A STUDY OF COMPOSITION OF KRAFT RECOVERY BOILER CARRYOVER PARTICLES USING AN ENTRAINDED FLOW REACTOR

by

Nanan Pathania

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

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0-612-62920-1
ABSTRACT

A Study of Composition of Kraft Recovery Boiler Carryover Particles using an Entrained Flow Reactor
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Carryover (unburned black liquor, char or smelt particles entrained in the flue gas during black liquor combustion) adheres to the heat transfer tube surfaces and forms deposits in kraft recovery boilers. Carryover deposition depends greatly on its liquid content, which, in turn, is a function of composition. Understanding the carryover composition and the parameters affecting the composition is important for optimizing recovery boiler performance. This work examined the effects of black liquor particle size, gas oxygen concentration, and the chloride and sulfur contents of black liquor on carryover composition. Carryover particles were produced using an Entrained Flow Reactor. The results show that the char, chloride, potassium and sulfide contents of carryover increased while the sulfate content decreased with an increase in black liquor particle size, and with a decrease in gas oxygen concentration. Chloride and potassium contents in carryover particles were less than those in the black liquor.
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1. INTRODUCTION

1.1 STATEMENT OF PROBLEM

Kraft recovery boilers are an important component of the chemical recovery process in the production of paper and paper board products. The main function of a kraft recovery boiler is to recover the cooking chemicals from the black liquor (by-product of chemical pulping) and to regenerate the sodium sulfide. The boiler also recovers the energy released during combustion of the organic material dissolved in the black liquor. The combustion of black liquor has the additional benefit of disposing of the lignin and other pulp mill waste components in an environmentally acceptable manner [1, 2].

As black liquor is sprayed into the boiler, some liquor droplets are carried up by the flue gases to the upper boiler. The droplets burn as they are entrained in the flue gas, and form carryover particles that may deposit on the heat transfer tubes. The accumulation of such fireside deposits can be extensive and causes serious problems. The deposits decrease the boiler thermal efficiency, impede the flue gas flow, and, in serious cases, may plug the flue gas passages leading to unscheduled shutdowns for cleaning. The economic and
Operational efficiency of the mill is adversely affected by unscheduled shutdowns [3, 4, 5, 6, 7, 8].

Deposits are composed mainly of three types of fly-ash particulates: carryover, fume and intermediate sized particles [9, 10]. Deposit composition and characteristics vary significantly from boiler to boiler. Within the boiler, it varies with location in the boiler, black liquor composition, operating conditions and the mechanism by which the deposit is formed [4, 10]. Inertial impaction of carryover particles (unburned black liquor or char entrained in the flue gas) on heat transfer surfaces is the dominant deposit formation mechanism in the superheater region and at the entrance of the generating bank. Carryover forms thick, hard and tenacious deposits that contain mainly sodium sulfate and sodium carbonate. Minor quantities of sodium chloride and equivalent potassium compounds are also present. In addition to carryover, fume deposits are found in the upper boiler, primarily in the generating bank and economizer regions [9, 10].

Fume results from the vaporization of sodium and potassium salts, followed by reactions with carbon dioxide and sulfur species in the combustion gases. Fume condenses and deposits in the upper boiler as the flue gas cools. Fume deposits tend to be soft, friable, white powders. Intermediate sized particles, ranging between 1 and 100 μm, are believed to form as a result of fragmentation of black liquor or char particles and/or ejection of material during combustion and char burning [11, 12, 13].

Carryover deposits are often found to accumulate massively in the superheater region and
at the entrance of the generating bank. They are formed as a result of inertial impaction of carryover particles. Carryover deposition remains a serious problem in many mills and often determines the ultimate limit of capacity of a recovery boiler.

1.2 CHOICE OF STUDIED PARAMETERS

Carryover deposition and accumulation depend on the tendency of the carryover particles to stick to heat transfer surface, particularly in the superheater and generating bank inlet. This tendency greatly depends on the liquid content of the carryover particles, which, in turn, is a function of chemical composition [14, 15]. Carryover particles burn as they travel with the flue gas stream through the oxidizing zone of the boiler and, as a result, their composition changes continuously. Understanding the change in composition would help to determine more accurately the particle sticky temperature, which is an important parameter in characterizing the fouling of the particles. The composition of carryover depends primarily on the state of combustion of the particle, which, in turn, depends on the liquor composition and physical properties, particle size and the flue gas temperature and composition. However, the composition of carryover has not yet been properly studied and no information is available on the change in carryover composition due to the abovementioned factors. In this study, the influence on carryover composition of particle size, oxygen concentration and liquor composition were examined. The importance of these factors to carryover composition is outlined below.

Black liquor droplet size ranges from 0.5 to 5 mm when sprayed into recovery boilers
Over this size distribution, droplet size strongly affects the rate of droplet combustion and thus its composition. A number of studies have been conducted on droplet size and distribution but their influence on carryover composition is unknown. The carryover composition as a function of particle size can be used to identify the proper droplet size distribution that produces relatively less sticky carryover.

Oxygen is required for black liquor combustion, and is supplied to recovery boilers as a part of primary, secondary and tertiary air [18]. Oxygen concentration varies from boiler to boiler and with location in the boiler. It is low in the lower boiler and increases with elevation in the boiler, and it is higher near air ports and infiltration openings. Changes in oxygen concentration can significantly alter the rate of black liquor burning [18], which affects the carryover composition. Therefore, the influence of changes in oxygen concentrations on carryover composition was examined.

Makeup chemicals are added to the black liquor before firing in a recovery boiler that changes the black liquor composition including the chloride and sulfur contents. Sulfur and chloride contents of black liquor differ not only from mill to mill but also within one mill over time [1, 19, 20]. Changes in chloride and sulfur contents of liquor can affect the black liquor combustion as both components take part in chemical reactions.

The need, therefore, exists for a systematic study on carryover composition, and the influence of particle size, oxygen concentration and liquor composition for better understanding of the fouling and plugging problems in recovery boilers.
1.3 RESEARCH OBJECTIVES

The objectives of the present work are:

1) to study the composition of carryover particles formed under a controlled combustion environment using the Entrained Flow Reactor.

2) to determine the effect of (a) black liquor feed particle size (b) oxygen concentration in the flue gas (c) chloride content of the black liquor, and (d) sulfur content of the black liquor on the carryover composition.

The present report has been divided into four major chapters. Relevant literature is reviewed in Chapter 2. It is subdivided into six sections that briefly describe the recovery boilers, black liquor combustion, the particulates formed during combustion, carryover formation and their chemistry, and black liquor combustion models. The experimental methodology is described in Chapter 3 and the experimental results and their pertinent discussion are presented in Chapter 4. Chapter 4 shows how the feed particle size, flue gas oxygen content, chloride and sulfur contents of the feed black liquor affect the carryover composition. Chapter 5 presents the practical implications of the findings of the present study. Chapter 6 and 7 list the conclusions, and the recommendations for future studies respectively.
2. LITERATURE SURVEY

2.1 KRAFT BLACK LIQUOR RECOVERY BOILERS

Black liquor is the by-product of chemical pulping in the pulp and paper mills. It contains the inorganic cooking chemicals along with organic material. Table (2-1) presents the range of elemental compositions of kraft black liquors from North American mills [21]. Black liquor is conventionally burned in a large combustion unit called a recovery boiler as schematically shown in Figure (2.1).

A recovery boiler has two main functions: to recover the inorganic cooking chemicals and to generate steam for the mill. It generates steam from the energy liberated during the combustion of organic material of black liquor and recovers cooking chemicals as smelt. The dual objective of recovering chemicals and energy makes the recovery boiler an essential, but complex, part of a kraft pulp mill [1, 2].
Figure 2.1: A Schematic diagram of a kraft recovery boiler.
Table 2-1: Elemental compositions of kraft black liquors from North American mills, the ranges are for virgin liquors, i.e. before the mix tank [21]

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>34 - 39</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3 - 5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>33 - 38</td>
</tr>
<tr>
<td>Sodium</td>
<td>17 - 25</td>
</tr>
<tr>
<td>Total Sulfur</td>
<td>3 - 7</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.1 - 2</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.2 - 2</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.04 - 0.2</td>
</tr>
<tr>
<td>Other</td>
<td>0.1 - 0.3</td>
</tr>
</tbody>
</table>

2.2 BLACK LIQUOR COMBUSTION IN RECOVERY BOILERS

Black liquor containing approximately 65-80% solids is fired into the recovery boiler furnace. It forms 0.5 to 5 mm droplets when sprayed into the recovery boiler furnace [1, 16, 17]. It burns mainly in four stages: 1) drying, 2) pyrolysis (also called devolatization), 3) char burning, and 4) smelt coalescence and reactions [17, 22]. Figure 2.2 shows the different stages of black liquor combustion [23].
Drying: During drying, most or all of the water in the black liquor droplet evaporates. The droplet swells slightly and reaches a temperature of 150°C rapidly as it begins to boil. The droplet temperature then rises slowly to 300°C approximately. All visible signs of boiling cease at the end of drying. This stage lasts for 1-2 seconds for an average size droplet and is more for bigger droplets. [17, 22].

Pyrolysis: During pyrolysis, liquor droplets swell considerably, and the volatile organic material along with about half of organic carbon in the liquor is released. The droplet
temperature rises rapidly during pyrolysis. It lasts typically for about 0.5-2 seconds for an average sized droplet in air and is more at reduced oxygen content. [17, 22].

**Char Burning:** At the end of pyrolysis, a solid char remains that contains residual organic carbon and inorganic material. The char then burns and some of the inorganic material is released during char burning. The droplet shrinks in size and the droplet temperature continues to rise as the char burns. It is usually the longest stage of black liquor combustion that lasts for about 1 to 6 seconds in air. [17, 22].

**Smelt Coalescence and reactions:** After char burning, a molten salt residue called smelt remains that is mainly composed of sodium sulfide and sodium carbonate. During the fourth stage, the inorganic material coalesces into a molten smelt bead and the subsequent reactions between the smelt bead and the surrounding gas take place. Sodium sulfide may be oxidized to sodium sulfate. The oxidation reactions also increase the droplet temperature by 100°C but it cools down slowly to furnace temperature after the completion of oxidation [17, 22].

In recovery boilers, the liquor droplets generally reach the char bed before the char burning stage ends. Therefore, all four stages may take place only in the droplets that are entrained in the flue gas stream.

Hupa *et al.* [17] indicated that during drying, heat is transferred to the particle from the
surrounding environment through a counter diffusing flow of water vapor. As with drying, the rate controlling step during pyrolysis is assumed to be heat transfer from the surroundings to the droplet. The combustible gases evolved during pyrolysis burn in an envelope that surrounds the particle. The envelope probably prevents oxygen from reaching the char until gas evolution by pyrolysis is finished. Only then, can oxygen diffuse to the carbon surface and react heterogeneously with it. Both carbon monoxide (CO) and carbon dioxide (CO$_2$) are formed by this reaction, but CO is the major product. CO diffuses back out of the particle and can react with oxygen to produce CO$_2$ in the gas phase surrounding the burning particle. Swelling of the particle during pyrolysis enhances external transport of oxygen during char burning phase. Swelling also enhances the internal transport mechanism by opening the pore structure. The oxygen transported to the particle is consumed at the surface or within the particle by char oxidation reactions, as well as in the gas boundary layer surrounding the burning particles by reacting with CO and hydrogen. At temperatures prevailing in the lower recovery boiler, the kinetic rates of char burning reactions are much faster than transport of oxygen to and into the char particles. Therefore, the rate of in-flight char burning is determined mainly by the rate at which oxygen reaches the particle surface [17].

\[
\frac{dC}{dt} = R_{O_2}
\]

where: \( \frac{dC}{dt} \) = rate of carbon consumption, kg/s

\( R_{O_2} \) = rate of carbon oxidation by oxygen, kg/s
2.3 PARTICULATES IN RECOVERY BOILERS

Black liquor combustion in recovery boilers produces large quantities of fly-ash particulates. Due to their low melting temperature, these particulates deposit and foul the heat transfer tubes in the upper boiler. There are three basic types of fly-ash particulates: 1) carryover 2) fume [3, 4, 10], and 3) intermediate size particles (or ejecta) [11, 12].

**Carryover:** Carryover results from the mechanical entrainment of burning black liquor droplets char or smelt particles in the flue gas stream [3, 4, 10]. Carryover particles may deposit on the heat transfer tubes in upper boiler depending on the composition, size and the temperatures of flue gas and the tube/deposit surface. The most important deposition mechanism for these particles is inertial impaction. Figure 2.3 shows the appearance of carryover deposits on a probe exposed in the superheater region of a recovery boiler. Carryover particles range in size from 0.1 to about 3 mm, and are usually pink, fused and hard [10]. In the recovery boiler, carryover quantity is much higher than fume and intermediate size particles in the superheater region. Carryover quantity can be reduced by proper liquor firing strategy and proper air distribution in the boiler.

**Fume:** In black liquor combustion, the term ‘fume’ refers to inorganic aerosol particles, which form as a result of condensation of volatilized inorganic salts. Fume particles are much smaller than carryover particles, typically from 0.1 to 1 μm [3, 4, 6, 9, 10]. These particles may condense and deposit in the upper boiler tubes in two ways: 1) directly from gas phase to form solid particles on the cooled surface of tubes, or 2) indirectly to
form solid particles in the flue gas stream, which then deposit on cool surfaces by thermophoresis and turbulent diffusion. Fume particles usually are white and soft as compared to carryover particles (Figure 2.3) [3, 4, 10].

*Figure 2.3:* Appearance of deposits on a probe exposed in the superheater region of a recovery boiler. Outer layer: carryover, inner layer: fume deposits.

**Intermediate size particles:** Intermediate size particles (ISP), also called ejecta, have size range of 1 to 100 μm. The formation mechanism of these particles is not well understood, however, it was suggested that they may be formed by a mechanical process in which particles break into small pieces either by fragmentation or ejection of some material from the burning black liquor droplets. It was also suggested that the eruption of water
vapors and pyrolysis gases from the surface film of the liquor drops eject tiny particles from the liquor droplet [10, 12, 13]. Kochesfahani studied the formation and composition of ISP during the char bed burning using a laboratory scale char bed reactor [11]. He suggested that ISP have a composition similar to that of oxidized smelt and found them to be rich in carbonate and lean in chloride, with a relatively low sulfate. He also suggested that large quantities of ISP are formed during char bed burning that may deposit significantly in the upper boiler. The most important deposition mechanism for ISP bigger than 10 μm is considered to be inertial impaction [11, 12, 13].

2.4 CARRYOVER DEPOSITION

Deposits in recovery boilers are a mixture of carryover and fume in proportions that vary with location in the recovery boiler [9, 10]. The width of arrows in figure (2-4) shows the relative amounts of carryover and fume deposits at various locations in the boiler [10]. In the lower superheater region, carryover is the dominant deposit on the windward side of the tube. In the upper superheater region close to entrance of the generating bank, the deposits consist of carryover and some fumes. In the back half of the generating bank and in the economizer region, fume becomes dominant. In the region of the superheater and the front half of the generating bank, the recovery boilers generally experience severe deposits that mainly consist of carryover [3, 4, 9, 10]. Sootblowers are used to remove the deposits with a high pressure steam jet. Sootblowers knock off fume deposits easily as they are soft but carryover deposits being hard are difficult to remove. Because of insufficient or ineffective sootblowing, massive accumulation of deposits occurs that may
Figure 2.4: Preferential formation of carryover and fume deposits in a recovery boiler [10].

plug the flue gas passages (Figure 2.5) and result in costly shutdown. Hence, carryover has been an issue of concern for the pulp and paper industry for decades.

Carryover deposition greatly depends on the stickiness of carryover particles. Here, stickiness is defined as the tendency of carryover particles to stick to the heat transfer surfaces upon impact. The stickiness of carryover depends on its liquid content, which was investigated as a function of chemical composition and thermal properties, under static conditions in the laboratory [14, 15, 24]. Therefore, the knowledge of carryover
composition is important to predict the carryover deposition in the superheater section of the recovery boilers.

Figure 2.5: Plugging of the flue gas passages at the generating bank inlet in a recovery boiler [10].

2.5 CARRYOVER CHEMISTRY

The composition of carryover is similar to partially or fully oxidized smelt as shown in Figure 2.6 [10]. A completely burned carryover contains mostly Na₂CO₃ and Na₂SO₄, together with some NaCl, and similar potassium compounds. If not completely burned, carryover may also contain unburned char, Na₂S, Na₂S₂O₃, and Na₂SO₃. After depositing on tubes, carryover composition may change due to reactions with the surrounding gases.
Na$_2$S may oxidize to form Na$_2$SO$_4$ (Reaction 2-1) and a portion of Na$_2$CO$_3$ may react with SO$_2$ and SO$_3$ in the flue gas to form Na$_2$SO$_4$ (Reaction 2-2).

![Before Deposition](image1)

![After Deposition](image2)

**Figure 2.6:** Typical composition (wt%) of carryover before and after deposition [4].

Chlorides may vaporize and convert to sulfates by reaction with SO$_2$, SO$_3$ and water vapor (Reactions 2-3 and 2-4). As a result of above reactions, carryover contains less sulfide, carbonate, and chloride, and more sulfate than oxidized smelt. Potassium content does not change. A typical carryover composition after depositing is shown in Figure (2-6) [10].
\[
\text{Na}_2\text{S} (s,l) + 2\text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s,l) \quad (2-1)
\]
\[
\text{Na}_2\text{CO}_3 (s,l) + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s,l) + \text{CO}_2 (g) \quad (2-2)
\]
\[
\text{NaCl} (s,l) \rightarrow \text{NaCl} (g) \quad (2-3)
\]
\[
2\text{NaCl} (s,l) + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 (s,l) + 2\text{HCl} (g) \quad (2-4)
\]

Carryover composition depends on many factors including the composition of as-fired black liquor, black liquor spray distribution, firing conditions in the lower furnace, location in the boiler, location on the tubes and flue gas composition.

### 2.6 BLACK LIQUOR COMBUSTION MODELS

A single particle heat transfer model for black liquor drop combustion was developed in 1995 by Verril & Wessel to predict the heating rate and internal temperature gradients as a function of furnace temperature and initial particle size [25, 26]. Model results for 2 mm liquor droplets fixed on a retaining wire, and 100 μm entrained particles gave agreement with experimental data [25]. The model was later used to predict trends in fume formation from 2 mm liquor drops as well as fine entrained particles [Verril & Wessel 1998]. The improvements to the model allowed more accurate prediction of fume composition, and demonstrated that the modeled reaction rates can be applied to predict full scale combustion behavior [23, 26]. A three-dimensional model was used to evaluate these reactions in context of a kraft recovery boiler.
An ash chemistry model was developed to predict the quantity and composition of particulates in recovery boilers: carryover, fume and intermediate sized particles [26]. The ash chemistry model was implemented in a three-dimensional model. Model predictions of total dust loading, and ash and flue gas compositions at the boiler exit were in agreement with field-test data [26]. The predicted composition of ash contained an increasing amount of sulfate and decreasing amount of carbonate in order of decreasing particle size. Fume was also enriched in chloride and potassium, while the carryover and intermediate sized particles were depleted of these elements. Modeling results suggested that physical ejection is the single most important phenomenon affecting particulate composition in recovery boilers [23, 26].

However, these results suggest that the model is useful for qualitatively understanding and evaluating how changes in operation affect boiler performance but further improvements and additional model validation are needed [26].
3. METHODOLOGY

3.1 ENTRAINDED FLOW REACTOR

In the present study, the University of Toronto Entrained Flow Reactor (EFR) was used to simulate the conditions that carryover particles experience during their passage through a kraft recovery boiler. The EFR, as shown in the figure 3.1, is a laminar, down-flow reactor consisting of a particle feeder, a gas combustion chamber, a long vertical heated section and a non-heated sampling section. The particle feeder consists of a horizontal belt conveyor and a water-cooled particle injector. The belt conveyor transports the dried black liquor particles at a constant rate to the top of the particle injector that introduces the particles into the top of the heated section of the reactor. The gas combustion chamber is located at the top of the heated section and is used to produce a hot flue gas stream, which entrains the particles and passes through the reactor. The heated section consists of five tubular furnaces that can be electrically heated to provide a hot environment for the black liquor particles to burn. The non-heated section is located at the bottom of the heated section and is provided to facilitate sample collection. The detailed description of the EFR [34] is presented in Appendix 1.
Figure 3.1: A schematic diagram of the University of Toronto Entrained Flow Reactor [34].
3.2 CHOICE OF FEED PARTICLES TO EFR

The composition of carryover depends primarily on the state of combustion of the particle; therefore, the combustion of black liquor particles should be complete. The dried black liquor particles or charred black liquor particles may be used to produce carryover particles. Dried black liquor particles form as a result of drying the black liquor, and drying and pyrolyzing the black liquor form charred black liquor particles [28]. Dried black liquor particles have higher heating value than charred black liquor particles since about 40% of the mass of black liquor solids is lost as pyrolysis gases during preparation of charred black liquor particles [17]. Since dried black liquor particles have higher heating value, they burn faster and completely in the EFR. The appearance of deposits produced in the EFR using dried black liquor particles was similar to those of recovery boiler superheater deposits (Figure 3.2). Fatemi also recommended for using dried black liquor particles to characterize the fouling tendency of black liquor using EFR [28].

3.3 PREPARATION OF DRIED BLACK LIQUOR PARTICLES

The glass jar containing the black liquor was heated in a water bath to about 80°C as shown in the figure 3.3. The liquor was stirred to make it fluid and well mixed. It was then, poured into the preheated stainless steel trays to form a thin sheet. Forming a thin sheet of black liquor increased the surface area that facilitated the drying by shortening the drying time and by preventing the non-uniformity caused by the precipitation of suspended salts in the liquor. The liquor trays were then placed in an oven controlled at 135°C to dry the liquor (described in section 3.4) as shown in the figure 3.4. After drying, the thin sheet of dried black liquor was
removed from the trays. It was then, ground and sieved into three different particle size ranges: 250-300 \( \mu m \), 425-500 \( \mu m \) and 600-710 \( \mu m \).

Figure 3.2: Appearances of deposits produced in EFR using dried black liquor particles (250-300 & 600-850 \( \mu m \)) and recovery boiler superheater deposits (at lower and upper superheater).
Figure 3.3: A glass jar containing black liquor that was preheated before drying.

Figure 3.4: Black liquor trays put in the oven, controlled at 135°C, for drying the liquor.
3.4 **BLACK LIQUOR DRYING TESTS**

Several tests were conducted to determine an optimum drying condition for black liquor. Black liquor was dried as explained above at different temperatures and for different durations of time. The black liquor was dried after 8 to 9 hours at 120°C, after 6 hours at 135°C and after 5 hours at 160°C. However, drying at 160°C appeared to result in the release of volatile compounds because weight loss of liquor exceeded its water content after 6 hours (Figure 3.5). Based on these results, the black liquor was dried at 135°C to prevent the loss of volatile components of the liquor.

![Figure 3.5: Weight loss of black liquor sample (BL 1) during drying.](image-url)
3.5 BLACK LIQUOR COMPOSITION

A single source of as-fired black liquor was used for all the experiments; however, four more types of black liquor samples were prepared by adding inorganic salts to the base liquor. Five liquor samples were used in the present study, which are named as BL 1, 2, 3, 4 and 5. BL 1 was the original base liquor to which different amounts of inorganic salts were added to change its composition. BL 2 and 3 were prepared by adding powdered sodium chloride to BL 1 while sodium sulfate (powdered) was added to prepare BL 4 and 5. The amounts of NaCl and Na₂SO₄ to be added to BL 1 were determined and weighed. They were added to liquor jar that was being heated in the water bath (Figure 3.2). The mixture was stirred to make it uniform and then dried in the oven as explained in the section 3.2. BL 2 and 3 were prepared by drying the liquor enriched with 1.65 and 4.12 wt % NaCl (equivalent to 1 and 2.5 wt % chloride) respectively. BL 4 and 5 were prepared by drying the liquor enriched with 11.1 and 22.2 wt % Na₂SO₄ (equivalent to 2.5 and 5 wt % sulfur) respectively.

Black liquor 1 (Base liquor) was the original black liquor.

Black liquor 2 (medium chloride liquor) = BL 1 + 1.65 wt% NaCl
Black liquor 3 (high chloride liquor) = BL 1 + 4.12 wt% NaCl
Black liquor 4 (medium sulfur liquor) = BL 1 + 11.1 wt% Na₂SO₄
Black liquor 5 (high sulfur liquor) = BL 1 + 22.2 wt% Na₂SO₄

The elemental compositions and the compositions expressed as mole ratio (%) of all five types of black liquor are shown in the tables 3-1 and 3-2 respectively.
Table 3-1: Elemental composition of different types of black liquor samples used in this study.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>BL 1</th>
<th>BL 2</th>
<th>BL 3</th>
<th>BL 4</th>
<th>BL 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, C (wt%)</td>
<td>32.4</td>
<td>32.4</td>
<td>32.4</td>
<td>32.4</td>
<td>32.4</td>
</tr>
<tr>
<td>Hydrogen, H (wt%)</td>
<td>3.49</td>
<td>3.49</td>
<td>3.49</td>
<td>3.49</td>
<td>3.49</td>
</tr>
<tr>
<td>Oxygen, O (wt%)</td>
<td>36.7</td>
<td>36.7</td>
<td>36.7</td>
<td>36.7</td>
<td>36.7</td>
</tr>
<tr>
<td>Sodium, Na (wt%)</td>
<td>18.9</td>
<td>19.5</td>
<td>20.5</td>
<td>22.5</td>
<td>26.1</td>
</tr>
<tr>
<td>Potassium, K (wt%)</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
<td>3.04</td>
</tr>
<tr>
<td>Chloride, Cl (wt%)</td>
<td>0.58</td>
<td>1.58</td>
<td>3.08</td>
<td>0.58</td>
<td>0.58</td>
</tr>
<tr>
<td>Total Sulfur, S (wt%)</td>
<td>4.47</td>
<td>4.47</td>
<td>4.47</td>
<td>6.97</td>
<td>9.97</td>
</tr>
</tbody>
</table>

The C, H and O contents of black liquor were determined by automated flash combustion and gas chromatography; Na and K were determined by atomic absorption spectroscopy; Cl and S were determined by titration with silver nitrate and barium perchlorate respectively.

Table 3-2: Composition of different types of black liquor samples used in this study, expressed as % mole ratio.

<table>
<thead>
<tr>
<th>COMPONENT</th>
<th>BL 1</th>
<th>BL 2</th>
<th>BL 3</th>
<th>BL 4</th>
<th>BL 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na/(Na+K), mole%</td>
<td>91.4</td>
<td>91.6</td>
<td>91.9</td>
<td>92.6</td>
<td>93.6</td>
</tr>
<tr>
<td>K/(Na+K), mole%</td>
<td>8.6</td>
<td>8.4</td>
<td>8.0</td>
<td>7.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Cl/(Na+K), mole%</td>
<td>1.82</td>
<td>4.8</td>
<td>8.95</td>
<td>1.55</td>
<td>1.35</td>
</tr>
<tr>
<td>S/(Na₂+K₂), mole%</td>
<td>31.1</td>
<td>30.1</td>
<td>28.8</td>
<td>41.2</td>
<td>48.8</td>
</tr>
</tbody>
</table>
3.6 BLACK LIQUOR BURNING USING EFR

The EFR was operated under desired operating conditions i.e. temperature and gas temperature, and allowed to reach the steady state. Dried black liquor particles were fed into the top of the EFR, using the particle feeder belt, at a constant rate of 4 gm/min (Figure 3.1). Figure 3.6 shows a scanning electron microscopic (SEM) photograph of the dried black liquor particles prior to being fed to the EFR. The particles burned as they traveled downward with the hot flue gas steam through the heated section of the EFR and formed carryover particles. The carryover particles were collected in the stainless steel trays in the non-heated section of the EFR, were dissolved in the water and analyzed for their char, sodium, potassium, chloride, carbonate, sulfate and sulfide contents.

Figure 3.6: A SEM picture of dried black liquor particles (600-710 μm) prior to being fed to the EFR.
Samples of carryover were also collected on the stainless steel coupon in the non-heated section of the EFR for observation using SEM. Figure 3.7 shows a SEM picture of carryover particles collected at the EFR exit.

![Figure 3.7: A SEM picture of carryover particles collected at the EFR exit](image)

Table 3-3 summarizes the types of black liquor used, black liquor particle size ranges, dried black liquor feeding rate to the EFR, flue gas oxygen concentration, flue gas temperature and the EFR wall temperature for all the experiments.
Table 3-3: Experimental Conditions used in the present study.

<table>
<thead>
<tr>
<th>BLACK LIQUOR TYPE</th>
<th>PARTICLE SIZE (micron)</th>
<th>GAS OXYGEN CONCENTRATION (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BL 1</td>
<td>250-300, 425-500, 600-710</td>
<td>2.85-3.6</td>
</tr>
<tr>
<td>BL 1</td>
<td>250-300, 425-500, 600-710</td>
<td>4.8</td>
</tr>
<tr>
<td>BL 1</td>
<td>250-300, 425-500, 600-710</td>
<td>8.5-8.6</td>
</tr>
<tr>
<td>BL 1</td>
<td>250-300, 425-500, 600-710</td>
<td>13.6</td>
</tr>
<tr>
<td>BL 2</td>
<td>250-300, 425-500, 600-710</td>
<td>4.8</td>
</tr>
<tr>
<td>BL 3</td>
<td>250-300, 425-500, 600-710</td>
<td>4.8</td>
</tr>
<tr>
<td>BL 4</td>
<td>425-500, 600-710</td>
<td>4.8</td>
</tr>
<tr>
<td>BL 5</td>
<td>425-500, 600-710</td>
<td>4.8</td>
</tr>
</tbody>
</table>
3.7 CARRYOVER CHEMICAL ANALYSIS

Carryover samples were analyzed for the major cations and anions using the standard analytical techniques as mentioned in Table 3-4.

Table 3-4: Methods of analysis used for analyzing the different components of the carryover.

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Methods of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char</td>
<td>Residue after filtering a solution of the sample</td>
</tr>
<tr>
<td>Sodium</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>Potassium</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>Chloride</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Automatic Acidimetric Titration</td>
</tr>
<tr>
<td>Sulfide</td>
<td>Automatic Acidimetric Titration</td>
</tr>
</tbody>
</table>
4. RESULTS AND DISCUSSION

The composition of carryover depends on the state of combustion of the black liquor particle, which in turn depends on the black liquor particle size, liquor composition and flue gas composition. In the present study, experiments were carried out to examine the effect of these parameters on carryover composition. Several experiments were conducted to produce carryover particles in the EFR, which were then analyzed for their composition.

In the present study, chloride, potassium, sulfide, sulfate and carbonate contents of carryover are normalized with total alkali content and thus are expressed as Cl/(Na+K), K/(Na+K), S/(Na+K+K₂), SO₄/(Na₂+K₂) and CO₃/(Na₂+K₂) mole% respectively. However, the char content is expressed as wt %. It should also be noted that in this study, S represents sulfide and S_{total} represents sulfur, i.e., S_{total} = S + SO₄.
4.1 EXPERIMENTAL REPRODUCIBILITY

To determine if the results were reproducible, triplicate experiments were conducted at the same operating conditions. Table 4-1 shows a reasonably good reproducibility for the carryover composition. Different researchers at the University of Toronto have studied the reproducibility of the experiments using the EFR previously and the results obtained were found to be reasonably reproducible [27, 28]

Table 4-1 shows the standard deviation and the coefficient of variation associated with the carryover composition obtained from three different runs for identical black liquor chemical composition and size distribution, under identical EFR operating conditions. The coefficient of variation was used in determining the error associated with each measurement, and in interpreting the results of the effect of examined variables on carryover composition.

The variations in the results can be due to several factors including: fluctuations in oxygen concentration of the flue gas; fluctuations in gas temperature and temperature reading; slightly varying composition of feeding particles; and minor variations in experimental technique.
Table 4-2: Triplicate carryover composition data obtained for one set of experimental conditions.

<table>
<thead>
<tr>
<th></th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Coefficient of Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Test Conditions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Oxygen Conc. (%)</td>
<td>13.6</td>
<td>13.6</td>
<td>13.6</td>
<td>13.6</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Gas temperature (°C)</td>
<td>932</td>
<td>935</td>
<td>938</td>
<td>935</td>
<td>3</td>
<td>0.3</td>
</tr>
<tr>
<td>Feed Particle Size (μm)</td>
<td>425-500</td>
<td>425-500</td>
<td>425-500</td>
<td>463</td>
<td>38</td>
<td>8.1</td>
</tr>
<tr>
<td><strong>Results</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Char (wt%)</td>
<td>0.14</td>
<td>0.15</td>
<td>0.13</td>
<td>0.14</td>
<td>0.01</td>
<td>7.9</td>
</tr>
<tr>
<td>Cl/(Na+K), mole%</td>
<td>0.46</td>
<td>0.45</td>
<td>0.48</td>
<td>0.46</td>
<td>0.01</td>
<td>3.0</td>
</tr>
<tr>
<td>CO₂/(Na₂+K₂), mole%</td>
<td>57.1</td>
<td>57.6</td>
<td>59.6</td>
<td>58.1</td>
<td>1.3</td>
<td>2.3</td>
</tr>
<tr>
<td>S/(Na₂+K₂), mole%</td>
<td>0.71</td>
<td>0.88</td>
<td>0.84</td>
<td>0.81</td>
<td>0.09</td>
<td>11.1</td>
</tr>
<tr>
<td>SO₄/(Na₂+K₂), mole%</td>
<td>40.3</td>
<td>36.2</td>
<td>35.3</td>
<td>37.3</td>
<td>2.7</td>
<td>7.2</td>
</tr>
<tr>
<td>Na/(Na+K), mole%</td>
<td>91.7</td>
<td>92.7</td>
<td>93.1</td>
<td>92.5</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>K/(Na+K), mole%</td>
<td>7.3</td>
<td>7.0</td>
<td>7.5</td>
<td>7.3</td>
<td>0.3</td>
<td>3.8</td>
</tr>
</tbody>
</table>
4.2 EFFECT OF BLACK LIQUOR PARTICLE SIZE

Black liquor forms 0.5 to 5 mm droplets when sprayed into the recovery boilers. The droplet size must be large enough to minimize carryover and small enough to avoid bed blackout and smelt-water contact [16, 17]. Black liquor droplet size strongly affects the rate of mass and energy transfer to and from the droplet, which, in turn, affects the rate of droplet combustion. Black liquor combustion rate directly influences the carryover composition.

In order to analyze the effect of black liquor particle size on carryover composition, dried black liquor particles of BL 1 having size ranges: 250-300 μm, 425-500 μm and 600-710 μm were burned in the EFR to form carryover. The carryover particles were collected in the stainless steel trays in the non-heated section of the EFR and their char, chloride, potassium, sulfide, carbonate and sulfate contents were determined. Figures 4.2.1 to 4.2.3 show the variations of carryover composition with particle size for experiments with a gas oxygen concentration of 4.8% while the results for experiments with oxygen concentration of 2.85-3.6% are shown in figures 4.2.4 to 4.2.6. Similar results were obtained at other oxygen concentrations that are shown in Appendix 2.
Figure 4.2.1: Effect of black liquor particle size on chloride and char contents of carryover
EFR conditions: 800°C and 4.8 % O₂; Particles: BL 1

Figure 4.2.2: Effect of black liquor particle size on potassium and sulfide contents of carryover
EFR conditions: 800°C and 4.8 % O₂; Particles: BL 1
Figure 4.2.3: Effect of black liquor particle size on sulfate and carbonate contents of carryover
EFR conditions: 800°C and 4.8 % O₂; Particles: BL 1

Figure 4.2.4: Effect of black liquor particle size on chloride and char contents of carryover
EFR conditions: 800°C and 2.85-3.6 % O₂; Particles: BL 1
Figure 4.2.5: Effect of black liquor particle size on potassium and sulfide contents of carryover EFR conditions: 800°C and 2.85-3.6 % O₂; Particles: BL 1

Figure 4.2.6: Effect of black liquor particle size on sulfate and carbonate contents of carryover EFR conditions: 800°C and 2.85-3.6 % O₂; Particles: BL 1
Figures 4.2.1 and 4.2.4 show that smaller particles had a lower char content, which suggests that they burn faster than larger particles. In addition, the chloride, potassium and sulfide contents of carryover particles increased as the size range of dried black liquor particles increased (Figures 4.2.1 to 4.2.5). It was also found that the particle size did not have any significant effect on carbonate content of the carryover but sulfate content decreased substantially with an increase in black liquor particle size (Figures 4.2.3 and 4.2.6). It was observed that not only did the carryover composition changes with particle size, but also the carryover formed by larger particles had a brown color as compared to white color of carryover formed by smaller particles.

The combustion rate depends on the rate of oxygen and energy transfer to the particle surface [17], which is directly proportional to the specific surface area of the particle. Smaller particles have higher specific surface area and thus have a higher burning rate than the larger particles. A higher burning rate results in a faster release of energy due to exothermic char combustion reactions (Reaction 4.2.1), which are expected to increase the temperature of the burning particle.

\[
\text{C (s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_{1200^\circ\text{C}} = -393 \text{ kJ} \quad \text{...(4.2.1)}
\]

Since high temperature and high specific surface area increase the rate of vaporization of NaCl and KCl (Reaction - 4.2.2), the chloride and potassium loss from smaller particles
is greater than from the larger particles. Therefore, the smaller particles had lower chloride and potassium contents.

\[ \text{NaCl (l,s) } \rightarrow \text{NaCl (g)} \] \( \ldots(4.2.2) \)

\[ \text{Na}_2\text{S (l,s) } + \text{2O}_2\text{(g) } \rightarrow \text{Na}_2\text{SO}_4\text{(l,s)} \] \( \ldots(4.2.3) \)

Similar reactions occur for equivalent potassium compounds.

High specific surface area and high temperature may also increase the rate of sulfide oxidation (Reaction - 4.2.3). As a result, smaller particles had higher sulfate and lower sulfide contents as compared to those of larger particles.

The results show that the presence of chloride and potassium in carryover increases with an increase in black liquor particle size. Chloride and potassium increase the quantity of liquid phase in carryover particles that makes them sticky [10, 14, 22, 24]. Sticky carryover deposit and accumulate on the heat transfer tubes in the superheater region. This may plug the flue gas passages and lead to costly shutdowns.
4.3 EFFECT OF OXYGEN CONCENTRATION

Black liquor combustion requires the addition of heat and oxygen to black liquor droplets. The heat is required to dry and pyrolyze the liquor, while the oxygen is required for burning of the organic material. Oxygen must be transported to the burning particle so that the solid organics react with oxygen. The burning rate is limited by transport of oxygen [17]; it is, therefore, necessary to know the effect of oxygen concentration in the gas.

The effect of oxygen concentration on the composition of carryover was examined for three black liquor particle sizes having ranges of 250-300 μm, 425-500 μm and 600-710 μm. Particles of black liquor sample 1 (Tables 3-1 and 3-2) were burned in the EFR at different oxygen concentrations and the carryover particles thus formed were analyzed for their chemical composition. The different oxygen concentrations used for this study are tabulated in Table 3-3. Figures 4.3.1 to 4.3.3 show the results for the particles of BL 1 having size range of 425-500 μm and similar results were obtained for other size ranges that are shown in Appendix 3.

Figures 4.3.1 and 4.3.2 show that the carryover formed in a higher oxygen environment had lower chloride, potassium and sulfide contents. It was also found that the carryover particles had lower char in an oxygen rich atmosphere (Figure 4.3.1). Figure 4.3.3 shows that the sulfate content of the carryover particles increased with an increase of oxygen concentration in the flue gas.
Figure 4.3.1: Effect of oxygen concentration on chloride and char contents of carryover. 
EFR conditions: 800°C; Particle size: 425-500 μm.

Figure 4.3.2: Effect of oxygen concentration on potassium and sulfide contents of carryover. 
EFR conditions: 800°C; Particle size: 425-500 μm.
Figure 4.3.3: Effect of oxygen concentration on sulfate and carbonate contents of carryover.
EFR conditions: 800°C; Particle size: 425-500 μm.

Results show that the carryover formed in a higher oxygen environment had a lower char, which suggests that they burn faster in that environment. Higher oxygen concentration in gas increases the rate of char burning. Since faster char burning increases the consumption of the char, a lower amount is left in the carryover particles. As discussed in Section 4.2, char burning reaction (Reaction 4.2.1) is exothermic and thus increases the temperature of the burning particle.

High temperature increases the rate of vaporization of NaCl and KCl (Reaction – 4.2.2), therefore, chloride and potassium contents of carryover particles are less at a higher
oxygen concentration. Such concentration would possibly increase the rate of sulfide oxidation (Reaction - 4.3.3) resulting in higher sulfate and lower sulfide contents of carryover.

Results show that the carryover formed at 13.6% oxygen concentration had lower carbonate content as compared to other oxygen concentrations. The reason for carbonate behavior is not clear but the intense burning at such a high oxygen concentration may lead to carbonate decomposition.
4.4 EFFECT OF BLACK LIQUOR CHLORIDE CONTENT

Chloride enters the chemical recovery cycle of the kraft mill via wood floated in seawater, makeup chemicals and pulp bleaching filtrates [19, 30]. Therefore, chloride is always present in carryover. The amount of chloride in carryover depends on many factors including the chloride content of black liquor. Chloride depresses the first melting point of the carryover particle and increases the quantity of liquid phase at any given temperature [14, 24]. Due to the significant influence of liquid phase on carryover stickiness, the presence of chloride can cause increased carryover deposition. Therefore, the knowledge of chloride behavior during black liquor burning is critical.

To study the effect of chloride on carryover composition, chloride was added to the black liquor in the form of sodium chloride (NaCl). Experiments were performed using three black liquor samples (BL 1, 2 and 3) containing 1.82, 4.8 and 8.95 mole% Cl/(Na+K) respectively (Table 3-2). The results obtained from these experiments are shown in Figures 4.4.1 to 4.4.5.
Figure 4.4.1: Effect of NaCl addition to black liquor on chloride and potassium contents of carryover. EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 2 & 3; Size: 425-500 μm.

Figure 4.4.2: Effect of NaCl addition to black liquor on sulfur and carbonate contents of carryover. EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 2 & 3; Size: 425-500 μm.
**Figure 4.4.3:** Effect of NaCl addition to black liquor on chloride and potassium contents of carryover. EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 2 & 3; Size: 600-710 μm.

**Figure 4.4.4:** Effect of NaCl addition to black liquor on sulfur and carbonate contents of carryover. EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 2 & 3; Size: 600-710 μm.
The results show that the addition of NaCl to the black liquor produced a substantial increase in the chloride and char contents of carryover (Figures 4.4.1, 4.4.3, and 4.4.5). On the other hand, the sulfur content of carryover decreased as NaCl was added (Figures 4.4.2 and 4.4.4). Addition of NaCl to black liquor did not produce any significant change in the potassium and carbonate contents of carryover.

Addition of sodium chloride increases the partial pressure of NaCl, this may result in a greater rate of NaCl vaporization (Reaction 4.3.4). Vaporization of NaCl requires heat that reduces the temperature of the burning particles. Since it is known that low
temperature favors sulfur release, lower temperature of high chloride particles causes more sulfur to release. Therefore, the sulfur content of high chloride particles is less. Lower particle temperature due to addition of NaCl, also lowers the rate of char burning, which would result in higher char content.
4.5 EFFECT OF BLACK LIQUOR SULFUR CONTENT

Ideally, in a recovery boiler process, all sulfur present in the black liquor would be transformed to sulfide. In recovery boilers, however, the sulfur is present as both sulfide and sulfate. A substantial part of sulfur is carried by the flue gases, mainly in the form of sulfate dust and sulfur-containing gases. These compounds increase the load on the electrostatic precipitator and may reduce the thermal efficiency of the boilers [17, 21, 29, 30].

The typical sulfur content of the black liquor is about 3 - 7 wt% as shown in Table (2-1). In addition to sulfur already present in the black liquor, sulfur enters the black liquor as a part of makeup chemicals including salt-cake (Na₂SO₄), elemental sulfur and precipitator dust. Since sulfur content varies with the addition of makeup chemicals, it is important to understand the effect of the addition of sulfur to the black liquor.

Figures 4.5.1 to 4.5.6 show how the carryover composition is affected by the addition of sodium sulfate to black liquor. Results show that the addition of sulfate to black liquor significantly changes the carryover composition. Figures 4.5.1 and 4.5.4 show that the chloride content of carryover decreased as the sulfate content of the black liquor increased while the char content increased. The potassium and sulfide contents decreased with an addition of sulfate to black liquor (Figures 4.5.2 and 4.5.5). The sulfate content of the carryover increased but the carbonate content decreased with an addition of sulfate to the black liquor (Figures 4.5.3 and 4.5.6).
Figure 4.5.1: Effect of Na₂SO₄ addition to black liquor on chloride and char contents of carryover
EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 4 & 5; Size: 425-500 μm.

Figure 4.5.2: Effect of Na₂SO₄ addition to black liquor on potassium and sulfide contents of carryover
EFR conditions: 800°C and 4.8% O₂; Particles: BL 1, 4 & 5; Size: 425-500 μm.
Figure 4.5.3: Effect of $\text{Na}_2\text{SO}_4$ addition to black liquor on sulfate and carbonate contents of carryover EFR conditions: $800^\circ\text{C}$ and 4.8% $\text{O}_2$; Particles: BL 1, 4 & 5; Size: 425-500 $\mu\text{m}$.

Figure 4.5.4: Effect of $\text{Na}_2\text{SO}_4$ addition to black liquor on chloride and char contents of carryover EFR conditions: $800^\circ\text{C}$ and 4.8% $\text{O}_2$; Particles: BL 1, 4 & 5; Size: 600-710 $\mu\text{m}$.
Figure 4.5.5: Effect of Na₂SO₄ addition to black liquor on potassium and sulfide contents of carryover. EFR conditions: 800°C and 4.8% O₂. Particles: BL 1, 4 & 5; Size: 600-710 μm.

Figure 4.5.6: Effect of Na₂SO₄ addition to black liquor on sulfate and carbonate contents of carryover. EFR conditions: 800°C and 4.8% O₂. Particles: BL 1, 4 & 5; Size: 600-710 μm.
Addition of $\text{Na}_2\text{SO}_4$ to the black liquor lowers the heating value of the liquor due to the dilution of its organic fraction. Lowering the liquor heating value results in a lower temperature of the burning particles. The increase in char content of high sulfate particles suggests that the particles had a lower temperature, resulting in more sulfur being released, which causes a decrease in sulfide content of the carryover.

The sulfur dioxide ($\text{SO}_2$) emissions from the burning black liquor particles depend primarily on the sulfur content of the black liquor and the temperature of the burning particles [29]. Addition of $\text{Na}_2\text{SO}_4$ increases the sulfur content and lowers the temperature of particles, resulting in an increase of $\text{SO}_2$ concentration in the gas surrounding the burning particles. The $\text{SO}_2$ along with $\text{O}_2$ and water vapor may react with $\text{Na}_2\text{CO}_3$ and $\text{NaCl}$ present in the particle to form $\text{Na}_2\text{SO}_4$ according to reactions 4.5.1 and 4.5.2 respectively [29, 30]. As a result, carbonate and chloride contents of carryover decrease while the sulfate content increases with the addition of $\text{Na}_2\text{SO}_4$ to black liquor.

$$\text{Na}_2\text{CO}_3 (l) + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (s, l) + \text{CO}_2 (g) \quad ...(4.5.1)$$

$$2 \text{NaCl (l,v)} + \text{SO}_2 (g) + \frac{1}{2}\text{O}_2 (g) + \frac{1}{2}\text{H}_2\text{O} (g) \rightarrow \text{Na}_2\text{SO}_4 (s, l) + 2\text{HCl (g)} \quad ...(4.5.2)$$
4.6 DEPLETION OF CHLORIDE AND POTASSIUM

A number of studies have been conducted on enrichment of chloride and potassium in fume but their depletion in carryover has not yet been studied. Experimental data obtained from the present study was used to determine chloride and potassium depletion in carryover and the influence of particle size, oxygen concentration and black liquor composition. A factor describing the enrichment/depletion is defined as the relative amount of chloride or potassium in the carryover (using total alkali as the basis) compared to that in the initial black liquor solids [18, 30].

Chloride Enrichment Factor (EFCl) = \[ \frac{[\text{Cl}/(\text{Na}+\text{K})]_{\text{carryover}}}{[\text{Cl}/(\text{Na}+\text{K})]_{\text{BLS}}} \]

Potassium Enrichment Factor (EFK) = \[ \frac{[\text{K}/(\text{Na}+\text{K})]_{\text{carryover}}}{[\text{K}/(\text{Na}+\text{K})]_{\text{BLS}}} \]

where: Cl = concentration of chloride (mole%)
Na = concentration of sodium (mole%)
K = concentration of potassium (mole %)
BLS = black liquor solids

If EF = 1, chloride or potassium concentration in carryover is equal to that of dry black liquor.

If EF > 1, carryover is enriched with chloride or potassium.

If EF < 1, carryover is depleted of chloride or potassium.
In Figures 4.6.1 to 4.6.3 a reference line was drawn at EF = 1 to compare the chloride or potassium concentrations of carryover and black liquor. Results show that the enrichment factors of chloride and potassium for carryover were less than one in all experiments, which suggests that the carryover is depleted of chloride and potassium. Chloride and potassium enrichment factors decreased with a decrease in particle size, and with an increase in oxygen concentration (Figures 4.6.1 and 4.6.2). Figures 4.6.3 and 4.6.4 show that the addition of chloride and sulfate to black liquor decreased the chloride enrichment factor in carryover but had no significant effect on potassium enrichment factor.

![Figure 4.6.1: Effect of particle size and oxygen concentration on chloride enrichment in carryover EFR conditions: 800°C; Particles: BL 1](image-url)
Figure 4.6.2: Effect of particle size and oxygen concentration on chloride enrichment in carryover EFR conditions: 800°C; Particles: BL 1

Figure 4.6.3: Effect of NaCl addition on chloride and potassium enrichments in carryover EFR conditions: 800°C; Particles: BL 1, 2 & 3; Size: 425-500 μm.
Figure 4.6.3: Effect of Na₂SO₄ addition on chloride and potassium enrichments in carryover EFR conditions: 800°C; Particles: BL 1, 4 & 5; Size: 425-500 μm.
5. IMPLICATIONS

The results obtained from the present study provide an insight into the carryover composition, however, it should be noted that the results have several relevant and practical implications to the operational problems encountered in the kraft recovery boilers. Since there are some differences between a recovery boiler and the entrained flow reactor, it is important to recognize the limitations of the application of the findings of the present study.

The results of the present study show that the particle size has a significant effect on the carryover composition; this may not be applied directly to the recovery boilers. When black liquor is sprayed into a recovery boiler, the black liquor droplets are distributed over a broad size range of 0.5 - 5 mm [16, 17]. In the entrained flow reactor, dried black liquor particles having size distribution between 250 - 710 μm were studied. This studied particle size distribution represents about 10% of the lower range of the droplet size
distribution found in recovery boilers. The extrapolation of results to higher sizes and its application in recovery boilers need appropriate caution.

Kochesfahani in his study of the formation of ISP suggested that large quantities of ISP are formed during char bed burning [11]. The results of the present study suggest that ISP have lower chloride and potassium contents because of their smaller size. Low chloride and potassium in ISP decrease their liquid content and make ISP less sticky. Therefore, ISP have less tendency to stick and deposit, and would be expected to cause less harm to the recovery boiler as compared to the larger particles (carryover).

The results also indicated that the addition of Na$_2$SO$_4$ to the black liquor decreased the chloride content of the carryover particles. Low chloride decreases the particle stickiness by lowering its liquid content. This seems to suggest that adding make-up saltcake to the black liquor can reduce the carryover deposition. On the other hand, this may increase the sulfur emissions.

The results suggest that any change in the studied parameters caused a change in the particle temperature resulting in different composition. The particle temperature, thus, plays a key role in determining the composition. The higher particle temperature produced carryover with lower char, chloride and potassium contents.

The results show that the small particles, high oxygen concentration and high sulfate content of black liquor cause the chloride content of the carryover to decrease. This
suggests that there is a corresponding increase in the chloride concentration in the flue gas, which causes higher enrichment of chloride in the precipitator catch. The precipitator catch is recycled into the recovery boiler by adding it to the black liquor. It was found in the present study that the addition of chloride to black liquor increased the chloride content of the carryover. The high chloride content of the carryover increases its liquid content, which makes the particles sticky resulting in increased carryover deposition and accumulation. The precipitator catch purging may help minimize the problem of carryover deposition and accumulation on the heat transfer tubes of the upper recovery boiler. The precipitator dust purging also results in the loss of sodium and sulfur that can be recovered as smelt in the boiler. Therefore, a compromise should be found between the detrimental and beneficial effects of precipitator catch purging.

The present study provides understanding of carryover composition and generally suggests careful regulation of black liquor droplet size, oxygen concentration and black liquor composition to control and prevent carryover deposition and accumulation. Any modification that will decrease the chloride and potassium contents of the carryover should be beneficial.
6. CONCLUSIONS

The present study on composition of the carryover particles formed under a controlled combustion environment using the Entrained Flow Reactor has led to the following conclusions:

1) Carryover particles are principally composed of sodium, carbonate and sulfate with small amounts of chloride, sulfide, char and potassium.

2) Smaller particles have lower char, chloride, potassium and sulfide contents, and have a higher sulfate content.

3) Carryover formed in a higher oxygen atmosphere has lower char, chloride, potassium and sulfide contents, and has a higher sulfate content.

4) Adding chloride to the black liquor results in higher chloride and char contents of carryover, and a lower sulfur content.
5) Chloride, potassium and carbonate contents in carryover decrease with the addition of sodium sulfate to the black liquor while the char and sulfate contents increase.

6) Carryover particles are depleted of chloride and potassium.

7) Chloride enrichment factor of carryover decreases with an increase of oxygen concentration, a decrease in particle size, and a decrease in particle size. It also decreases with an addition of sodium chloride and sodium sulfate to the black liquor.
7. RECOMMENDATIONS

Based on the results obtained from the present study, several interesting factors require further consideration and investigations. These factors are briefly outlined below:

1) Due to the influence of potassium on the liquid content of the particles, the effect of potassium on carryover composition should be determined. This would be beneficial in predicting the fouling tendency of the carryover.

2) The entrained flow reactor should be modified to get oxygen concentrations lower than 2.85 % and experiments should be conducted to determine the effect of reducing conditions on the carryover composition.

3) Experiments should be conducted to collect carryover at different sampling ports of the EFR. The results obtained from these experiments will simplify the interpretation and will be beneficial in the validation of the present findings.

4) The heat transfer model should be developed to evaluate the carryover composition, their liquid content and the stickiness. This model then should be tailored to the conditions found in the actual recovery boiler.
REFERENCES


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APPENDIX 1: ENTRAINED FLOW REACTOR

The EFR, as shown in Figure 3.1, is a laminar, down-flow reactor consisting of five high temperature tubular furnaces that form a continuous unit that operates at temperatures as high as 1350°C. The EFR consists of a particle feeder, a gas combustion unit, a long vertical heated section, a non-heated sampling section, a gas exhaust system and a data acquisition and control system.

Particle Feeder: The feeder consists of a 0.3 m wide by 1.2 m long belt conveyor that transports particles at a mass flow rate as low as 0.5 g/min to the top of a water cooled particle injector. A flow of pressurized carrier air ensures the flow of the particles into the injector. The injector passes through the gas combustion unit and a ceramic honey-comb which is used to provide a uniform gas flow, and introduces the particles into the first zone of the heated section at the top of the reactor [27].

Gas Combustion Unit: The gas combustion unit is located at the top of the heated section of the reactor. It is equipped with an Eclipse Thermojet natural gas burner that has a maximum heat input capacity of 44 kW. Natural gas is burned at a flow rate of about 1 to 25 m³/hr. The combustion gases are tangentially mixed with the dilution air to produce gas of desired volume with a temperature up to 1200°C [27].

The temperature and the flow rate of the inlet gas to the heated section are controlled through two independent control loops. The first control loop manipulates the gas valve
to achieve the desired flow rate setpoint. The combustion air valve is coupled with the gas valve and provides stoichiometric combustion air plus 10% additional air for complete combustion. The second control loop manipulates the dilution valve to achieve the desired temperature setpoint. Each control loop is provided with a flow indicator and controller. The flow rates of natural gas, combustion air and dilution air to the combustion chamber are all indicated as the inlet flow rates at 25°C. Three R-type thermocouples are located in ports 120° apart at the bottom of the combustion chamber to measure the temperature of the inlet gas to the heated section. Multiple temperature measurements are provided to ensure a complete mixing of the combustion gas and even inlet gas temperature to the heated section. The gas then passes through a honeycomb flow straightener, installed at the top of the first furnace of the heated section to provide a uniform gas flow in the reactor [27].

**Heated Section**: The heated section is an assembly of five split-shell tube furnaces that form a continuous vertical unit. Each furnace is 1.22 m high, 0.3 m ID and 0.61 m OD; each can be electrically heated to a maximum temperature of 1350°C. A mullite tube of 1.22 m high, 0.18 m ID, 0.22 m OD is placed axially in each furnace. Between adjacent furnaces, there is a 0.1 m non-heated insulated space which accommodates an observation/sampling port, and which supports the mullite tube. The temperature of each furnace is monitored by two R-type thermocouples, and each furnace is controlled independently using a temperature controller [27].
**Non-heated Sampling Section**: This section is located between the bottom of the heated section and the exhaust system and is provided to facilitate sample collection and optical measurements. The non-heated section consists of an insulated chamber, placed on a stainless steel base located 10.2 cm above the well mouth of the exhaust system. The insulated chamber minimizes the heat loss by convection, while providing suitable conditions for optical measurement [27].

**Gas Exhaust System**: The combustion gas is exhausted from the reactor to the atmosphere via an induced draft fan located on the roof of the building. The draft inlet, located about 0.5 m below the last furnace, is designed for a flow rate of 2500 standard m³/hr, a flow rate much greater than the reactor exhaust gas flow rate [27].

**Data Acquisition and Control System**: A control panel is provided for the gas combustion unit in order to control the temperature and the flow rate of the gas leaving the combustion chamber. A labview date acquisition program is used to monitor the particle feed rate, the burner combustion gas temperature and flow rate, five furnace temperatures, the probe surface temperature and the deposit weight [27].
APPENDIX 2

Figure A2.1: Effect of black liquor particle size on chloride and char contents of carryover
EFR conditions: 800°C and 8.5-8.6 % O₂; Particles: BL 1

Figure A2.2: Effect of black liquor particle size on potassium and sulfide contents of carryover
EFR conditions: 800°C and 8.5-8.6 % O₂; Particles: BL 1
Figure A2.3: Effect of black liquor particle size on sulfate and carbonate contents of carryover
EFR conditions: 800°C and 8.5-8.6 % O₂; Particles: BL 1

Figure A2.4: Effect of black liquor particle size on chloride and char contents of carryover
EFR conditions: 800°C and 13.6 % O₂; Particles: BL 1
Figure A2.5: Effect of black liquor particle size on potassium and sulfide contents of carryover EFR conditions: 800°C and 13.6 % O₂; Particles: BL 1

Figure A2.6: Effect of black liquor particle size on sulfate and carbonate contents of carryover EFR conditions: 800°C and 13.6 % O₂; Particles: BL 1
Figure A3.1: Effect of oxygen concentration on chloride and char contents of carryover. EFR conditions: 800°C; particle size: 250-300 μm.

Figure A3.2: Effect of oxygen concentration on potassium and sulfide contents of carryover. EFR conditions: 800°C; particle size: 250-300 μm.
**Figure A3.3:** Effect of oxygen concentration on sulfate and carbonate contents of carryover. EFR conditions: 800°C; particle size: 250-300 μm.

**Figure A3.4:** Effect of oxygen concentration on chloride and char contents of carryover. EFR conditions: 800°C; particle size: 600-710 μm.
Figure A3.5: Effect of oxygen concentration on potassium and sulfide contents of carryover. EFR conditions: 800°C; particle size: 600-710 μm.

Figure A3.6: Effect of oxygen concentration on sulfate and carbonate contents of carryover. EFR conditions: 800°C; particle size: 600-710 μm.