized. At time $\approx$ 122 minutes the bed pressure drop began to decrease in magnitude at a rate of 0.99 inches of water per hour. At time $\approx$ 136 minutes the bed pressure drop began to increase in magnitude at a rate of 1.37 inches of water per hour. At time $\approx$ 141 minutes the magnitude of the bed pressure drop decreased rapidly. The experiment was terminated shortly thereafter. The change in the magnitude of the bed pressure drop could be the result of either defluidization or agglomeration or both. The thermocouple at the height of the bottom pressure tap (probe # 4) was decreasing in temperature which would indicate defluidization. However, bed material agglomerated during this experiment which may have instigated the bed pressure drop fluctuations.

The carbon dioxide concentration averaged 12.75% after the methane flow was induced. The oxygen concentration remained at 0% for the portion of the experiment when reducing conditions were present. The carbon monoxide and sulfur dioxide concentrations were higher than the calibrated peak values of the respective monitors.

The experiment ended because the bed temperature at several thermocouple probe locations was reaching the maximum allowable value of 1700 °F (925 °C). Also, the bed pressure drop and moving average bed pressure data indicated either defluidization or agglomeration was taking place. Upon removal of the bed material, one golf ball size

Figure 5.10 Agglomerate formed under reducing conditions with sand as the bed material.

agglomerate, shown in Figure 5.10, was retrieved. The agglomerate was located just under the surface of the bed at the center of the combustor. The agglomerate appeared to be composed of coal char and coal ash with very little sand present. The agglomerate was blackish-gray in color.

5.4 Oxidizing conditions with limestone as bed material

This experiment was performed under oxidizing conditions using approximately the same amount of excess air as industrial-scale boilers. The experiment is a baseline case to be compared with tests performed under reducing conditions. A minimum equivalence ratio of 1.20, or 120% theoretical air, was maintained throughout the experiment. Air and nitrogen

combined to achieve a fluidization gas flow rate of 13.5 scfm. Illinois #6 coal was used as the fuel. Figures 5.11 through 5.14 display the data obtained during this experiment. The data include temperatures, bed pressure drop, and exhaust gas composition.

An average bed temperature of 1575 °F (860 °C) was experienced during most of the test. The temperature increase at time $\approx$ 52 minutes corresponds to the completion of the endothermic calcination reaction. At time $\approx$ 225 minutes the temperature at thermocouple probe #1 began to decrease due to large ash particles defluidizing. The initial location for defluidization differs between this test and the test reported above that used sand as the bed material. It is unclear why defluidization begins at the center of the combustor when limestone is used and at the wall when sand is used as the bed material.

The initial decrease in the magnitude of the bed pressure drop is also a result of the calcination reaction. The subsequent increase in the bed pressure drop magnitude is a result of the sulfation reaction. At time $\approx$ 190 minutes the bed pressure drop stabilizes at a value of 1.6 inches of water. At time $\approx$ 230 minutes the bed pressure drop began to decrease in magnitude. Although this decrease is small compared to instances when agglomerates occur, it is unclear why the decrease occurred in this experiment.

During the calcination of the limestone, the carbon dioxide concentration exceeded the peak calibrated value of 15.0%. As the experiment progressed the carbon dioxide concentration decreased at a rate of 0.33% per hour while the oxygen concentration increased at a rate of 0.34% per hour. A possible explanation for the change in oxygen and carbon dioxide concentrations involves the sulfation reaction. The amount of oxygen consumed to

Figure 5.11 Combustor temperatures for equivalence ratio of 1.20 (120% theoretical air).
(a) thermocouple probe #10, (b) thermocouple probe #1.

Figure 5.12 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 1.20 (120% theoretical air).

Figure 5.13 Exhaust gas composition for equivalence ratio of 1.20 (120% theoretical air).

Figure 5.14 Exhaust gas composition for equivalence ratio of 1.20 (120% theoretical air).

complete the sulfation reaction will decrease as the calcium oxide is depleted. The result will be an increase in oxygen and decrease in carbon dioxide as discussed above. A low carbon monoxide concentration was experienced throughout the experiment. The sulfur dioxide concentration was approximately zero until time ≈ 60 minutes. At this time the concentration began to increase linearly at a rate of 260 ppm per hour. At time ≈ 135 minutes the sulfur dioxide concentration continued to increase linearly at a new rate of 645 ppm per hour. There is no explanation for the change in the rate of increase.

5.5 Reducing conditions and methane plume with limestone as bed material

This experiment was performed under reducing conditions. It is hypothesized that these conditions are similar to those which may occur in industrial size boilers. An equivalence ratio of 0.50, or 50% theoretical air, was achieved and then maintained throughout the remainder of the experiment. Additionally, a methane plume was induced, as it was in the test with sand as the bed material, to simulate highly reducing conditions, which may occur near coal feed points in industrial scale boilers. Air and nitrogen combined to achieve a fluidization gas flow rate of 13.5 scfm. Pittsburgh #8 coal was used as the fuel. Figures 5.15 through 5.18 display the data obtained during this experiment. The data include bed temperatures, bed pressure drop, and exhaust gas composition.

Bed temperatures ranged from 1525 to 1650 °F (830 to 900 °C) after the calcination reaction was complete. The temperature increase at time ≈ 70 minutes was the result of completion of the endothermic calcination reaction. At time ≈ 65 minutes the temperature at

Figure 5.15 Combustor temperatures for equivalence ratio of 0.50 (50% theoretical air). (a) thermocouple probe #10, (b) thermocouple probe #1, (c) thermocouple probe #2, (d) thermocouple probe #3, (e) thermocouple probe #4.

Figure 5.16 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.17 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.18 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

thermocouple probe #1 began to decrease due to defluidization. Subsequent defluidization occurred at thermocouple probe #2 (time $\approx$ 105 minutes). Just prior to experiment termination the temperatures at the remainder of the thermocouple probes began a rapid decrease. This decrease is attributed to agglomeration.

The initial decrease in the magnitude of the bed pressure drop is also a result of the calcination reaction. The bed pressure drop then stabilized at a value of 1.2 inches of water until time $\approx$ 92 minutes when its magnitude began to decrease until the experiment was terminated. The decrease in bed pressure drop was likely due to agglomeration of the bed material.

During the calcination of the limestone the carbon dioxide concentration exceeded the peak calibrated value of the carbon dioxide monitor. A steady-state value was never achieved as the carbon dioxide concentration decreased as the desired condition of 50% theoretical air was achieved and then began to increase shortly after the methane plume was initiated. The oxygen concentration decreased to zero and remained at that value for the remainder of the experiment.

The carbon monoxide concentration increased at a rate of 1.36% per hour until the peak calibration value of 0.8% was exceeded. The sulfur dioxide concentration remained below 100 ppm until reducing conditions were achieved at which time the sulfur dioxide concentration began to increase beyond the calibrated peak value of 1500 ppm. At time $\approx$ 84 minutes the sulfur dioxide concentration began to decrease at a sporadic rate until the experiment was terminated. The SO_2 concentration decrease may be the result of the sulfur

being released as hydrogen sulfide (H_2S) which can not be detected with the present gas analysis setup.

The experiment ended because the bed temperature at several thermocouple probe locations was decreasing uncontrollably. Also, the bed pressure drop and moving average bed pressure data indicated either defluidization or agglomeration was taking place. Upon removal of the bed material, agglomerates ranging from marble to golf ball in size were retrieved. The agglomerates are shown in Figure 5.19. The agglomerates were located approximately 4 inches above the distributor plate at the center of the combustor. The agglomerates appear to be composed of coal char and coal ash with limestone particles covering the surface. The agglomerates were a blackish-gray color with a half-coated white surface.

Figure 5.19 Agglomerate formed under reducing conditions with limestone as the bed material.

5.6 Reducing conditions with limestone as bed material

This experiment was performed under reducing conditions. It is hypothesized that these conditions are similar to those which may occur in industrial size boilers. An equivalence ratio of 0.50, or 50% theoretical air, was achieved and then maintained throughout the remainder of the experiment. A methane plume was not utilized during this experiment to determine if agglomerates would form without the highly reducing zone or if this experiment would be analogous to the experiment with the sand bed when no agglomerates formed (Section 5.2). Air and nitrogen combined to achieve a fluidization gas flow rate of 13.5 scfm. Pittsburgh #8 coal was used as the fuel. Figures 5.20 through 5.23 display the data obtained during this experiment. The data include temperatures, bed pressure drop, and exhaust gas composition.

Bed temperatures ranged from 1575 to 1650 °F (860 to 900 °C) after the calcination reaction was complete. The temperature increase at time $\approx$ 50 minutes was the result of completion of the calcination reaction. At time $\approx$ 58 minutes the temperature at thermocouple probe #1 began to decrease due to defluidization. Subsequent defluidization occurred at thermocouple probe #2 (time $\approx$ 77 minutes), thermocouple probe #3 (time $\approx$ 83 minutes), and thermocouple probe #4 (time $\approx$ 89 minutes). Just prior to experiment termination the temperatures at the remainder of the thermocouple probes began a rapid decrease. This decrease is attributed to agglomeration.

The initial decrease in the magnitude of the bed pressure drop is also a result of the calcination reaction. The bed pressure drop then stabilized at a value of 1.2 inches of water until time $\approx$ 68 minutes when its magnitude began to decrease until the experiment was

Figure 5.20 Combustor temperatures for equivalence ratio of 0.50 (50% theoretical air). (a) thermocouple probe #10, (b) thermocouple probe #1, (c) thermocouple probe #2, (d) thermocouple probe #3, (e) thermocouple probe #4.

Figure 5.21 Bed pressure drop and modified moving-average bed pressure drop for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.22 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

Figure 5.23 Exhaust gas composition for equivalence ratio of 0.50 (50% theoretical air).

terminated. The decrease in the magnitude and increase in the fluctuations of the bed pressure drop were likely due to agglomeration of the bed material.

During the calcination of the limestone the carbon dioxide concentration exceeded the peak calibrated value of the carbon dioxide monitor. A quasi-steady-state value of 12% was achieved shortly after the desired condition of 50% theoretical air was achieved. The carbon dioxide concentration began to increase at time ≈ 85 minutes until the end of the experiment. The oxygen concentration decreased to zero and remained at that value for the remainder of the experiment.

The carbon monoxide concentration increased at a rate of 0.63% per hour until the peak calibration value and eventually the detecting limit of the monitor were exceeded. The sulfur dioxide concentration remained below 100 ppm until reducing conditions were achieved at which time the sulfur dioxide concentration began to increase beyond the calibrated peak value of 1500 ppm.

The experiment ended because the bed temperature at several thermocouple probe locations was increasing at a rapid rate. Also, the bed pressure drop and moving average bed pressure data indicated either defluidization or agglomeration was taking place. Upon removal of the bed material, agglomerates ranging from marble to golf ball in size were retrieved. The agglomerates are similar to those shown in Figure 5.19. The agglomerates were located approximately 3 to 4 inches above the distributor plate scattered across the cross-section of the combustor. The agglomerates appear to be composed of coal char and coal ash with limestone particles covering the surface. The agglomerates were a blackish-gray color with a half-coated white surface.

5.7 Discussion

Baseline tests were conducted under oxidizing conditions. No agglomerates were expected and no agglomerates were formed during these experiments. Agglomerates were expected for experiments conducted in a reducing atmosphere. However, agglomerates were retrieved for most, but not all, experiments conducted under reducing conditions. A methane plume was required to form agglomerates for experiments conducted under reducing conditions with sand as the bed material. Thus, a lower equivalence ratio was required to form agglomerates in a bed of sand as opposed to a bed of limestone. It is hypothesized that additional reactions involving calcium compounds increased the agglomeration tendency of the bed material when limestone was used.

Data acquisition equipment was used to monitor and record combustor operating parameters including bed temperature, bed pressure drop, and exhaust gas emissions. It has also been determined that bed temperatures and bed pressure drop may be used to detect and monitor agglomerate formation.

Thermocouple probes (locations listed in Table 3.1) located throughout the bed material are used to monitor the mixing condition of the bed. Uniform bed temperatures are characteristic of a well-mixed bed. A temperature gradient within the bed indicates partial defluidization of the bed may be occurring, generally near the distributor plate. Large diameter ash particles may settle out of the actively fluidized bed and come to rest at the bottom of the bed. The combusting coal particles and hot bed material are unable to interact with the defluidized particles, which results in decreasing temperatures near the distributor

plate. Experiments show (Sections 5.1, 5.2, and 5.4) that defluidization of bed material does not lead to agglomeration.

Pressure taps located 2 and 4 inches above the distributor plate measure the bed pressure drop. The bed pressure drop (Δp) is directly related to the weight of the material (W) located between the pressure taps and inversely related to the cross-sectional area (A) of the combustor by the following equation:

$$\Delta p = \frac{W}{A} \quad [25].$$

Also, once fluidization is achieved, the magnitude of the bed pressure drop is relatively independent of the fluidization gas flow rate and, therefore, remains constant. The bed pressure drop magnitude will change if the density of the material between the taps changes or if bed material defluidizes between the taps. With limestone as the bed material, the magnitude of the bed pressure drop decreased as the limestone calcined due to the decreased density of calcium oxide (CaO) compared to calcium carbonate (CaCO_3). In contrast, the sulfation of the calcium oxide to calcium sulfate (CaSO_4) resulted in an increase in the bed pressure drop due to the larger density of the calcium sulfate compared to the calcium oxide.

Bed material agglomeration was observed to cause abnormal fluctuations and/or a decrease in the magnitude in the bed pressure drop. Such irregularities in the bed pressure drop may be used to detect and monitor agglomerate formation. As agglomerates grow, they may become too large to remain supported by the fluidizing gas. The agglomerated particles

may then contribute to slugging, jetting, or defluidization of the bed material. A slugging or jetting bed may result in abnormal pressure drop fluctuations. A magnitude decrease of the bed pressure drop indicates defluidization.

A method employed to monitor changes in the magnitude of the bed pressure drop and detect agglomerates is based on a modified moving average analysis of the bed pressure drop data. A moving average is calculated by determining the statistical mean of the current data point and a given number of previous data points. When a new data point is recorded the oldest data point is dropped to enable determination of the mean using the same number of data points each time. The modified moving average is calculated by subtracting the average of the last ten data points from the average of the last one-hundred data points. The modified moving bed pressure drop average for a given data point is determined by the following equation:

$$\Delta p[n] = \frac{\sum_{j=0}^{100} \Delta p[n-j]}{100} - \frac{\sum_{k=0}^{10} \Delta p[n-k]}{10}$$

During steady-state operation the difference between the ten and one-hundred moving point averages should be small, on the order of ± 0.03 inches of water. Instability within the combustor due to agglomeration, evidenced as increased pressure drop fluctuations or change in bed pressure drop magnitude, can be recognized as larger deviations from zero, on the magnitude of ± 0.15 inches of water. A positive value of the modified moving average

indicates the bed pressure drop is decreasing in magnitude while a negative value indicates the bed pressure drop is increasing in magnitude over time.

The exhaust gas composition is representative of the conditions under which combustion is taking place. For baseline tests, excess oxygen will be present for equivalence ratios larger than one. For tests conducted under reducing conditions, equivalence ratios less than one, the oxygen level will be at or near zero. Carbon dioxide levels are dependent on fuel flow rate and oxygen availability and does not give a direct indication of combustion conditions. Carbon monoxide will be emitted in high concentrations (beyond the calibrated peak value of the monitor) during experiments with an equivalence ratio less than unity but will have a relatively low concentration during baseline experiments. Sulfur dioxide emissions are greater than the calibrated peak value of the monitor for experiments which utilize a sand bed. When limestone is used as the bed material, sulfur dioxide is virtually non-existent in the exhaust gas stream. However, as the experiment proceeds and calcium oxide is consumed, sulfur dioxide emissions will increase. If combustion takes place at an equivalence ratio less than unity, the sulfation reaction may not proceed as it would under oxidizing conditions. It is possible that calcium sulfate already formed can decompose to calcium oxide, sulfur dioxide (SO_2), or hydrogen sulfide (H_2S) [26]. NO_x emission data were not utilized for this research.

Analyses of agglomerates formed in the laboratory-scale fluidized bed combustor indicate iron, in the form of FeO or FeS , may have acted as a flux for the aluminosilicate ash. As a result of the fluxing reaction, a viscous material comprised of iron, aluminum, and silicon may “flow” over other bed particles making the surface of the bed particles “sticky.” Bed particles may adhere to the “sticky” bed particles resulting in an agglomerate. The results of the

laboratory-scale combustor agglomerate analyses resemble analyses of agglomerates retrieved from the Iowa State circulating-fluidized bed combustor [4, personal communication with Dr. Robert Dawson, 1995].

CHAPTER 6

CONCLUSIONS

Experiments performed support the hypothesis that a reducing atmosphere during fluidized bed coal combustion contributes to the formation of agglomerates. A summary of these experiments can be found in Table 5.1. Reducing conditions are imposed by controlling the amount of combustion air supplied to the combustor, 50% of theoretical in these experiments. It is hypothesized the reducing conditions induced in the laboratory-scale fluidized bed combustor simulate conditions which may be found in industrial size boilers. These localized reducing conditions may arise from either poor lateral bed mixing or oxygen-starved conditions due to the coal feed locations.

Analyses of agglomerates formed in both the Iowa State University circulating fluidized bed combustor and the laboratory-scale fluidized bed combustor reveal a material high in iron, silicon, and aluminum coated bed particles and acted as a bonding agent. These results support the hypothesis that reducing conditions present during combustion lead to the presence of iron in a reduced state of FeS or FeO. The reduced iron acts as a flux for the aluminosilicate ash resulting in a viscous substance which may “flow” over other bed particles making the surface of these particles “sticky.” Bed particles may adhere to the “sticky” surface of the coated particles resulting in an agglomerate.

Agglomerates formed in the laboratory scale combustor as the equivalence ratio approached 0.50 and a methane plume was utilized. However, with 50% theoretical air

conditions without the methane plume, agglomerates were formed in the limestone bed but not in the sand bed. It is possible that reactions with calcium compounds contribute to the agglomerating tendency of the limestone bed. The absence of calcium compounds in the sand bed requires a lower equivalence ratio for agglomerate formation. In this study a methane plume was utilized to reduce the equivalence ratio below 0.50.

Data acquired from equipment which monitor the operating conditions of a combustor may be used to detect agglomerate formation. Deviations from steady-state operating conditions in bed pressure drop and/or bed temperature may indicate the presence of agglomerates. These deviations may be observed as bed temperature swings or a change in magnitude of the bed pressure drop and/or increased bed pressure drop fluctuations. Interpretation of the bed pressure drop was made more straight-forward by employing a moving-average difference method. During steady-state operation the difference between the moving point averages should be close to zero, within ± 0.03 inches of water. Instability within the combustor, experienced once agglomerates begin to form, can be recognized as larger deviations from zero, on the magnitude of ± 0.15 inches of water.

Several modifications to the laboratory-scale combustor would be beneficial for further study of agglomeration during fluidized bed coal combustion. First, a method to remove coal ash from the bottom of the combustor would allow longer combustion tests giving greater similarity to steady-state conditions found in industrial-scale boilers. Also, coal ash removal would eliminate, or at least limit, defluidization which may inhibit the ability to utilize bed pressure drop readings for monitoring agglomerate formation. Second, an additional pressure tap would improve agglomerate monitoring capabilities. The three pressure taps present

allow 4 inches of vertical bed coverage starting 2 inches above the distributor plate. An additional pressure tap near the distributor plate would increase the vertical bed coverage and would improve agglomerate monitoring capabilities. Third, additional thermocouple probes would enable the combustor operator to monitor bed temperature to ensure no temperature excursions occur due to poor bed mixing.

Results obtained using the laboratory-scale combustor may be applied to industrial-scale combustors. The method of feeding coal into industrial-scale combustors is of utmost importance. If coal feed is limited to one location localized reducing zones may occur. Such localized reducing zones may lead to agglomeration as shown by this research. It is also important to maintain a well-mixed bed. Poor bed mixing may lead to fuel rich zones or local hot spots and subsequent agglomeration.

More research should be conducted to further develop and test remedial actions after agglomeration occurs. Such actions include increasing the equivalence ratio, which would diminish the possibility of reducing conditions. Another action includes increasing the fluidization gas flow rate. The effect would be the same as first mentioned, increasing equivalence ratio, if air was the fluidization gas. Also, the effect would be increased bed mixing which would diminish the possibility of localized reducing zones and might possibly break up agglomerates through particle collisions.

REFERENCES

- [1] Congalidis, J. P. and Georgakis, C. "Multiplicity patterns in atmospheric fluidized bed coal combustors." *Chemical Engineering Science*, 36(9), 1529-1546, 1981.
- [2]. Oakey, J. E., Minchester, A. J., and Stringer, J. "Ash deposition in atmospheric-pressure fluidised-bed combustion systems." *Journal of the Institute of Energy*, 208-219, February, 1989.
- [3] Radovanovic, M. "Introduction." In Fluidized Bed Combustion. M. Radovanovic, ed.; Hemisphere Publishing Corporation: New York, 1986.
- [4] Dawson, M. R., Miller, D. J., and Buttermore, W. H. "Bonded deposit formation during high-sulfur coal utilization in a circulating fluidized bed boiler." In Processing and Utilization of High-Sulfur Coals III, R. Markuszewski and T. D. Wheelock, eds.; Elsevier: Amsterdam, 1990.
- [5] Dawson, M. R. and Brown, R. C. "Bed material cohesion and loss of fluidization during fluidized bed combustion of midwestern coal." *Fuel*, 71, 585-592, May, 1992.
- [6] Mann, M. D., Galbreath, K. C., and Kalmanovitch, D. P. "The role of ash chemistry and operating parameters on ash agglomeration and deposition in the fbc systems." In Inorganic transformations and ash deposition during combustion. American Society of Mechanical Engineers, 773-789, 1992.
- [7] Tao, F. F., Lamb, C. W., and Plumlee, K. W. "Sintering phenomena of coal ash in fluidized bed gasifier." In Fluidization and Fluid-Particle Systems: Theories and Applications. American Institute of Chemical Engineers, 79(222), 75-82, 1983.
- [8] Manzoori, A. R. and Agarwal, P. K., "Agglomeration and defluidization under simulated circulating fluidized-bed combustion conditions." *Fuel*, 73(4), 563-568, 1994.
- [9] Skrifvars, B. J., Hupa, M., Backman, R., and Hiltunen, M. "Sintering mechanisms of FBC ashes." *Fuel*, 73(2), 171-176, 1994.
- [10] Arastoopour, H., Huang, C. S., and Weil, S. A., "Fluidization behavior of particles under agglomerating conditions." *Chemical Engineering Science*, 43(11), 3063-3075, 1988.

- [11] Basu, P. and Sarka, A. "Agglomeration of coal ash in fluidized beds." *Fuel*, 62, 924-926, August, 1983.
- [12] Ekinici, E., Yardim, F., and Atakul, H. "Temperature profiles in a lignite flotsam-rich fluidized bed." *Fuel*, 62, 191-197, February, 1988.
- [13] Rozelle, P. L., and Scaroni, A. W. "Bed agglomeration and ash disposal for anthracite fired fluidized-bed combustors." In Proceedings 9th International Conference on Fluidized Bed Combustion. J. Mustonen, ed.; The American Society of Mechanical Engineers: New York, 1987.
- [14] Marinov, V., Marinov, S. P., Lazoarov, L., and Stefanova, M. "Ash agglomeration during fluidized bed gasification of high sulfur content lignites." *Fuel processing technology*, 31, 181-191, 1992.
- [15] Nowok, J. W., Benson, S. A., Jones, M. L., and Kalmanovitch, D. P. "Sintering behaviour and strength development in various coal ashes." *Fuel*, 69, 1020-1028, August, 1990.
- [16] Williamson, J., West, S. S., and Laughlin, M. K. "The behaviour of bed material during fluidized bed gasification: The effects of mineral matter interactions." *Fuel*, 73(7), 1039-1046, 1994.
- [17] Ghaly, A. E., Ergudenler, A., and Laufer, E. "Study of agglomeration characteristics of silica sand-straw ash mixtures using scanning electronic microscopy and energy dispersion X-ray techniques." *Bioresource Technology*, 48, 127-134, 1994.
- [18] Raask, E. Mineral Impurities in Coal Combustion. Hemisphere Publishing Corporation: New York, 1985.
- [19] Atakul, H., Oner, G., and Yardim, M. F. "Fluidized bed combustion research in Turkey." *Energy Sources*, 15, 1-15, 1993.
- [20] Valk, M. "Fluidized Bed Combustors." In Fluidized Bed Combustion. M. Radovanovic, ed.; Hemisphere Publishing Corporation: New York, 1986.
- [21] Atakul, H. and Ekinici, E. "Agglomeration of Turkish lignites in fluidised-bed combustion." *Journal of the Institute of Energy*, 56-61, March, 1989.
- [22] Ekinici, E., Yardim, F. "Temperature profiles in a lignite flotsam-rich fluidized bed." *Fuel*, 67, 1-15, February, 1988.

- [23] Srinivasachar, S., Helble, J. J., Ham, D. O., and Domazetis, G. "A kinetic description of vapor phase alkali transformations in combustion systems." *Progressive Energy Combustion Science*, 16, 303-309, 1990.
- [24] "Illinois Basin Coal Information System." Illinois State Geological Society, 1993.
- [25] Kunii, D. and Levenspiel, O. Fluidization Engineering. Butterworth-Heinemann: Boston, 1991.
- [26] Oh, J. S. and Wheelock, T. D. "Reductive decomposition of calcium sulfate with carbon monoxide: reaction mechanism." *Ind. Eng. Chem. Res.*, 29, 544-550, 1991.
- [27] Rasmussen, R. "Installation and operation of two CFB boilers at ISU." In Processing and Utilization of High-Sulfur Coals IV, P. R. Dugan, D. R. Quigley, and Y. A. Attia, eds.; Elsevier: Amsterdam, 1991.
- [28] Noble, S. "The effects of equivalence ratio on agglomeration in fluidized bed combustors." M.S. Thesis, Iowa State University, 1993.