A Fundamental Study of the Effect of Alkali Salts on Deposition in Biomass Boilers

by

Atif Vaniyambadi

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Chemical Engineering and Applied Chemistry
University of Toronto

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Abstract

The accumulation of deposits on tube surfaces in the superheater regions of biomass boilers is a concern as it affects boiler efficiency. This work examines the effect of alkali salts (mainly potassium chloride, KCl) on ash deposition on tube surfaces in biomass boilers using an Entrained Flow Reactor (EFR) at the University of Toronto. The effect of KCl mixed with silica, fly ash, and other oxides on deposition is studied. The deposition is found to increase with an increase in molten phase and the particles do not accumulate on the probe surface if there is no molten phase. These results are different compared to those obtained for recovery boilers. The carryover ash in recovery boilers requires a liquid content of 15 - 20% for the particles to deposit on the heat transfer surfaces. In the biomass boiler scenario, however, the deposition increases almost linearly with increasing liquid content.
ACKNOWLEDGEMENTS

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Last but not least, I would like to thank my parents Parvez Vaniyambadi and Thasneem Kothwal, for their unconditional love and support throughout this study. I dedicate this thesis to them.
# Table of Contents

1.0 Introduction .................................................................................................................... 1
  1.1 Biomass energy as a renewable source ................................................................. 1
  1.2 Biomass fly ash problem ..................................................................................... 3
  1.3 Motivation and objective ................................................................................. 5

2.0 Literature Review ........................................................................................................ 9
  2.1 Biomass Boiler Operation ................................................................................... 9
  2.2 Biomass Fuel Properties .................................................................................. 10
  2.3 Ash Properties of Biomass Fuel ....................................................................... 13
  2.4 Ash Deposition ..................................................................................................... 14
    2.4.1 Problems ........................................................................................................ 14
    2.4.2 Ash deposition mechanism ........................................................................... 15
    2.4.3 Deposit stickiness ........................................................................................ 19
    2.4.4 Hardening ..................................................................................................... 22
    2.4.5 Deposit removal ........................................................................................... 22
  2.5 Differences between recovery boiler and biomass boiler ash ......................... 23

3.0 Methodology .................................................................................................................. 26
  3.1 Materials ................................................................................................................ 26
  3.2 Experimental Setup .............................................................................................. 27
    3.2.1 Entrained Flow Reactor (EFR) .................................................................... 27
    3.2.2 Air Jet Blow-off Apparatus ......................................................................... 29
  3.3 Experimental Procedure ....................................................................................... 30
    3.3.1 Mechanically mixing .................................................................................. 30
    3.3.2 Well mixing ............................................................................................... 30
    3.3.3 Separately injecting .................................................................................... 31
  3.4 Air Jet Peak Impact Pressure (PIP) vs. Distance Correlation .............................. 33

4.0 Results & Discussion .................................................................................................... 35
  4.1 Experimental Reproducibility ............................................................................. 35
  4.2 Effect of KCl on Silica Deposition ...................................................................... 36
    4.2.1 KCl – silica mixtures at various EFR temperatures ....................................... 36
    4.2.2 Mechanically mixed .................................................................................... 37
List of tables

Table 1. Fuel and Ash Properties for selected biomass [13, 14] .............................................. 11
Table 2. Ash property between recovery and biomass boiler [13, 41] ........................................ 23
Table 3. Fly ash composition analyzed using XRF ........................................................................ 26
Table 4. Experimental reproducibility of the deposits and PIP of the deposits at 800°C EFR
temperature and 400 psig ........................................................................................................... 35
Table 5. A table showing the input data to LabJet model .............................................................. 67
Table 6. A table showing the output data for 400 psig .................................................................. 68
List of figures

Figure 1. Overview of a Pulp Mill (Courtesy: Valmet) .............................................................. 1
Figure 2. Common types of boilers (Courtesy: Babcock & Wilcox) ........................................... 3
Figure 3. A schematic diagram of a biomass boiler highlighting the fly ash deposition in superheater tubes (Courtesy: Kvaerner Pulping) ..................................................................... 4
Figure 4. Effect of liquid content on deposition in recovery boilers [6] ...................................... 6
Figure 5. A schematic representation of the hypothesis for this study; highlighting the different particle – particle interaction scenarios .................................................................................. 7
Figure 6. A schematic of a bubbling fluidized bed boiler (Courtesy: Babcock and Wilcox) ...... 10
Figure 7. Particle flow around a cylindrical tube [33, 34] .......................................................... 16
Figure 8. Particle collision probability [33] .................................................................................. 18
Figure 9. Appearance of deposit cones at various temperatures [41] ........................................ 20
Figure 10. A schematic of an experiment apparatus by Isaak [46] ............................................... 21
Figure 11. Interaction between fouling and non-fouling ash [4] .................................................. 25
Figure 12. Experimental setup of an EFR, which simulates conditions in the superheater regions of biomass boilers [57] .................................................................................................. 27
Figure 13. A schematic of Air Jet Blow-Off Apparatus [57] ........................................................ 29
Figure 14. An illustration showing the preparation steps for mechanically mixed feed mixtures 30
Figure 15. An illustration showing the steps for preparing well mixed feed mixtures ............... 31
Figure 16. An illustration showing the separate injection of chemicals to the EFR .................... 32
Figure 17. A curve showing the Peak Impact Pressure (PIP) of the air jet as a function of nozzle distance [59] .................................................................................................................. 34
Figure 18. A graph showing the deposition of KCl – silica mixtures for varying EFR temperatures .............................................................................................................................. 37
Figure 19. Deposition curve for mechanically mixed KCl – silica samples (probe temperature: 565°C) ................................................................................................................................. 38
Figure 20. Appearance of deposit on the probe surface for KCl - SiO2 mechanical mixtures ..... 39
Figure 21. Deposition curve for well mixed KCl – silica samples (probe temperature: 565°C) .. 40
Figure 22. Deposition curve for separately injected KCl – silica samples (probe temperature: 565°C) ............................................................................................................................... 41
Figure 23. Deposition curve combining all the mixing strategies for KCl – silica samples ......... 42
Figure 24. Deposition curve for mechanically mixed KCl - silica mixture for 0 to 100 wt% KCl compositions .................................................................................................................. 44
Figure 25. SEM image for mechanically mixed feed sample ......................................................... 45
Figure 26. SEM image for mechanically mixed deposit sample ..................................................... 45
Figure 27. SEM image for well mixed feed sample ......................................................................... 46
Figure 28. SEM image for well mixed deposit sample ................................................................. 47
Figure 29. A graph showing K/Si molar ratio for the mechanically mixed and well mixed feed and deposit samples .................................................................................................... 48
Figure 30. A graph showing the effect of varying the particle size of silica on KCl – silica deposition ................................................................................................................................. 50
Figure 31. A graph showing the effect of varying probe temperature on KCl – silica deposition 51
Figure 32. Deposition curve for mechanically mixed KCl – fly Ash mixtures (probe temperature: 565°C) ................................................................................................................................. 52
Figure 33. Deposition curve for well mixed KCl – fly Ash mixtures (probe temperature: 565°C) ................................................................................................................................. 53
Figure 34. A graph showing the effect of varying probe temperature on KCl – fly Ash deposition ................................................................................................................................. 54
Figure 35. Deposition curve for mechanically mixed KCl mixtures with different chemicals (CaO, K₂SO₄, fly Ash, and silica) ................................................................................................................................. 55
Figure 36. Deposition curve of mechanically mixed alkali salts mixtures (KCl & K₂SO₄) with silica (probe temperature: 565°C) ................................................................................................................................. 57
Figure 37. Deposition curve of mechanically mixed alkali salts mixtures (KCl & K₂CO₃) with silica (probe temperature: 565°C) ................................................................................................................................. 57
Figure 38. Deposit removal for KCl - silica deposits using the air jet blow-off apparatus ....... 58
Figure 39. Schematic of the pitot tube setup for deposit removal study [60] ..................... 66
Figure 40. A curve showing the calculated model of Peak Impact Pressure (PIP) of the air jet as a function of nozzle outlet distance ................................................................................................. 67
Figure 41. TGA profile of dry KCl powder ...................................................................................... 69
Figure 42. Phase diagram of K₂Cl₂ – K₂SO₄ mixtures showing the composition point where the feed sample was prepared (63 mol% K₂SO₄ and 37 mol% K₂Cl₂) [18] ................................................................. 70
Figure 43. Phase diagram of KCl – K₂CO₃ mixtures showing the composition point where the feed sample was prepared (68 mol% K₂CO₃ and 32 mol% KCl) [18] ................................................................. 70
1.0 Introduction

1.1 Biomass energy as a renewable source

A typical pulp and paper mill requires about 20 to 35 GJ of steam and 700 to 1000 kWh of energy per air dry metric ton (ADMT) of pulp produced [1]. This energy is required to dry pulp and paper products, heat water and process liquors, concentrate spent cooking liquor (black liquor), and run equipment and buildings. Out of these energy requirements, about 60 to 70% are generally self-supplied by burning concentrated black liquor in recovery boilers, while the remaining 30 to 40% is supplied by burning biomass in biomass boilers (Figure 1) [1]. Natural gas and coal are also co-fired in biomass boilers to supplement the steam and power. Currently, due to the depletion of global fossil fuels, there is a need to find alternatives to maximize energy production at mills while at the same time minimize environmental impacts.

Figure 1. Overview of a Pulp Mill (Courtesy: Valmet)
Biomass such as forest residues (bark), energy crops, agricultural residues (rice/wheat straw), and wood wastes are a promising alternative to fossil fuels because it represents a large amount of renewable resources. In Canada, about 6% of the overall energy is provided by bio-energy, which mainly comes from the pulp and paper industry [2]. According to a report by the International Energy Agency (IEA), a 30 MW power station fuelled by biomass produced from 11,250 ha of plantations can provide approximately 30,000 houses with electricity [3].

Electricity is generated from biomass through a combustion process where hot flue gases provide heat for producing high pressure steam which subsequently drives a turbine. There are four boiler types used in mills. They are pulverized fuel boilers, grate-fired boilers, bubbling fluidized bed boilers, and circulating fluidized bed boilers [4]. Pulverized fuel boilers are mainly used for coal and are only occasionally used to fire biomass. Biomass has been commercially burned in stoker-fired or grate-fired boilers since the 1960s (Figure 2). However, since the 1990s, advances in fluidized bed technology have enabled fluidized bed boilers to be the primary boilers at mills for burning large quantities and types of biomass.
1.2 Biomass fly ash problem

Hog-fuel is the solid fuel that is typically burned in biomass boilers. Hog-fuel is a mixture of different types of biomass such as saw dust, energy crops, wood, agricultural waste, forest residue, animal residue, straw, and bark. In addition, primary sludge, secondary sludge (biosludge), and/or deinked sludge are also burned in biomass boilers.

Since feedstocks with different chemical and physical properties are used, one of the problems associated with biomass boilers is the variation in the ash content and composition that is generated. While the carbon (C), oxygen (O), and hydrogen (H) elements of biomass on a dry basis are relatively constant, with 45 – 50 wt% C, 40 – 44 wt% O, and 5 – 6 wt% H; the moisture content, the ash content, and the ash composition vary depending on the source and storage conditions of the biomass feedstock [4]. For instance, burning bark produces more ash, calcium
(Ca), and potassium (K) as compared to the other parts of the tree. Compared to wood, agricultural residues such as rice/wheat straw, corn waste, etc. contains more ash, alkali, chlorine (Cl), and sulphur (S). A large amount of silicon (Si) is present in rice husk, while a large amount of nitrogen (N), phosphorous (P), and sulphur (S) is present in chicken litter.

As a consequence of using different feedstocks, a serious operational problem associated with burning biomass fuels is the production of fly ash, which consists of silicates/oxides and alkali/alkaline earth compounds in the form of chlorides and sulphates. When these particles interact with one another and/or with other compounds of ash, they lower the melting temperature of ash particles and lead to partial melting. When these partially molten ash particles become entrained in the flue gas, they collide with the steam generating heat transfer surfaces forming deposits [4]. The ash deposits build up on the boiler wall tubes, superheater tubes, and the generating bank tubes where high temperature flue gas prevails, thus affecting the thermal efficiency of the boiler. The deposits (Figure 3) also cause plugging and corrosion, leading to unscheduled maintenance and cleaning of tubes and/or tube removal [4, 5].

![Figure 3. A schematic diagram of a biomass boiler highlighting the fly ash deposition in superheater tubes (Courtesy: Kvaerner Pulping)](image-url)
1.3 Motivation and objective

Fly ash in biomass boilers predominantly consists of inorganic materials with some organic portion (unburned carbon). It is generally divided into mixtures of three types of particles: (1) fume particles (mostly alkali salts) formed from the condensation of particles that are vaporized or volatized in-flight in the boilers or on other fly ash particle surfaces as the flue gas cools, (2) inorganic particles such as Si, Al, Ca, etc. that are in the form of oxides, and (3) unburned carbon residues that are entrained in the flue gas.

Previous studies have shown that burning black liquor in recovery boilers produces carryover ash particles which have a significant effect on the deposition rate on the tube surfaces; and on the ability of a sootblower jet to remove the deposits. Shenassa and Mao [6, 7] found that in order for the carryover ash particles to be sticky, the particles must contain 15 – 20% liquid; although for a deposit to be promptly removed by a sootblower jet, it must contain less than 40% liquid (Figure 4). Understanding the liquid content in the particles makes it possible to predict if the particles in recovery boilers are sticky and form strong deposits at a particular location based on the black liquor composition and flue gas temperature. Results also showed that the ash particles on recovery boilers mainly consist of alkali salts (> 99%) and this causes them to be sticky on the superheater tubes as the melting temperature of common alkali salts in recovery boilers is below 800°C.
Figure 4. Effect of liquid content on deposition in recovery boilers [6]

The liquid requirement of 15 – 20%, however, is not the same for conditions in biomass boilers. This is because fly ash particles in biomass boilers are mostly made of silicates and oxides, and with a minimal content of alkali salts (KCl, K₂SO₄, NaCl etc.) varying from 2 to 10% depending on the source of the biomass burned.

It is not clear how fly ash particles deposit on the superheater tubes in biomass boilers. Therefore, this study focuses on the deposition mechanism between particles (i.e., interactions between particles), mainly silica and alkali salts. Silicates/oxides are non-fouling ash chemicals and major components of fly ash that have high melting temperatures, while alkali salt is a fouling ash chemical which has a low melting temperature. It is hypothesized that when an alkali salt is mixed with silicates/oxides, then deposition will occur on the superheater tube regions of the boilers. The deposition may occur due to one of four particle interaction scenarios (Figure 5), as discussed below.
In scenario (1), the alkali salt would become molten due to its low melting temperature. Silicates would remain solid due to their high melting temperature. The molten alkali salt would adhere on the superheater tubes first, and then silicates would stick on the molten alkali salt causing deposition. In scenario (2), the molten alkali salt would attach to the surface of the silicates and then together they would adhere to the superheater tubes leading to deposition. In scenario (3), the alkali salt and the silicate particle would chemically react to form an alkali-silicate mixture; and then stick on the superheater tubes. In the case of scenario (4), the alkali salt could be absorbed inside the pore walls of the silicates and then adhere to the superheater tubes.

Thus, the objective of this work is to systematically study the effect of alkali salts on deposition, by determining the effect of alkali salts on silica, fly ash, and other compounds. In addition, a preliminary deposition removal study on the effect of the alkali salt on silica is conducted.
This thesis consists of four major sections. The relevant literature is discussed in chapter 2, methodology in chapter 3, results and discussion in chapter 4, and conclusions in chapter 5. The literature review covers a fundamental understanding of biomass boiler operation, biomass fuel and ash properties, ash deposition and removal, and ash property comparison between recovery boilers and biomass boilers. The methodology describes the experimental setup used in this study. Chapter 4 discusses the results obtained in this study and compares the results to the hypothesis stated earlier. Chapter 5 summarizes and concludes the thesis highlighting the key findings of the work.
2.0 Literature Review

2.1 Biomass Boiler Operation

Biomass boilers in pulp mills are generally referred to as hog-fuel boilers or power boilers. These boilers can be as high as an eight storey building, and depending on the boiler that is used, they can produce power as high as 500 MW [8]. Biomass is fed into the boiler in the presence of excess air for the complete combustion process to take place. Combustion takes place in the high temperature lower furnace section and the heat released during combustion heats up the flue gas in the boiler. This flue gas passes through the steam generating bank tubes in the superheater area of the boiler located at top levels. The water in the generating bank tubes is heated and steam at saturated temperature and pressure is produced. This steam passes through the superheater tubes where the hot flue gases provide heat to produce high pressure superheated steam. After passing through the superheater area, the flue gases pass through the economizers or heat exchangers where the heat from the flue gases is captured and transferred to the boiler feed-water. At this stage of the boiler, the flue gases have lost most of their heat and they pass through the electrostatic precipitator area where fly ash and particulate matter are captured. Finally, the flue gases exit the boiler via the stack. A schematic of a fluidized bed boiler can be seen in Figure 6.
2.2 Biomass Fuel Properties

Typical biomass fuels burned in boilers are wood, energy crops, agricultural waste, straw, saw dust, forest residue, and grass [4, 9]. Understanding the fuel characteristics is important as biomass feed affects fly ash deposition during combustion as well as plays a key role in boiler design and operation [10, 11]. The properties of biomass are generally given by proximate and ultimate analysis [12]. Proximate analysis provides the char, volatility, and ash content in a fuel while ultimate analysis provides a composition of the elements such as C, H, O, Cl, etc. Table 1 below shows the proximate and ultimate analysis of some biomass fuels.
Table 1. Fuel and Ash Properties for selected biomass [13, 14]

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<th>Fuel Type</th>
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<th>Furniture waste</th>
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<th>Forest residues</th>
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<td>SO₃</td>
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<td>1.00</td>
<td>2.78</td>
<td>1.24</td>
<td>4.40</td>
<td>0.44</td>
<td>2.08</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P₂O₅</td>
<td>1.97</td>
<td>0.50</td>
<td>7.44</td>
<td>1.41</td>
<td>1.26</td>
<td>4.50</td>
<td>2.72</td>
<td>0.43</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Undetermined</td>
<td>0.73</td>
<td>-0.78</td>
<td>2.78</td>
<td>2.68</td>
<td>1.82</td>
<td>2.32</td>
<td>1.39</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td></td>
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</tr>
</tbody>
</table>
Table 1 shows that biomass fuels have a large amount of volatile matter (>60%), but have a low heating value because of high oxygen content (> 30%). The heating value is defined as the energy content of biomass on a dry basis. Biomass fuels generally have low heating value because of higher oxygen content compared to carbon and hydrogen, thus leading to a lower energy density. The heating value generally decreases with increasing moisture content. The moisture content of biomass fuels is high varying from 10 – 70%, and affects the combustion and volume of flue gas produced per energy unit [12]. High moisture content can cause ignition problems, and affect combustion temperature and require a longer residence time for drying in the combustor [4, 12]. On the other hand, the volatile matter of biomass fuels is high ranging from 60 – 90% and this causes the biomass fuels to burn faster as they rapidly consume oxygen during the combustion of volatiles [4]. However, the most serious problem in the biomass boiler is ash formation, as discussed in the next section.

2.3 Ash Properties of Biomass Fuel

The ash content in boilers varies from one biomass fuel to another, ranging from <1% in saw dust to as high as 20% in rice straws and husks [13, 14]. Table 1 shows the ash composition for different biomass fuels. Biomass ash contains alkali and alkaline earth metals with high potassium (K) and calcium (Ca) content, and low aluminum (Al) and sulphur (S) content. The presence of K is a concern because when K interacts with other compounds of biomass ash, it lowers the melting temperature and leads to the molten phase in the ash [14 – 16]. For example, pure silica (SiO$_2$) has a melting temperature of 1713°C, but the presence of K leads to the formation of K$_2$Si$_4$O$_9$ which melts at around 767°C [17]. In the presence of sulphur, alkali can form alkali sulphates on the combustor heat transfer surfaces. For instance, a mixture of K$_2$SO$_4$ and KCl start to melt at 694°C (42.5 mole% K$_2$SO$_4$), even though the pure compounds have a melting point of 1069°C (K$_2$SO$_4$) and 775°C (KCl) [18]. Since the gas temperature in the superheater regions of the combustors range from 700 to 900°C, there is a higher chance of fly ash particles to become molten and stick on tube surfaces due to the presence of K [4].

Chlorine (Cl) is another significant concern in biomass fuels that lead to ash deposition. Chlorine reacts with the alkali material to form alkali chlorides [13]. The low melting
temperatures of chloride compounds (example: 775°C for KCl) causes the alkali chlorides to deposit and form a sticky layer on the heat transfer surfaces [19, 20]. Consequently, fly ash particles stick to this layer, resulting in the growth of the ash deposits [21].

There are considerable amounts of silica in biomass fuels as well ranging from 15 to 70% of the ash content (Table 1) [16]. Silicates mixed with alkali/alkaline metals could melt or sinter at 800–900°C during the combustion process [22]. These alkali silicates tend to deposit on the boiler walls or the heat transfer surfaces, causing fouling/corrosion even at a low fusion temperature (<700 °C) [23]. Furthermore, the presence of heavy metals such as Zn, Pb, and Cd [24, 25] in some solid fuels (such as recycled tires) can also affect the ash melting behaviour as well as fouling and corrosion processes on boiler walls and in the combustor [26, 27]. Through reactions with Cl, these heavy metals form gaseous compounds during the combustion process, and eventually form aerosols and agglomerate or condense on fly ash particles when the flue gas temperature cools [26, 27].

2.4 Ash Deposition

2.4.1 Problems

Ash deposition leads to problems in boilers when biomass materials are fired [14, 28]. The problems are:

1) **Boiler usage efficiency**: There is a decrease in efficiency of boiler usage due to the formation of agglomerates. The ash particles agglomerate when the low melting compounds such as K, Na, S, and Ca begin to form a kind of coating in the bottom ash particles (which is partly molten), and eventually bind with each other [29]. For example, bed agglomeration causes de-fluidization in fluidized bed boilers, which would result in decreased boiler usage efficiency. Moreover, deposition of ash on heat transfer surfaces will inhibit the boiler heat transfer, leading to a decrease in the boiler thermal efficiency.
2) **Boiler equipment damage:** The growth of ash deposits restricts the flow of flue gas throughout the boiler, especially in the heat transfer surfaces, steam tubes, and tube bundles. This restriction could damage the components of the combustion system. Moreover, the ash deposits could cause corrosion damage at high temperatures.

3) **Unscheduled maintenance:** Severe ash deposits in steam tubes, hoppers, and grates lead to unscheduled shutdown of boiler equipment to clear deposits [30]. Tobiasen et al. [31] for example, reported that severe slagging occurred in a full-scale boiler burning straw pellets, leading to system shutdown within only a few weeks of being started.

### 2.4.2 Ash deposition mechanism

When ash particles collide on the heat transfer surfaces, they either stick or rebound. If they stick, they form deposits that accumulate and become stronger with time. In two review papers, Baxter and DeSollar [22, 32] identified that there are four mechanisms for ash deposition on heat transfer surfaces. They are: (1) inertial impaction, (2) thermophoresis, (3) condensation of vaporized inorganic compounds, and (4) chemical reaction.

1) **Inertial impaction**

Inertial impaction is typically the primary source of deposition on the heat transfer tubes. As seen in Figure 7, inertial impaction occurs when the gas is passing around the tube in a curved streamline fashion. The curved streamline causes the particles to have a curvilinear motion.
The curvilinear motion of the particle is characterized by a dimensionless number called the Stokes number [35]. The Stokes number is defined as the ratio of the distance the particles travels before fully adapting to the changing streamlines around the obstacle (i.e., the tube) [4].

\[ Stk = \frac{S}{d_c} \]  \hspace{1cm} (2-1)

In this equation:

Stk = Stokes number;
S = particle stopping distance;
d_c = tube characteristic dimension;

The particles follow the streamline perfectly if the Stokes number approaches zero, and the particles resist changing their direction with the streamline if the Stokes number is increasing. However, equation (2-1) above was originally developed only for conditions when the Reynolds number (Re) was less than 1. Hence, Israel and Rosner [35] introduced the effective Stokes number (Stk_{eff}), which accounts for the effect of a non-Stokesian flow regime.
The non-Stokesian correlation factor is defined as [34, 36, 37]:

\[
\omega = 18.99 \times Re_p^{\frac{-2}{3}} - 47.77 \times \tan^{-1}\left(\frac{0.3975 \times Re_p^{\frac{1}{5}}}{Re_p}\right) \quad (2-3)
\]

\[
Re_p = \frac{\rho_p D_p u_p}{\mu_g} \quad (2-4)
\]

In these equations:

Stk_{eff} = effective Stokes number;
\omega = non-Stokesian correlation factor;
Re_p = particle reynolds number;
\rho_g = gas density;
u_p = gas velocity.

Inertial impaction takes place when the momentum of the particle towards the tube is large enough to overcome the drag forces produced by the flue gas. The collision probability (\eta) of the particle on the tube is defined as the ratio of the particles that collide on the cylinder to the particles that pass through a projected area of the cylinder [34]. The probability is generally a function of the effective Stokes number and is determined by inertia:

\[
\eta = \left\{1 + 1.54 \times (Stk_{eff} - 0.125)^{-1} - 0.538 \times (Stk_{eff} - 0.125)^{-2} + 0.202 \times (Stk_{eff} - 0.125)^{-3}\right\}^{-1} \quad (2-5)
\]

Figure 8 shows the collision probability as a function of effective Stokes number.
The particle capture efficiency is described as the amount of the particle mass passing through the projected area of the tube over the deposit mass that is captured on the tube. However, not all particles that collide with the tube will deposit, some particles rebound. Therefore, the particles that rebound are quantified by the adhesion efficiency. The adhesion efficiency is defined as the mass of the particles that deposit on the tube to the mass of the particles that strike the tube [32, 36]. Adhesion efficiency can also be defined as the ratio of the particle capture efficiency to the collision probability [36].

2) **Thermophoresis**

Thermophoresis is the process of particle motion in a gas due to a temperature gradient. The temperature gradient is formed when the hot gases flow over the cold heat transfer surfaces. In a uniform gaseous medium, the molecular movement of the particles on the hot side is greater than on the colder side. This imbalance leads to a net force (a thermophoretic force) which pushes the particles from the hotter side and results in the deposition of the particle on the colder surface [38]. Thermophoretic deposits are composed of fine grain (sub-micron) ash particles and are distributed evenly around the tube surface as compared to deposits formed through inertial
impaction. The rate of thermophoretic deposits decreases over time due to the decrease in the temperature gradient. Deposit accumulation on the tube surface leads to the decrease in temperature gradient [39]. Since thermophoresis is dependent on temperature gradient, it is generally a predominant force in the initial stages of the deposition, but less so in the later stages.

3) **Condensation**

Deposition by condensation is relevant only when temperatures higher than the dew point of a substance exist in the boiler [33]. The dew point of a substance is the temperature at which the vapour condenses into liquid. Vapour condenses to form liquid droplets after diffusion into the surface boundary layer. Deposits are subsequently formed on the surface when some of the liquid droplets move closer to the surface by diffusion [33]. In general, condensation occurs more on the trailing edge of the tube compared to the leading edge and this is because condensation is driven by temperature gradient [39].

4) **Chemical reaction**

Chemical reaction is another mechanism that leads to ash deposits. A chemical reaction generally involves a heterogeneous chemical reaction between the gas and the deposits [22]. The most important chemical reaction with respect to ash deposits are (i) sulphation of alkali metals, (ii) formation of alkali-silicates, and (iii) combustion of the residual carbon [22, 32].

2.4.3 **Deposit stickiness**

Deposits in boilers have two distinct melting temperatures: the first melting temperature where the first liquid phase in the deposits appear and the complete melting temperature where the deposits are completely molten [33]. Tran [40] defined two other temperatures when considering deposit accumulation; they are the sticky temperature and the radical deformation temperature (or slagging temperature). Both these temperatures lie between the first melting temperature and the complete melting temperature as seen in Figure 9. The temperature above which the deposits contain enough liquid phase to become sticky is called the sticky temperature and the temperature above which the liquid content in the deposits are so high that the deposits become
fluid is called slagging temperature [33]. Figure 9 shows the temperature regions of the deposits depicted in a conical form.

![Temperature Regions of Deposits](image)

**Figure 9.** Appearance of deposit cones at various temperatures [41]

The deposit sticky region (i.e., the region where most of the deposits accumulate) is the temperature region between the lower limit of the sticky temperature and the upper limit of the slagging temperature. Outside of this temperature region, the deposits either do not have enough liquid content to stick or they are completely molten where the deposits flow and do not build up [40, 41].

However, the stickiness of a particle depends on both the stickiness of the colliding ash particle and the stickiness of the surface [42 – 44]. Hence, not all particles that collide on the tube surface stick to it. The tendency for a particle to stick depends on many variables such as flue gas temperature and velocity, tube and deposit temperature, particle composition, striking angle, surface characteristics, and size.
A measure of deposit stickiness was developed by Isaak et al. [45, 46] through an experimental apparatus shown in Figure 10. Experiments were conducted by contacting a cast deposit pellet with synthetic deposits and metal substrates. This method was developed to simulate the stickiness of the carryover particle to a metal surface. In this method, the adhesion of the particle demonstrated the magnitude of the force required to separate the cast pellet from the metal surface. Isaak [46] found that the presence of liquid phase was necessary for strong adhesion to take place. The strength of the stickiness was minimal when the deposits and the substrate surfaces were in solid form. The study showed that a minimum liquid content of 10 to 20% for rough pellet surfaces and approximately 7% for smoother surfaces was required for strong adhesion to occur. Moza and Austin [47] experimented with synthetic ash (SiO$_2$, Al$_2$O$_3$, CaO, Fe$_2$O$_3$) on cooled steel substrates, and found that the interfacial region between the ash and the substrate needed to be in liquid form for strong deposits to occur.

![Figure 10](image.png)

**Figure 10.** A schematic of an experiment apparatus by Isaak [46]

In another study, Shenassa [6] conducted experiments to confirm that for the deposits to become sticky in recovery boilers, the ash particles must contain a minimum 15% liquid content (Figure 4).
2.4.4 Hardening

During initial deposit formation, ash sticks to the surface by van der Waals, thermophoretic, interfacial, electrostatic, and capillary forces, and also through mechanical interlocking on the rough surface [16, 48, 49]. The deposits gradually become harder over time and are difficult to remove. The adhesion strength of the deposits is dependent on the contact area, the chemical bonding, and the mechanical interlocking [50]. Condensation and chemical reactions also increase the adhesion strength of the deposits by increasing the contact area by several orders of magnitude [22]. The process that leads to the increase in deposit strength is known as sintering. Since the deposit strength is not investigated in this thesis, the hardness of deposits is not discussed further.

2.4.5 Deposit removal

The most common method applied to control deposit build-up is sootblowing [49, 51]. A sootblower is a rotating long lance tube which discharges high pressure steam as it advances into the boiler [52]. It provides jet energy from a full-expansion nozzle for deposit removal. The performance of the sootblower is determined by measuring the peak impact pressure (PIP) of the nozzle. The PIP is measured by a pitot tube along the centerline of the nozzle outlet. Due to the deceleration of the surrounding fluid and the decline of the jet energy, the PIP decreases as the distance from the nozzle exit is increased [53, 54].

In general, three categories of factors affect sootblowing efficiency. The first category includes the nozzle design, the nozzle blowing sequence, the distance between the nozzle and the deposit, and the jet arrangement [55, 56]. The second category includes the deposit particle size, deposit adhesion strength (i.e., deposit composition and temperature), and the tube temperature [56]. Mao et al. [57] found that the PIP required to remove the deposit increases sharply with increase in chloride content in the deposit. In another study, Piroozmand et al. [58] found that the strength of the deposits is strongly related to the particle size. Mao et al. [7] studied the effect of particle size and liquid content on deposit removability. From this study, it was concluded that the deposits formed from smaller particles were much stronger than from larger particles for a fixed
liquid content. In addition, it was shown that the particles that contain high liquid content formed stronger deposits than those with low liquid content. Finally, the third category that affects soot blowing performance relates to the interaction between the jet and the deposit, and the deposit removal mechanisms [55]. If the deposits are brittle, there are four different removal mechanisms. They are brittle fracture, debonding, vibration, and thermal shock.

### 2.5 Differences between recovery boiler and biomass boiler ash

Problems associated with fly ash deposition on heat transfer surfaces in boilers are inevitable due to the large quantity and the low melting temperature of the ash content. From recovery boiler carryover ash deposition studies, it was found that the ash particles required a liquid content of around 15 – 20% for the deposits to stick on the heat transfer surfaces [33]. However, data from recovery boiler studies cannot be applied to biomass boilers. This is because of differences in the boiler feed and ash properties. Table 2 below shows the differences in the ash property.

<table>
<thead>
<tr>
<th>Ash Property</th>
<th>Recovery Boiler</th>
<th>Biomass Boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ash content in fuel</td>
<td>40 - 50 wt%</td>
<td>1 – 6 wt%</td>
</tr>
<tr>
<td>Alkali content in ash</td>
<td>&gt;99 wt%</td>
<td>2 – 10 wt%</td>
</tr>
<tr>
<td>Major ash components</td>
<td>Alkali salts (mainly Na₂SO₄ and Na₂CO₃)</td>
<td>Silicates, oxides, alkali salts (KCl)</td>
</tr>
<tr>
<td>Particles</td>
<td>Uniform</td>
<td>Non-uniform</td>
</tr>
</tbody>
</table>

As seen in Table 2, when burning black liquor in recovery boilers, the ash content is about 40 – 50 wt%, whereas burning biomass fuel produces very little ash around 1 – 6 wt%. The ash component in the recovery boiler carryover particles consists mainly of alkali salts (> 99 wt%) such as Na₂SO₄ and Na₂CO₃. They have melting temperatures between 500 – 800°C, and since the temperature of the flue gas around the superheater regions of the boilers are at this range, these alkali salts melt and stick on the heat transfer surfaces.
Biomass fly ash particles, on the other hand, are generally mixtures of compounds mostly made of silicates and oxides, and very little alkali salts (< 5 wt%) depending on the source of the biomass fuel burned. Alkali compounds have a low melting temperature (500 – 800°C), whereas silicates/oxides have high melting temperatures (> 1300°C).

Thus, due to the differences in compounds in the ash particles from the recovery and biomass boilers, the liquid content requirement of 15 - 20% in carryover ash particles in recovery boilers cannot be applied to biomass boilers. Therefore, there is a need to study the sticky temperature of fly ash particles in biomass boilers as the ash melting temperature is dependent on compounds in the feedstock.

Theis [4] compared the deposition behaviours of fly ash for three biomass feedstocks – straw, peat, and bark with different chemical compositions. The study found that straw had a high tendency to foul compared to bark and peat, as straw has large amounts of alkali compounds (such as K₂O and Na₂O). The study showed that when fouling ash interacts with non-fouling ash, there is a tendency for the non-fouling ash to foul. Peat was recognized as the non-fouling ash, and straw and bark were recognized as fouling ash. Mixtures of straw with peat behaved differently than mixtures of bark with peat. The results showed a non-linear deposition behaviour and concluded that when good ash (non-fouling ash) and bad ash (fouling ash) are mixed, different fouling tendencies occur with different types of ash (Figure 11). For instance, peat-straw mixtures can burn up to 70% straw without encountering any increased deposition, while peat-bark mixtures can only burn up to 50% bark.
Most of the studies that have investigated ash deposition in biomass boilers state that alkali metals such as K are the major reason for the deposits to occur on the superheater tube surfaces. Therefore, this study focuses on experimentally studying the deposition mechanism of fly ash particles where silica (non-fouling ash) is mixed with KCl (fouling ash). Silica is chosen as it is one of the major components of fly ash and melts at a higher temperature (1700°C); and KCl is chosen as it melts at 775°C (the region where the gas temperature is between 700 and 900°C). The particles interaction between these chemicals will help in interpreting fly ash formation and growth.
### 3.0 Methodology

#### 3.1 Materials

The materials primarily used in this work were i) fine granules of silica (SiO$_2$), and ii) analytical grade crystalline potassium chloride (KCl) from Fisher Scientific. Both chemicals were ground and sieved to the desired particle size. Other chemicals used for this study were analytical grade K$_2$SO$_4$, K$_2$CO$_3$, and CaO powders from Fisher Scientific with over 99.9% purity.

The fly ash used for this study was from a pulp mill. The fly ash was analyzed using x-ray fluorescence (XRF) and found to have a low Cl content. Table 3 below shows the chemical properties of the fly ash particles.

**Table 3.** Fly ash composition analyzed using XRF

<table>
<thead>
<tr>
<th>Composition</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$</td>
<td>35.0</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>14.1</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>13.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>12.1</td>
</tr>
<tr>
<td>CaO</td>
<td>10.3</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>5.70</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>4.35</td>
</tr>
<tr>
<td>MgO</td>
<td>1.91</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>1.65</td>
</tr>
<tr>
<td>MnO</td>
<td>1.13</td>
</tr>
<tr>
<td>Cl</td>
<td>0.37</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.61</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.17</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>0.06</td>
</tr>
<tr>
<td>CoO</td>
<td>0.01</td>
</tr>
<tr>
<td>CuO</td>
<td>0.01</td>
</tr>
<tr>
<td>Undetermined</td>
<td>0.72</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>
3.2 Experimental Setup

The experimental setup used for this study was the Entrained Flow Reactor (EFR) and the air jet blow-off apparatus. The sample particles were fed into the EFR to simulate similar conditions the fly ash particles experience in biomass boilers. The deposition process was determined by the particles that were collected on the air-cooled probe at the bottom of the EFR and the removability of the deposits on the probe was determined by blowing the deposits using the air jet blow-off apparatus.

3.2.1 Entrained Flow Reactor (EFR)

The EFR at the University of Toronto as seen in Figure 12 is a downward-flow reactor which is 9-metres in height and has an inner diameter of 18 cm.

![Figure 12. Experimental setup of an EFR, which simulates conditions in the superheater regions of biomass boilers [57]](image-url)
The EFR consists of a sample feeder, a natural gas combustion unit, a long-vertical heated section, and a non-heated sampling section. An electromagnetic weight cell, a data acquisition system and control, and an air-cooled probe comprise the auxiliary equipment included in the EFR system. The detailed descriptions of the design and operating conditions are explained by Shenassa [33], and the following section gives a brief review of the EFR.

1) **Sample feeder:** The sample feeder consists of a 0.3 m wide by 1.2 m long conveyer belt where the particles are fed. The particle feed rate is controlled by the conveyer belt speed which in turn is run by a motor. The particles then pass through a double-layered stainless steel water cooled injector and a flow of pressurized carrier air ensures the particles flow inside the injector.

2) **Natural gas combustion unit:** The gas combustion unit located at the top of the vertical heated section is equipped with a natural gas burner. The gas produced from the burner is mixed with dilution air to produce a hot gas stream that reaches temperatures as high as 1100°C. The hot gas passes through a ceramic honey comb which provides a uniform gas flow through the EFR. The hot gas that exits the combustion unit carries the sample particles and flow down the EFR to the first heated vertical section.

3) **Long vertical heated section:** The long-vertical heated section consists of five tubular furnaces which form into a continuous unit. Each furnace is electrically heated to temperatures as high as 1100°C and has a mullite tube. Each mullite tube between the adjacent furnaces is supported by non-heated insulated fire bricks. The hot environment required to burn the particles is provided in this heated section.

4) **Non-heated sampling section:** The non-heated sampling section is located at the bottom of the last vertical heated section and is used for deposit collection and measurements. The internal diameter of the non-heated section is 18 cm and the section is insulated by bricks to minimize heat lost by convection. The burned particles that fall to the bottom of the EFR are deposited on the air-cooled probe. The probe is connected to an
electromagnetic weight cell which measures the mass and transmits to the Labview data acquisition system. The weight cell has an accuracy of ±0.1 g. The data acquisition system is also utilized to monitor the conveyor belt speed, gas combustion temperature and flow rate, dilution air flow rate, the furnace temperatures, and the probe temperature.

3.2.2 Air Jet Blow-off Apparatus

The air blow-off jet is used to determine the minimum peak impact pressure (PIP) required to remove deposits on the EFR probe. The air jet in the apparatus is mounted on a manual hoisting table that sits on a slide close to the probe. Compressed air is supplied through the nozzle from the cylinders. A pressure regulator on the second compressed air cylinder controls the supplied air pressure at the nozzle inlet, and the nozzle outlet is at atmospheric pressure. The PIP is increased by moving the nozzle closer to the probe. Figure 13 shows a diagram of the air jet blow-off apparatus coupled with the EFR. [57, 59]

![Figure 13. A schematic of Air Jet Blow-Off Apparatus [57]](image-url)
3.3 Experimental Procedure

For this study, the feed samples were prepared by different mixing methods. The purpose of the different mixing methods was to simulate the different conditions the fly ash particles experience in biomass boilers. Three methods were employed in this study: mechanical mixing, well mixing, and separately injecting.

3.3.1 Mechanically mixing

This method was used to examine the effect of deposition if the chemicals are physically mixed in the biomass boiler but not bound together. The rationale is that once the samples are fed, the alkali salt will melt and form a layer on the probe and then the silica particle would stick to this layer. In this method, the two different chemicals were transferred to a plastic container where they were physically mixed by shaking the bottle. Figure 14 shows how the KCl and silica were added to a beaker and transferred to the plastic container where they were physically mixed.

![Figure 14. An illustration showing the preparation steps for mechanically mixed feed mixtures](image)

3.3.2 Well mixing

This method was employed to examine the effectiveness of the alkali salt on deposition when it is well mixed (adsorbing on the surface) with silica. The rationale is that once the samples are fed into the boiler, the alkali salt adsorbed on the surface of the silica particle would melt and stick on the probe capturing the entire silica particle (similar to hypothesis 2 - Figure 5). In this method, the two chemicals were added to the beaker and then water was added to form a slurry-
like solution. The slurry mixture was then transferred to an aluminum container and dried overnight at 90°C in an oven as seen in Figure 15. After the mixture was dried, it was crushed and ground to the desired particle size and fed into the EFR.

![Illustration showing the steps for preparing well mixed feed mixtures](image)

**Figure 15.** An illustration showing the steps for preparing well mixed feed mixtures

### 3.3.3 Separately injecting

In this method, the chemicals were fed separately to the EFR by splitting them on the conveyer belt [59]. This method was used to examine the effectiveness of the alkali salt when the alkali salt and the silica particles were introduced separately to the boiler. Figure 16 shows this method.
Figure 16. An illustration showing the separate injection of chemicals to the EFR
In all runs, a total feed of 50 g was added to the EFR at a rate of 2.5 g/min. The feed mixtures were sieved below 300 µm and the EFR temperature was set at 800°C until otherwise specified. The reason for choosing the EFR temperature of 800°C was because KCl melts at 775°C; and a molten phase was desired for the deposition study. The probe temperature for the runs was at about 565°C. The gas velocity at the EFR exit was 1.8 m/s while the average particle velocity was estimated to be around 2 m/s. The deposits that were collected on the probe were originally measured in grams (g). However, the deposition results for this study is shown in grams of deposit collected over the surface area of the probe, and over the gram of feed added (stated as g/m²/g-feed). The projected surface area on the 1 inch probe in an 18 cm internal diameter at the EFR bottom was calculated to be 0.0071 m². The deposits were then analyzed using a Scanning Electron Microscope (SEM).

3.4 Air Jet Peak Impact Pressure (PIP) vs. Distance Correlation

Pophali et al. [60] determined the PIP of the air jet as a function of distance from the nozzle outlet using a laboratory pitot tube. Using the setup, a PIP profile of the air jet as a function of nozzle distance was measured [59]. A curve fit line was added to the plot as seen in Figure 17. A schematic and description of the setup can be seen in Appendix A.
Using the PIP profile as mentioned above, Kaliazine et al. [55] developed a mathematical model called LabJet to measure the PIP of the air jet as a function of distance for different design pressures. An inlet air pressure of 400 psig was utilized in this study. Figure 40 in Appendix B shows the calculated PIP against nozzle outlet distance for 400 psig inlet pressure. The data table of the LabJet model at 400 psig can also be seen in Appendix B.
4.0 Results & Discussion

4.1 Experimental Reproducibility

The reproducibility of the experiments was examined by measuring the deposit mass collected on the probe for the same feed composition and particle size distribution under the same EFR operating conditions. The reproducibility of the air jet blow-off apparatus was determined by measuring the PIP of the deposits at the same supplied inlet pressure and the same nozzle. Table 4 below shows the experimental conditions and the results obtained from the reproducibility study. The deposit mass for the seven 20 wt% KCl - silica samples for a particle size less than 300 µm at 800°C EFR temperature had an average of 1.80 ± 0.13 g/m²/g-feed with a coefficient of variation of 7.3%. The average PIP of the deposits was 126 ± 8.4 psig with a coefficient of variation of 6.6%. The coefficient of variation was utilized to determine the percent error associated with each measurement.

Table 4. Experimental reproducibility of the deposits and PIP of the deposits at 800°C EFR temperature and 400 psig

<table>
<thead>
<tr>
<th>Run #</th>
<th>Probe Temp. (°C)</th>
<th>Deposition (g/m²/g-feed)</th>
<th>PIP of deposit (psig)</th>
</tr>
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</table>

Furthermore, experiments were conducted to determine the capture efficiency of the feed particles when it is falling down the EFR. The capture efficiency for three 20 wt% KCl – silica samples had an average of 80 ± 1% with a coefficient of variation of 2.4%.
4.2 Effect of KCl on Silica Deposition

In this section, the effect of KCl with silica on deposition is discussed. KCl was mechanically mixed with silica for varying EFR temperatures. KCl and silica were then well mixed and separately injected into the EFR to study the deposition for different sample preparation methods. The results from the different feed mixtures were compared to the hypothesis that was stated earlier in the objective section. Moreover, the effect of deposition on varying particle size of silica and varying probe temperature were looked at in this section.

4.2.1 KCl – silica mixtures at various EFR temperatures

Experiments were carried out by feeding mechanical mixtures of KCl and silica at various EFR temperatures. Figure 18 shows the effect of deposition on the probe for varying EFR temperatures (800°C, 850°C, and 900°C). When only silica was fed to the EFR at 800°C (i.e., a mixture with 0 wt% KCl), only a small amount of deposit (0.01 g/m²/g-feed) accumulated on the probe and was easy to remove. This is because silica has a high melting temperature (1700°C) and does not melt at 800°C.

When the feed was mixed with KCl in increasing amounts (0 to 20 wt%), the results obtained were different depending on the temperature. Below 775°C (the melting temperature of KCl), the amount of deposit on the probe was close to zero, similar to when only silica was added to the EFR at 800°C. This is because there was no molten phase present in the system. However, at 800°C, the deposition increased with KCl and it remained at high values for higher EFR temperatures (850°C and 900°C). At EFR temperatures above 800°C, KCl melts and sticks on the probe since it has a melting point of 775°C. The silica then adheres to the molten KCl leading to the formation of the deposits. As more KCl is added to the total feed, a larger amount of deposits are accumulated on the probe since there is more molten KCl present in the system. However, a slight reduction in deposit accumulation was observed as the EFR temperature was increased. This was due to the vaporization of KCl at temperatures above the melting temperature. Thermal Gravimetric Analysis/ Differential Scanning Calorimetry (TGA/DSC) was
utilized to examine the thermal behaviour of KCl and this loss in KCl (weight %) due to vaporization can be seen in Appendix C.

![Graph showing the deposition of KCl – silica mixtures for varying EFR temperatures](image)

**Figure 18.** A graph showing the deposition of KCl – silica mixtures for varying EFR temperatures

### 4.2.2 Mechanically mixed

From Figure 18, the deposition data at 800°C EFR temperature was obtained and deposition as a function of KCl concentration in the feed was plotted (Figure 19). From the figure, it can be observed that the addition of KCl in the feed mixture increased the deposition rate in a linear-like fashion.
Figure 19. Deposition curve for mechanically mixed KCl – silica samples (probe temperature: 565°C)

Figure 20 shows the appearance of deposit obtained on the probe for different wt% of KCl in the feed. The 0wt% KCl in the feed sample was used as a baseline as there was no deposit accumulated on the probe. From the figure, it can be seen that the amount of deposit increases with increasing KCl in the feed (i.e., appearance of silica on the probe).
Figure 20. Appearance of deposit on the probe surface for KCl - SiO₂ mechanical mixtures

4.2.3 Well mixed

Since the results for mechanically mixed KCl – silica samples showed a linear-like increase in deposition, experiments were conducted to examine if different sample preparation methods would lead to different deposition trends. For this experiment, KCl and silica were mixed to simulate one of the possible particle interactions occurring in biomass boilers, that is, fly ash particles physically bound with each other on the particle surfaces before striking the heat transfer surfaces in the boilers. In this experiment, KCl and silica were physically bound through the well mixing method. Samples were prepared by mixing KCl and silica in water and drying overnight in an oven at 90°C. The mixture was then crushed and ground to the desired particle size (< 300 µm) before being fed into the EFR. Similar to the mechanically mixed samples, the
KCl composition in the total feed was increased from 0 to 20 wt%. Figure 21 shows the deposition curve for well mixed KCl - silica samples. The figure shows that the curve has a polynomial-like rise in deposition with increasing KCl composition in the feed.

![Deposition Curve](image)

**Figure 21.** Deposition curve for well mixed KCl – silica samples (probe temperature: 565°C)

### 4.2.4 Separately Injected

In this experiment, another possible scheme for particle interaction in biomass boilers was simulated, i.e., fly ash particles are individually entrained in the flue gas in the boiler before striking the heat transfer surfaces. KCl and silica particles were fed separately by splitting them on the conveyor belt. Figure 22 shows the deposition curve for the separately injected KCl and silica particles into the EFR. The curve shows that the deposition increased in a linear-like fashion with an increase in KCl composition in the feed. This increase in deposition was similar to the mechanically mixed deposition curve (Figure 19).
When the deposition curves of the three mixing methods were plotted in one curve (Figure 23 below), it can be seen that the deposition rates for all methods were similar. Increasing the amount of liquid phase in the mixture (molten KCl) resulted in more deposit accumulation. If the KCl particle is completely molten, then the 20 wt% KCl in the feed means 20% liquid phase, and 15 wt% KCl in the feed means 15% liquid phase and so on. From previous work on the recovery boiler, Shenassa [33] found that a liquid content of over 15% was required for the carryover ash particles to start deposition on the heat transfer surfaces. Here, however, in the biomass boiler scenario, that was not the case and even a small liquid % was enough for the deposition to take place. This was one of the major differences that were determined for the biomass boiler in contrast to the recovery boiler. The deposition curve of the KCl and silica particles (Figure 23) in this study appears to show a linear-like trend whereas the carryover ash particle deposits in the recovery boiler had a step increase at 15 - 20% liquid content and eventually reached a plateau at 40% as displayed in Figure 4. This difference in deposition trend between the boilers could be because of differences in the ash particles. The carryover ash particles in the recovery boilers are homogenous and could chemically react to form alkali salts mixtures in the presence of the high
temperature flue gas ranging between 500 – 800°C at the superheater regions of the boilers. This alkali salts mixture would then stick on the probe surface only if they are above a liquid content of 15% in the mixture. Below 15%, there is not enough adhesion capacity on the mixture for the particles to stick on the heat transfer surfaces. On the other hand, the particles in biomass boilers are non-homogenous, meaning they are individual chemical particles (silica and KCl respectively). They deposit on the probe in a linear-like trend because KCl is the only chemical that melts due to its low melting temperature (775°C) and form a molten layer on the probe when they strike the probe surface. The silica particles then adhere on this molten layer. The more amount of KCl that is present in the system, the more amounts of deposit stick on the probe.

Furthermore, some differences in the deposition curves for different mixing methods can be seen. A polynomial-like increase in deposition is observed for the well mixed case as opposed to the linear-like increase in the mechanically mixed and separately injected case. It can be seen that the polynomial-like increase in deposition for well mixed samples is only for low concentrations from 0 to 10 wt% KCl, and then after 10 wt% KCl, there is a linear-like increase in deposition. This could be because of errors in sample preparation for low concentrations. When the well
mixed samples are prepared and dried in the oven, not all of the KCl particles are adsorbed on the surface of the silica. There are some KCl particles that usually precipitate out during the drying process. Due to this, there might be some particles that are lost in the sample preparation. In addition, there might also be some individual KCl particles in the well mixed mixture since not all the KCl particles stick on the silica particles.

Another reason for low deposition for low concentrations for well mixed case (0 to 10 wt% KCl) could be because of particle size and weight. When the well mixed feed mixture is fed into the EFR, the KCl particles that are adsorbed on the surface of the silica could stick to other individual KCl particles in-flight and increase the particle size. An increase in particle size could increase the weight of the particles. The heavier particles would have a higher momentum on them to bounce away from the probe or the molten KCl layer on the probe surface might not be strong enough to hold the heavier particles in place.

But regardless of the mixing method that is used, the results seem to suggest that the deposition increases with increases in the liquid phase. Figure 24 further shows the increase in deposition as the KCl wt% is increased from 0 to 100 wt% in the feed.
Figure 24. Deposition curve for mechanically mixed KCl - silica mixture for 0 to 100 wt% KCl compositions

4.2.5 SEM images and K/Si molar ratios of mechanical and well mixed samples

Figure 25 and Figure 26 shows the SEM images for a 20 wt% KCl in silica mechanically mixed feed and deposit sample. As seen on the feed sample (Figure 25), KCl and silica particles are separate, and are distinguished by their color and brightness. The KCl is the brighter particle while the silica is the darker particle. In contrast to the feed sample, the SEM image of the deposit sample (Figure 26) is different. The KCl and silica particles are not separate in the deposit sample, and the KCl particle is sticking on the silica particle. The structure of the KCl particle in the deposit sample is different as opposed to the feed sample. The difference in the structure of the KCl particle is because KCl becomes molten (melting point of 775°C) when passed through the EFR temperature of 800°C. KCl becomes liquefied while passing through the EFR, and then solidifies at the EFR exit on the probe as the probe temperature is 565°C (well below the melting temperature of KCl). On the other hand, the silica particle structure on the deposit sample remained identical to the feed sample as silica has a melting point of around 1700°C and did not melt.
Figure 25. SEM image for mechanically mixed feed sample

Figure 26. SEM image for mechanically mixed deposit sample
Similarly, Figure 27 & Figure 28 shows the SEM images for a 20 wt% KCl in silica well mixed feed and deposit sample. In comparison to the SEM images of the mechanically mixed samples, the SEM images of the well mixed samples are different. The KCl particles in the mechanically mixed feed sample were separate (Figure 25), whereas the KCl particles in the well mixed feed sample (Figure 27) are not separate, and are adsorbed on the surface of the silica particles. The main difference, however, is that the silica particles in the well mixed deposit sample are covered entirely by the KCl particles (Figure 28). This is because when the well mixed sample is fed into the EFR, the KCl that is bound on the surface of the silica becomes molten at 775°C, and this causes the silica particles to adhere to the liquid KCl. Thus, as more molten KCl particles fall down the EFR, they build up on top of one another covering the silica particle.

![Figure 27. SEM image for well mixed feed sample](image)

Figure 27. SEM image for well mixed feed sample
Moreover, potassium (K) and silicon (Si) contents in the feed and the deposit samples of the mechanically mixed and the well mixed methods were analyzed. Figure 29 below shows the analysis results for the K/Si molar ratio in the feed and the deposit. The K/Si ratios for the mechanically mixed samples were very high compared to the well mixed samples. The K/Si deposit ratio for mechanically mixed samples becomes steady at around 3.5 for increasing K/Si feed ratio. Even though the deposit mass increases with an increase of KCl in the feed (seen in Figure 19 above), the K/Si deposit ratio reaches to a steady value after a certain K/Si feed ratio (0.10 onwards). This implies that after a certain feed ratio, both the K and Si concentrations on the deposit are the same even though the deposit mass is increasing. In addition, the high ratio means that there are small amounts of Si in the sample, while K is very high. Small amounts of Si mean small amounts of silica in the sample. Hence, it is likely that there is a very little amount of silica sticking on the KCl in the mechanically mixed samples.

On the contrary, the K/Si ratio for the well mixed deposits were small (i.e., close to 0.6), which means that the amount of silica in the well mixed deposits is higher than the KCl. A larger amount of silica in the well mixed deposit could be due to the KCl particles that are adsorbed on
the silica particles capturing the entire silica particle when they fall down the EFR. This can be seen in the SEM image of the well mixed deposit sample above (Figure 28). In addition, the molten KCl layer on the probe might also capture other individual silica particles in the feed thus leading to a higher silica amount in the deposits.

Furthermore, the K/Si deposit ratio for the well mixed samples seems to reach a steady value similar to the mechanically mixed deposits. This suggests that even for well mixed deposit samples, the K and Si concentrations are the same with increasing K/Si feed ratio. Therefore, from the results, it can be concluded that only small amounts of silica adhere to the KCl in mechanically mixed samples; whereas a larger amount of silica adheres for the well mixed samples.

**Figure 29.** A graph showing K/Si molar ratio for the mechanically mixed and well mixed feed and deposit samples
4.2.6 Comparison of deposition results to the hypothesis

The mechanically mixed and well mixed deposits of the KCl - silica mixtures were compared to the hypothesis scenarios in Figure 5. From the SEM images of the mechanically mixed deposit sample (Figure 26), it can be seen that the mechanically mixed deposition is similar to scenario (1). This is because the KCl and silica particles are separate in the feed sample and are only adhered together on the surface in the deposit sample. On the other hand, for the well mixed deposition, the SEM image (Figure 28) show that they follow scenario (2) and scenario (4). The reason is that there is a possibility for the KCl particles to be absorbed first inside the silica pores (scenario 4) and then cover the silica surface completely (scenario 2) as more KCl particles would accumulate on top of one another. Therefore, it can be concluded that the mechanically mixed and well mixed depositions follow scenario (1), scenario (2), and scenario (4) from the hypothesis in Figure 5.

4.2.7 Effect of particle size on deposition

Figure 30 below shows the effect of particle size on deposition for the mechanically mixed samples of 10 wt% KCl in silica. The KCl samples were sieved to obtain particles below 300 µm. The silica particle sizes were varied from 200 µm to 800 µm for particles with medians of 260 µm, 363 µm, 513 µm, and 725 µm respectively. As seen in Figure 30, the deposition decreased with an increase in particle size of silica. An example that can be compared to this effect is of sand particles with different sizes that are thrown on to adhesive paper. If the sand particles are small, then the adhesion strength of the paper is strong enough allowing for the sand particles to stick to the paper. If the sand particles are large, the adhesion strength is not strong enough for the sand particles to stick to the paper, and therefore, they bounce away from the paper. Furthermore, this effect of particle size was also seen for different compounds mixed with KCl. This is discussed later in section 4.4.1.
4.2.8 Effect of probe temperature on deposition

The effect of changing the probe temperature on the deposition was determined. Figure 31 shows the amount of deposits collected on the probe for different compositions (10 wt% and 20 wt% KCl in silica) and varying probe temperatures at an EFR temperature of 800°C. The probe temperature was changed by adjusting the amount of air passing through the probe. The temperature was reduced by increasing the flow rate of air through the probe and vice versa. From Figure 31, it can be seen that a very minimal amount of deposits were accumulated on the probe for a probe temperature below 400°C (< 0.3 g/m²/g-feed). When the temperature was increased above 400°C, an increase in deposition was observed until the maximum probe temperature of 565°C was attained by the EFR. The results suggest that very little molten KCl particles stick on the probe if the probe temperature is below 400°C. However, larger amount of molten particles stick on the probe if the temperature is above 400°C. This implies that the thermal boundary layer on the probe surface can hold only minimal amounts of molten particles and once it reaches the threshold, the molten particles that fall down the EFR freeze, solidify, and bounce away from the probe surface. As the probe temperature is increased, the thermal
boundary layer on the probe is hot and the temperature gradient between the molten particle and the surface is lower allowing for the molten particles to stick on the probe. Therefore, larger amount of deposition occurs with increasing probe temperature.

![Graph showing the effect of varying probe temperature on KCl - silica deposition](image)

**Figure 31.** A graph showing the effect of varying probe temperature on KCl - silica deposition

### 4.3 Effect of KCl on Fly Ash Deposition

In this section, the effect of KCl with fly ash on deposition was discussed. The fly ash used in this study was from a pulp mill. KCl was mixed with the fly ash in similar methods as the KCl - silica mixtures (i.e., mechanically mixed and well mixed). The operating condition for these mixtures was the same as the KCl - silica mixtures at EFR temperature of 800°C and probe temperature of 565°C. The results for the different mixing methods of KCl with fly ash were compared to the hypothesis and discussed. Moreover, the effect of varying probe temperature on deposition was studied.
4.3.1 Mechanical mixed and well mixed deposition

In a similar manner to the experiments between the KCl and the silica, experiments were conducted by mechanically and well mixing KCl with fly ash at different compositions. The compositions were varied from 0 to 20 wt% KCl in the feed. The deposition curves of the mechanically mixed and the well mixed mixtures can be seen in Figure 32 and Figure 33 respectively. The results demonstrate an increase in deposition with an increase in KCl (molten phase). Similar to the trends for the KCl - silica mixtures, the deposition shows a linear-like increase for the mechanically mixed samples, and a polynomial-like increase for the well mixed samples.

![Deposition curve for mechanically mixed KCl – fly Ash mixtures (probe temperature: 565°C)](image)

**Figure 32.** Deposition curve for mechanically mixed KCl – fly Ash mixtures (probe temperature: 565°C)
4.3.2 Effect of probe temperature on fly ash deposition

The effect of varying probe temperature on deposition for the 20 wt% KCl in fly ash particles was studied. The results in Figure 34 showed a similar trend to that of Figure 31 for the KCl-silica mixtures, where there were minimal deposits for temperatures below 400°C and the accumulation of significant deposits starting only above 400°C. The deposition increased with increasing probe temperature. However, it was observed that the deposition rate for KCl-fly ash mixtures were higher than the KCl-silica mixtures. This could be because of different compounds such as other alkali salts and oxides present in fly ash which would have reacted with KCl leading to a higher deposition. Moreover, another difference in the deposition rate could be due to the differences in the average particle sizes of fly ash (75 µm) and silica (260 µm). This is discussed below in section 4.4.1.
4.4 Effect of Alkali mixtures on Deposition

Experiments were conducted by mixing KCl with other compounds present in the biomass fly ash particles. The effect of KCl on deposition with these compounds was investigated. Furthermore, the effect of an alkali salt mixture with silica on deposition was discussed. The alkali salts, potassium sulphate (K$_2$SO$_4$) and potassium carbonate (K$_2$CO$_3$), were mixed and prepared with KCl separately.

4.4.1 KCl mixtures with other chemicals

As seen in Figure 35, experiments were conducted by mechanically mixing KCl with other impurities generally present in the biomass fly ash particles. KCl was mixed with calcium oxide (CaO) and potassium sulphate (K$_2$SO$_4$). The deposition trend for these mixtures was compared with the KCl - silica and KCl - fly ash mechanical mixtures. As per the previous deposition curves, a similar linear-like deposition trend was observed here. However, there were differences
in deposition for different chemical mixtures. For instance, the deposition for the KCl – CaO mixtures did not start at zero but rather at 1.24 g/m²/g-feed. This difference in deposition can be observed for other KCl chemical mixtures as well. KCl - fly ash mixtures started deposition at 0.14 g/m²/g-feed, while K₂SO₄ and SiO₂ mixtures started at around zero. In spite of these differences in the starting point of the chemical mixtures, it can be observed that the deposition was increasing in a linear-like trend and that they had similar slopes with different intercepts.

![Figure 35. Deposition curve for mechanically mixed KCl mixtures with different chemicals (CaO, K₂SO₄, fly Ash, and silica)](image)

The difference in the starting point of the deposition could be because of differences in the physical properties of the chemicals such as shape, size, and bulk density. CaO and fly ash, for instance, have an average particle size of 40 µm and 75 µm respectively. K₂SO₄ and SiO₂, on the other hand, have an average particle size of 190 µm and 260 µm. CaO and fly ash particles are light and fluffy-like in nature compared to K₂SO₄ and SiO₂ which are heavier and are packed well together. This was further confirmed by measuring the bulk density in the lab. For instance, CaO has a bulk density of 0.51 g/cm³, fly ash at 0.61 g/cm³, K₂SO₄ at 1.6 g/cm³, and SiO₂ at 1.8 g/cm³. The lighter particles have a low momentum force when they fall down the EFR, and
therefore, instead of bouncing away from the probe, the particles sit on the surface of the probe. This can be seen for the lighter CaO particles where they start deposition at 1.24 g/m²/g-feed for 0 wt% KCl – CaO mixture (i.e., no molten phase). The fly ash, K₂SO₄, and SiO₂ are heavier compared to CaO and they have enough momentum force on them for the particles to bounce away from the probe when there is no molten phase (0 wt% KCl). Therefore, the fly ash, K₂SO₄, and SiO₂ particles accumulate on the probe only in the presence of a molten phase.

### 4.4.2 Alkali salts mixtures with silica on deposition

Mixtures of KCl and K₂SO₄, and mixtures of KCl and K₂CO₃ with silica on deposition are discussed in this section. Figure 36 shows the effect of the alkali salts mixture (KCl and K₂SO₄) on deposition. The mixture was prepared at 63 mole% K₂SO₄ and 37 mole% K₂Cl as highlighted in Figure 42 from the phase diagram in Appendix D. The mixture was heated in a muffle furnace at 1100°C; and then solidified, crushed, and ground to the required particle size (< 300 µm). Since the EFR is run at 800°C, the mixture was prepared at this composition (i.e., 63 mole% K₂SO₄ and 37 mole% K₂Cl) because from the phase diagram, it is known that the alkali salts melt at 770°C for this point (highlighted in figure). This was done to study the effect of deposition for the alkali salts mixtures in contrast to only KCl that was studied earlier.

As seen in Figure 36 below, a similar linear-like trend in the deposition was observed. This suggested that the molten phase is indeed responsible for deposition to take place, and an increase in the molten phase leads to an increase in the deposition. Similarly, another alkali salts mixture (KCl and K₂CO₃) was prepared with a composition of 68 mole% K₂CO₃ and 32 mole% KCl where they are completely molten below 800°C. This is highlighted in the phase diagram of KCl and K₂CO₃ (Figure 43) in Appendix D. The result, as seen in Figure 37, was the same as the previous cases where increasing the molten phase increased the deposition.
Figure 36. Deposition curve of mechanically mixed alkali salts mixtures (KCl & K₂SO₄) with silica (probe temperature: 565°C)

Figure 37. Deposition curve of mechanically mixed alkali salts mixtures (KCl & K₂CO₃) with silica (probe temperature: 565°C)
4.5 Deposit removability by air blowing

A preliminary study was conducted to determine the deposit removability. Mixtures of KCl and silica were fed into the EFR at 800°C and the deposits collected at probe temperature of 565°C were blown by the air jet blow-off apparatus. Figure 38 shows the effect of air blowing the deposits for increasing KCl content in the feed. There was no peak impact pressure (PIP) at 0 wt% KCl in the feed mixture as there was no deposit accumulated. The PIP of the deposits appeared to increase slightly with increase in KCl in the feed. The result suggests that the strength required to remove the deposits is increasing for increasing KCl concentrations in the feed.

Figure 38. Deposit removal for KCl - silica deposits using the air jet blow-off apparatus
5.0 Conclusions

The overall objective of this thesis was to study the deposition mechanism of a fouling biomass ash (alkali salt) with a non-fouling ash (silicates/oxides). This was conducted by systematically studying the effect of KCl with silica, fly ash, and other oxides on deposition for varying particle composition and temperature. The results obtained were compared to the hypothesis to give a better understanding of the deposition mechanism.

The deposition results were obtained using the laboratory-scale Entrained flow reactor (EFR) at University of Toronto. The EFR was chosen as it simulates the conditions the fly ash particles experience in the superheater regions of biomass boilers. The deposition removal results were acquired with an air jet blow-off apparatus. The air jet blow-off apparatus was used to determine the minimum peak impact pressure (PIP) required to remove the deposits from the probe. Scanning Electron Microscopy images were obtained to understand the interactions between particles. The experiments showed that there is an interaction between KCl (fouling ash) and silica, and other oxides (non–fouling ashes). The main conclusions are as follows:

- Mixing KCl with silica, fly ash, and other oxides results in an increase in deposition with increasing KCl concentration in the feed. This is because the KCl becomes molten at 775°C. As a result, the deposition increases with the increase in molten (liquid) phase.

- The particles accumulate on the probe surface if there is a molten phase (even small liquid %) contrary to the ash particles in recovery boilers where they accumulate only when the liquid content is above 15%.

- Increasing the particle size of the silica in the KCl – silica mixture results in the decrease in deposition on the probe surface. There were differences in deposition rates for different KCl chemical mixtures (i.e., KCl mixed with CaO, fly ash, and K₂SO₄). This was because of differences in the physical properties of the compounds such as shape, size, and density.
• With regards to the effect of temperature on deposition, minimal deposits were observed on the probe surface when the probe temperature was below 400°C. Significant deposits started to occur only above 400°C, and the deposition was increasing with increasing probe temperature until the maximum attainable temperature of 565°C. Moreover, the deposition rate remained the same when the EFR temperature was increased from 800 to 900°C. There was a slight reduction in deposition, and this was due to the loss of KCl in the form of vaporization at higher temperatures.

• Deposition experiments of silica with alkali salts mixtures (mixtures of KCl and K₂SO₄, and mixtures of KCl and K₂CO₃) shows a similar increasing trend. The results further show that the molten phase is the main factor for the deposition to occur on the probe surface.

• A preliminary deposit removal study for the KCl – silica deposits show that the PIP required to remove the deposits was increasing slightly with increasing KCl concentration in the feed.

Even though the experiments were conducted to study the fundamental mechanism of particle-particle interaction on deposition, it should be noted that other factors such as sintering, erosion, corrosion, shedding, or sootblowing will also play a key role in deposition. However, the experiments conducted in the EFR for this study are useful as it gives a starting point in the understanding of the deposition mechanism in biomass boiler superheater tubes that is particles accumulate on the tubes if they contain a molten phase (even small liquid %) and increasing the molten phase leads to an increase in deposition.
Bibliography


Appendices

Appendix A: PIP Air Jet vs. Nozzle Distance using a Pitot Tube

The pitot tube is used to determine the peak impact pressure (PIP) of the air jet as described by Pophali et al. The tube is 33 cm long with the tip outer diameter of 0.32 cm and the inner diameter of 0.20 cm. Compressed air from two cylinders is supplied to a solenoid valve which provides the air jet from the nozzle exit. A schematic of the pitot tube arrangement can be seen below in Figure 39 [59, 60].

Figure 39. Schematic of the pitot tube setup for deposit removal study [60]
Appendix B: PIP curve and data table for 400 psig using LabJet

**Figure 40.** A curve showing the calculated model of Peak Impact Pressure (PIP) of the air jet as a function of nozzle outlet distance

**Table 5.** A table showing the input data to LabJet model

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Appendix C: TGA Profile of Potassium Chloride

Figure 41. TGA profile of dry KCl powder
Appendix D: Phase Diagrams

Figure 42. Phase diagram of KCl₂ – K₂SO₄ mixtures showing the composition point where the feed sample was prepared (63 mol% K₂SO₄ and 37 mol% KCl₂) [18]

Figure 43. Phase diagram of KCl – K₂CO₃ mixtures showing the composition point where the feed sample was prepared (68 mol% K₂CO₃ and 32 mol% KCl) [18]