A STUDY OF THE

COMPOSITION OF CARRYOVER PARTICLES

IN KRAFT RECOVERY BOILERS

by

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A thesis submitted in conformity with the requirements

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ABSTRACT

Carryover particles are partially/completely burned black liquor particles entrained in the flue gas in kraft recovery boilers. Understanding how carryover particles form and deposit on heat transfer tube surfaces is critically important in the design and operation of a recovery boiler. The tendency for a carryover particle to deposit on a tube surface depends on the particle temperature and composition at the moment of impact. This study was the first to examine systematically how carryover particle composition changes with the black liquor chemistry and burning conditions.

The effect of black liquor composition and particle size, gas composition (O₂ and SO₂ concentrations) and temperature on the composition of carryover particles were studied using an Entrained Flow Reactor (EFR). Field studies were conducted on three operating boilers, where an air-cooled probe was used to collect carryover samples at the superheater entrance.

The results show that the chloride (Cl) and potassium (K) contents in carryover particles were linearly proportional to their contents in black liquor. Cl and K were depleted during black liquor
combustion due mainly to the vaporization of NaCl and KCl. The depletion of Cl is about three times greater than that of K. The significant depletion of Cl implies that carryover particles contain much less Cl, and hence, are less sticky than previously expected from black liquor composition.

A dynamic model was also developed to predict the composition of carryover particles as a function of black liquor composition and burning conditions. Based on the data obtained experimentally in this study, the kinetic equations for the oxidation of sulphide available in the literature were modified and incorporated into the model to improve its sulphide and sulphate predictions. The model predicts the main components of carryover particles formed in both the EFR and three operating recovery boilers reasonably well, except for the K content, which is slightly over-predicted at high O₂ concentrations (or high particle temperatures).

Based on the predicted composition, it is possible to determine the thermal properties of carryover and to assess its fouling propensity in the boiler. The information helps boiler manufacturers and operators to identify locations in the boiler where massive carryover deposition may occur and to devise appropriate control strategies to minimize fouling and to improve boiler thermal efficiency.
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NOMENCLATURE

The parameters in the equations presented in this report are all defined in alphabetical order as follows:

\( A_p \): Particle surface area (\(m^2\))
\( A_s \): Particle specific surface area (\(m^2/g\))
\( C_D \): Drag force coefficient (dimensionless)
\( C_s \): Particle interface gas concentration (\(mol/m^3\))
\( C_\infty \): Bulk gas concentration (\(mol/m^3\))
\( E_1, E_2, E_3 \): Activation energy in Kobayashi equation for sulphur (\(J/mol\))
\( E_4, E_5 \): Activation energy in Kobayashi equation for carbon (\(J/mol\))
\( K_g \): Mass transfer coefficient (\(m^2/s\))
\( Gr \): Grashof number (dimensionless)
\( Nu \): Nusselt number (dimensionless)
\( P_{sat} \): Pure component vapour pressure (kPa)
\( P_t \): Bulk gas total pressure (kPa)
\( Q_{cons} \): Rate of heat consumed inside the particle (W)
\( Q_{devol} \): Rate of heat consumed during the devolatilization (W)
\( Q_{gen} \): Rate of heat generated inside the particle (W)
\( Q_{in} \): Rate of heat into the particle (W)
\( Q_{out} \): Rate of heat going out of the particle (W)
\( Q_{phase} \): Rate of heat required for the phase change of inorganics (W)
\( R \): Gas constant (\(J/mol/K\))
\( Re \): Reynolds number (dimensionless)
\( R_{c-char} \): Rate of carbon converted to char during devolatilization (g/s)
\( R_{c-g} \): Rate of carbon converted to gas during devolatilization (g/s)
\( R_{cond} \): Conductive heat transfer resistance (\(m^2 K/W\))
\( R_{conv} \): Convective heat transfer resistance (\(m^2 K/W\))
\( R_{CO2} \): Rate of carbon reacting with \(CO_2\) during the char burning stage (mole/s)
\( R_{CO3} \): Rate of carbon reacting with alkali carbonate during the char burning stage (mole/s)
\( R_{H2O} \): Rate of carbon reacting with \(H_2O\) during the char burning stage (mole/s)
$R_i$: Rate of reaction for species $i$ (g/s)
$R_{O2}$: Rate of carbon reacting with $O_2$ in the char burning stage (mole/s)
$R_S$: Rate of alkali sulphide oxidation (mole/s)
$R_{SO4}$: Rate of carbon reacting with alkali sulphate in the char burning stage (mole/s)
$R_{s-char}$: Rate of sulphur going to char within devolatilization (g/s)
$R_{s-g}$: Rate of sulphur going to gas within devolatilization (g/s)
$\text{R}_{\text{rad}}$: Radiation heat transfer resistance ($m^2$ K/W)
$\text{R}_t$: Total heat transfer resistance ($m^2$ K/W)

$S_{\text{max}}$: Particle swelling ratio at the end of devolatilization stage (dimensionless)
$S_{\text{min}}$: Particle shrinking ratio for the smelt, at the end of char burning (dimensionless)

$T_f$: Film temperature (K)
$T_{\text{flame}}$: Flame temperature (K)
$T_p$: Particle bulk temperature (K)
$T_{\text{gas}}$: Gas bulk temperature (K)

$V_p$: Particle volume ($m^3$)
$V_s$: Slip velocity (m/s)

$X_{\text{char}}$: Extent of char burning (dimensionless)
$X_{\text{devol}}$: Extent of devolatilization (dimensionless)
$Y_{O2}$: Oxygen mole fraction in gas (dimensionless)

$\Delta H_c$: Heat of combustion for pyrolyzed gases (J/g)

$a_1, a_2$: Constants in Kobayashi equation for carbon (1/s)
$b_1, b_2, b_3$: Constants in Kobayashi equation for sulphur (1/s)

$C_{H2O}$: Concentration of water vapour at surface of particle (mole/m$^3$)
$C_{H2}$: Concentration of hydrogen at surface of particle (mole/m$^3$)
$C_{CO}$: Concentration of carbon monoxide at surface of particle (mole/m$^3$)
$C_{CO2}$: Concentration of carbon dioxide at surface of particle (mole/m$^3$)

$C_{\text{p,inorg}}$: Heat capacity at constant pressure for the inorganics in black liquor (kJ/K/mole)
$C_{\text{p,g}}$: Heat capacity at constant pressure for the gas phase (kJ/K/mole)
$C_{\text{p,org}}$: Heat capacity at constant pressure for the organics in black liquor (kJ/K/mole)
$C_{\text{p,p}}$: Heat capacity at constant pressure for the particle (kJ/K/mole)

$d_p$: Particle diameter ($\mu$m)
$d_{p,ini}$: Particle initial diameter ($\mu$m)

$f_g$: Stoichiometric CO/O$_2$ ratio (dimensionless)
g: Acceleration of gravity (m²/s)
h_{\text{con.}}: Convective heat transfer coefficient (W/m²/K)
h_{\text{rad.}}: Radiation heat transfer coefficient (W/m²/K)
h_i: Enthalpy of reaction i (kJ/kg)
k_f: Flame efficiency factor
kc_1,kc_2: Constants in Kobayashi equation for carbon (dimensionless)
ks_1,ks_2,ks_3: Constants in Kobayashi equation for sulphur (dimensionless)
k_{\text{gas}}: Conductivity of gas (W/m/K)
k_p: Conductivity of particle (W/m/K)
m_p: Mass of particle (g)
n_i: number of moles of species i reacted (dimensionless)
p_{O2}: Oxygen partial pressure (kPa)
u_g: Gas velocity (m/s)
u_p: Particle velocity (m/s)
x_i: mole fraction of species i in liquid or solid phase (dimensionless)
x_{Na_2SO_4}: mole fraction of Na_2SO_4 in liquid or solid phase (dimensionless)
y_i: mole fraction of species i in gas phase (dimensionless)
\alpha_1,\alpha_2: Constants in Kobayashi equation for carbon (1/s)
\beta_1,\beta_2,\beta_3: Constants in Kobayashi equation for sulphur (1/s)
\beta: Coefficient of thermal expansion (1/K)
\rho_g: Density of gas (kg/m³)
\rho_p: Density of particle (kg/m³)
\mu_g: Viscosity of gas (m²/s)
\sigma: Stefan-Boltzmann constant (W/m²/K)
\nu_g: Kinematic viscosity of gas (m²/s)
[i]: Amount of species i (mole)
[i]_{ini}: Initial amount of species i (mole)
CHAPTER 1: INTRODUCTION

1.1. Background

Black liquor is the by-product of the kraft chemical pulping process. It contains almost all of the inorganic cooking chemicals along with the lignin and other organic matter separated from the wood in a digester. Concentrated black liquor, with a solids content of 65 to 85%, is burned in a kraft recovery boiler (Figure 1-1) to recover the pulping chemicals and to generate steam. On spraying the concentrated black liquor into the boiler, small droplets with the size range of 0.1 to 5.0 mm are produced. While most particles fall onto the char bed at the bottom of the boiler where they burn, a portion is carried up by the flue gas toward the convection heat transfer tubes in the upper furnace [1, 2].

Entrained black liquor droplets, called carryover, burn in-flight in four overlapping stages: drying, devolatilization (pyrolysis), char burning, and smelt oxidation when there is excess oxygen. At the entrance of the superheater region, carryover particles are partially or completely burned and may become partially or completely molten depending on the degree of combustion and temperature [1]. As a result, they may be sticky and form deposits on tube surfaces. The accumulation of carryover deposits on tube surfaces causes fouling and decreases the boiler heat transfer efficiency. In severe cases, deposits plug flue gas passages, leading to an unscheduled shutdown of the boiler for waterwashing.

The tendency of carryover particles to deposit depends greatly on the liquid content of the particles at the moment of impact, which, in turn, is a function of particle temperature and composition, particularly the chloride (Cl) and potassium (K) contents [3,4]. The temperature
and composition of a carryover particle continuously change as the particle goes through the various stages of combustion, and, they also depend on the composition of the black liquor from which the carryover particle originated, the boiler operating conditions, the gas temperature and composition, and the residence time of the particle inside the boiler.

![Diagram of a Kraft Recovery Boiler](image)

**Figure 1-1** Schematic diagram of a kraft recovery boiler [18].

### 1.2. Problem Definition and Objectives

Knowledge of the composition of carryover particles allows the prediction of the particle liquid content, from which its stickiness and deposition tendency can be determined. The relationship
between carryover stickiness and liquid content is well-understood [3]; however, it is difficult to estimate the liquid content of the carryover particle prior to its deposition on a tube surface, since this requires the composition of carryover particle, which is unknown.

It is difficult to sample carryover particles in order to determine their composition due to the hostile environment in an operating boiler. In addition, the composition of carryover particles changes continuously with their residence time in the boiler, and also with the composition of black liquor and boiler operating conditions. It will be beneficial if the composition of carryover particles can be estimated. There are many CFD models available for the combustion of black liquor in a recovery boiler. However, none of them predicts the composition of carryover particles.

Therefore, a substantiated model is required to predict the composition of carryover particles prior to their deposition, and also to analyze the effect of operational parameters on the composition of the particles. The model enables boiler designers and operators to calculate the melting temperature of the carryover particles in order to assess the deposition conditions in the boiler, and to minimize plugging, and, hence, the number of the unscheduled shutdowns of the boiler.

Therefore, the objectives of this study were:

1) to relate the composition of carryover particle to the composition of as-fired black liquor and burning conditions; and
2) to develop a model which predicts the composition of the carryover particles based on the composition of black liquor and burning conditions.

The work performed to achieve the objectives is explained in detail in this document. The relevant literature review is discussed in Chapter 2 where the combustion of black liquor is discussed in order to understand how it may affect the composition of carryover particles. It is followed by explanation of different types of black liquor combustion models currently available to broaden the knowledge of the art of the modeling in this category. Part I of the study is presented in Chapters 3 and 4 where the methodology and the results of the laboratory study using the EFR are discussed. This part presents the results of the investigation on the effect of black liquor composition and particle size and gas composition on the carryover composition.

Part II of the study is presented in Chapters 5 and 6 where the technique of the sampling and the results of field study are discussed. The final part of the document (Chapter 7 and 8) includes the formulation and the results of the dynamic carryover composition model which is constructed on the same basis as the black liquor combustion models with a focus on the prediction of carryover composition. The document is concluded with the summary of the entire work presented in Chapter 9.
CHAPTER 2: LITERATURE SURVEY

2.1 General

As mentioned in Chapter 1, the composition of carryover particles is a function of the composition of black liquor, and the operating conditions of the boiler which determine the burning conditions. Therefore, knowledge of the composition of black liquor particles and the combustion of the black liquor in the boilers are required in order to study the composition of the carryover particles. A literature survey was conducted on the composition of black liquor, the combustion stages of black liquor, and the composition of carryover particles. This chapter also reviews the different types of the existing recovery boiler and black liquor combustion models that are theoretically very close to the carryover model developed in this study. It should be noted that none of the existing models are capable of predicting the carryover composition.

2.2 Composition of Black Liquor

The chemical composition of black liquor varies over a wide range depending on its source. Variables include the wood source and pulping chemicals, and diverse pulping practices. The organic materials in the wood react with the pulping chemicals resulting in the formation of complex mixture of organic materials bound with inorganic species such as sodium (Na) and potassium (K) compounds. As a result, black liquor contains 30 to 40% inorganic, and 30 to 40% organic materials, with the balance water [5]. The exact chemical composition of black liquor is usually not known, since it requires elaborate experimental procedures. As a result, it is more common to describe the composition of black liquor in its elemental form.
A typical elemental analysis of black liquor is shown in Table 2-1. This composition changes from mill to mill and time to time. C, H, and O originate from lignin and extractives of the wood, and exist in the black liquor in different forms of organo-inorganic structures. S originates from pulping chemicals; i.e. Na₂S, and wood, and exists in many different forms of inorganics, including sulphide, sulphate, thiosulphate, and sulphite; and in many different forms of organics that are usually referred to as organosulphur including mercaptans.

As shown in Table 2-1, unlike many other fuels, black liquor contains a high level of inorganic elements such as Na, K, and Cl, which makes the black liquor a unique fuel. Na and K are in different forms of organosalt materials including dissolved lignin bound with Na and K, while Cl is mostly in the form of NaCl and KCl. Na is a process element, while K and Cl are the most important non-process elements in the black liquor. The presence of K and Cl lowers the melting temperature of the residue of black liquor combustion, and, as a result, fly ash becomes molten and sticky in the upper furnace. Therefore, K and particularly Cl are seen as the key elements in the plugging of recovery boilers.

Table 2-1. A typical elemental analysis of kraft black liquor [6].

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt% based on solids content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>35.0</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>3.3</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>35.7</td>
</tr>
<tr>
<td>Sulfur (S)</td>
<td>4.0</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>19.7</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>1.6</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>0.6</td>
</tr>
<tr>
<td>Inert (Ca, Mg, Pb, N, etc.)</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The molar ratio of S to Na in black liquor determines the concentrations of S and Na in the flue gas of a recovery boiler [6]. The sulphidity of the pulping liquor and the high concentration of the oxidized sulphur salts (Na₂SO₄, Na₂S₂O₃, etc.) in the recovery cycle increase the S/Na ratio. In an ideal case, all S and Na compounds leave the recovery boiler in the form of Na₂S and Na₂CO₃; i.e. smelt. In practice, the process is more complicated and depends on the operating conditions, including gas temperature and composition.

2.3 Combustion of Black Liquor in Recovery Boilers

As mentioned in Chapter 1, concentrated black liquor with a solids content from 65% to 85% is sprayed into the recovery boiler through nozzles that produce droplets in the size range of 0.1 to 5.0mm [7]. These droplets start to dry and burn as soon as they form in the boiler. The laboratory study on the combustion of black liquor has shown that the black liquor particles burn in four stages: drying, devolatilization, char burning, and smelt oxidation [7]. As shown in Figure 2.1, the size of a particle changes as the combustion proceeds: swelling during drying and devolatilization and shrinking during char burning, while the size does not change during smelt oxidation [7]. For better understanding of the combustion of the black liquor particles, each stage of the combustion is reviewed.

2.3.1 Drying

Black liquor with a moisture content of 15% to 35% dries as it is exposed to the hot environment of the boiler. Drying is a heat transfer controlled process which lasts up to 2 seconds, depending on the initial size of the droplet [7]. At this stage, the droplet swells by a factor of roughly 1.5,
making the droplet porous, which increases the particle specific surface area. This enhances the rate of heat transfer into the particle [7,9].

![Relative Size of Particles]

**Figure 2-2** Changes in the particle size at different stages of the combustion of a black liquor particle [7,8].

### 2.3.2 Devolatilization

Devolatilization is a far more complex process than drying. Due to the high temperature in the boiler, organo-salt materials with high molecular weight start to break down into gases, charred carbon, and inorganics [8].

\[
\text{Black Liquor Solids} \rightarrow \text{Volatile (g)} + \text{Carbon (s)} + \text{Inorganics (s)} \quad \text{Reaction (2-1)}
\]
The exact mechanisms of the reactions in this stage are not well understood, and many reactions have been suggested following various laboratory studies [10,11,12]. The volatiles are released in the form of light gases including CH$_4$, H$_2$, CO, H$_2$O, CO$_2$, H$_2$S, and mercaptans. Tar is also produced during devolatilization as the primary product. It is rapidly decomposed resulting in the formation of gases such as CO$_2$, CO, H$_2$, light hydrocarbons, H$_2$S, mercaptans, NO and NH$_3$ [7].

These gaseous products leave the particle, and the rate of their release depends on the particle temperature and the rate of mass transfer from the surface of the particle to the surrounding gas. Under reducing conditions, the produced gases leave the particle and do not burn, while, under oxidizing conditions, they start to burn at the surface of the particle and produce a flame starting at a temperature of about 550°C [7,13]. The flame isolates the particle from the surrounding gas. As a result, the particle is enveloped in a much hotter environment which enhances the rate of heat transfer into the particle. This will result in an increase in the rate of devolatilization. The flame disappears at the end of devolatilization stage when the volatile compounds are not released any further from the particle [8].

The formation of the gaseous materials inside the particle increases the particle internal pressure leading to the further swelling of the particle. As a result, the particle diameter reaches 2 to 3 times its initial diameter [8]. The rate of increase in the size of the particles depends on the rates of chemical reactions during devolatilization, the rates of the heat transfer between the particle and gas, particle initial size, and gas temperature [13].
Some of the C and H in the black liquor particle end up in the gas phase in the form of CO, CO₂, CH₄, and H₂; however, a fraction of the C stays in the particle in the form of char and carbonate. Char, a combustible material; stays in the particle and is burned off during the char burning stage. Carbonate is formed as a result of the reaction between CO₂ and alkali oxides; i.e. Na₂O and K₂O. A fraction of carbonate (about 6% in weight) may exist in the black liquor as a result of an inefficient recovery process during recaustisizing, where carbonate (Na₂CO₃ and K₂CO₃) ideally is converted into hydroxide (NaOH and KOH).

Much of the S released during the combustion of black liquor is released at the devolatilization stage. Gaseous sulphur species including H₂S, COS, CS₂, SO₂, mercaptans, and disulphides have been identified as pyrolysis products in a number of studies [10,14]. These studies have shown that the sulphur release depends mainly on the temperature, and the release mostly occurs at temperatures below the first melting point of the particle, at about 600°C. At temperatures above 600°C, the inorganics melt and cover the surface of the particle which limits the release of the sulphur. Experimental studies have shown that the portion of S that stays in the particle is mainly in the form of sulphide [14].

Relatively little Na, K, and Cl are vaporized due to low particle temperature during the devolatilization stage compared to higher particle temperature during char burning [15]. By the end of the devolatilization stage, Na and K are mainly in the form of carbonate, sulphate, and sulphide, while small amounts of Na and K are in the form of sodium chloride (NaCl) and potassium chloride (KCl). The potassium components usually follow reactions occurring for the sodium components, and, as a result, they are not discussed separately.
Na$_2$S and Na$_2$SO$_4$ are formed during the devolatilization stage. It is shown by Sricharoenchaikul et al that sulphide and sulphate are produced as a result of the decomposition of the thiosulphate and sulphite during devolatilization stage [14].

\[
\text{Na}_2\text{S}_2\text{O}_3 (s,l) \rightarrow \text{Na}_2\text{SO}_3 (s,l) + \text{S} (s) \quad \text{Reaction (2-2)}
\]

\[
4\text{Na}_2\text{SO}_3 (s,l) \rightarrow \text{Na}_2\text{S} (s,l) + 3 \text{Na}_2\text{SO}_4 (s,l) \quad \text{Reaction (2-3)}
\]

### 2.3.3 Char Burning

After devolatilization, the particle contains combustible organic carbon; i.e. char, and inorganic salts. The char is composed of roughly 80% carbon, 20% oxygen, and a small amount of hydrogen [8]. Char burning is a less complex process than devolatilization, but involves several parallel reactions. The char reacts mainly with CO$_2$, H$_2$O, and O$_2$ in the flue gas and Na$_2$CO$_3$ and Na$_2$SO$_4$ in the particle.

The reactions between char and CO$_2$ and H$_2$O occur in a reducing environment and are usually the dominant reactions at the early stages of char burning [16,17]. The reaction between char and O$_2$ occurs in an oxidizing environment. The rates of reactions between char and CO$_2$, H$_2$O, and O$_2$ are controlled by the rate of diffusion of the oxidizing agents; i.e. CO$_2$, H$_2$O, and O$_2$ to the particle.

\[
\text{C} (s) + \text{CO}_2 (g) \rightarrow 2 \text{CO} (g) \quad \text{Reaction (2-4)}
\]

\[
\text{C} (s) + \text{H}_2\text{O} (g) \rightarrow \text{CO} (g) + \text{H}_2 (g) \quad \text{Reaction (2-5)}
\]

\[
\text{C} (s) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{CO} (g) \quad \text{Reaction (2-6)}
\]
The reactions between char and alkali carbonate and sulphate are known respectively as carbonate and sulphate reduction [18,19]. At high temperatures and under reducing conditions, about 10% of char burns as a result of the reactions between char and carbonate and sulphate. As a result of the carbonate reduction reactions (Reaction 2-7 and similarly for K$_2$CO$_3$), elemental alkali (Na and K) are produced that diffuses into the gas in the elemental form or oxidized (Na$_2$O or K$_2$O), where there is excess oxygen at the surface of the particle. Therefore, carbonate reduction reactions is an important mechanism for alkali depletion during char burning [18]. As a result of sulphate reduction (Reaction 2-8) sulphate is reduced to sulphide [19].

\[ 2 \text{C}(s) + \text{Na}_2\text{CO}_3(s,l) \rightarrow 2 \text{Na}(g) + 3 \text{CO}(g) \]  
\text{Reaction (2-7)}

\[ 2 \text{C}(s) + \text{Na}_2\text{SO}_4(s,l) \rightarrow \text{Na}_2\text{S}(s,l) + 2 \text{CO}_2(g) \]  
\text{Reaction (2-8)}

Sulphate may also be reduced either by CO, resulting in the production of sulphide and CO$_2$ or by H$_2$, resulting in the production of sulphide and water vapor. However, the rates of these reactions are so slow compared to the rate of the reduction of sulphate by char [18,19].

During char burning, the particle temperature increases further and at a temperature above the melting point of the inorganics (above 550C), the particle becomes partially molten. As a result, molten ash partially covers the surface of the particle and prevents it from a direct contact with the gas [9]. In these conditions, the rate of reaction between the molten sulphide and O$_2$ becomes faster than the oxidation of char resulting in the formation of sulphate [9].
The produced sulphate then reacts with the char according to Reaction 2-8, resulting in the oxidation of carbon. Reactions 2-8 and 2-9 are repeated in sequence as long as carbon exists in the particle.

In a reducing environment, sulphide may undergo a reaction with carbonate which contains oxygen. The reaction between sulphide and carbonate is less likely to occur in carryover particles which are traveling in an oxidizing environment.

During the char burning stage, the particle temperature exceeds the gas temperature and may reach as high as 1200°C [7]. At this high temperature, inorganic materials with low melting temperatures; e.g. NaCl and KCl, are vaporized. This is the main mechanism for the depletion of Cl during black liquor combustion. The depletion of Cl is mainly controlled by the equilibrium vapour pressure of NaCl at the surface of the particle and the mass diffusion of the vaporized species from the surface of the particle to the surrounding gas [9].
As the char burning proceeds and the char is burned off, particle temperature increases and the particle becomes molten. As a result, the molten material coalescence and the particle diameter shrinks by a factor of about six [7]. Depending on the particle size and burning conditions, the char burning stage lasts between 1 and 6 seconds. At the end of char burning stage, the particle is completely molten, and contains alkali carbonate, sulphide, sulphate, and chloride [7].

2.3.4 Smelt Oxidation

At this stage, the sulphide is oxidized into sulphate according to Reaction 2-9 resulting in a decrease in the sulphide content and an increase in the sulphate content of the particle. This reaction is highly exothermic, helping the particle to either maintain its high temperature or increase its temperature depending on the particle sulphide content.

Other reaction that may occur at the smelt oxidation stage is the sulphation of alkali carbonate (Reaction 2-12) and alkali chloride (Reaction 2-13). The rates of these two reactions depend on the concentration of SO$_2$ at the surface of the particle.

\[
\text{Na}_2\text{CO}_3\text{(s,l)} + \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{Na}_2\text{SO}_4\text{(s,l)} + \text{CO}_2\text{(g)} \quad \text{Reaction (2-12)}
\]

\[
2\text{NaCl\text{(s,l)}} + \text{SO}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} + \text{H}_2\text{O\text{(g)}} \rightarrow \text{Na}_2\text{SO}_4\text{(s,l)} + 2\text{HCl\text{(g)}} \quad \text{Reaction (2-13)}
\]

During the smelt oxidation stage, the particle temperature is high, allowing the vaporization of NaCl (and KCl) to occur. This leads to further depletion of Cl during this stage. At the end of this stage, the particle is completely oxidized and contains alkali carbonate, sulphate, and chloride.
2.4 Composition of Carryover Particles

The composition of carryover particles varies from the composition of the original black liquor to the composition of the completely oxidized smelt, depending on the degree of combustion. The particle may contain char and alkali carbonate, sulphate, sulphide, and chloride [4]. Many field and laboratory studies have been conducted to determine the composition of carryover particles in the boiler prior to their deposition on the heat transfer tubes in the upper furnace [1,7,21,22,23,24].

Tran et al. in 1983 [1] showed that the composition of the samples collected from the boilers are affected by the compositions of carryover particles and fume. Thus the deposit has a composition that varies from the composition of pure carryover particles to the composition of fume alone, depending on the location of sampling. Samples collected at the superheater region have mostly the same composition as the carryover particles, while samples collected after generating bank are rich in fume and have the same composition as the fume. They found that carryover contains less sodium sulphate, sodium chloride, and potassium salts but more sodium carbonate and sodium hydroxide in comparison to fume.

Hupa et al [22] and Janka et al [24] conducted field studies and showed that the highest level of the carbonate was found in the deposits at the superheater, decreasing as the sampling point is moved downstream. They also showed that the lowest level of Cl and K are typically found in the deposits collected in the superheating region, increasing as the sampling point is moved downstream.
Figure 2-3 shows the composition of a carryover deposits collected from a boiler [25]. It is hard to judge whether this is the composition of carryover particles prior to its deposition. The composition changes from boiler to boiler and time to time, as the operating conditions and as-fired black liquor composition change. Moreover, the collected deposit samples on the probes may become contaminated with fume at the sampling time and, also, the composition of the sample may change with time due to the oxidation and sulphation reactions occurring between the deposits and flue gas species [21, 25].

![Pie chart showing composition of deposits](image)

**Figure 2-3** A typical composition of deposits in the upper furnace [25].

In laboratory studies, a single particle technique developed by Hupa et al. [7] was used to study the combustion of black liquor particles in order to determine the composition of carryover particles at different burning conditions. Many of these studies elucidate the combustion of a single black liquor particle as a function of black liquor composition and burning conditions [26,27,28]. Using this technique, Verrill et al [15] found that about 20% of sodium is lost and small particles called ejecta (later called intermediate sized particles, ISP) are released during the combustion of black liquor particles. One of the main problems with the single particle technique was that the results were limited to large particles of above 2mm in diameter.
Different types of entrained flow reactors [3, 14] were also used to study the composition of carryover particles. The entrained flow reactors were limited to the particles less than 700µm, and were mostly used to understand the kinetics involved in the combustion of the black liquor particles. The entrained flow reactor (EFR) at the University of Toronto was used previously to study the effect of black liquor particle size, gas O\textsubscript{2} concentration, the amount of Cl and sulphur in black liquor on the composition of the carryover particles [3, 29]. The results of these studies showed that the carryover particles are mainly made of carbonate and sulphate and small amount of sulphide, chloride, and potassium salts. It was also shown that the composition of carryover particles changes with black liquor particle size and composition, and gas O\textsubscript{2} concentration.

These studies also showed that as the black liquor particle size increased, carryover particles contained more char, Cl, K, sulphide, and carbonate, but contained less sulphate. The carryover particles contained less chloride, potassium, carbonate, and sulphide but more sulphate as the O\textsubscript{2} concentration increased [29].

The results of these studies showed how the composition of the particles at the exit of the EFR might vary with a change in the main variables, including black liquor composition and size and gas composition. However, none of them could determine the exact composition of carryover particles prior to their deposition. It is also of interest to know whether there is (is not) any correlation between the composition of carryover particles and the composition of black liquor and burning conditions. This will enable us to predict the composition of carryover particle by knowing the composition of black liquor and burning conditions.
2.5 Numerical Models

Several models have been presented for the combustion of a single black liquor droplet in the recovery boilers. They are classified as either non-isothermal or isothermal.

2.5.1 Isothermal models

In this modeling approach, a one-resistance heat transfer (only external) model is used to calculate the particle temperature. This approach is useful for small particles with Bi less than 0.1 where it is assumed that internal heat transfer resistance is negligible compared to the external heat transfer resistance. This means that the particle temperature does not change radially and is represented by one temperature. Because of its simplicity, the isothermal approach was the first method used to simulate the combustion of single black liquor droplet in the recovery boiler.

The model developed by Merriam in 1980 was the first recovery boiler model [39]. In his model, Merriam used coal combustion data to simulate the combustion of black liquor, due to the lack of data for the combustion of black liquor. He modeled the combustion of black liquor in the char bed and predicted the recovery boiler gas composition. The model was useful for the combustion of black liquor in the lower furnace, but it was not intended for the prediction of the composition of carryover particles.

Many other models were developed in the early 1980’s but they all used the coal combustion data to model the combustion of black liquor particles in recovery boilers. The approach was not suitable for use particularly during devolatilization stage when particles swell. A better
understanding of the combustion of black liquor particle through Hupa et al work [7,26,27,28] helped the model developers to better simulate the combustion of black liquor.

Walsh [40] used isothermal approach to model the combustion of black liquor. He considered that drying is a heat transfer controlled step and devolatilization is controlled by particle initial dry solids content, particle size, and O₂ concentration. During char burning, he assumed that the char and inorganics react only with oxygen. This simple model was a step forward in the development of the models that simulate the combustion of black liquor in recovery boilers.

Kulas [41] developed his model based on the Walsh model with the addition of the reaction between the char and CO₂ in the char burning stage in the modeling of the combustion of black liquor. Kulas concluded that the O₂ is mostly consumed by the gaseous materials leaving the particle including CO and H₂ and does not reach the surface of the particle. The model developed by Wag et al. [37] was based on the model developed by Frederick (presented in Non- Isothermal Models Section) with the addition of the carbonate and sulphate reductions during the char burning stage. The results of the model developed by Wag et al were in the approval of the Kulas results showing that the reaction between char and O₂ is negligible compared to the reactions between char and CO₂ and H₂O.

### 2.5.2 Non-Isothermal models

This group of models uses a two-resistance approach to calculate the particle temperature. The approach uses both internal and external heat transfer resistances to solve the energy balance equation in order to find the particle temperature. The internal heat transfer resistance is considered for particles that are thermally large, with a Biot number (Bi) greater than 0.1. Bi is
defined as the ratio of internal (conductive) heat transfer resistance to the external (convective and radiation) heat transfer resistance of a particle [30], namely:

\[
Bi = \frac{R_{\text{internal}}}{R_{\text{external}}}
\]  

(2.1)

where \( R_{\text{internal}} \) and \( R_{\text{external}} \) are the internal and external heat transfer resistances, respectively. When Bi is greater than 0.1, the internal heat transfer resistance can be assumed to be much larger than the external heat transfer resistance. This means that the heat transfer within the particle controls the overall heat transfer, and that a temperature gradient exists within the particle. This approach is particularly relevant when the particle size is large resulting in a radial change in the particle temperature.

Harper [31] was the first to use non-isothermal approach to predict the rate of the sulphur release during devolatilization stage. His model was not applicable to the boiler conditions and was limited to the temperatures below 700°C.

The combustion of black liquor droplets in recovery boilers was modeled by Wessel et al. [32] using a non-isothermal approach. In their model [called COMO], the mass and energy balance equations along with the kinetics equations were solved using an implicit finite difference (control volume) method. They considered that the combustion of the black liquor occurs in four overlapping stages of drying, devolatilization, char burning, and smelt oxidation.

In the drying stage, they considered internal conduction and thermal radiation heat transfer to calculate the particle temperature. The evaporation of water was assumed to be controlled by the
mass diffusion of water vapour to the gas, while the Stefan blowing effect was employed to calculate the mass transfer coefficient.

In the devolatilization stage, they used the same approach as the drying stage with the addition of kinetic equations to calculate the rates of the release of the sulphur and carbon to the gas and char. The kinetic equations used were those developed by Wag et al [33]. In the char burning and smelt oxidation stages, they assumed that char reacts with CO$_2$, H$_2$O, O$_2$, Na$_2$SO$_4$, and Na$_2$CO$_3$, and sulphide is oxidized to sulphate when excess oxygen is available at the surface of the particle. The original model was modified in a couple of stages by Verrill et al. [34] with a main focus on the mechanisms of intermediate size particles formation.

COMO was used later by Mahinpey et al. [35] to simulate the combustion of black liquor particles burned in the EFR at the University of Toronto in order to examine the capability of the COMO in the prediction of carryover composition. Mahinpey et al. showed that the model overpredicts the carbonate, sulphide, Cl and K contents and underpredicts the sulphate content, when the predicted results were compared with the EFR experimental results obtained by Pathania et al [29].

Frederick et al. simplified the non-isothermal approach through the assumption of isothermal bulk temperature, but with a different surface temperature for the particle [9]. This approach was the result of a combination of the isothermal and non-isothermal assumptions and became attractive to model developers in the 1990’s. Models presented by Horton [36], Frederick et al. [13], Wag et al. [37], and Grace et al. [38] were all based on this approach.
The Frederick approach can be used for small particles, with a Bi number smaller than 0.1. In this approach, reactions were assumed to take place at the particle bulk temperature and the transport properties of gases for the heat transfer coefficients were calculated using the particle surface temperature. Both drying and devolatilization were assumed to be controlled by heat transfer to the particle. Swelling during devolatilization and shrinking during the char burning stages were also used in the model. The program included the gasification of char by CO$_2$, H$_2$O, and O$_2$ during the char burning stage. This approach was successful in simulating black liquor combustion, but it was not developed and hence may not be suitable, for use in the prediction of carryover composition.

Although, these models made significant contributions to the simulation of the combustion of black liquor particles in recovery boilers with a specific focus on the combustion of the char and the release of sulphur, none of them were developed for the prediction of the composition of carryover particles.
PART 1: LABORATORY STUDY
CHAPTER 3: METHODOLOGY

The composition of carryover particles depends mainly on the composition and size of black liquor particles, and the composition and temperature of flue gas. The main objective of the laboratory experiments was to find a correlation between the carryover composition and black liquor composition and burning conditions. To obtain the correlation, an Entrained Flow Reactor (EFR) at the University of Toronto was used to study the effect of some key parameters, listed below, on the composition of carryover particles:

1) black liquor chloride (Cl) and potassium (K) contents;
2) oxygen (O₂) concentration;
3) sulphur dioxide (SO₂) concentration;
4) dried black liquor particle size;
5) EFR temperature.

3.1 The EFR

The EFR, shown in Figure 3-1, is a laminar down-flow reactor that consists of a particle feeder, a natural gas combustion chamber, a vertical radiation furnace, a non-heated exit section, and a temperature-controlled probe used for particle deposition rate studies.

The particle feeder consists of a horizontal speed-controlled belt conveyor, a funnel, and a water-cooled tube for injecting the particles to the reactor. The mass rate of the feed was controlled by the speed of the conveyor, and the length of the dried black liquor distributed on the belt (the width and height was limited). The particles fell down into a funnel at the end of the feeding belt. A supplementary flow of air was used to overcome the buoyancy effect of the hot gases from the
inside of the EFR, in order to push the particles down through the feeding tube at the top of the EFR.

For the sulphur dioxide study, SO$_2$ at a concentration of 10% (balance N$_2$) was injected into the top of the EFR from a high-pressure gas cylinder. The flow rate of the SO$_2$ stream was controlled using a valve and a flow meter at the top of the EFR. The concentration of SO$_2$ at four different elevations (at the unheated zones between each furnace) and at the exit of the EFR was measured using a gas analyzer.

Figure 3-1 Schematic diagram of the EFR at University of Toronto.
Natural gas was burned inside the combustion chamber with 10% excess air to produce a hot gas stream which was the carrier for the particles in the EFR. An extra flow of air (dilution air) was added into the combustion chamber in order to control the gas temperature at a specified setpoint. The flue gas at the exit of the combustion chamber flowed through a flow straightener (honeycomb) resulting in a uniformly distributed laminar flow of gas in the EFR.

The vertical furnace consisted of five independently controlled, electrically heated radiation zones. The wall temperature at each radiation furnace was controlled at a specified setpoint using electronic controllers which regulated the power supply to the EFR, and the temperature of each furnace was recorded separately on a computer. A non-heated zone was located below the radiation furnaces at the exit of the EFR for collecting samples. The samples were either left to deposit on an air-cooled temperature-controlled probe, or collected on a tray depending on the purpose of the study. The design and operating procedure of the EFR have been discussed in detail by Shenassa et al. [3].

3.2 Sample Selection and Preparation

Eight black liquor samples were collected from different kraft pulp mills. To cover a wide range of chloride and potassium contents in the black liquor samples, the samples were used either as-is (designated as BL), or were mixed with various amounts of the correspondent boiler precipitator dust (designated as BL+Dust), or were mixed with various amounts of KCl (designated as BL+KCl). Dust or KCl was weighed and dissolved in water, then, mixed with the black liquor. The black liquor samples were heated to 90 °C in a hot water bath to decrease the sample viscosity, and, then, agitated using a stainless steel rod until it was well-mixed.
The samples were poured over preheated stainless steel trays to form a thin layer. The trays were left inside an oven set at 130°C for a minimum 6 hours or until the samples were dry. The oven temperature must be kept below 145°C to prevent the loss of volatile components [29]. The dried samples were removed from the trays and kept in a dry, and closed container such as ziplock plastic bags. The dried samples were ground using a manual screw grinder, and, then, sieved to separate particles into specified size ranges of 150 to 300µm, 300 to 425µm, 300 to 500µm, 425 to 600µm, and 600 to 710µm.

### 3.3 Sample Chemical Composition

The chemical composition measurement techniques used to measure element or component contents in the black liquor, dust, and carryover samples are defined in Table 3-1. A full chemical analysis was carried out only on two black liquor samples. The rest of the black liquor samples, as-is or mixed with precipitator dust or KCl, were analyzed for their sodium (Na), potassium (K), and chloride (Cl) contents. The results of these measurements are shown in Tables 3-2 and 3-3. The concentration of some defined species in either black liquor or carryover samples is expressed in mole % as follows:

- **Sodium**: \( \text{mole}\% \frac{\text{Na}}{\text{Na}+\text{K}} \)
- **Potassium**: \( \text{mole}\% \frac{\text{K}}{\text{Na}+\text{K}} \)
- **Chloride**: \( \text{mole}\% \frac{\text{Cl}}{\text{Na}+\text{K}} \)
- **Carbonate**: \( \text{mole}\% \frac{\text{CO}_3}{\text{Na}_2+\text{K}_2} \)
- **Sulphate**: \( \text{mole}\% \frac{\text{SO}_4}{\text{Na}_2+\text{K}_2} \)
- **Sulphide**: \( \text{mole}\% \frac{\text{S}}{\text{Na}_2+\text{K}_2} \)
The total amount of sulphur in carryover particles was calculated as the sum of sulphate and sulphide contents.

\[
\text{Total sulphur: } \frac{\text{mole\% } S_{\text{total}}}{(\text{Na}_2+\text{K}_2)} = \frac{\text{mole\% } (\text{S+SO}_4)}{(\text{Na}_2+\text{K}_2)}
\]

Table 3-1 Sample analysis techniques

<table>
<thead>
<tr>
<th>Element</th>
<th>Technique of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, Hydrogen, Oxygen, and Total Sulphur (in Black Liquor)</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>Sodium and Potassium</td>
<td>Atomic Absorption Spectroscopy</td>
</tr>
<tr>
<td>Chloride and Sulfate</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>Sulfide and Carbonate</td>
<td>Automatic Acidimetric Titration</td>
</tr>
</tbody>
</table>

Table 3-2 Elemental analysis of the black liquor samples 1 and 2 (in wt%) from two different mills.

<table>
<thead>
<tr>
<th>Element</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon, C</td>
<td>33.0</td>
<td>32.5</td>
</tr>
<tr>
<td>Hydrogen, H</td>
<td>3.12</td>
<td>2.85</td>
</tr>
<tr>
<td>Oxygen, O</td>
<td>33.7</td>
<td>40.2</td>
</tr>
<tr>
<td>Sulphur, S</td>
<td>4.68</td>
<td>3.5</td>
</tr>
<tr>
<td>Sodium, Na</td>
<td>20.3</td>
<td>20.9</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>2.93</td>
<td>0.83</td>
</tr>
<tr>
<td>Chloride, Cl</td>
<td>0.78</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Table 3-3 Sodium, potassium, chloride, and ash contents in black liquor samples (in wt%).

<table>
<thead>
<tr>
<th>Black Liquor Sample</th>
<th>Sodium</th>
<th>Potassium</th>
<th>Chloride</th>
<th>Ash Content @ 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 (S1)</td>
<td>20.3</td>
<td>3.0</td>
<td>0.8</td>
<td>56.9</td>
</tr>
<tr>
<td>Sample 2 (S2)</td>
<td>17.1</td>
<td>0.9</td>
<td>0.2</td>
<td>59.8</td>
</tr>
<tr>
<td>Sample 3 (S3)</td>
<td>17.2</td>
<td>1.0</td>
<td>2.9</td>
<td>47.9</td>
</tr>
<tr>
<td>Sample 4 (S4)</td>
<td>20.6</td>
<td>1.9</td>
<td>0.5</td>
<td>53.4</td>
</tr>
<tr>
<td>Sample 5 (S5)</td>
<td>19.0</td>
<td>2.7</td>
<td>0.5</td>
<td>55.6</td>
</tr>
<tr>
<td>Sample 6 (S6)</td>
<td>20.0</td>
<td>2.5</td>
<td>1.8</td>
<td>54.8</td>
</tr>
<tr>
<td>Sample 7 (=S5+5% Dust1)</td>
<td>18.6</td>
<td>2.8</td>
<td>0.5</td>
<td>56.2</td>
</tr>
<tr>
<td>Sample 8 (= S5+10% Dust1)</td>
<td>18.4</td>
<td>3.0</td>
<td>0.8</td>
<td>58.3</td>
</tr>
<tr>
<td>Sample 9 (= S5+20% Dust1)</td>
<td>16.3</td>
<td>3.0</td>
<td>0.7</td>
<td>60.9</td>
</tr>
<tr>
<td>Sample 10 (=S2+1% KCl)</td>
<td>14.1</td>
<td>1.5</td>
<td>0.9</td>
<td>53.6</td>
</tr>
<tr>
<td>Sample 11 (= S2+3% KCl)</td>
<td>13.4</td>
<td>2.2</td>
<td>1.76</td>
<td>58.7</td>
</tr>
<tr>
<td>Sample 12 (=S1+2%KCl)</td>
<td>12.6</td>
<td>4.9</td>
<td>3.8</td>
<td>54.9</td>
</tr>
<tr>
<td>Sample 13 (=S6+20% Dust2)</td>
<td>17.4</td>
<td>3.0</td>
<td>2.1</td>
<td>61.3</td>
</tr>
<tr>
<td>Sample 14 (S14)</td>
<td>19.9</td>
<td>2.9</td>
<td>1.2</td>
<td>Not Measured</td>
</tr>
<tr>
<td>Sample 15 (S15)</td>
<td>21.1</td>
<td>1.9</td>
<td>1.1</td>
<td>Not Measured</td>
</tr>
</tbody>
</table>
3.4 EFR Test Conditions

The EFR wall and gas temperatures were set at the same value in all experiments; therefore, they are both referred as the EFR temperature in this report. The natural gas combustion products from the combustion chamber were mixed with various amounts of dilution air to produce a gas stream that flowed through the EFR with a velocity of about 1.8 (±0.1)m/s, and to obtain different O$_2$ concentrations. Dried black liquor particles were fed into the EFR at a mass flow rate of 10g/min. The particles were either left to deposit on an air-cooled probe (designated as deposit) or collected on a tray (designated as carryover) at the exit of the EFR. The probe was controlled at 500°C and deposits were exposed to the downward flowing gas for about 10min.

Table 3-4 summarizes the EFR operating conditions for all experiments conducted in this study. In the experiments in which the effect of SO$_2$ concentration, EFR temperature, and black liquor particle size were investigated, the black liquor samples were selected based on their compositions and availabilities.
Table 3-4 *The EFR operating conditions for all different experiments.*

<table>
<thead>
<tr>
<th>Study</th>
<th>Black Liquor Sample Used</th>
<th>EFR Temperature (°C)</th>
<th>O$_2$%</th>
<th>SO$_2$%</th>
<th>Black Liquor Particle Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black Liquor Composition</td>
<td>All Samples Listed In Table 3-3</td>
<td>800</td>
<td>12.3</td>
<td>&lt;2ppm</td>
<td>300-500</td>
</tr>
<tr>
<td>O$_2$ Concentration</td>
<td>Samples S1,S2,S3,S4,S5,S6</td>
<td>800</td>
<td>1.6-12.5%</td>
<td>&lt;2ppm</td>
<td>300-500</td>
</tr>
<tr>
<td>SO$_2$ Concentration</td>
<td>Sample S14</td>
<td>800</td>
<td>12.5</td>
<td>0-800ppm</td>
<td>150-300, 300-425, 425-600, 600-710</td>
</tr>
<tr>
<td>Black Liquor Particle Size</td>
<td>Sample S1</td>
<td>800</td>
<td>12.5</td>
<td>0-800ppm</td>
<td>150-300, 300-425, 425-600, 600-710</td>
</tr>
<tr>
<td>EFR Temperature</td>
<td>Samples S1 and S15</td>
<td>700, 800, 900, 1000</td>
<td>12.5</td>
<td>132</td>
<td>300-500</td>
</tr>
</tbody>
</table>
CHAPTER 4: LABORATORY RESULTS AND DISCUSSION

The conditions at which the experiments were performed in the EFR were described in Chapter 3 (Table 3-4). The collected carryover particles at the exit of the EFR were analyzed for their chemical compositions. The results of the analyses are discussed in this chapter after evaluating the reproducibility of the experiments.

4.1 Experimental Reproducibility

Since it was difficult to produce dried black liquor particles with a uniform particle size, particles with a wide size range, 300 to 500 µm, were used in the experiments. This size range was obtained by grinding (using a manual screw grinder) and sieving (using a shaker) of the dried black liquor samples. The prepared particles were then fed into the EFR where they were burned and formed carryover particles. At each step of the experiments, there was a chance for error in the obtained data, the total effect of these individual errors is an error in the final results. Therefore, the reproducibility of the experiments was examined to define the experimental error and to check that this error is small enough to allow valid conclusions to be drawn.

4.1.1 Particle size distribution

The size distribution of three dried ground black liquor samples was studied to examine the reproducibility of the sample preparation method. The study was performed on the black liquor samples 3, 4, and 6 that were available at the time. As shown in Figure 4.1, it was possible to use the technique used to prepare samples of a reasonably similar particle size distribution from three different black liquors.
Figure 4-1 The particle size distribution of three black liquor samples using sieving technique.

Figure 4-2 Dried black liquor particles used in the experiments.
4.1.2 Experimental reproducibility

Triplicate experiments were performed under the same EFR operating conditions for the black liquor sample 3. The variation percentage for gas temperature, O\(_2\) concentration, and carryover composition were below 5%, which is an acceptable level of variation in the parameters listed in Table 4-1. Since the O\(_2\) concentration in this set of experiments was high, the sulphide content in the carryover particles was small. As a result, a small absolute difference in the sulphide content measured in the carryover has resulted in a large percent variation. Thus this high variability should not be considered as a sign of the poor measurement of the sulphide content in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Temperature (°C)</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>800</td>
<td>0</td>
<td>0.0</td>
</tr>
<tr>
<td>Gas Oxygen Content (O(_2)%</td>
<td>12.0</td>
<td>12.5</td>
<td>12.4</td>
<td>12.3</td>
<td>0.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Na/(Na+K) mole %</td>
<td>97.2</td>
<td>97.3</td>
<td>97.7</td>
<td>97.4</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>K/(Na+K) mole %</td>
<td>2.8</td>
<td>2.7</td>
<td>2.5</td>
<td>2.7</td>
<td>0.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Cl/(Na+K) mole %</td>
<td>2.7</td>
<td>2.4</td>
<td>2.5</td>
<td>2.5</td>
<td>0.1</td>
<td>4.9</td>
</tr>
<tr>
<td>S(^-)/(Na(_2)+K(_2)) mole %</td>
<td>0.07</td>
<td>0.26</td>
<td>0.22</td>
<td>0.18</td>
<td>0.10</td>
<td>55.7</td>
</tr>
<tr>
<td>SO(_4)/(Na(_2)+K(_2)) mole %</td>
<td>38.8</td>
<td>37.1</td>
<td>37.7</td>
<td>37.9</td>
<td>0.7</td>
<td>1.9</td>
</tr>
<tr>
<td>CO(_3)/(Na(_2)+K(_2)) mole %</td>
<td>58.5</td>
<td>61.1</td>
<td>60.0</td>
<td>59.8</td>
<td>1.1</td>
<td>1.8</td>
</tr>
</tbody>
</table>

4.2 Effect of Cl and K Contents

As shown in Figure 4-3, the Cl content in carryover is lower than that in the black liquor, with the Cl content in carryover being only about 30% of that in the black liquor feed particles. This result indicates that a portion of Cl was depleted during the combustion of black liquor particles.
Depletion of Cl may occur as a result of direct vaporization and/or sulphation of Cl components; i.e. NaCl and KCl.

\[
\text{NaCl}_{(s,l)} \rightarrow \text{NaCl}_{(g)} \quad \text{Reaction (2-11)}
\]

\[
2 \text{NaCl}_{(s,l)} + \text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{Na}_2\text{SO}_4(s,l) + 2\text{HCl}(g) \quad \text{Reaction (2-13)}
\]

Similar reactions are expected for KCl. Since the concentration of SO\textsubscript{2} in the EFR when SO\textsubscript{2} was not injected, was negligible, the sulphation of Cl components (Reaction 2-13) can not be considered as a major mechanism of the depletion of Cl. As a result, the vaporization of NaCl and KCl become the main mechanism for the depletion of Cl.

Figure 4-3 shows a linear relationship between the Cl content in carryover particles and the content in black liquor. This is what would be expected if the vaporization process obeyed Raoult’s Law, which states that the partial pressure of a vaporizing substance is equal to the vapour pressure of a pure component times its mole fraction in the condensed phase [5]. Since the partial pressures of the Cl components; i.e. NaCl and KCl, increase linearly with their concentrations in the particle, the rate of the vaporization of Cl also increases linearly. Therefore, the concentration of Cl species remaining in the particle is linearly proportional to its original concentration in the black liquor.

A similar linear relationship to that of Cl content was obtained for K content (Figure 4-4). However, the K content in carryover was about 80% of that in black liquor, and so the depletion of K in the carryover was much less than that of the Cl. There are two potential mechanisms for
the depletion of K during the combustion of black liquor: 1) vaporization of KCl, and 2) reduction of potassium carbonate (K$_2$CO$_3$) during char burning stage (Reaction 4-1).

The vaporization of KCl follows Raoult’s Law, and result in a linear change in K content similar to that of Cl content, while the reduction of K$_2$CO$_3$ occurs at a rate linearly proportional to the K$_2$CO$_3$ concentration and exponentially proportional to the particle temperature (Reaction 4-1). The K$_2$CO$_3$ concentration is a function of black liquor composition and varies from sample to sample, whereas the particle temperature is mainly controlled by O$_2$ concentration. Black liquor samples burned at the same O$_2$ concentration most likely reach the same temperature. Thus, the rate of reaction between K$_2$CO$_3$ and char increases only linearly with K$_2$CO$_3$ concentration. The linear relationship between the K in carryover and that in black liquor suggests that both
mechanisms; i.e. the vaporization of KCl and the reduction of K$_2$CO$_3$ by char, are the main causes of K depletion.

\[
2\text{ C(s)} + \text{ K}_2\text{CO}_3(\text{s,l}) \rightarrow 2\text{ K(g)} + 3\text{ CO(g)}
\]

Reaction (4-1)

\[
R_{\text{CO}_3} = 1.00 \times 10^9 [\text{K}_2\text{CO}_3] e^{(-\frac{2.44 \times 10^5}{RT_f})}
\]

(4-1)

Figure 4-4 Effect of black liquor K content on K content in carryover particles. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C and 12.3% oxygen concentration).

The similar results for both Cl and K contents among different samples; i.e. BL, BL + Dust, and BL + KCl, suggests that the amounts of Cl and K in carryover particles are proportional to their concentrations in black liquor, and their origins do not have any effect on their behaviour during the combustion of the black liquor.
The results presented above were for the particles burned in the EFR set at 800°C and an oxygen concentration of 12.3%. The results are expected to vary at different oxygen concentrations.

4.3 Effect of $O_2$ Concentration

The EFR was operated in four different $O_2$ concentrations of 1.7, 6.2, 9.5, and 12.3%. The results at 12.3% oxygen concentration have been presented in Section 4.2.

4.3.1 Effect of $O_2$ concentration on Cl and K contents

As shown in Figure 4-5, at any oxygen concentration, the Cl content in carryover particles has a linear relationship with its content in black liquor. As the $O_2$ concentration decreases, however, there is a smaller proportional decrease in Cl content. As discussed in the previous section, the only mechanism for Cl depletion is expected to be vaporization of NaCl and KCl. Since the particle temperature decreases as the $O_2$ concentration decreases, less vaporization of NaCl and KCl occurs, which results in less Cl depletion.

Figure 4-6 shows a similar result for K content to those for Cl content at different $O_2$ concentrations. In all cases, there is a linear relationship between the K content in the carryover and its content in the black liquor. At all different $O_2$ concentrations, the depletion of K was much smaller than that of Cl. As discussed in the previous section, two mechanisms; i.e. vaporization of KCl and reduction of $K_2CO_3$, are responsible for the depletion of K.
Figure 4-5 Effect of $O_2$ concentration on the relationship between Cl content in carryover particle and its content in black liquor. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).

Figure 4-6 Effect of $O_2$ concentration on the relationship between K content in carryover particle and its content in black liquor. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).
The term “enrichment factor” is often used to indicate the relative amounts of Cl and K in any given sample compared to those in the black liquor. Therefore, this term easily shows the fraction of each element remaining in the particle at the end of combustion. In this work, the enrichment factor for Cl (EF_{Cl}) is defined as the ratio of the Cl content (in mole%) in the sample divided by Cl content in the black liquor. Similarly, the enrichment factor for K (EF_{K}) is defined as the ratio of K content in the sample divided by K content in the black liquor. An enrichment factor equal to one means no loss has occurred and the amount of either Cl or K in the sample is equal to its initial amount in the black liquor. An enrichment factor equal to zero indicates a full loss of the elements from the particles. The enrichment factor of Cl or K (EF_{Cl} or EF_{K}) is represented by the slope of the lines which goes through data points in Figures 4-5 and 4-6.

\[ EF_{Cl} = \text{Line slope for Cl in Figure 4.5} \quad (4.2) \]

\[ EF_{K} = \text{Line slope of for K in Figure 4-6} \quad (4.3) \]

Figure 4-7 shows that the enrichment factors of Cl and K decreased with an increase in O_2 concentrations, which is as a result of an increase in the vaporization of NaCl and KCl as the O_2 concentration increases. In order to determine whether there is any correlation between the depletion of Cl and K, the term depletion factor is defined here.

The term “depletion factor” is used to indicate the relative amounts of Cl and K depleted from the samples. In this work, the depletion factor for Cl or K (DF_{Cl} or DF_{K}) is defined as the ratio of the amount of Cl or K (in mole%) depleted from the sample during the combustion of the black liquor divided by the amount of initial Cl or K in the black liquor. The amount of Cl or K
depleted from the sample can be calculated by subtracting the Cl or K content in the sample from
the initial Cl or K content in the black liquor. A depletion factor for either Cl or K equal to zero
means no depletion has occurred and the concentration of either Cl or K in the sample is equal to
its initial concentration in the black liquor, and, a depletion factor for either Cl or K equal to one
indicates a full depletion of either Cl or K from the samples.

![Figure 4-7](image-url)

**Figure 4-7** Effect of O$_2$ concentration on the enrichment factor of Cl and K in carryover particle.
(dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).

Using the EF$_{\text{Cl}}$ and EF$_{\text{K}}$ values, the depletion factor of chloride (DF$_{\text{Cl}}$) and the depletion factor of
potassium (DF$_{\text{K}}$) for carryover particles can be obtained as:

\[
\text{DF}_{\text{Cl}} = 1 - \text{EF}_{\text{Cl}} \quad (4.4)
\]

\[
\text{DF}_{\text{K}} = 1 - \text{EF}_{\text{K}} \quad (4.5)
\]
Figure 4-8 shows the relationship between DF$_K$ and DF$_{Cl}$. is linear with DF$_K$ is one-third of DF$_{Cl}$, on average. The results of chemical analysis show that Na compounds are mostly in the form of Na$_2$CO$_3$ and Na$_2$S or Na$_2$SO$_4$ (depending on the degree of oxidation), and only a small portion is in the form of NaCl. Similar results are expected for K compounds, i.e. K is mainly in the form of K$_2$CO$_3$ and K$_2$S or K$_2$SO$_4$ and only a small portion of it will be in the form of KCl. Since K$_2$CO$_3$ and K$_2$SO$_4$ have much lower vapour pressures than KCl and NaCl [41,42], more K is expected to remain in the particle than Cl.

If the vaporizations of KCl and NaCl were the only mechanisms for the depletion of K and Cl, and they occurred at the same rate, the depletion of K should have been only about one-ninth of that of Cl. This preferentially greater depletion of K compared to that expected from vaporization of KCl implies that the existence of other K depletion mechanisms. One possible mechanism is the greater rate of K$_2$CO$_3$ reduction by carbon (or char) compared to that of Na$_2$CO$_3$ reduction under strong reducing conditions, as will be discussed in the Section 8.1.3 of this thesis.

4.3.2 Effect of O$_2$ concentration on carbonate, sulphide, and sulphate contents

This section discusses the effect of oxygen concentration on sulphide, sulphate, and carbonate contents in carryover particles produced from four different black liquor samples. Figure 4-9 shows that carryover particles contained the highest sulphide content at the lowest O$_2$ concentration tested (1.7%). As the O$_2$ concentration increased, the sulphide content in carryover particles decreased and approached zero at an O$_2$ concentration of about 12.3%. Consistent results were obtained for all four samples.
Figure 4-8 Depletion factors of Cl and K in carryover particle at different O$_2$ concentrations. (for dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).

Figure 4-9 Effect of O$_2$ concentration on sulphide content in carryover particles of four different black liquor samples. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).
As shown in Figure 4-10, sulphate content in the carryover particles increased with an increase in O₂ concentration, which is the opposite trend to that for the sulphide content. A comparison of the change in the sulphide and sulphate contents indicates a different rate of change for these two components. For example, in sample S1, the sulphide content decreased from 10 mole% at 1.7% O₂ to about zero at 12.3% O₂ (10 mole% decrease), (Figure 4-9), while sulphate content increased from 17 mole% at 1.7%O₂ to 45 mole% at 12.3% O₂ (28 mole% increase), (Figure 4-9), which is close to three times the decrease in sulphide content. This means that sulphide oxidation is not the only mechanism for the formation of sulphate. The increase in sulphate content in the particles formed at high O₂ concentrations is due to the greater sulphur retention in the particles formed at high temperatures. This is more apparent in Figure 4-11 which shows the total sulphur contents in all four samples increased as the O₂ concentration increased.

![Figure 4-10](image_url)

**Figure 4-10** Effect of O₂ concentration on sulphate content in carryover particles of four different black liquor samples. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).
Figure 4-11 Effect of $O_2$ concentration on total sulphur content in carryover particles of four different black liquor samples. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).

Figure 4-12 shows the effect of $O_2$ concentration on the carbonate content in carryover particles. The results of all four samples were consistent showing that the carbonate content in carryover decreased as the $O_2$ concentration increased. The decrease in the carbonate content is essentially the same as the total increase in total sulphur content in carryover particles. For example in sample S1, the carbonate content decreased from 72 mole% to 54 mole% while the total sulphur content increased from 26 mole% to 44 mole%, both with a 18% change but in opposite directions.

The decrease in carbonate content could have been resulted from three mechanisms: 1) the sulphation of carbonate (Reaction 2-12) as a result of the reaction between the carbonate and $SO_2$ in the gas, 2) the reduction of carbonate as a result of the reaction between the carbonate and char, and 3) the higher sulphur retention in the particles formed at high $O_2$ concentrations which
lowers the carbonate formation. The concentration of SO$_2$ at the exit of the EFR was measured to be below 2ppm. Therefore, the rate of sulphation of carbonate (Reaction 2-12) is not expected to be significant at this low SO$_2$ concentration.

$$\text{Na}_2\text{CO}_3 (l,s) + \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4 (l,s) + \text{CO}_2 (g) \quad \text{Reaction (2-12)}$$

The significant of the reaction between the carbonate and char and the degree of the sulphur retention at high O$_2$ concentrations (high particle temperature) are not well known. Therefore, it is not possible to distinguish which of these mechanisms is the main mechanism that results in a decrease in the particle carbonate content.

![Figure 4-12](image)

**Figure 4-12** Effect of O$_2$ concentration on carbonate content in carryover particles of four different black liquor samples. (dried black liquor particles in a particle size range of 300 to 500µm burned in the EFR set at 800°C).
4.4  Effect of SO₂ Concentration

As mentioned in Chapter 2, it is believed that reaction between SO₂ and carryover particles results in the sulphation of carbonate and Cl (Reactions 2-12 and 2-13), which will affect the composition of the particles. The effect of SO₂ in the EFR was studied to determine whether these two reactions occur in the EFR and how SO₂ may affect the composition of carryover particles. In this study, the particles were either left to deposit on a probe (designated as deposit) or collected on a tray (designated as carryover) at the exit of the EFR. Experiments were performed for four different size ranges, however, only the results of the 150 to 300µm size range are discussed here; all other size ranges showed similar trends as presented in Appendix A.

Figure 4-13 shows the effect of SO₂ on the Cl and K contents in the deposit and carryover. As expected, the K content in the deposit and carryover did not show any significant change with SO₂. The Cl content for both deposit and carryover did not change with SO₂ either, indicating no interaction between SO₂ in the gas and Cl in the carryover particles and deposits. The results suggest that the sulphation reaction (Reaction 2-13) could not have been responsible for the depletion in Cl of carryover particles and deposits.

\[
\text{2 NaCl}_{(s,l)} + \text{SO}_2_{(g)} + \frac{1}{2} \text{O}_2_{(g)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Na}_2\text{SO}_4_{(s,l)} + 2 \text{HCl}_{(g)} \quad \text{Reaction (2-13)}
\]

Figure 4-14 shows that the sulphide contents in the carryover particles and deposits were very low (below 2%) at all different SO₂ concentrations, which indicate the particles were completely burned and almost oxidized before deposition. Due to the low level of sulphide in the samples, the effect of SO₂ on the sulphide content could not be determined; however, no effect from SO₂ on the sulphide content is expected. The results in Figure 4-14 also shows that the sulphate
contents in both the carryover particles and deposits increased with an increase in the SO$_2$ concentration. The increase in sulphate content was higher in the deposit than in the carryover particles in the presence of SO$_2$, implying that the capture of SO$_2$ continued after the deposition of carryover particles on the probe.

Figure 4-15 shows that the carbonate contents in both the carryover particles and deposits decreased with an increase in SO$_2$ concentration. A comparison of the carbonate content with the total sulphur contents in both carryover and deposits suggest that the decrease in carbonate content was essentially the same as the increase in the total sulphur content. These results are consistent with the fact that the sulphation of carbonate in an environment rich in O$_2$ and SO$_2$ occurs which leads to the consumption of carbonate and the formation of sulphate in the samples.
Figure 4-14 Effect of SO₂ on the sulphide and sulphate contents in deposit and carryover for the black liquor particles in a size range of 150 to 300µm (EFR set at 800°C with O₂ concentration of 12.5%, and probe temperature of 500°C).

Figure 4-15 Effect of SO₂ on the Cl and K contents in deposit and carryover for the black liquor particles in the size range of 150 to 300µm (EFR set at 800°C with O₂ concentration of 12.5%, and probe temperature of 500°C).
The results presented in Figures 4-13 for Cl content and 4-15 for carbonate content shows that the presence of SO\textsubscript{2} in the EFR did not affect the Cl content in the carryover particles, while it caused a decrease in the carbonate content. This is in good agreement with the equilibrium calculation results presented by Salmenoja and Makela [43], who showed that alkali carbonates (Na\textsubscript{2}CO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3}) are sulphated prior to alkali chlorides (NaCl and KCl) in an environment containing SO\textsubscript{2}. As a result, it may be concluded that the sulphation of Cl in the carryover particles and deposits may not be observed as long as these samples contain carbonate.

4.5 Effect of EFR Temperature

Previous results showed that the sulphide content at high O\textsubscript{2} concentrations was very low (close to zero); therefore, it was not measured in this set of experiments. The carbonate content of the samples was not measured either, since it was assumed that the carbonate content in the samples was the balance between the Cl and sulphate contents and 100 (all in mole %) in each sample.

Figures 4.16 and 4.17 show that an increase in the EFR temperature lowered the Cl and K contents in the carryover particles. As the EFR temperature increases, the vapour pressures of Cl and K components (NaCl and KCl) increase leading to higher vaporization of Cl and K components. As a result, more Cl and K are lost during the combustion and less remains in the particle.

To better understand the trend of change in the level of Cl and K in samples with different compositions, the Cl and K content are normalized using the term “enrichment factor”. This term was already defined in Section 4.3.1 and is used here for the Cl and K in the carryover and
Figure 4-16 Effect of the EFR Temperature on Cl Content in Carryover Particles.

Figure 4-17 Effect of the EFR Temperature on K Content in Carryover Particles.
deposit samples. Figure 4.18 shows that the EF\textsubscript{Cl} and EF\textsubscript{K} of carryover and deposits decreased with an increase in EFR temperature and that EF\textsubscript{Cl} was much lower than EF\textsubscript{K}. This trend is expected since the higher EFR temperature results in a more loss of Cl and K from the particle leading to lower enrichment factors for Cl and K. The results confirm those found in the experiments discussed in Section 4.3.1, which showed a much lower enrichment factor of Cl than that of K.

The results show the Cl enrichment factor was the same for both samples, while the K enrichment factor of sample S15 was lower than that of sample S1. This is puzzling, since sample S1 contains more carbonate and less sulphate than sample S15 (Figure 4-19), the K depletion should be greater (or K enrichment factor be lower) for sample S1 than sample S15. No explanation can be made for this finding.

![Figure 4-18](image-url)  
*Figure 4-18 Effect of the EFR temperature on the enrichment factors of Cl and K in carryover particle.*
Figure 4-19 shows an increase in the sulphate content of both samples with an increase in EFR temperature. There are two main reasons for this: 1) particles formed at elevated temperatures retained more sulphur, and 2) carbonate may decompose at high temperatures, leading to an increase in sulphate content. Information collected from the mills indicated that sample S1 contained more sulphur than sample S15. The results show that sample 1 from a mill with a higher sulphidity (about 42%) contained more sulphate than sample S15 from a mill with a lower sulphidity (about 36%). In spite of the different levels of sulphidity of the samples, the sulphate content of these two samples increases at the same rate with the EFR temperature.

While sample S1 contained more sulphur than sample S15, both of them showed the same enrichment factors for the Cl. This indicates that the sulphur content in the black liquor did not affect the depletion of the Cl, resulting in the same value of enrichment factors for both samples.

![Graph showing effect of EFR temperature on sulphate content in carryover particles](image.png)

**Figure 4-19** Effect of the EFR temperature on sulphate content in carryover Particles.
4.6  Effect of Black Liquor Particle Size

Small particles burn faster and may reach higher temperatures than large particles. Therefore, it is expected that the composition of the carryover particles at the superheater entrance of a recovery boiler vary depending on the particle size. The EFR was used to study the effect of the black liquor particle size on the composition of carryover particles. Figure 4-20 shows that the black liquor particle size did not greatly affect the Cl and K contents in carryover particles. This result is in apparent contradiction with previous work [29] which showed that smaller particles had greater depletion of K and Cl than the larger particles. The higher depletion was attributed to the higher burning temperature of smaller particles, but there is no evidence to proof it.

As will be presented later in Figure 7.3, the vapour pressures of NaCl and KCl are very low at temperatures below 1000°C. Therefore, the rates of vaporization of NaCl and KCl, as the main mechanism of the Cl and K depletions, will be negligible at particle temperatures below 1000°C. The level of particle temperature (at least above 1000°C) and the period of the time that the particle stays above 1000°C are the key parameters determining the loss of Cl and K. Small particles may experience a different temperature profile than the large particles, but the results shown in Figure 4-20 indicates that the net effect of the level of the particle temperature and the period of the time staying at that temperature are the same for both small and large particles.

Figure 4-21 shows that the black liquor particle size did not appreciably affect the sulphate and carbonate contents in carryover particles either, while it caused an increase in the sulphide content. The increase in the sulphide content was expected since the larger particles leave the EFR faster than small particles and do not become completely burned and oxidized.
Figure 4-20  Effect of black liquor particle size on Cl and K contents in the carryover particles formed in the EFR set at 800 °C and O₂ concentration of 12.5%.

Figure 4-21  Effect of black liquor particle size on the sulphide, sulphate, total sulphur, and carbonate contents in carryover particles at O₂ concentrations of 12.5%.
4.7 Summary

A systematic study using the EFR was conducted to examine the correlation between the carryover composition and black liquor composition at different burning conditions. The results show that:

1- Cl and K contents in carryover particles are lower than those in the black liquor;
2- both Cl and K contents in carryover are linearly proportional to those in the black liquor.
3- The vaporization of NaCl and KCl is the main cause of the depletion of Cl from carryover particles in the EFR, while the vaporization of KCl and reduction of K$_2$CO$_3$ with char can both lead to the depletion of K;
4- Cl and K depletions is independent of the origin of the Cl and K in the black liquor;
5- K depletion is about 1/3 of Cl depletion. If vaporization is the only mechanism for the depletion of K and Cl, a much lower depletion ratio is expected. This implies that the depletion of K as a result of K$_2$CO$_3$ reduction by char is significant;
6- the Cl and K contents in carryover particles decreases with an increase in O$_2$ concentration (which would increase burning intensity and temperature of the particle);
7- carryover particles formed in an environment with high O$_2$ concentration contain less sulphide, less carbonate, but more sulphate than the particles formed in an environment with low O$_2$ concentration;
8- the carryover particles contain more sulphur as the particle temperature increases. This is consistent with what is known about sulphur retention in recovery boilers;
9- the SO$_2$ concentration did not affect the Cl and K contents in carryover particles;
10- sulphide was almost fully oxidised at an O₂ concentration of 12.5% and did not change significantly with an increase in SO₂ concentration, but it was increased with an increase in the black liquor particle size; 

11- the sulphation of carbonate increases with an increase in SO₂ concentration, leading to an increase in sulphate content of carryover particles; 

12- carbonate is sulphated when exposed to SO₂, while Cl is not; 

13- Cl, K, and carbonate contents in the carryover particle decrease, while the sulphate content increases with an increase in the EFR temperature; 

14- at 12.5% O₂, black liquor particle size did not show a significant effect on the composition of carryover particles; 

15- among the test variables (black liquor size, EFR temperature, gas composition), O₂ concentration (particle temperature) has the most significant effect on the composition of carryover particles followed by the EFR temperature.
PART 2: FIELD STUDY
CHAPTER 5: BOILERS DATA AND SAMPLING PROCEDURE

To compliment the experimental results, two field studies were conducted on three operating recovery boilers. A specially designed air-cooled probe was used to collect carryover particles at the entrance to the superheater region at each boiler. Samples of smelt, as-fired black liquor, and precipitator dust from each boiler were also collected and analyzed for comparison. The boiler data and sampling technique are presented in this chapter.

5.1 Boiler Data

Tests were performed on a recovery boiler at a kraft mill in Ontario, Canada (Boiler A) and on two recovery boilers at a Southern US mill (Boilers B and C). Boilers with different firing loads and operating conditions were chosen where possible. The availability of the boilers was a main limitation in the selection process. Relevant boiler data and operating parameters are listed in Table 5-1.

<table>
<thead>
<tr>
<th>Boiler</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacturer</td>
<td>CE</td>
<td>Ahlstrom</td>
<td>CE</td>
</tr>
<tr>
<td>Type</td>
<td>Two-drum 3-level air</td>
<td>Single-drum 4-level air</td>
<td>Two-drum 3-level air</td>
</tr>
<tr>
<td>Black liquor firing load (tons of dry solids/day)</td>
<td>1900</td>
<td>1300</td>
<td>2200</td>
</tr>
<tr>
<td>Solids content (%)</td>
<td>72</td>
<td>72</td>
<td>71</td>
</tr>
<tr>
<td>Steam Production (tonnes/hr)</td>
<td>270</td>
<td>190</td>
<td>330</td>
</tr>
<tr>
<td>Steam Temperature (°C)</td>
<td>420</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Steam Pressure (Bar)</td>
<td>64</td>
<td>41</td>
<td>41</td>
</tr>
<tr>
<td>Excess O₂ (%)</td>
<td>2.2</td>
<td>2.2</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Table 5-1 Key Boiler Data and Operating Parameters.
5.2 Sampling Technique

An air-cooled probe equipped with a gas analyzer and thermocouples was used to collect carryover samples. Since the collected deposits on the probe may react with the gas and change their composition, the probe was left inside the boiler for different periods of time to examine the change in deposit composition. Boiler operating data were monitored and collected from data collection system (DCS) continuously to assure that boiler operating conditions were stable before starting the sampling.

5.2.1 Carryover sampling

The carryover sampling probe is shown in Figure 5-1. It consists of two concentric, type 310 stainless steel pipes. The outer pipe is 50mm in inner diameter and 3.3m long. The inner pipe, 25mm in inner diameter and 3.5m long, is equipped with a removable sampling tip, a thermocouple embedded on the tip, and a cooling system that regulates the air flow through the inner probe to keep the sampling tip at a desired temperature. The outer pipe acts as a shield to minimize the condensation of fume on the area of the sampling tip where carryover is collected. A small tube is inserted through the inner pipe to collect gas samples.

![Figure 5-1: Air-cooled sampling probe used for collecting carryover particles from operating boilers.](image)
The probe was inserted in each boiler through the side walls at the entrance of the superheater region at the bull nose elevation, as shown in Figure 5-2. The collecting end of the probe was inserted about three meters into the furnace. The inner pipe was kept inside the outer shield pipe when the probe was first inserted into the boiler. When the tip temperature reached about 500°C, the inner pipe was pushed out of the shield pipe to expose the sampling tip to the gas. This procedure was necessary in order to prevent condensed material (fume) from depositing on the sampling tip while it was still “cool”.

Figure 5-2. Location of Carryover Sampling Probe in Boiler B (arrow).
When the sampling time was over, the inner pipe was pulled back into the shield pipe before the entire probe was taken out of the boiler. Cooling air was allowed to flow through the inner pipe to quickly cool the probe. The sampling tip with deposit was removed from the probe and placed in a zip-lock bag. This procedure was necessary in order to minimize the oxidation of the collected deposits on the sampling tip.

### 5.2.2 Gas sampling

Gas samples were taken during the heating period of the carryover sampling probe, using a small tube inserted through the inner pipe. During that period, the cooling air flowing through the probe into the furnace was shut off to facilitate accurate gas temperature measurements and to prevent the gas sample from being “contaminated” by the cooling air. The gas temperature was measured using a Type K thermocouple embedded on the tip of the sampling probe (Figure 5-1). O₂ and SO₂ concentrations in the flue gas were measured by extracting the flue gas through the gas-sampling tube and analyzing it using a portable O₂ and SO₂ analyzer.

The gas temperature and O₂ and SO₂ concentrations at the sampling locations are shown in Table 5-2. The flue gas temperature in Boiler A was the highest, followed by Boiler B and Boiler C. The O₂ and SO₂ concentrations were similar in all three boilers.

**Table 5-2 Gas temperature and composition at the sampling site in boilers A, B, and C.**

<table>
<thead>
<tr>
<th>Boiler</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature ºC</td>
<td>900</td>
<td>863</td>
<td>815</td>
</tr>
<tr>
<td>O₂ concentration (%)</td>
<td>2.0</td>
<td>2.2</td>
<td>2.0</td>
</tr>
<tr>
<td>SO₂ concentration (ppm)</td>
<td>not measured</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>
5.3 Chemical Analysis

Samples of as-fired black liquor, smelt, and electrostatic precipitator dust were collected concurrent with carryover sampling. The black liquor samples were analyzed for sodium (Na), potassium (K) and chloride (Cl), while the carryover, smelt, and precipitator dust samples were analyzed for Na, K, Cl, sulphate (SO$_4$), sulphide (S), and carbonate (CO$_3$). The concentrations of these defined species in the samples are expressed in mole %, for example mole % Na/(Na+K), as explained in Section 3.4.
CHAPTER 6: FIELD RESULTS AND DISCUSSION

The chemical composition of all samples collected from three recovery boilers was analyzed and the results are discussed in this chapter.

6.1 Samples Chemical Compositions

Table 6-1 shows Na, K, and Cl contents in the as-fired black liquor samples. Boilers B and C had a similar black liquor composition, reflecting the fact that they are in the same mill. Boiler A had a lower Cl content and a higher K content compared to Boilers B and C. These as-fired black liquor concentrations were used in the calculation of Cl and K enrichment factors in the carryover, smelt, and precipitator dust samples.

Table 6-2 shows the compositions of carryover, smelt and precipitator dust samples collected from boilers A, B and C. Unfortunately, samples taken from boiler B were contaminated with fume when the probe was left inside the boiler for 12 minutes. Therefore, this result does not follow the expected trend for deposit samples. Figure 6-1 shows the difference in the appearance of deposits samples after exposing the probe in boiler B for 3 and 12 minutes. The 12-minute sample was whiter and appeared to be less fused when compared to the 3-minute sample.

Table 6-1 As-fired black liquor and flue gas analyses at the sampling locations.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Boiler A</th>
<th>Boiler B</th>
<th>Boiler C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, wt% d.s.</td>
<td>18.1</td>
<td>19.3</td>
<td>20.0</td>
</tr>
<tr>
<td>K, wt% d.s.</td>
<td>3.7</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Cl, wt% d.s.</td>
<td>0.6</td>
<td>1.1</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table 6-2 Chemical composition (in wt.%) of the samples taken from boilers A, B, and C.

<table>
<thead>
<tr>
<th>Boiler A</th>
<th>Sampling Time (min.)</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>SO₄</th>
<th>S</th>
<th>CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carryover</td>
<td>1</td>
<td>27.54</td>
<td>4.20</td>
<td>0.37</td>
<td>24.30</td>
<td>0.45</td>
<td>22.80</td>
</tr>
<tr>
<td>Carryover</td>
<td>3</td>
<td>27.94</td>
<td>4.16</td>
<td>0.29</td>
<td>26.75</td>
<td>0.44</td>
<td>21.97</td>
</tr>
<tr>
<td>Carryover</td>
<td>5</td>
<td>32.08</td>
<td>4.61</td>
<td>0.26</td>
<td>33.47</td>
<td>0.43</td>
<td>23.57</td>
</tr>
<tr>
<td>Carryover</td>
<td>7</td>
<td>29.50</td>
<td>4.59</td>
<td>0.43</td>
<td>20.65</td>
<td>0.50</td>
<td>27.85</td>
</tr>
<tr>
<td>Carryover</td>
<td>10</td>
<td>28.84</td>
<td>4.20</td>
<td>0.39</td>
<td>23.59</td>
<td>0.29</td>
<td>25.31</td>
</tr>
<tr>
<td>Smelt</td>
<td>N/A</td>
<td>32.84</td>
<td>5.65</td>
<td>0.70</td>
<td>3.91</td>
<td>5.76</td>
<td>33.56</td>
</tr>
<tr>
<td>Dust</td>
<td>N/A</td>
<td>24.20</td>
<td>6.63</td>
<td>2.01</td>
<td>53.65</td>
<td>0.00</td>
<td>1.57</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boiler B</th>
<th>Sampling Time (min.)</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>SO₄</th>
<th>S</th>
<th>CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carryover</td>
<td>3</td>
<td>32.87</td>
<td>2.72</td>
<td>0.92</td>
<td>27.60</td>
<td>0.03</td>
<td>26.80</td>
</tr>
<tr>
<td>Carryover</td>
<td>6</td>
<td>31.73</td>
<td>2.60</td>
<td>0.85</td>
<td>28.79</td>
<td>0.05</td>
<td>24.71</td>
</tr>
<tr>
<td>Carryover</td>
<td>9</td>
<td>32.63</td>
<td>2.73</td>
<td>0.96</td>
<td>30.64</td>
<td>0.05</td>
<td>24.83</td>
</tr>
<tr>
<td>Carryover*</td>
<td>12</td>
<td>31.56</td>
<td>2.74</td>
<td>1.66</td>
<td>25.10</td>
<td>0.13</td>
<td>26.13</td>
</tr>
<tr>
<td>Smelt</td>
<td>N/A</td>
<td>41.67</td>
<td>4.19</td>
<td>2.05</td>
<td>9.05</td>
<td>7.53</td>
<td>35.91</td>
</tr>
<tr>
<td>Dust</td>
<td>N/A</td>
<td>28.76</td>
<td>5.11</td>
<td>4.26</td>
<td>57.79</td>
<td>0.16</td>
<td>1.48</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Boiler C</th>
<th>Sampling Time (min.)</th>
<th>Na</th>
<th>K</th>
<th>Cl</th>
<th>SO₄</th>
<th>S</th>
<th>CO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carryover</td>
<td>3</td>
<td>32.02</td>
<td>2.72</td>
<td>0.85</td>
<td>34.89</td>
<td>0.16</td>
<td>21.19</td>
</tr>
<tr>
<td>Carryover</td>
<td>6</td>
<td>32.89</td>
<td>2.77</td>
<td>0.88</td>
<td>36.54</td>
<td>0.31</td>
<td>20.88</td>
</tr>
<tr>
<td>Carryover</td>
<td>9</td>
<td>32.35</td>
<td>2.71</td>
<td>0.80</td>
<td>36.47</td>
<td>0.39</td>
<td>20.11</td>
</tr>
<tr>
<td>Carryover</td>
<td>12</td>
<td>32.49</td>
<td>2.73</td>
<td>0.78</td>
<td>37.36</td>
<td>0.44</td>
<td>19.55</td>
</tr>
<tr>
<td>Smelt</td>
<td>N/A</td>
<td>40.50</td>
<td>3.84</td>
<td>1.65</td>
<td>9.34</td>
<td>6.36</td>
<td>36.31</td>
</tr>
<tr>
<td>Dust*</td>
<td>N/A</td>
<td>30.57</td>
<td>5.02</td>
<td>2.60</td>
<td>59.38</td>
<td>0.17</td>
<td>3.98</td>
</tr>
</tbody>
</table>

*: contaminated samples
Figure 6-1 Carryover deposits not contaminated (3 minute exposure) and contaminated (12 minute exposure) with fume taken from boiler B.

6.2  Enrichment Factors of Cl and K

The term “enrichment factor” was already defined in Section 3.2.1, this is used here to calculate the enrichment factor for chloride (EF$_{\text{Cl}}$) and for potassium (EF$_{\text{K}}$) for the samples. Figure 6-2 shows EF$_{\text{Cl}}$ and EF$_{\text{K}}$ in carryover deposits collected from boilers A, B, and C, along with those for smelt (shown at time = 0). In all cases, the enrichment factors were less than one, indicating that both carryover deposits and smelt in each boiler contained less Cl and K than the as-fired black liquor of the boiler.

The average EF$_{\text{Cl}}$ value was about 0.79 for smelt (ranging from 0.7 to 0.86), and significantly lower (about 0.5) for carryover deposits (ranging from 0.27 to 0.54). In each boiler, no significant difference in EF$_{\text{Cl}}$ value was observed between carryover deposits from different sampling times, except for the 12-minute sample from Boiler B, which showed a significantly higher EF$_{\text{Cl}}$ value than other carryover deposit samples. As mentioned in Section 6.1, this outlier (noted with an asterisk (*)) in Figure 6-2 was caused by the contamination of the sample by fume deposits which usually contain much more Cl and K than carryover deposits.
Figure 6-2 Enrichment factors for: a) chloride and b) potassium in carryover deposits and smelt collected from boiler A, B, and C (oxidized smelt shown at time = 0).
Similar results were obtained for potassium, although the average EF$_K$ value was higher than the average EF$_{Cl}$ value. It was close to one for smelt, but varied between 0.8 and 0.9 for carryover deposits. The higher EF$_K$ value compared to EF$_{Cl}$ value is due to the fact that potassium compounds are not only in the form of KCl, but also K$_2$SO$_4$, K$_2$S and K$_2$CO$_3$, none of which is appreciably volatile. However, chloride can be in the form of NaCl and KCl, which are much more volatile than other alkali compounds.

Note also in Figure 6-2 that extrapolation of the carryover sample data to zero sampling time gives EF$_{Cl}$ and EF$_K$ values significantly lower than those from smelt. This is plausible since carryover particles are exposed to a more oxidizing atmosphere and a higher temperature than smelt in the lower furnace. High temperatures cause more Cl and K to vaporize and be lost from the particles.

Depletion factors of Cl and K for each sample was calculated using Equations 4-3 and 4-4. The results shown in Table 6.3 indicate that the depletion of Cl is about 3 to 4 times greater than that of K. The results are similar to those obtained using the EFR (presented in Section 4.3), implying that the field and experimental results are in good agreement.

**Table 6.3** Depletion factors of Cl and K for three recovery boilers of A, B, and C.

<table>
<thead>
<tr>
<th>Boiler</th>
<th>Depletion Factor of Cl (DF$_{Cl}$)</th>
<th>Depletion Factor of K (DF$_K$)</th>
<th>DF$_{Cl}$/DF$_K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.55</td>
<td>0.14</td>
<td>3.93</td>
</tr>
<tr>
<td>B</td>
<td>0.53</td>
<td>0.18</td>
<td>2.94</td>
</tr>
<tr>
<td>C</td>
<td>0.48</td>
<td>0.13</td>
<td>3.69</td>
</tr>
</tbody>
</table>
Figure 6-3 shows the average EF$_K$ values versus the average EF$_{Cl}$ values for black liquor, smelt, carryover particles, and precipitator dust samples taken from boilers A, B, and C. By definition, as-fired black liquor samples have an enrichment factor of one. Carryover deposits and smelt samples have enrichment factors of less than one, since they contain less Cl and less K than the black liquor sample. Precipitator dust samples, which are the condensed gaseous inorganics, mostly Cl and K components, are significantly enriched in Cl and K, and thus have enrichment factors of much greater than one. The correlation between EF$_K$ and their respective EF$_{Cl}$ of these samples appears to be linear for boilers A and B. These results are consistent with the results presented with Janka et al. [24].

The results obtained from Boiler C did not fall on a straight line, since the precipitator dust taken from this boiler showed lower EF$_{Cl}$ than what was expected. A gray colour and presence of some large particles in this sample indicated that it was contaminated probably by the presence of an old deposit sample removed from a tube by sootblowers. Carryover particles have an EF$_{Cl}$ less than 1, and the addition of carryover particles to the precipitator dust would lower the EF$_{Cl}$ of the dust samples. The straight line shown in Figure 6.3 (for boilers A and B) goes through the data points of carryover, smelt, black liquor, and precipitator dust. Therefore, drawing a line through data points of carryover, smelt, and black liquor for Boiler C will give us an idea where the expected data point for the dust sample may fall. This line (designated as Expected) is shown on Figure 6-3c as a dashed line.
Figure 6-3 Correlation between the enrichment factor of Cl and K for as-fired liquor, smelt, carryover, and dust from a) boiler A and b) boiler B.
Figure 6-3 (cont’d) Correlation between the enrichment factor of Cl and K for as-fired liquor, smelt, carryover, and dust from c) boiler C.

6.3 Concentrations of S, SO₄, and CO₃

Carryover samples contained little sulphide and a much larger amount of sulphate when compared to smelt (Table 6-2). This is expected since carryover is formed in a more oxidizing atmosphere and at a higher temperature than smelt in the lower furnace. In order to enable a comparison between carryover composition and smelt composition, the sulphide content was converted to sulphate which was then added to the original sulphate content of the samples. The sum of the “converted” sulphate and the original sulphate are expressed as total sulphate.

Figure 6-4 shows the total sulphate and carbonate contents of carryover samples from boilers A, B, and C, along with the composition of oxidized smelt (shown in these figures at time = 0), which was taken to be the composition of smelt with all sulphide converted to sulphate. The carryover deposits contained more total sulphate and less carbonate than oxidized smelt. The
total sulphate content in the carryover samples increased slightly while the carbonate content decreased with the sampling time. This indicates that sulphation of carbonate occurred, lowering the carbonate content, and increasing the total sulphate content. The results also suggest that although some sulphation of the carbonate in carryover deposits may have occurred on the probe, the majority of the sulphation occurred during black liquor combustion, before the deposition of the particles on the probe.

Note also in Figure 6-4 that while the total sulphate and carbonate contents of oxidized smelt in Boilers B and C were similar (which is expected since these boilers were burning the same black liquor at the same pulp mill), the total sulphate content of carryover in Boiler C was significantly higher than in Boiler B. This, together with the higher carbonate content of the boiler C precipitator dust (Table 3), suggests that Boiler C may have been operated at a higher temperature in the lower furnace than Boiler B. Higher temperatures minimize sulphur release and thus more sulphur is retained in the carryover.
Figure 6-4 Total sulphate and carbonate content of the oxidized smelt and carryover deposit from a) boiler A and b) boiler B (oxidized smelt shown at time = 0).
Figure 6-4 (cont’d) Total sulphate and carbonate content of the oxidized smelt and carryover deposit from c) boiler C (oxidized smelt shown at time = 0).

6.4 Summary

Field studies were conducted to examine the composition of carryover particles in three recovery boilers using a specially-designed air-cooled probe. Samples of as-fired black liquor, smelt, and precipitator dust from each boiler were also analyzed for comparison. The results of the studies can be summarized as follows:

1) carryover particles and smelt contain less Cl and K than the as-fired black liquor, while the degree of the depletion of Cl and K is much higher in carryover particles than smelt;

2) the depletion of Cl is about 3 to 4 times greater than the depletion of K, which is similar to data obtained from the EFR experiments;
3) there is a linear relationship between the Cl and K contents of smelt, carryover, black liquor and precipitator dust in each boiler;

4) the results of the field studies show that the composition of carryover particles does not change significantly with the sampling time; and

5) carryover particles are leaner in Cl and K and contain less carbonate and more sulphate than oxidized smelt. Therefore, it can be concluded that oxidized smelt does not give a reasonable approximation of carryover composition.
PART 3: MODEL DEVELOPMENT
CHAPTER 7: CARRYOVER COMPOSITION MODEL

Carryover composition is required to estimate the tendency of the particles to deposit. This enables assessment of the deposition conditions in kraft recovery boilers. It is difficult to obtain in situ carryover samples and quickly determine their composition; however, the composition of carryover particles can be predicted using a numerical model that considers the combustion of black liquor particles under boiler operating conditions. One of the main challenges in the prediction of carryover composition has been the lack of validated kinetic equations used to model the chemical reactions occurring during the combustion stages.

The main objective of this chapter was to develop a dynamic model that can predict the composition of carryover particles. Time varying particle kinetic, mass and energy equations were solved to predict the composition and temperature of a single particle in an evolving environment. Available kinetic equations were used as a basis to formulate the combustion of a black liquor particle. The model was evaluated and modified using the experimental data collected in the tightly controlled EFR environment.

7.1 General Approach

A model has been developed to predict carryover composition as it travels through the EFR or a boiler based on initial black liquor composition and particle combustion. Initial particle composition is defined on an elemental basis and is assumed to include carbon (C), hydrogen (H), oxygen (O), sulphur (S), sodium (Na), potassium (K), and chlorine (Cl). These individual elements are all assumed to be converted to specified chemical compounds during the
combustion stages. Four different overlapping stages are considered for the combustion of a single black liquor particle: drying, devolatilization, char burning, and smelt oxidation (Figure 7.1). The drying stage is omitted for the combustion of dried black liquor in the EFR.

Figure 7.1 Stages of the combustion of a black liquor particle [34].

C, S, H, and O are assumed to pyrolyze during devolatilization stages, while Na, K, and Cl form inorganic materials involved in the reactions occurring during char burning and smelt oxidation stages. It is assumed that Cl leaves the particle due to the vaporization of NaCl and KCl and this mechanism is assumed to obey Raoult’s Law. It was also assumed that K leaves the particle due to the vaporization of KCl and reduction of K₂CO₃ with char. The preliminary results of the
calculation in this study did not show a significant rate for the depletion of the K. However, the EFR and field results showed that K was depleted during the combustion of the black liquor, and its depletion rate was approximately one third of that of Cl. Therefore, in this model, it was then assumed that the rate of depletion of K is one third of the rate of the depletion of Cl in order to calculate the K content in the carryover particle.

The Biot number (Bi) of the dried black liquor particles was calculated, and it was found that the particles smaller than 1mm (used for this study) had Bi below 0.1, indicating that the heat resistance inside the particle was negligible compared to the heat resistance between the particle and gas. Therefore, since most black liquor droplets are smaller than 1 mm, one single temperature was assigned for the particle. A set of algebraic and differential equations were derived from the governing transient kinetic, mass and energy equations defined for the combustion of the particles.

Particle position through the EFR or the boiler was based on a particle terminal velocity estimate as described in Section 7.2. The governing kinetic and mass balance equations are developed in Section 7.3, while the energy equation is developed in Section 7.4. Discretized forms of the mass and energy equations are given in Section 7.5. Model assumption, initial and boundary conditions are defined in Section 7.6. The solution procedure to predict particle temperature and composition as it travels through the EFR or boiler is listed in Section 7.7. The sensitivity of results to the time step is discussed in section 7.8.
7.2 Particle Velocity

Gravitational, buoyancy, and drag forces act on a particle traveling in a gas stream. Gravitational force is always downward and pulls the particle down, while the buoyancy force is always upward and pulls the particle up. However, the direction of the drag force depends on the direction of the slip velocity. The slip velocity is the velocity that the surface of a particle experiences when the relative velocity between a stream of fluid and a particle is non-zero. When the slip velocity is upward, the drag force is upward, and vice versa. In the EFR, for example, when the particle has a velocity below the gas velocity, the slip velocity is downward and so is the drag force (Figure 7.2-a), and vice versa; when the particle has a velocity greater than the gas velocity, the slip velocity is upward and so the drag force (Figure 7.2-b).

![Figure 7.2 Forces acting on a) a falling particle moving slower than the gas and b) either a falling particle moving faster than the gas or an entrained particle by a gas moving slower than the gas.](image)

Either way, the particle velocity is calculated based on a force balance on a traveling particle [47].

\[
\sum \vec{F} = \vec{F}_G + \vec{F}_B + \vec{F}_D = \frac{d\vec{V}_p}{dt} \tag{7.2}
\]
where $V_p$ is the particle velocity and $F, F_G, F_B,$ and $F_D$ are respectively balance, gravitational, buoyancy, and drag forces acting on the particle and are calculated from the following equations:

\[ F_G = -\frac{1}{6} \pi \rho_p d_p^3 g \]  
\[ F_B = \frac{1}{6} \pi \rho_s d_p^3 g \]  
\[ F_D = \frac{1}{8} \pi \rho_s d_p^2 C_D \left| \vec{V}_p - \vec{V}_s \right| \]

where $\rho_p$ and $\rho_s$ are respectively particle and gas densities, $d_p$ is the particle diameter, $g$ is gravitational acceleration, $C_D$ is the drag force coefficient, and $V_s$ is the slip velocity. Particle density is assumed to be the ratio of the particle mass to the particle volume. The method of calculation of particle mass and volume is discussed in Section 7.3.

The value of the slip velocity ($V_s$) is calculated as:

\[ V_s = \left| V_g - V_p \right| \]

where $V_g$ is the gas velocity and is defined as the initial condition in this model and particle velocity is calculated as it follows.

Drag force coefficient is obtained for spherical particles with $1 < \text{Re} < 100$ as [47]:

\[ C_D = \frac{24}{\text{Re}_p} \left( 1 + 0.197 \text{Re}_p^{0.63} + 2.6 \times 10^{-4} \text{Re}_p^{1.38} \right) \]

where Reynolds number ($\text{Re}$) for a particle is defined as:
\[ \text{Re}_p = \frac{\rho_g V_s d_p}{\mu_g} = \frac{V_s d_p}{v_g} \quad (7.8) \]

In this equation, \( \mu_g \) and \( v_g \) are the gas dynamic viscosity and kinematics viscosity, respectively.

Incorporating Equations 7.3, 7.4, and 7.5 into Equation 7.2, and assuming upward forces are positive and downward forces are negative, gives:

\[ \frac{1}{6} \pi \rho_p d_p^3 g + \frac{1}{6} \pi \rho_g d_p^3 g + \frac{1}{8} \pi C_D \rho_g d_p^2 \left( \frac{V_s}{V} \right) = \frac{d \tilde{V}_p}{dt} \quad (7.9) \]

A solution to Equation 7.9 gives the particle velocity. For a special condition, when the particle reaches its terminal velocity, the external forces acting on the particle are balanced, which means Equation 7.9 equals zero. Under this special condition, a solution to this equation gives the particle slip velocity as:

\[ \tilde{V}_{s,t} = \pm \left( \frac{4d_p (\rho_p - \rho_g) g}{3C_D \rho_g} \right)^{0.5} \quad (7.10) \]

Therefore, when the particle travels at its terminal velocity, its velocity becomes:

\[ V_p = V_t = V_g \pm \left( \frac{4d_p (\rho_p - \rho_g) g}{3C_D \rho_g} \right)^{0.5} \quad (7.11) \]

The sign in Equations 7.10 and 7.11 is positive for the EFR conditions and is negative for the recovery boiler environment.
### 7.3 Governing Kinetics and Mass Transfer Equations

Particle mass transfer is calculated taking into account the resistances from chemical reaction kinetics and mass transfer between the particle and surrounding gas. The rates of chemical reactions during combustion of the particle are calculated to obtain the concentrations of some defined species; e.g. sulphate and carbonate. The reactions occurring during the combustion of a black liquor particle are discussed below as the particle goes through four overlapping stages of: drying, devolatilization, char burning, and smelt oxidation. Devolatilization and char burning stages are respectively assumed to initiate when water evaporation (during drying stage) and carbon conversion into gas and char (during devolatilization) reach 90% of completion. While char burning and smelt oxidation are not separated and the oxidation of sulphide occurs whenever there is excess oxygen at the surface of the particle.

#### 7.3.1 Drying

In the drying stage, no reaction occurs and only water is evaporated. The rate of evaporation is controlled by the diffusion of the water from the surface of the particle to the surrounding gas, and is calculated as [30].

\[
R_{H2O} = K_{g,H2O} A_p (C_s - C_{\infty})_{H2O}
\]  

(7.12)

where \( R_{H2O} \) is the rate of evaporation in mole/s, \( K_{g,H2O} \) is the mass transfer coefficient of water vapour in the gas phase, \( A_p \) is the particle surface area, and \( C_{H2O,s} \) and \( C_{H2O,\infty} \) are the concentration of water vapour at the surface of the particle and in the surrounding gas far from the particle, respectively.
The mass transfer coefficient of water vapour from the surface of the particles to the surrounding gas is calculated using the Sherwood number ($Sh$) for a spherical particle at laminar flow with Reynolds number below 100 [47].

$$Sh_{H_2O} = \frac{K_{g,H_2O} d_p}{D_{H_2O,g}} = 2 + 0.569(GrSc)^{0.25} + 0.347(Re_{p, Sc})^{0.62} \quad (7.13)$$

where $D_{H_2O,g}$ is diffusivity of water vapour in the gas phase, $Gr$ is the Grashof number, $Sc$ is the Schmidt number, and $Re_p$ is the Reynolds number, and are calculated using Equations 7.14, 7.15, and 7.8, respectively.

$$Gr = \frac{g}{V_g^2} d_p^3 (T_{gas} - T_p) \beta \quad (7.14)$$

$$Sc = \frac{V_g}{D_{H_2O,g}} \quad (7.15)$$

where $\beta$ is coefficient of thermal expansion. For an ideal gas, $\beta$, is the inverse of film temperature ($T_f$) [11],

$$\beta = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right) = \frac{1}{T_f} \quad (7.16)$$

and Equation 7.14 becomes:

$$Gr_{id} = \frac{g}{V_g^2} d_p^3 \left( \frac{T_{gas} - T_p}{T_f} \right) \quad (7.17)$$
To calculate the rate of evaporation, it is assumed that the concentration of water vapour in the

gas phase is negligible \( (C_{H2O,g}=0) \). The concentration at the surface of the particle is calculated

using the ideal gas law, and assuming that the water vapour partial pressure is equal to its pure

vapour pressure.

\[
P^{H2O(g)} = P_{vap} = C_{H2O,s} RT_p (1 - S)
\] (7.18)

where \( P^{H2O(g)} \) and \( P_{vap} \) are respectively water partial and pure vapour pressures, \( R \) is gas constant,

and \( S \) is the black liquor solids content. The vapour pressure (in Pascal) at different gas

temperatures is [48]:

\[
P^{H2O,g} = \left(2.9 \times 10^{-6} T_p^3 - 2.839 \times 10^{-4} T_p^2 + 9.401 \times 10^{-3} T_p\right) \times 10^5
\] (7.19)

Rearrangement of Equation 7.18 gives the vapour concentration at the surface of the particle as:

\[
C_{H2O,s} = \frac{P_{vap}}{RT_p (1 - S)}
\] (7.20)

The equation used to calculate the rate of evaporation of water during drying stage is

summarized in Table 7.1.

**Table 7.1 Rate equation used during the drying stage.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equation (mole/s)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2O(l) \rightarrow H_2O(g) )</td>
<td>( R_{H2O} = K_{g,H2O} A_p C_{H2O,s} )</td>
<td>(7.21)</td>
</tr>
</tbody>
</table>
7.3.2 Devolatilization

The drying stage is assumed to conclude at a solids content of 90%, when the devolatilization stage begins. During devolatilization, black liquor decomposes into gas and char. It is assumed that all H and some C, O, and S leave the particle in different forms of gaseous materials including H₂, H₂S, CH₄, CO, CO₂, and H₂O; while Na, K, and Cl do not volatilize and remain in the particle. The releases of C, S, H, and O are dependent on local process conditions and were determined by temperature dependent Kobayashi-type equations.

The Kobayashi-type equation is a simple empirical model used to predict the decomposition of volatile carbon and sulphur materials during the devolatilization stage of the combustion of black liquor particles. In this approach, the decomposition is described by two parallel irreversible reactions that both produce volatile and solid products. The volatile products leave the particle and burn in the gas phase, and the solid products remain in the particle in the form of char. The advantage of the Kobayashi equation is that it can describe the dependence of char yield on the particle temperature history.

The devolatilization stage is an endothermic process, and its rate is determined by the rate of heat transfer to the particle. It is assumed that this stage requires 800 kJ/kg to occur [49]. The diameter of the particle is assumed to expand up to three times its initial value during devolatilization and is expressed by Equation 7.22 [7].

\[
d_p = d_{p,\text{ini}} + (S_{\text{max}} - 1)d_{p,\text{ini}}(X_{\text{devol}})
\]  

(7.22)
where $d_{p,ini}$ is particle initial diameter, $S_{max}$ is the particle’s maximum swelling ratio at the end of the devolatilization ($=3$), and $X_{devol}$ is the degree of the extent of devolatilization stage [7].

7.3.2.1 Sulphur Conversion

The sulphur in the black liquor is assumed to exist initially in five different forms: sulphate (10%), thiosulphate (36%), sulphite (15%), sulphide (5%), and organic sulphur (34%) [6]. During devolatilization, alkali thiosulphate and sulphite decompose according to the following reactions [14]:

\[
\begin{align*}
\text{Na}_2\text{S}_2\text{O}_3 (s,l) & \rightarrow \text{Na}_2\text{SO}_3 (s,l) + \text{S} (s) \quad \text{Reaction (7-1)} \\
4\text{Na}_2\text{SO}_3 (s,l) & \rightarrow \text{Na}_2\text{S} (s,l) + 3 \text{Na}_2\text{SO}_4 (s,l) \quad \text{Reaction (7-2)}
\end{align*}
\]

Since there is no equation available to determine the rates of Reactions 7-1 and 7-2, it is assumed that their rates are equal to the rate of sulphur release during devolatilization multiplied by their molar ratios (of thiosulphate or sulphite) to the pyrolyzable sulphur. The elemental sulphur formed in Reaction 7-1 is assumed to be added to the organic sulphur.

Of the different forms of sulphur, only organic sulphur is pyrolyzable. The pyrolyzable sulphur is converted into gas and char. The gaseous portion leaves the particle in the form of H$_2$S. The charred portion stays in the particle in the form of alkali sulphide. Equations 7.23 and 7.24 are the Kobayashi-type equations used to calculate the rates of sulphur conversion (in g/s) into the char ($R_{S-char}$) and gas ($R_{S-gas}$), respectively [33].
\[ R_{S_{-char}} = (\beta_1 k_{s1} + \beta_2 k_{s2} + \beta_3 k_{s3})[S] \] (7.23)

\[ R_{S_{-gas}} = ((1 - \beta_1)k_{s1} + (1 - \beta_2)k_{s2} + (1 - \beta_3)k_{s3})[S] \] (7.24)

where,

\[ k_{s1} = b_1 e^{-\frac{E_1}{RT}} \] (7.25)

\[ k_{s2} = b_2 e^{-\frac{E_2}{RT}} \] (7.26)

\[ k_{s3} = b_3 e^{-\frac{E_3}{RT}} \] (7.27)

The values for \( b_1, b_2, b_3, \beta_1, \beta_2, \beta_3, E_1, E_2, \) and \( E_3 \) are 4, 125, 5.6 \times 10^5, 0, 0.8, 0.24, 200, 1500, and 8300, respectively. The \( b \) values and \( k \) values are coefficients in 1/s, \( \beta \) values are constants and dimensionless, \( E \) values are activation energy in J/mole, and \([S]\) is the total amount of pyrolyzable sulphur in gram. These coefficients were determined based on the fitted curve presented in Figure 7.3 [7]. The data presented in Figure 7.3 are the experimental results from Brink, Clay, Cantrell, and Forssen who performed the experiments using six different black liquor samples designated as Liq A to Liq G on the graph.

### 7.3.2.2 Carbon conversion

The carbon in the black liquor is assumed to be initially in the form of pyrolyzable carbon and alkali carbonate. The pyrolyzable carbon is converted into gas and char. The gaseous portion leaves the particle in the form of CO, CO\(_2\), and CH\(_4\) in the molar proportions of 60\%, 37\%, and 3\%, respectively [33].
Figure 7.3 Percentage of sulphur released from various black liquor samples burned at different oven temperatures [7].

The charred portion stays in the particle in the form of burnable carbon which is usually called char. Equations 7.28 and 7.29 are the Kobayashi-type equations used to calculate the rates of carbon conversion (in g/s) into the gas and char, respectively [50].

\[
R_{C-g} = (\alpha_1 k_{c1} + \alpha_2 k_{c2})[C] \\
R_{C-char} = ((1 - \alpha_1) k_{c1} + (1 - \alpha_2) k_{c2})[C]
\]

(7.28)

(7.29)

where,

\[
k_{c1} = a_1 e^{\left(-\frac{E_r}{RT}\right)}
\]

(7.30)

\[
k_{c2} = a_2 e^{\left(-\frac{E_r}{RT}\right)}
\]

(7.31)
The values for \( a_1, a_2, \alpha_1, \alpha_2, E_4, \) and \( E_5 \) are 3.0, 1.0\( \times 10^6 \), 0.18, 0.6, 4.7\( \times 10^{-7} \), and 1.0\( \times 10^4 \), respectively [49]. The \( a \) values and \( k \) values are coefficients in 1/s, \( \alpha \) values are constants and dimensionless, and \( E \) values are activation energy in J/mole, and \( [C] \) is the total amount of pyrolyzable carbon in gram.

### 7.3.2.3 Hydrogen conversion

All hydrogen in the black liquor is assumed to be converted to \( \text{H}_2, \text{H}_2\text{S} \) and \( \text{CH}_4 \) in the gas phase. The rates of formation of \( \text{H}_2\text{S} \) and \( \text{CH}_4 \) are linked to the rates of sulphur and carbon (the \( \text{CH}_4 \) portion) release to the gas, and the balance of hydrogen is assumed to end up in the gas in the form of \( \text{H}_2 \) [38].

### 7.3.2.4 Oxygen conversion

The oxygen in the black liquor is either fixed in the inorganics, including carbonate, sulphate, sulphite, and thiosulphate, or is in the pyrolyzable organic matters. The pyrolysis of the organic matters is assumed to result in the release of the oxygen in the form of \( \text{CO} \) and \( \text{CO}_2 \) [38].

The rate equations used for the reactions during the devolatilization stage are summarized in Table 7.2.
Table 7.2 Rate equations used for the reactions during devolatilization stage.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equation (mole/s)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(pyrolyzable S)(_{\text{s}}) → Gaseous S components</td>
<td>[R_{S-\text{char}} = (100 \times e^{-\frac{1500}{RT_p}} + 1.36 \times 10^5 \times e^{-\frac{5300}{RT_p}}) \times [S]]</td>
<td>(7.32)</td>
</tr>
<tr>
<td>(pyrolyzable S)(_{\text{s}}) → Sulphide in Char</td>
<td>[R_{S-\text{char}} = (4 \times e^{-\frac{200}{RT_p}} + 0.25 \times e^{-\frac{1500}{RT_p}} + 4.26 \times 10^5 \times e^{-\frac{8300}{RT_p}}) \times [S]]</td>
<td>(7.33)</td>
</tr>
<tr>
<td>(pyrolyzable C)(_{\text{s}}) → Gaseous C components</td>
<td>[R_{C-\text{char}} = (0.54 \times e^{-\frac{4.7 \times 10^{-7}}{RT_p}} + 6.0 \times 10^5 \times e^{-\frac{1.3 \times 10^7}{RT_p}}) \times [C]]</td>
<td>(7.34)</td>
</tr>
<tr>
<td>(pyrolyzable C)(_{\text{s}}) → Char</td>
<td>[R_{C-\text{char}} = (2.46 \times e^{-\frac{4.7 \times 10^{-7}}{RT_p}} + 4.0 \times 10^5 \times e^{-\frac{1.3 \times 10^7}{RT_p}}) \times [C]]</td>
<td>(7.35)</td>
</tr>
<tr>
<td>(pyrolyzable O)(_{\text{s}}) → Gaseous O components</td>
<td>[R_O = \left(R_{C-\text{gas}} + R_{C-\text{char}}\right) \times \frac{n_O}{n_C}]</td>
<td>(7.36)</td>
</tr>
<tr>
<td>(pyrolyzable H)(_{\text{s}}) → Gaseous H components</td>
<td>[R_H = \left(R_{C-\text{gas}} + R_{C-\text{char}}\right) \times \frac{n_H}{n_C}]</td>
<td>(7.37)</td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3) (s,l) → Na(_2)SO(<em>3) (s,l) + S(</em>{\text{s}})</td>
<td>[R_{\text{Na}<em>2\text{S}<em>2\text{O}<em>3} = \left(R</em>{C-\text{gas}} + R</em>{C-\text{char}}\right) \times \frac{n</em>{\text{Na}_2\text{S}_2\text{O}_3}}{n_C}]</td>
<td>(7.38)</td>
</tr>
<tr>
<td>K(_2)S(_2)O(_3) (s,l) → Na(_2)SO(<em>3) (s,l) + S(</em>{\text{s}})</td>
<td>[R_{\text{K}<em>2\text{S}<em>2\text{O}<em>3} = \left(R</em>{C-\text{gas}} + R</em>{C-\text{char}}\right) \times \frac{n</em>{\text{K}_2\text{S}_2\text{O}_3}}{n_C}]</td>
<td>(7.39)</td>
</tr>
<tr>
<td>2 Na(_2)SO(_3) (s,l) → Na(<em>2)S(</em>{\text{s}}) (s,l) + Na(_2)SO(_4) (s,l)</td>
<td>[R_{\text{Na}<em>2\text{SO}<em>3} = \left(R</em>{C-\text{gas}} + R</em>{C-\text{char}}\right) \times \frac{n_{\text{Na}_2\text{SO}_3}}{n_C}]</td>
<td>(7.40)</td>
</tr>
<tr>
<td>2 K(_2)SO(_3) (s,l) → K(<em>2)S(</em>{\text{s}}) (s,l) + K(_2)SO(_4) (s,l)</td>
<td>[R_{\text{K}<em>2\text{SO}<em>3} = \left(R</em>{C-\text{gas}} + R</em>{C-\text{char}}\right) \times \frac{n_{\text{K}_2\text{SO}_3}}{n_C}]</td>
<td>(7.41)</td>
</tr>
</tbody>
</table>
7.3.3 Char burning and smelt oxidation

During the char burning stage of combustion, carbon in the black liquor may be consumed by reaction with CO$_2$, H$_2$O, O$_2$, Na$_2$CO$_3$, or Na$_2$SO$_4$. The reactions between the carbon and CO$_2$ and H$_2$O (Reactions 7-3 and 7-4) dominate in a reducing environment when the concentration of oxygen at the surface of the particle is low [16,17,18,19]. The rate of reactions between char and CO$_2$ and H$_2$O are controlled by the rates of the mass diffusion of CO$_2$ and H$_2$O to the surface of the particle, respectively.

\[
\begin{align*}
C_{(s)} + H_2O_{(g)} & \rightarrow CO_{(g)} + H_2_{(g)} & \text{Reaction (7-3)} \\
C_{(s)} + CO_2_{(g)} & \rightarrow 2CO_{(g)} & \text{Reaction (7-4)}
\end{align*}
\]

The reaction between char and oxygen (Reaction 7-5) occurs only when there is excess oxygen at the surface of the particle (an oxidizing environment). The reaction rate is controlled by the mass diffusion of oxygen to the surface of the particle, where oxygen reacts first with combustion gases, CO and H$_2$, near the surface, before reacting with char to form CO [33].

\[
C_{(s)} + \frac{1}{2}O_2_{(g)} \rightarrow CO_{(g)} & \text{ Reaction (7-5)}
\]

The reduction of alkali carbonate is an important mechanism for char combustion and for alkali depletion during char burning. At temperatures above 700°C and under a reducing condition, sodium carbonate is reduced by char to produce sodium vapour and CO [18].

\[
2C_{(s)} + Na_2CO_3 \rightarrow 2Na_{(g)} + 3CO_{(g)} & \text{ Reaction (7-6)}
\]
Alkali sulphate reduction is another mechanism for char combustion and for the reduction of sulphate to sulphide during char burning. In the presence of char at high temperatures, sodium sulphate is reduced by char to produce sodium sulphide and CO$_2$ [51].

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

Reaction (7-7)

CO and CO$_2$ may also be formed as a result of Reactions 7-6 and 7-7, respectively [33]. For simplicity and availability of the equations for the rate of these reactions, it is assumed that the product of Reaction 7-6 is in the form of CO and the product of Reaction 7-7 is in the form of CO$_2$. Produced CO reacts with oxygen at the surface of the particle and is converted into CO$_2$.

If there is excess oxygen at the surface of the particle during and after char burning, sulphide is oxidized to sulphate [33]. The rate of this reaction is controlled by the mass diffusion of O$_2$ to the surface of the particle. O$_2$ reacts with sulphide quickly and the reaction is exothermic, which is the main cause of the increase in particle temperature during and after the char burning stage.

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

Reaction (7-8)

The rates of sulphide oxidation are expressed using Equations 7.60 to 7.63 (listed in Table 7.5), which are modified forms of the equations previously reported by Wag [33]. The modifications were performed as a part of the model development for a better prediction of the model in the EFR environment. The EFR experiments showed that no appreciable sulphide was formed in the carryover particles at 12.5% O$_2$. Therefore, the original coefficients in equations 7.60 to 7.63
were changed to obtain zero sulphide content in the particles formed at this O\textsubscript{2} level. Same coefficients were used in the model at all different O\textsubscript{2} concentrations.

The rate expressions for the reactions occurring during char burning and smelt oxidation stages used in the model are listed in Table 7.5. Similar reactions to Reactions 7-6, 7-7, and 7-8 occur for K\textsubscript{2}CO\textsubscript{3}, K\textsubscript{2}SO\textsubscript{4}, and K\textsubscript{2}S. Due to the lack of data, the rates for potassium components are assumed to be the same as the rates for sodium components.

The diameter of the particle is assumed to shrink to 0.65 times its initial value at the end of the char burning stage and is expressed by Equation 7.42 [7].

\[
d_p = d_{p,ini} S_{\min} \left\{ 1 + \left[ \left( \frac{S_{\min}}{S_{\max}} \right)^3 - 1 \right] X_{\text{char}} \right\}^{1/3}
\]  

(7.42)

where \(d_{p,ini}\) is particle initial diameter, \(S_{\min}\) is the minimum shrinking ratio at the end of the char burning stage (=0.65), and \(X_{\text{char}}\) is the degree of the extent of char burning stage [7].

7.3.3.1 Release of Na, K, and Cl

Na, K, and Cl are released from black liquor during and after char burning. Na is released in the form of elemental Na due to the carbonate reduction (Reaction 7-6) and in the form of NaCl due to the vaporization of NaCl (Reaction 7-9). Similarly, K is released in the form of elemental K due to the reduction of K\textsubscript{2}CO\textsubscript{3} (Reaction 7-10) and in the form of KCl due to the vaporization of KCl (Reaction 7-11). When the particle is at elevated temperatures, NaCl and KCl vaporize and leave the particle, which result in Cl release [51].
\[
\text{NaCl}_{(s,l)} \rightarrow \text{NaCl}_{(g)} \quad \text{Reaction (7-9)}
\]
\[
2 \text{C} \text{(s)} + \text{K}_2\text{CO}_3 \text{(s,l)} \rightarrow 2 \text{K}_{(g)} + 3 \text{CO}_{(g)} \quad \text{Reaction (7-10)}
\]
\[
\text{KCl}_{(s,l)} \rightarrow \text{KCl}_{(g)} \quad \text{Reaction (7-11)}
\]

The release of Na, K, NaCl, and KCl are controlled by the diffusion of these species from the surface of the particle to the surrounding gas. The rates of vaporization for each species were calculated using equation 7-43, similar to that used for the drying stage.

\[
R_i = K_{i,g} A_p \left( C_{i,s} - C_{i,\infty} \right) \quad (7.43)
\]

where \(i\) is either Na, K, Cl, NaCl, or KCl, \(R_i\) is the rate of vaporization in mole/s, \(K_{i,g}\) is the mass transfer coefficient, \(A_p\) is the particle surface area, and \(C_{i,s}\) and \(C_{i,\infty}\) are respectively the concentration of species at the surface of the particle and in the surrounding gas far from the surface of the particle.

To calculate the rate of vaporization of each species, it is assumed that: 1) the concentrations of species in the gas phase are negligible (\(C_{\infty}=0\)); 2) the gas phase is ideal; and 3) molten smelt obeys Raoult’s Law. The mass transfer coefficient of each species from the surface of the particles to the surrounding gas is calculated using Equation 7.44. This equation is from an empirical equation corrected for the Stefan blowing effect, which considers the effect of the heat transfer on the mass transfer of the species from the surface of a particle to the surrounding gas [30].
\[ K_{i,g} = \frac{h_{\text{conv}}}{\rho_g C_{p,g}} \left( \frac{k_g}{\rho_g C_{p,g} D_i} \right)^2 \]  

(7.44)

where \( k_g \) is gas conductivity, \( C_{p,g} \) is gas heat capacity, \( h_{\text{conv}} \) is convective heat transfer coefficient, and \( D_i \) is the diffusivity of the inorganic species; including NaCl, KCl, in the gas phase. \( h_{\text{conv}} \) is calculated using rearranged form of Equation 7.71 presented in Section 7.4.1.

The concentrations of NaCl or KCl at the surface of a particle (\( C_{i,s} \)) is determined by the product of the mole fraction of each species and total gas concentration.

\[ C_{i,s} = y_i C_{t,g} \]  

(7.45)

where the mole fraction of each species, \( y_i \), is calculated using Raoult’s Law (Equation 7.46) and total gas concentration, \( C_{t,g} \), is calculated using ideal gas law (Equation 7.47). Raoult’s law states that the partial pressure of a vaporizing substance is equal to the pure component vapour pressure times the mole fraction in the solid phase \([30]\).

\[ y_i P_i = x_i P_i^{\text{sat}}. \]  

(7.46)

\[ C_{t,g} = \frac{P_t}{RT_p} \]  

(7.47)

The vaporization process is assumed to occur at an atmospheric pressure. Mole fraction of NaCl (or KCl) in the inorganics, \( x_i \), is known; therefore, only, NaCl (or KCl) pure component vapour pressure, \( P_i^{\text{sat}} \), is required to calculate \( y_i \). The vapor pressure of NaCl (or KCl) is calculated using the Antoine equation \([30]\):
\[
\log(p_{i}^{\text{sat}}) = A - \frac{B}{T + C}
\]  
(7.48)

where A, B, and C are constants and listed in Table 7.3 [41]. Figure 7.4 shows the agreement between the vapour pressures of NaCl and KCl calculated using the Antoine equation and the data from the literature [41].

**Table 7.3** Antoine equation constants for NaCl and KCl [41].

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B (K)</th>
<th>C (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (860-1240 K)</td>
<td>3.6</td>
<td>5200</td>
<td>-317.4</td>
</tr>
<tr>
<td>NaCl (1138-1738 K)</td>
<td>5.1</td>
<td>8388</td>
<td>-82.6</td>
</tr>
<tr>
<td>KCl (1094 – 1680 K)</td>
<td>4.8</td>
<td>7440</td>
<td>-122.7</td>
</tr>
</tbody>
</table>

**Figure 7.4** Comparison of the calculated (solid lines) and reference data (datapoint) [41] of the vapour pressures of NaCl and KCl.
7.3.3.2 Sulphation of Carbonate

Sulphation of carbonate in an oxidizing environment is the main mechanism of the conversion of carbonate to sulphate (Reaction 7-12). This reaction occurs at high temperatures and is controlled by the mass diffusion of SO₂ to the surface of the particle and the mass diffusion of CO₂, as a product of the reaction, from the surface of the particle. The concentration of SO₂ in the gas phase is not calculated in this model; therefore, it is assumed that carbonate vaporizes at a temperature above 950 °C during char burning and smelt oxidation. The gaseous Na₂CO₃ is decomposed to Na₂O and CO₂ at the surface of the particle. Na₂O reacts with SO₂ in the gas and condenses in the form of Na₂SO₄, while CO₂ leaves the particle and ends up in the gas phase. Therefore, the rate of vaporization of Na₂CO₃ from the surface of the particle to the surrounding gas defines the rate of the sulphation of Na₂CO₃.

\[
\text{Na}_2\text{CO}_3 (s,l) + \text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{Na}_2\text{SO}_4(s,l) + \text{CO}_2 (g) \quad \text{Reaction (7-12)}
\]

The rate of vaporization of Na₂CO₃ is calculated similar to that described for the vaporization of NaCl. Equation 7.43 is used to calculate the rate of vaporization of Na₂CO₃. Equations 7.44, and 7.45 are respectively used to calculate the mass transfer coefficient and the particle surface concentration of Na₂CO₃. A similar approach to that of NaCl is used to calculate the vapour pressure of Na₂CO₃ at the particle surface. Table 7.4 lists the vapour pressure of Na₂CO₃ at different temperatures [42]. A Claussius type equation is assumed to fit the data. The logarithm of vapour pressure (in bar) is plotted against the inverse of absolute temperature (in K) to obtain the constants of the Claussius equation. The equation is the same as the Antoine equation, Equation 7.47, where C is zero. The result of curve fitting determines the values of 4.03.
(dimensionless) and 8303 K for constants A and B, respectively. Figure 7.5 shows the agreement between the calculated results and the values from literature [42].

The rate equations of the reactions defined during the char burning and smelt oxidation stages are listed in Table 7.5. $A_s$ in equations listed in Table 7.5 is the particle specific surface area and it is assumed to be 120 m$^3$/g of particle [33].

<table>
<thead>
<tr>
<th>$P_{\text{sat}}$ (mmHg)</th>
<th>0</th>
<th>1.5</th>
<th>3</th>
<th>5.5</th>
<th>8.5</th>
<th>14</th>
<th>21.5</th>
<th>29</th>
<th>44</th>
<th>66</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$ ($^\circ$C)</td>
<td>950</td>
<td>1000</td>
<td>1050</td>
<td>1100</td>
<td>1150</td>
<td>1200</td>
<td>1250</td>
<td>1300</td>
<td>1350</td>
<td>1400</td>
</tr>
</tbody>
</table>

**Table 7.4 Vapour pressure of pure Na$_2$CO$_3$[42].**

**Figure 7.5** Comparison of the calculated (solid line) and reference values (data point) [42] of the vapour pressure of Na$_2$CO$_3$. 
Table 7.5 Rate equations used for the reactions during char burning and smelt oxidation stages.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equation (mole/s)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) )</td>
<td>( R_{H_2O} = 1.60 \times 10^7 A_s[C]^\frac{c_{H_2O}}{c_{H_2O} + 1.42c_{H_2}} e^{-\frac{2.10 \times 10^4}{RT_p}} )</td>
<td>(7.49)</td>
</tr>
<tr>
<td>( C(s) + CO_2(g) \rightarrow 2 CO(g) )</td>
<td>( R_{CO_2} = 3.94 \times 10^8 A_s[C]^\frac{c_{CO_2}}{c_{CO_2} + 3.4c_{CO}} e^{-\frac{2.30 \times 10^4}{RT_p}} )</td>
<td>(7.50)</td>
</tr>
<tr>
<td>( C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g) )</td>
<td>( R_{O_2} = 3.00 \times 10^3 A_s[C]^\frac{c_{O_2}}{c_{O_2}} e^{-\frac{1.80 \times 10^4}{RT_p}} )</td>
<td>(7.51)</td>
</tr>
<tr>
<td>( 2C(s) + Na_2CO_3(s,l) \rightarrow 2Na(g) + 3CO(g) )</td>
<td>( R_{CO} = 1.00 \times 10^9 [Na_2CO_3]^\frac{c_{Na_2CO_3}}{c_{Na_2CO_3}} e^{-\frac{2.44 \times 10^8}{RT_p}} )</td>
<td>(7.52)</td>
</tr>
<tr>
<td>( 2C(s) + K_2CO_3(s,l) \rightarrow 2K(g) + 3CO(g) )</td>
<td>( R_{CO_3} = 1.00 \times 10^9 [K_2CO_3]^\frac{c_{K_2CO_3}}{c_{K_2CO_3}} e^{-\frac{2.44 \times 10^8}{RT_p}} )</td>
<td>(7.53)</td>
</tr>
<tr>
<td>( 2C(s) + Na_2SO_4(s,l) \rightarrow Na_2S(s,l) + 2CO_2(g) )</td>
<td>( R_{SO_4} = 3.79 \times 10^3 [x_{Na_2SO_4}]^{1.4}[C]^\frac{c_{Na_2SO_4}}{c_{Na_2SO_4}} e^{-\frac{6.62 \times 10^4}{RT_p}} )</td>
<td>(7.54)</td>
</tr>
<tr>
<td>( 2C(s) + K_2SO_4(s,l) \rightarrow K_2S(s,l) + 2CO_2(g) )</td>
<td>( R_{SO_4} = 3.79 \times 10^3 [x_{K_2SO_4}]^{1.4}[C]^\frac{c_{K_2SO_4}}{c_{K_2SO_4}} e^{-\frac{6.62 \times 10^4}{RT_p}} )</td>
<td>(7.55)</td>
</tr>
<tr>
<td>( NaCl(s,l) \rightarrow NaCl(g) )</td>
<td>( R_{NaCl} = K_{NaCl,s} A_p \left( C_{NaCl,s} \right) )</td>
<td>(7.56)</td>
</tr>
<tr>
<td>( KCl(s,l) \rightarrow KCl(g) )</td>
<td>( R_{KCl} = K_{KCl,s} A_p \left( C_{KCl,s} \right) )</td>
<td>(7.57)</td>
</tr>
<tr>
<td>( Na_2CO_3(s,l) + SO_2(g) + \frac{1}{2} O_2(g) \rightarrow Na_2SO_4(s,l) + CO_2(g) )</td>
<td>( R_{Na_2CO_3} = K_{Na_2CO_3,s} A_p \left( C_{Na_2CO_3,s} \right) )</td>
<td>(7.58)</td>
</tr>
<tr>
<td>( K_2CO_3(s,l) + SO_2(g) + \frac{1}{2} O_2(g) \rightarrow K_2SO_4(s,l) + CO_2(g) )</td>
<td>( R_{K_2CO_3} = K_{K_2CO_3,s} A_p \left( C_{K_2CO_3,s} \right) )</td>
<td>(7.59)</td>
</tr>
<tr>
<td>( Na_2S(s,l) + 2O_2(g) \rightarrow Na_2SO_4(s,l) )</td>
<td>( R_s = 1.13 \times 10^4 A_s[Na_2S]^\frac{c_{Na_2S}}{c_{Na_2S}} e^{-\frac{1.80 \times 10^4}{RT_p}} )</td>
<td>(7.60)</td>
</tr>
</tbody>
</table>

reducing environment (beginning of char burning stage)

<table>
<thead>
<tr>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s = 3 \times 10^5 A_s[Na_2S]^\frac{c_{Na_2S}}{c_{Na_2S}} e^{-\frac{1.80 \times 10^4}{RT_p}} )</td>
</tr>
</tbody>
</table>

oxidizing environment
Table 7.5 (Cont’d) Rate equations used for the reactions during char burning and smelt oxidation stages.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Equation (mole/s)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}<em>2\text{S}</em>{(s,l)} + 2\text{O}<em>2</em>{(g)} \rightarrow \text{K}_2\text{SO}<em>4</em>{(s,l)}$</td>
<td>$R_s = 1.13 \times 10^4 A_s [K_2S] p_{O_2} e^{-\frac{1.80 \times 10^8}{RT_p}}$ (reducing environment (beginning of char burning stage))</td>
<td>(7.62)</td>
</tr>
<tr>
<td></td>
<td>$R_s = 3 \times 10^4 A_s [K_2S] p_{O_2} e^{-\frac{1.80 \times 10^8}{RT_p}}$ (oxidizing environment)</td>
<td>(7.63)</td>
</tr>
</tbody>
</table>

7.3.4 Particle mass balance

As mentioned in Section 7.2, it is assumed that the particle initially has the same composition as the black liquor containing C, H, O, S, Na, K, and Cl. Therefore, the mass of the particle is assumed to be the summation of the mass of each element.

$$m_p = \sum_{j=1}^{k} m_j$$  \hspace{1cm} (7.64)

where $m_p$ is the mass of the particle, $m_j$ is the mass of element $j$, and $k$ is the total number of elements (equal 7) in the particle. The initial mass of each element is calculated by the product of the mass fraction of each element and total initial mass of the particle. The mass of each element is updated as the particle undergoes the combustion stages and its composition changes. The rate of change of mass of each element is calculated using the rate of reactions.

$$\frac{d(m_j)}{dt} = \sum_{i=1}^{n} \nu_j R_{ij}$$  \hspace{1cm} (7.65)
where $\nu_j$ is the net stoichiometric coefficient (product minus reactant) of element $j$ in reaction $R_{ij}$, and $R_{ij}$ is the rate of reaction $i$ where element $j$ is involved. $\nu_j$ is positive for products and negative for reactants.

Each of the elements is defined to be in specific chemical forms as listed in Table 7.6. The components get involved in reactions defined in Sections 7.3.1 to 7.3.3. The initial concentrations of these components are set as initial conditions and, then, are recalculated using the same equation as 7.65 to update their concentrations. The moisture in the particle is treated separately as described in Section 7.3.1.

**Table 7.6** Forms of the elements considered in the dry particle.

<table>
<thead>
<tr>
<th>Element</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon (C)</td>
<td>CO, CO$_2$, CH$_4$, Na$_2$CO$_3$, and K$_2$CO$_3$,</td>
</tr>
<tr>
<td>Hydrogen (H)</td>
<td>H$_2$ and CH$_4$</td>
</tr>
<tr>
<td>Oxygen (O)</td>
<td>CO, CO$_2$, Na$_2$SO$_4$, K$_2$SO$_4$, Na$_2$CO$_3$, and K$_2$CO$_3$,</td>
</tr>
<tr>
<td>Sulphur (S)</td>
<td>H$_2$S, Na$_2$S, K$_2$S, Na$_2$SO$_3$, K$_2$SO$_3$, Na$_2$S$_2$O$_3$, K$_2$S$_2$O$_3$, Na$_2$SO$_4$, and K$_2$SO$_4$</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>Na, Na$_2$S, Na$_2$SO$_3$, Na$_2$S$_2$O$_3$, Na$_2$SO$_4$, and NaCl</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>K, K$_2$S, K$_2$SO$_3$, K$_2$S$_2$O$_3$, K$_2$SO$_4$, and KCl</td>
</tr>
<tr>
<td>Chloride (Cl)</td>
<td>NaCl and KCl</td>
</tr>
</tbody>
</table>
7.4 **Governing Energy Equations**

A two-resistance heat transfer model which includes convective and radiation heat transfer resistances between the particle and gas, is used to calculate the particle temperature. The heat generated or consumed due to the reactions is also incorporated into the energy balance equation. The particle energy balance equation can be expressed as follows [30]:

\[
\frac{d(mC_p T_p)}{dt} = Q_{trans} + Q_{source}
\]

(7.66)

where \( m_p, C_{p,p}, \) and \( T_p \) are respectively the particle mass, heat capacity, and temperature, and the \( Q \) terms on the right hand side of Equation 7.66 are described below.

\( Q_{trans} \) is the heat transferred between the particle and gas. It is the sum of the convective and radiation heat transfer, \( Q_{g \leftrightarrow p} \), and the heat loss from the particle due to the mass transfer of the combustion gases, \( Q_{leave} \).

\[
Q_{trans} = (Q_{g \leftrightarrow p} - Q_{leave})
\]

(7.67)

\( Q_{g \leftrightarrow p} \) is determined by:

\[
Q_{g \leftrightarrow p} = \frac{A_p (T_{gas} - T_p)}{R_t}
\]

(7.68)

where \( R_t \) is the total heat transfer resistance and is the sum of the convective, \( R_{conv} \), and radiation \( R_{rad} \), heat transfer resistances.

\[
R_t = R_{conv} + R_{rad}
\]

(7.69)
where,

\[
R_{\text{conv}} = \left( \frac{Nu \, k_{\text{gas}}}{d_p} \right)^{-1}
\]  \hspace{1cm} (7.70)

\[
R_{\text{rad}} = \left( \frac{Q_{\text{rad}}}{T_{\text{gas}} - T_p} \right)^{-1}
\]  \hspace{1cm} (7.71)

The Nusselt number (Nu) in Equation 7.70 is calculated using an empirical equation for forced convection over a sphere.

\[
Nu = \frac{h_{\text{conv}} \, d_p}{k_p} = 2.0 + 0.39 Gr_{id}^{0.25} + 0.37 \, Re_p^{0.6}
\]  \hspace{1cm} (7.72)

where, Grashof (Gr_{id}) and Reynolds (Re_p) numbers are calculated using equations 7.17 and 7.8, respectively.

The radiation heat transfer, Q_{rad}, in Equations 7.71 is calculated according to the Stefan-Boltzman equation [30]:

\[
Q_{\text{rad}} = \alpha A_p \left( T_{\text{gas}}^4 - T_p^4 \right)
\]  \hspace{1cm} (7.73)

where \( \sigma \) is the Stefan-Boltzmann constant, \( A_p \) is the particle surface area, and \( T_{\text{gas}} \) and \( T_p \) represent the absolute gas and particle temperature, respectively.

\( Q_{\text{leave}} \) in Equation 7.67 is calculated using:
\[ Q_{\text{leave}} = \sum_{i=1}^{n} n_i C_{p,j} T_p \]  

(7.74)

where \( n_j \) and \( C_{p,j} \) are, respectively, the number of the moles and heat capacity of each of the gas species that leaves the particle, and \( T_p \) is the particle absolute temperature.

There are three types of heat involved during particle combustion: 1) heat consumed during the devolatilization, \( Q_{\text{devol}} \), 2) heat consumed as a result of the phase change in the inorganics, \( Q_{\text{phase}} \), and 3) heat produced or consumed as a result of the reactions occurring during the char burning and smelt oxidation stages, \( Q_{\text{gen}} \).

\[ Q_{\text{source}} = Q_{\text{devol}} + Q_{\text{gen}} + Q_{\text{phase}} \]  

(7.75)

800 kJ/kg is assumed to be consumed during the devolatilization stage [45]. This amount of heat consumed is proportional to the rate of carbon conversion during devolatilization. \( Q_{\text{phase}} \) is solved based on the enthalpy required for the phase change of the inorganics at their melting temperatures. Enthalpy data is obtained from HSC software [52].

Since most reactions occurring during char burning and smelt oxidation are exothermic, the heat source is identified as generated (\( \text{gen} \)) rather than consumed and is calculated as follows:

\[ Q_{\text{gen}} = \sum R_i h_i \]  

(7.76)
where, \( i \) represents the species, \( R_i \) is the rate of each reaction and is calculated using the equations shown in Tables 7.1, 7.2, and 7.5, and \( h_i \) is the enthalpy of the correspondent reactions and is obtained from the HSC software.

When the particle temperature reaches 450 °C, a flame is assumed to surround the particle [13]. Under this condition, the bulk gas temperature is replaced by the flame temperature. The following empirical equation is used to calculate the non-adiabatic flame temperature (in °C) at different oxygen concentrations [33].

\[
T_{\text{flame}} = T_{\text{gas}} + \frac{0.232 k_f f_g \Delta H_c Y_{O_2}}{0.21 C_p}
\]  

(7.77)

where \( k_f \) is flame efficiency factor with a value of 0.12 for black liquor burning in an oxidizing environment; \( f_g \) is stoichiometric ratio of CO to \( O_2 \) with a value of 1.75; \( \Delta H_c \) is heat of combustion of pyrolyzed gases with a value of 10 kJ/g; \( Y_{O2} \) is the mole fraction of \( O_2 \) in gas; and \( C_p \) is heat capacity of the gas with a value of 1.17 J/g/°C. Substitution of these values into Equation 7.77 gave the following simplified equation:

\[
T_{\text{flame}} = T_{\text{gas}} + 1983 Y_{O_2}
\]  

(7.78)

### 7.5 Discretization of Mass and Energy Balance Equations

The mass balance equation, Equation 7.65, is discretized as:

\[
m_{p,i} = m_{p,i-\Delta t} + \sum_{j=1}^{k} \sum_{\nu=1}^{n} V_{f_i R_{ij}} \Delta t
\]  

(7.79)
where the rates of reactions are calculated at new temperature \((T_{p,t})\) and old compositions (compositions at \(t-\Delta t\)).

The energy balance equation is discretized and is solved using the Golden Section Search method.

\[
\frac{\left(mC_p T\right)_{p,t} - \left(mC_p T\right)_{p,t-\Delta t}}{\Delta t} = Q_{\text{trans},t} + Q_{\text{source},t}
\]

The subscripts \(t\) and \(t-\Delta t\) represent the new and old time, respectively. \(Q_{\text{trans}}\) and \(Q_{\text{source}}\) are calculated using the equations defined in Section 7.4.

### 7.6 Model Assumptions and Boundary and Initial Conditions

#### 7.6.1 Model assumptions

Particle shape, growth, velocity, temperature distribution, thermal combustion stage, and composition assumptions during combustion are listed below.

1. the particle is spherical;

2. the particle swells to three times its initial diameter at the end of the devolatilization stage [7], and shrinks to two third of its initial diameter at the end of the char burning stage [7];

3. the particle travels at its terminal velocity. This assumption is justified in Appendix B;

4. the particle temperature is uniform (Bi<0.1). This assumption in justified in Appendix C;
5. when the particle temperature reaches 450 °C, a flame surrounds the particle until 90% of pyrolyzable carbon has been converted into gas or char during devolatilization [17]. As long as the particle is surrounded by the flame, the bulk gas temperature in the energy balance equations is assumed to be the same as the flame temperature;

6. carbon in the black liquor is in the form of either organic (pyrolyzable) or alkali (Na and K) carbonate (non-pyrolyzable) [38].

7. sulphur in the black liquor is in the form of: sulphin (10%), thiosulphate (36%), sulphite (15%), sulphate (5%), and pyrolyzable organic sulphur (34%) [7];

8. pyrolyzable sulphur, which ends up in the char, is in the form of sulphin [14]; and

9. the inorganic compounds; including carbonate, sulphate, sulphinide, and Cl are split between Na and K based on the molar ratio of Na and K in the particle.

**7.6.2 EFR boundary and initial conditions**

The following conditions apply to the EFR environment as the initial and boundary conditions:

1. the EFR is operated at gas velocity of 1.8 m/s,

2. the EFR is operated at a fixed temperature of 800 °C, unless otherwise mentioned;

3. the gas temperature is the same as the EFR temperature;

4. the model black liquor (feed has the same composition as the black liquor sample 1, shown in Table 3.3, and a size of 400µm;

5. the feed is totally dry, and so the drying stage is omitted in the model;
6. the initial particle temperature is 150 °C. This is the particle temperature at the exit of the feeding tube at the top of the EFR (Figure 3-1);

7. the particle enters the EFR at its terminal velocity;

8. the height of the EFR is 6.3 m;

9. the particle cools down to a temperature of about 550°C after leaving the EFR.

7.6.3 Boiler boundary and initial conditions

The following conditions apply to the boiler environment as the initial and boundary conditions for a particle traveling upward from the black liquor spray nozzles toward the generating bank entrance:

1) the as-fired black liquor solids content is 72%;
2) the initial particle temperature is 150 °C, which is the black liquor temperature at the spray nozzles;
3) the gas temperature at the black liquor spray nozzles elevation is 1300°C, which is based on the CFD results of Wessel et al. [32];
4) the gas temperature at the entrance of the superheater tubes is set 900°C based on field study results;
5) the gas temperature changes linearly from the black liquor spray nozzles to the generating banks entrance;
6) the gas velocity is assumed to be 8m/s, which is the average calculated gas velocity in the boilers where the field study was conducted;
7) the distance between the black liquor spray nozzles and the sampling location at the entrance of the superheater region is 28m;

8) the initial particle size is 650µm;

9) the particle stays at 600°C after reaching the superheater entrance. This was the temperature of the probe at the time of the sampling; and,

10) the average oxygen concentration is assumed to be 2.5%.

The thermal boundary conditions for the boiler simulation are based on the CFD predictions presented by Wessel et al. [32]. The CFD model simulated the temperature, velocities, etc. in a boiler with a cross section area of 10m by 10m. Temperature values were extracted from the temperature profiles at different locations in the boiler and are presented in Figure 7.6.

Figure 7.6 shows that the gas temperature from the black liquor spray nozzles to the generating bank entrance approximately changes linearly, and the following equation is used to calculate the gas temperature at different elevations for the present boiler study.

\[
T_g = \left( T_L - T_{\text{gun}} \right) \frac{x}{L} + T_{\text{gun}}
\]  

(7.81)

where \( T_g \), \( T_{\text{gun}} \), and \( T_L \) are gas temperatures at elevation of x, at black liquor spray gun location, and at elevation of L generating bank entrance, respectively. Black liquor spray nozzles elevation is used as the reference (zero) elevation to calculate the elevations x and L.
Figure 7.6 Change in the gas temperature inside a boiler from a CFD modeling [32].

7.7 Solution Procedure

All algebraic equations and the kinetic, mass and energy balance equations are written in different subroutines and solved in the TK solver software. The transient kinetic and mass balance equations were solved using the 4th order Runge-Kutta method [44] (see Appendix D), while the energy balance equation was discretized and solved using Golden Section Search method [45] (see Appendix E). The mass and energy equations were solved to obtain the particle composition and temperature simultaneously at each time step. The model has been coded in a tool kit environment called TK Solver [46]. All particle and gas physical properties are calculated using the equations listed in Appendix F. Constants are listed in Table 7.7. The equations are listed in Appendix G, where the subroutines of the model are provided.
Table 7.7 The value of the constants used in the model.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stephan Boltzman</td>
<td>å</td>
<td>W/m2/K4</td>
<td>5.67E-8</td>
</tr>
<tr>
<td>Gas constant</td>
<td>R</td>
<td>J/mol/K</td>
<td>8.3142</td>
</tr>
<tr>
<td>Kobayashi coefficients</td>
<td>-</td>
<td>-</td>
<td>Listed in Sections 7.2.2.1 and 7.2.2.2</td>
</tr>
<tr>
<td>Reaction rate coefficients</td>
<td>-</td>
<td>-</td>
<td>Listed in Table 7.5</td>
</tr>
</tbody>
</table>

The software solves the equations as is described as follows:

1) set time to zero, \( t=0 \);

2) set initial position to zero, \( l=0 \);

3) set particle initial mass, \( m_{p,t=0} \);

4) define initial and boundary conditions, see sections 7.6.2 and 7.6.3 for EFR and Boiler conditions, respectively;

5) define constants including the coefficients of the kinetic equations, see Tables 7.1, 7.2, and 7.5;

6) define elemental composition of black liquor;

7) calculate assumed reaction compounds and elements, see Section 7.3;

8) define time step (\( \Delta t \));

9) calculate terminal velocity of particle \( V_t \) and set particle velocity to terminal velocity, \( V_p = V_t \);

10) calculate the rate of heat transfer from the gas to the particle, \( Q_{\text{trans},t=0} \), see Equation 7.67;
11) set the rates of reactions, see Tables 7.1, 7.2 and 7.5, to zero (no change in particle mass);

12) calculate temperature at \( t = \Delta t \) based on explicit expression of the energy equation,

\[
T_{p,t=\Delta t} = T_{p,t=0} + \frac{\Delta t(Q_{g\rightarrow p,t=0})}{mC_{p,t=0}} \quad T_{p,t=\Delta t} = T_{p,t=0} + \frac{\Delta t(Q_{g\rightarrow p,t=0})}{mC_{p,t=0}} \text{ simplified from equation 7.80;}
\]

13) calculate position at \( t = \Delta t \), \( l = V_p \Delta t \);

14) store current time \( t = \Delta t \), position \( l = V_p \Delta t \), and particle temperature \( T_{p,t=\Delta t} \);

15) define new time, \( t = t + \Delta t \); \( \Delta t \);

16) as part of the Golden Section Search method, lower temperature \( (T_l) \) and upper temperature \( (T_h) \) limits are required to estimate the new temperature \( T_{p,t} \). Depending on the gas temperature two conditions exist: a) when gas temperature is greater than the particle temperature; \( T_l = T_{p,i} \) and \( T_h = T_{g,t} - \frac{Q_{g\rightarrow p,t=\Delta t}}{(h_{conv,t=\Delta t} + h_{rad,t=\Delta t}) A_{t=\Delta t}} \text{ where}
\[
h_{rad} = \frac{Q_{rad}}{(T_g - T_p)} \text{ and b) when gas temperature is greater than particle}
\]

\[
T_l = T_{p,i} \text{ and } T_h = T_{p,t=\Delta t} + \frac{Q_{g\rightarrow p,t=\Delta t}}{(6k_{t=\Delta t} A_{t=\Delta t} d_{p,t=\Delta t})};
\]

17) further, as part of the Golden Section two new temperatures between the interval \([T_l, T_h]\)

are determined: \( T_{p,new1} = 0.382(T_h - T_l) + T_l \) and \( T_{p,new2} = (1 - 0.382)(T_h - T_l) + T_l \). Repeat

steps 18 to 22 for both \( T_{p,new1} \) and \( T_{p,new2} \);

18) calculate the rates of reactions, see Tables 7.1, 7.2 and 7.5, using Runge-Kutta Method;

the rates are calculated at new temperature and old composition;

19) calculate the new mass of the particle, \( m_{p,t} \), using Equation 7.79;

20) calculate the rate of heat transfer from the gas to the particle, \( Q_{trans,t} \), see Equation 7.67;
21) calculate the RHS and LHS of the energy equation, Equation 7.80,

22) calculate the squared difference between the RHS and LHS of the energy equation (\(\Delta^2\));

23) if \(|T_{p,new1} - T_{p,new2}|\) is greater than \(1 \times 10^{-12}\) °C then reset the temperature limits as: a) if \(\Delta_{\text{new1}}^2 < \Delta_{\text{new2}}^2\), then \(T_l = T_{p,i}\) and \(T_h = T_{\text{new2}}\) and b) if \(\Delta_{\text{new1}}^2 > \Delta_{\text{new2}}^2\), then \(T_l = T_{\text{new1}}\) and \(T_h = T_{\text{h,old}}\). Repeat steps 17 to 23.

24) calculate new position, \(l = l + V_p \Delta t\);

25) store current time (\(t\)), position (\(t = \tau_p \Delta \tau\)), and particle temperature (\(T_{p,t}\));

26) if \(t\) is less than the maximum distance (depending on the case studied either the EFR height or the distance between the black liquor spray nozzles and the generating bank entrance) loop through steps 15 to 26; otherwise,

27) terminate program.

### 7.8 Time Step Sensitivity Analysis

The composition changes when the particle temperature changes. The most significant change in the composition occurs when the particle reaches its peak temperature. Therefore, the effect of time step on the particle peak temperature is calculated to find the optimum time step for the calculation.

Table 7.8 shows the effect of the time step on the particle peak temperature. It is shown that when time step goes below 0.01, the particle temperature does not show any significant change, and, therefore, this can be used as an optimum value for the time step.
Table 7.8 *The effect of time step selection on the particle peak temperature.*

<table>
<thead>
<tr>
<th>Time step, $\Delta t$ (s)</th>
<th>0.05</th>
<th>0.04</th>
<th>0.03</th>
<th>0.02</th>
<th>0.01</th>
<th>0.009</th>
<th>0.008</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle Temperature (°C)</td>
<td>869.4</td>
<td>1087.1</td>
<td>1124.8</td>
<td>1221.1</td>
<td>1224.3</td>
<td>1224.9</td>
<td>1225.1</td>
</tr>
</tbody>
</table>
CHAPTER 8: MODEL RESULTS AND DISCUSSION

The black liquor combustion model was run under different EFR and boiler conditions and for different black liquor compositions. Section 8.1 focuses on EFR predictions. In the second section, the model is applied to simulated black liquor combustion in a typical recovery boiler. The concentrations of species such as Na are expressed in mole % (or mole% Na/(Na+K)) as explained in detail in Section 3.4.

8.1 Prediction in EFR Environment

Black liquor samples were dried prior to being fed to the EFR and consequently the simulations begin at the devolatilization stage. The standard EFR conditions simulated are listed in Section 7.6.2 and the standard black liquor composition was that of sample 1, see Table 3.3. The particle temperature and composition variation through the EFR are discussed in Sections 8.1.1 and 8.1.2 under the standard conditions. Sections 8.1.3 to 8.1.5 present and discuss the effects of varying the EFR temperature and O₂ content, and particle composition and size. A sensitivity analysis on initial conditions is presented in Section 8.1.7. Model results for three other black liquor samples are listed in Appendix H for further comparison.

8.1.1 Particle temperature along the EFR

Figure 8.1 shows the particle temperature as a function of position. The particle temperature increases during devolatilization, and exceeds the bulk gas temperature of 800°C due to the high local temperature environment around the particle after the formation of a flame. As the char burning starts, the flame disappears; however, the energy released due to the combustion of the
char causes a further increase in the particle temperature. The particle reaches its highest temperature at the smelt oxidation stage where a significant amount of heat is released due to the oxidation of sulphide. When the particle is completely oxidized, it cools down to the gas temperature. The particle temperature rapidly decreases after leaving the EFR, where the non-heated zone of the EFR is located and air at room temperature is mixed with the exiting gases.

![Graph showing particle temperature vs. EFR length](image)

**Figure 8.1.** Predicted particle temperature as it burns in the EFR set at 800°C and 12.5% $O_2$.

The combustion of the standard black liquor sample under different EFR inlet conditions was previously simulated using COMO, a black liquor combustion model developed by Babcock & Wilcox, [32]. In this earlier study, dried black liquor particles were assumed to enter the EFR at room temperature, not 150 °C. The predictions of the particle temperature of the two models are compared in Figure 8.2. As the particle enters the EFR and is heated to a temperature at which...
devolatilization begins, a difference in the predicted particle temperature using this model and COMO is observed.

![Graph showing temperature profile](image)

**Figure 8.2** A comparison of the predicted particle temperature profile using this model and COMO for a black liquor particle in a size of 400 µm burned at 800°C and 12.5%O₂.

Since devolatilization is an endothermic process, a slower increase in the predicted particle temperature by COMO could be due to a higher heat requirement for the devolatilization stage in COMO than that in the present model. In both models, Kobayashi-type equations are used to calculate the rates of the reactions occurring during the devolatilization stage. However, COMO calculates the heat required for each reaction separately based on the products, while this model considers a fixed heat of 800 kJ/kg to be consumed by all reactions occurring during the devolatilization stage. The required heat of devolatilization was varied in the current model between 500 to 2000 kJ/kg and little effect on the particle temperature profile was observed.
Heat of devolatilization does not account for the difference between the present temperature predictions and those of COMO during the first half of the devolatilization stage.

After the flame forms at approximately 450 °C, the particle temperature predicted by COMO rises more rapidly, and, then, reaches the same temperature predicted by the present model at the beginning of the char burning stage. This rapid increase in the particle temperature could be as a result of a higher rate of devolatilization prediction in COMO. This is evident if the time when the particle reaches the peak temperature are compared, in which the particle reaches the peak temperature earlier in COMO than the time predicted in this current model. The slow increase in the particle temperature at low temperatures and the rapid increase of the particle temperature at high temperatures indicate that the coefficients used in the Kobayashi-type equations may not be valid at low temperatures. As a result, a very low rate of devolatilization is predicted at low temperatures and a very high rate of devolatilization is predicted at higher temperatures. Overprediction at high temperature results in higher release of light gases which burn at the surface of the particle resulting in a much hotter environment around the particle. This acts as a cocatalytic reactions until organic materials are decomposed and only char remains in the particle, when the devolatilization stage ends.

At the beginning of the char burning stage, COMO predicts a slower increase in the particle temperature than the present model likely due to a lower assumed energy release during char burning. As char burning ends and smelt oxidation starts, COMO predicts a much more rapid increase in temperature than the present model, indicating a higher heat release due to the oxidation of sulphide. Both models predict maximum particle temperatures slightly above
1200°C. The decrease in particle temperature proceeds at similar rates after the maximum temperature is reached.

8.1.2 Particle composition along the EFR

K and Cl contents are first presented based on an initial set of K rate equations. Due to poor agreement with measured values, the K rate equations were modified to the form presented in Section 7. The revised kinetic rate results are present later in this section. Figure 8.3 shows the initial predicted K and Cl contents as a function of position for the standard black liquor sample burned in the EFR at 800°C and 12.5% O\textsubscript{2}. The model predicts no change in the particle K content. The concentration of K is expressed in mole% which is the ratio of moles of K to the summation of the moles of Na and K. The mechanisms of the loss of Na and K are reviewed in order to find out the reasons for this unexpected K prediction by the model. Two mechanisms are assumed for the depletion of K: loss due to the vaporization of KCl and elemental loss due to the reduction of K\textsubscript{2}CO\textsubscript{3} with char. The same mechanisms are assumed for the depletion of Na: loss due to the vaporization of NaCl and elemental loss due to the reduction of Na\textsubscript{2}CO\textsubscript{3} with char.

The rates of vaporization of KCl and NaCl are calculated using Equations 7.57 and 7.56, respectively. KCl has higher pure vapor pressure than NaCl, which gives relatively higher concentration of KCl at the surface of the particle than that of NaCl. But, a lower diffusivity because of KCl’s larger molecule size, gives a smaller diffusivity, which, in turn, leads to a smaller mass transfer coefficient for KCl. As a result, the product of concentration and mass transfer coefficient does not give a much higher vaporization rate of KCl compared to that of NaCl. Therefore, the rates of vaporization of NaCl and KCl become the same.
On other hand, due to insufficient data, it is assumed that the rates of reduction for both Na$_2$CO$_3$ and K$_2$CO$_3$ are the same, corrected by the molar ratio of K and Na in the particle. This means that the rate of reduction by char of Na$_2$CO$_3$ and K$_2$CO$_3$ is the same. As a result, proportional amounts of elemental Na and K are depleted due to the reduction of Na$_2$CO$_3$ and K$_2$CO$_3$ by char during the combustion of a black liquor particle.

Since both Na and K change at the same ratio, by dividing the moles of K by the sum of moles of Na and K to get mole%, the mole% of K becomes the same as its initial mole% in the black liquor, indicating no change in K content. Thus, in order to improve the prediction of K content, it requires the use a higher rate for K$_2$CO$_3$ reduction than that for Na$_2$CO$_3$ reduction.

In this study, equilibrium calculations were performed using HSC Chemistry software [53] to examine whether a higher amount of K than Na would be observed for the system containing char, Na$_2$CO$_3$, and K$_2$CO$_3$. The results are presented in Section 8.1.3.

Figure 8.4 shows predicted K and Cl content as a function of position for liquor sample S1 and EFR operating conditions after performing modification on the calculation of K content and linking its depletion to the depletion of Cl. No change in the K and Cl contents are predicted during the devolatilization stage, since the particle temperature is not high enough to result in the vaporization of K and Cl components; i.e. NaCl and KCl. K and Cl contents decrease during char burning and the early stage of smelt oxidation when the particle temperature is high. As smelt oxidation proceeds, the particle temperature decreases resulting in less vaporization of K and Cl components, and K and Cl contents remain steady as the particle exit the EFR.
Figure 8.5 shows the variations in the sulphide, sulphate, sulphite, and thiosulphate contents of the particle along the EFR. During the early period of the devolatilization stage, sulphite and thiosulphate are converted into sulphide and sulphate according to Reactions 7.1, and 7.2. Sulphide is also formed due to the decomposition of organo-sulphur material. When the sulphite and thiosulphate decomposition is over, the sulphate content does not change and stays constant, while the sulphide content still shows an increase due to the decomposition of organo-sulphur materials, and, then, remains constant.

![Figure 8.3 Changes in K and Cl contents during combustion of a black liquor particle in a size of 400 µm burned at 800°C and 12.5%O₂ (before modification of K content calculation).](image-url)
At the beginning of the char burning stage, the sulphide content increases due to the reduction of sulphate with char. However, the sulphate is reduced to sulphide, the net sulphate content increases as a result of two mechanisms. The first mechanism is the reduction of carbonate by char which would result in a decrease in the carbonate content. A decrease in the carbonate content increases the mole percent of the sulphate content. The second mechanism is the sulphation of carbonate by $SO_2$, which results in the formation of sulphate. These two mechanisms result in a net increase in the sulphate content. As the char burning finishes and smelt oxidation starts, the sulphide is oxidized and the sulphate content increases further.

Figure 8.4 Changes in K and Cl contents during combustion of a black liquor particle in a size of 400 µm burned at 800°C and 12.5%$O_2$ (after modification of K content calculation).
Figure 8.6 shows that the carbonate content slightly decreases and, then, increases during devolatilization stage. At the very early stage of devolatilization, the rate of formation of sulphide and sulphate (with a delay) is much higher than the rate of formation of carbonate, resulting in a decrease in the carbonate mole%. But, soon, the rate of the formation of carbonate becomes much higher than the rate of the formation of sulphide and sulphate, which results in an increase in the carbonate content. During the char burning and smelt oxidation stages, the carbonate content in the particle decreases as a result of the reduction and sulphation reactions. Figure 8.5 also shows that the particle’s total sulphur content initially decreases as a result of the release of sulphur to the gas during devolatilization stage, and then, increases as a result of the sulphation of carbonate during char burning and smelt oxidation stages.
Figure 8.6 Changes in carbonate and total sulphur contents during the combustion of a black liquor particle in a size of 400 µm burned at 800°C and 12.5%O₂.

The results presented above are for the particles burned at an EFR temperature of 800°C and an oxygen concentration of 12.5%. They are expected to be different at various EFR oxygen concentrations and temperatures.

8.1.3 Reduction of Carbonate By Char

In order to examine whether the carbonate reduction by char will result in higher release of K than Na, equilibrium concentrations of a mixture of char, Na₂CO₃, and K₂CO₃ were calculated using the HSC Chemistry software. In this study, all compounds involved were assumed to exist in one single condense phase, i.e. do not form solid-solid solutions with one another particularly at low temperatures. Reactions 7-6 and 7-10 are expected to occur between the char and carbonates.
2 C\(_{(s)}\) + Na\(_2\)CO\(_3\) → 2 Na\(_{(g)}\) + 3 CO\(_{(g)}\) \hspace{1cm} \text{Reaction (7-6)}

2 C\(_{(s)}\) + K\(_2\)CO\(_3\)\(_{(s,l)}\) → 2K\(_{(g)}\) + 3 CO\(_{(g)}\) \hspace{1cm} \text{Reaction (7-10)}

Since 4 moles of carbon (char) is required for a complete reduction of one mole of Na\(_2\)CO\(_3\) and one mole of K\(_2\)CO\(_3\), the equilibrium concentrations of a mixture containing 4 moles of char, 1 mole of Na\(_2\)CO\(_3\), and 1 mole of K\(_2\)CO\(_3\) at temperatures between 25 and 1500 °C was calculated using HSC Chemistry program. As shown in Figure 8.7, the equilibrium concentrations of the species did not change at temperatures below 650 °C indicating no reaction between char and carbonates. At temperatures above 650°C, char reacts with the carbonates lowering the concentrations of both K\(_2\)CO\(_3\) and Na\(_2\)CO\(_3\). The lower concentration of K\(_2\)CO\(_3\) than that of Na\(_2\)CO\(_3\) suggests that more K\(_2\)CO\(_3\) reacts with char than Na\(_2\)CO\(_3\), resulting in the formation of more elemental K than elemental Na in the system.

With the addition of the sulphides (1 mole of Na\(_2\)S and 1 mole of K\(_2\)S) to the system described earlier (containing 4 moles of carbon and 1 mole of each carbonate), Reaction 8.1 occurs in the system. The formation of K\(_2\)CO\(_3\) as a result of Reaction 8.1 increases its concentration in the system leading to a greater release of K than that of Na (Figure 8.8).

\[ \text{K}_2\text{S} + \text{Na}_2\text{CO}_3 \rightarrow \text{K}_2\text{CO}_3 + \text{Na}_2\text{S} \hspace{1cm} \text{Reaction (8-1)} \]

Therefore, in the study of the carbonate reduction with char, Reaction 8.1 should also be considered. This reaction results in higher concentration of K\(_2\)CO\(_3\) than when carbonate is split between Na and K according to their molar ratio. Consideration of Reaction 8.1 will result in a greater K release than that of Na, as shown in Figure 8.9.
Figure 8.7 Release of elemental Na and K as a results of reduction of carbonates with char (Equilibrium calculation using HSC Chemistry).

Figure 8.8 Concentrations of elemental Na and K, char, carbonates, and sulphides in the presence of sulphide (Equilibrium calculation using HSC Chemistry Program).
8.1.4 Predicted Effect of $O_2$ Concentration

This section presents the model prediction on the effect of the $O_2$ concentration on the carryover composition for a dried black liquor particle of size 400$\mu$m burned at 800°C in the EFR environment. The $O_2$ concentration was varied between 1 and 12.5% and the predicted results are compared with the EFR results presented in Chapter 6.

8.1.4.1 Effect of $O_2$ Concentration on Particle Temperature

Figure 8.10 shows that as the $O_2$ concentration decreases from 12% to 6%, the particle peak temperature decreases. The particle peak temperature appears constant between $O_2$ concentrations of 6% and 2%. As the $O_2$ concentration decreases, it takes longer for the particle
to reach the peak temperature, and at 2% O₂, the particle reaches the peak temperature just at the exit of the EFR. This is consistent with the experimental observation that the particles burned at low O₂ concentrations were still burning and splashed on the collecting tray, while the particles burned at high O₂ concentrations were completely burned and solidified when they hit the collecting tray at the exit of the EFR.

Figure 8.10 Particle temperature along the EFR for a black liquor in a size of 400 µm burned at 800°C and at different O₂ concentrations.

8.1.4.2 Effect of O₂ Concentration on K and Cl Contents

Figure 8.11 shows the effect of O₂ concentration on K and Cl contents for a particle at the exit of the EFR. The model assumed the rate of K depletion is one-third to the rate of Cl depletion, and, as a result, they both show similar trends during the combustion of the black liquor. The model predicts that the Cl content in the particle decreases as the EFR oxygen concentration increases.
As shown in Figure 8.10, an increase in the $O_2$ concentration leads to an increase in the particle temperature. The vapour pressure of NaCl and KCl increases with temperature resulting in a higher rate of vaporization for these two components, and a greater depletion for Cl.

![Graph showing Mole% of Potassium and Chloride against $O_2$ %]

Figure 8.11 *Predicted (solid line) and experimental (symbols) K and Cl contents of a particle burned at different $O_2$ concentrations, collected at the exit of the EFR.*

There is good agreement between the predicted and experimental results for the Cl content, which suggests that the assumption that vaporization of NaCl and KCl is the main mechanism for Cl depletion is valid. A good prediction for the Cl content leads to a reasonably good prediction for the K content, particularly at low $O_2$ concentrations. However, K content in the carryover particle is slightly overpredicted at high $O_2$ concentrations. As mentioned earlier, the depletion of K is assumed to be a third of that of Cl. This is an average value obtained from the EFR experiments performed on 16 black liquor samples burned at different operating conditions.
This ratio varies slightly by black liquor composition and burning conditions. The overprediction of K may indicate that the ratio might be slightly higher than a third at high O₂ concentration.

8.1.4.3 Effect of O₂ Concentration on Carbonate, Sulphate, and Sulphide Contents

The predicted EFR exit results show the same trend as the experimental results for the variation of carbonate, sulphate and sulphide components with O₂ concentration, (Figure 8.12). The carbonate and the sulphide contents decrease with O₂ concentration, while the sulphate content increases. Excellent agreement is observed at O₂ concentrations below 11%. As discussed above, as the O₂ concentration increases, the particle temperature increases and the combustion process advances more rapidly. Above 11% O₂ concentration, the sulphide content is completely oxidized and no further increase in carbonate and sulphate contents are predicted.

Figure 8.12 Predicted (solid line) and experimental (datapoint) carbonate, sulphate, and sulphide contents of a particle burned at different O₂ concentrations.
A comparison between the rate of decrease in the sulphide content and the rate of increase in the sulphate content shows that they are unbalanced. The greater increase in the sulphate content in the particles burned at high \( \text{O}_2 \) concentrations is due to higher retention of sulphur in the particles and the sulphation of carbonate. This argument is supported by Figure 8.13 where the decrease in carbonate content is essentially the same as the increase in total sulphur content.

![Figure 8.13 Predicted carbonate and total sulphur contents of a particle burned at different \( \text{O}_2 \) concentrations.](image)

8.1.5 Predicted effect of EFR temperature

Figure 8.14 shows the variation of Cl and K content with EFR temperature at an elevated \( \text{O}_2 \) concentration of 13%. Based on the above discussion, an overprediction of the sulphate content and an underprediction of the K, Cl, and carbonate contents for the particles formed at high \( \text{O}_2 \) concentration is expected. At EFR temperatures below 700°C no change in K and Cl
contents in the carryover particles is predicted. The black liquor is just charred and does not burn at this temperature, and, as a result, no depletion of K and Cl is predicted.

As the EFR temperature exceeds 700°C, the model predicts an abrupt depletion of K and Cl contents then a weak further depletion of K and Cl with higher EFR operating temperatures. Not enough experiments were performed at low temperatures; therefore, the abrupt predicted change in depletion of K and Cl at 700 °C cannot be confirmed by the experimental results. The slow further increase in depletion with operating temperature above 750 °C is in agreement with the trend in the experimental results. Once the particle begins to burn the particle temperature dominates, and the EFR temperature has a minimal effect.

![Figure 8.14 Predicted (solid line) and experimental (datapoint) values of K and Cl of a particle in a size of 400µm burned at different EFR temperatures at 12.5% O₂.](image-url)
Figure 8.15 shows the predicted and experimental results for the sulphate contents in the carryover particles. The model predicts a low level of sulphate in the carryover particles formed at temperatures below 700 °C. As mentioned in the above paragraph, a high level of char is predicted in the particle burned at temperatures below 700°C. High level of char prevents the oxidation of sulphur to sulphate, and, as a result, the level of sulphate is predicted to be very low. As the EFR temperature exceeds 700°C, a rapid increase in the sulphate content is predicted and the predicted results approach the experimental results. At temperatures above 750°C, the model predicts a slight increase in the sulphate content, which is the same trend as the experimental results. This small increase in the sulphate content could be as a result of the sulphation of carbonate that is accelerated at higher temperatures or higher retention of sulphur in the particle at elevated temperatures.

Figure 8.16 shows that the carbonate content does not change significantly at temperatures below 700°C at which the carbonate is already formed and not consumed. After a sharp change at a temperature of about 725°C, the carbonate content decrease slightly with the EFR temperature. The sharp change in the carbonate content is as a result of the significant reduction of carbonate by char during the char burning stage and the slight change is as a result of the sulphation of carbonate after char burning stage at elevated temperatures. The sulphide content shows a similar trend to that of the carbonate content; however, the sulphide content increases slightly before the sharp decrease at 725°C. The small increase in the sulphide content is as a result of the sulphate reduction during char burning. As was expected, the sulphide is oxidized and becomes zero at temperatures above 750°C.
Figure 8.15 Predicted (solid line) and experimental (datapoint) value of the sulphate of a particle in a size of 400µm burned at different EFR temperature at 12.5% O₂.

Figure 8.16 Predicted values of the carbonate and sulphide of a particle in a size of 400µm burned at different EFR temperature at 12.5% O₂.
8.1.6 Predicted effect of black liquor particle size

As shown in Figure 8.17, the K and Cl contents are predicted to decrease initially and then increase slowly as the black liquor particle size increases. The model predicts the K and Cl contents close to the experimental results; however, the model overpredicts the K content for the small particles. Figure 8.15 shows that the maximum particle temperature decreases as particle size decreases and the particle stays at elevated temperature for a shorter time. This led to less depletion of K and Cl at the smaller particle sizes.

The position that the maximum temperature is reached occurs further down in the EFR as the particle size increases. At the largest particle size, the maximum is predicted beyond the exit of the EFR, where they are still burning. Shorter residence times and increasingly incomplete combustion become dominant for larger particles, resulting in less depletion of K and Cl with particle size for particles above 450µm. The results presented in Figure 8.18 are consistent with the observation that the larger particles were still burning, while the smaller particles were completely burned and solidified, an indication of lower temperature, when they hit the collecting tray at the exit of the EFR.
Figure 8.17 Predicted (solid line) and experimental (datapoint) values of K and Cl in carryover particle formed from black liquor particles at different sizes burned at 800°C and 12.5%O₂.

Figure 8.18 Predicted temperature for the particles with a size of 250, 450, and 650µm burned in the EFR operated at 800°C and 12.5%O₂.
Figure 8.19 shows the predicted results for the carbonate, sulphate, and sulphide contents in carryover particle as the black liquor particle size changes. The carbonate content initially decreases and then increases with the black liquor particle size. As mentioned in the previous paragraph, particles have different temperature profile depending on their sizes. The temperature of large particles increases very slowly; however, it reaches much higher than the temperature of small particles. Very large particles reach much higher temperature, but leave the EFR just when they reach the peak temperature. As a result, very small and very large particles experience the elevated temperatures for a short period of time, which results in less reduction and less sulphation of carbonate, resulting in higher amount of carbonate in the particles. In contrast, the mid size particles in a range of 350 to 550 µm experience relatively high temperatures for a longer periods of time, which results in more reduction and more sulphation of carbonate, resulting in lower amount of carbonate in the particles.

![Figure 8.19](image-url)

**Figure 8.19** Predicted (solid line) and experimental (datapoint) values of the carbonate, sulphate, and sulphide in carryover particle formed from black liquor particles at different sizes burned at 800°C and 12.5%O₂.
The model predicts an increase and then a decrease in sulphate content, as the black liquor particle size increases. An inverse effect is predicted for the sulphide content. For 200µm particles, the model predicts high sulphide content and low sulphate content in the particle. However, as the experimental results show, it is expected that the sulphide in the small particles become completely oxidized. The model prediction indicates that the kinetic equation used in this model underpredicts the rate of the oxidation of sulphide for the small particles. This is not a surprise, since the kinetic equations used in this model are temperature dependent and the results presented in Figure 8.18 shows that small particles do not reach a temperature as high as larger particles. This results in an overprediction of the sulphide content and the underprediction of the sulphate content for the small particles.

### 8.1.7 Sensitivity analysis on initial conditions

The sensitivity of the particle composition to the particle initial temperature was tested. No significant effect of initial temperature on particle composition was observed for a temperature range between 20 to 250°C. This temperature range brackets the possible temperature range of particles exiting the feeder tube and entering the EFR.

### 8.2 Recovery Boiler Environment

The results of the boiler model are compared with the results of the field study for boiler A presented in Chapter 4. The results of the other two boilers are presented in Appendix I. During the field study, the sampling probe was left inside the boiler for different periods of time, and the results showed, in average, no significant change in carryover composition with sampling time. Therefore, the results of the sampling at 1min are compared with the model results.
Figure 8.20 shows the model and field study results of the K and Cl contents in the carryover particles. The model results show that the K and Cl contents decrease rapidly in the boiler and then remain constant. The rapid changes occur when the particle burns and reaches a very high temperature. After that, the particle cools down to the gas temperature, and the rate of change decreases and becomes small. The predicted results indicates that it takes about four seconds for the particle to reach the sampling point, where no further significant change was predicted after the deposition of the particle on the probe.

A comparison of the model and experimental results shows that the model underpredicted the K content, while it closely predicted the Cl content. As mentioned in Chapter 7, it is assumed that the depletion of Cl is three times greater than the depletion of the K. However, in this particular boiler, it was found the rate of depletion of Cl was about 3.9 times greater than that of the K. This led to a lower depletion of K in the boiler, while the model predicted a higher rate of depletion of K. This resulted to the underprediction of K content in the carryover particles.

Figure 8.21 shows the predicted and field study results of the carbonate, sulphate, and sulphide contents in the carryover particle. These components show significant changes at a few seconds in the boiler, when the particle burns and reaches elevated temperatures. A sudden increase in the carbonate content right after entering the boiler is as a result of the formation of carbonate during the devolatilization stage. After reaching a peak, the carbonate content starts to decrease because of carbonate reduction and sulphation reactions which occurs during the char burning and smelt oxidation stages. This results in the conversion of carbonate into sulphate. The sulphate initially is reduced to sulphide during devolatilization and, then, is formed as a result of the oxidation of
sulphide and the sulphation of carbonate during char burning and smelt oxidation. The oxidation of the sulphide also results in a decrease in the sulphide content, as the model predicts.

![Graph showing potassium and chloride contents over time](image)

**Figure 8.20** Predicted (solid line) and field (datapoint) results of the K and Cl contents in the carryover particles formed in the recovery boiler A.

After 4 seconds, when the particle reaches the sampling point, the carbonate decreases and sulphate increases gradually while the sulphide is almost completely oxidized and shows no further change. The changes in carbonate and sulphate contents result from the sulphation of carbonate. As shown in Figure 8.21, the model predicts the carbonate, sulphate, and sulphide contents in good agreement to the experimental results.
8.3 Summary

The combustion of a single dried black liquor particle was studied to develop a dynamic model that predicts the composition of carryover particles. The model predicts the composition of carryover particles as a function of the initial elemental and composition of black liquor and burning conditions. Kinetics, mass transfer, and energy balance equations are coded in TK Solver environment. All differential equations from kinetics and mass balance are solved using Fourth-order Runge-Kutta method and the energy balance equation is solved using Golden Section Search method.
The kinetic equation for the sulphide oxidation obtained from the literature was modified according to the experimental results obtained from this study in order to get a better prediction for the sulphide and sulphate contents in carryover particles.

Due to lack of information, the rate of depletion of K as a result of the reduction of $K_2CO_3$ by char was assumed to be at the same rate as the rate of depletion of Na as a result of the reduction of $Na_2CO_3$ by char. This assumption results in the prediction of the same rate of depletion for K as the Na. The results of equilibrium calculations using HSC Chemistry Program show that when the same number of moles of $K_2CO_3$ and $Na_2CO_3$ are reduced by char, the gas phase contains more elemental K than elemental Na. This implies that the reduction of $K_2CO_3$ by char occurs at a higher rate than that of $Na_2CO_3$. The calculation results, however, need to be verified experimentally before they can be applied with confidence.

In this study, the K content of carryover particles was calculated based on the empirical relationship obtained, i.e. the depletion of K is one-third of the depletion of Cl.

A comparison of experimental data and the model results indicated that the model successfully predicts the effect of the black liquor Cl and K contents, $O_2$ concentration, the EFR temperature, and the black liquor particle size on the composition of carryover particles formed in the EFR. The model results show that the particle temperature exceeds the surrounding gas temperature and, depending on the $O_2$ concentration, the particle temperature reaches above 1200°C at its peak. The results also show that it takes longer for the particle to reach its peak temperature as the $O_2$ concentration decreases.
Small particles are predicted to reach a peak temperature and to cool down to the gas temperature earlier than larger particles. The model predicts that it takes longer for the larger particles to reach a peak temperature, but their peak temperature is higher than that of smaller particles. The carryover particles formed in the EFR are predicted to be only charred when the EFR temperature is below 750°C.

The model also successfully predicts the composition of carryover particles formed in the boiler environment. The boiler results show that the composition of the carryover particle changes significantly at the early stage of the combustion, when the particle temperature is high, and, then, changes slightly after the deposition of carryover particle on the tube (or sampling probe) surface.
CHAPTER 9: SUMMARY, CONCLUSIONS, AND IMPLICATIONS

As black liquor is sprayed and burned in a kraft recovery boiler, a fraction of the liquor spray droplets is entrained in the flue gas, burns and forms carryover particles. Depending on temperature and composition, carryover particles may form hard deposits on heat transfer surfaces in the upper section of the boiler, drastically reduce the boiler thermal efficiency, and hinder the flue gas flow. While the composition of carryover particles is needed to assess the propensity of deposit buildup (fouling) on the tube surface, it is often not available due to the difficulty in collecting representative samples from operating recovery boilers, as well as in preserving the collected samples for subsequent chemical and thermal analyses. This thesis work is the first to systematically study how the composition of carryover particles changes during the black liquor combustion and how it may be related to the composition and burning conditions of the black liquor from which the carryover particles originated.

The composition of carryover was studied over a wide range of black liquor composition and burning conditions. Experiments were performed in the laboratory using an entrained flow reactor (EFR) to produce carryover particles from various black liquor samples, and in three operating recovery boilers using a specially-designed probe to collect carryover samples. A dynamic model was developed to predict the composition of a carryover particle as it is formed during the combustion of a dried black liquor particle. The predicted composition was tested against experimental values obtained from both EFR and field studies.
Results of EFR experiments show that the chloride (Cl) and potassium (K) contents in carryover particles were linearly proportional to their respective contents in the black liquor. Both Cl and K were depleted markedly during black liquor burning at a rate that increased with an increase in O₂ concentration (or temperature) in the gas. The depletion of Cl was about three times greater than that of K. These EFR results suggest that vaporization of alkali chloride is the main cause of Cl and K depletion from carryover particles.

Carryover particles formed at a high O₂ concentration (or high temperature) contained also less sulphide (S), less carbonate (CO₃), but more sulphate (SO₄) than carryover particles formed in a low O₂ concentration. In the presence of SO₂ in the gas, the CO₃ content in carryover particles was lower, while the Cl content remained unchanged. These findings are consistent with thermodynamic predictions which suggest that NaCl and KCl would not be converted into Na₂SO₄ and K₂SO₄ until all the carbonates (Na₂CO₃ and K₂CO₃) in the particles have been completely sulphated.

Similar results were obtained for carryover samples collected from operating recovery boilers. These field studies further show that the composition of carryover particles did not change significantly with sampling time, and that carryover contained less Cl, less K, less CO₃ and more SO₄ than oxidized smelt. In each boiler, there was a clear linear relationship between the Cl and K contents of smelt, carryover, black liquor, and precipitator dust. This relationship can be useful for the prediction of Cl and K contents in carryover, based on their contents in black liquor, smelt and precipitator ash.
The significant depletion of Cl and K in carryover particles is an important finding. It implies that carryover contains much less Cl and somewhat less K, and consequently, is less sticky than previously expected from black liquor composition. Since the sticky temperature of the particles is dramatically lowered by Cl only in the first few mole% Cl/(Na+K), the much lower Cl content of carryover implies that the removal of Cl from the liquor system through various ash treatment methods is much more effective in controlling of fouling/plugging in recovery boilers than previously thought.

In the development of the dynamic model, the kinetic equations for sulphide oxidation obtained by Wag [33] were first modified based on the experimental data obtained in this study, and then incorporated into the model to improve its sulphide and sulphate predictions. The model predicted the main components of carryover particles formed in both the EFR and recovery boilers reasonably well, except for the K content, which was over-predicted particularly at high O$_2$ concentrations (or high temperatures).

The over-prediction of K content was due to the assumptions in the model that the depletion of K is one-third of the depletion of Cl according to the results obtained in this study, and that the rate of K$_2$CO$_3$ reduction by char (carbon) is the same as that of Na$_2$CO$_3$ reduction by char. While the second assumption may not be valid, it was necessary due to the lack of kinetic equations for calculating the rate of reduction of K$_2$CO$_3$ by char. The over-prediction of K content in carryover particles implies that the rate of K$_2$CO$_3$ reduction by char must be higher than that of Na$_2$CO$_3$ reduction. Although the higher rate of K$_2$CO$_3$ reduction by char has been confirmed by equilibrium calculations using HSC, it needs to be verified experimentally and the kinetic
equations for K$_2$CO$_3$ reduction by char are required in order for the model to predict the K content more accurately.

A comparison of experimental data and model predictions shows that:

1. the model successfully predicts the effects of black liquor particle size and Cl and K contents, O$_2$ concentration and EFR temperature on carryover composition;
2. the particle temperature may exceed 1200°C depending on O$_2$ concentration. At lower O$_2$ concentrations, it takes longer for the particle to reach its peak temperature;
3. small particles reach the peak temperature and cool down to the surrounding gas temperature more quickly than large particles; and
4. the composition of carryover changes significantly at the early stage of combustion when the particle temperature is high, and becomes stable after the particles have deposited on the sampling probe surface.

Despite its inability to completely predict the composition of carryover particles obtained in this study, the model is still a useful predictive tool for determining the composition of carryover as a function of black liquor composition and burning conditions to a sufficient accuracy. The predicted composition can be used to determine the melting behaviour of carryover, and to assess its fouling propensity in the recovery boiler, if the flue gas temperature is known. The information helps boiler manufacturers, boiler operators and mill engineers to identify locations where massive deposit accumulation may occur in the boiler, and to devise appropriate control strategies to minimize fouling, improve boiler thermal efficiency, and avoid unscheduled boiler shutdowns due to plugging.
PUBLICATIONS


REFERENCES


46. TK Solver, version 5.0, developed by Universal Technical Systems Inc.


53. HSC Chemistry, version 5.0, developed by Outokumpu Research Oy.
APPENDICES
Appendix A: Effect of SO$_2$ on Carryover Composition with Different Initial Sizes

The effect of SO$_2$ on carryover and deposit compositions with initial particle size in a range of 150 to 300 µm was discussed in Chapter 4.4. The effect of SO$_2$ on carryover and deposit compositions with initial particle size in a range of 300 to 425 µm, 425 to 600 µm, and 600 to 710 µm is presented here.

Figure A-1 Effect of SO$_2$ on the Cl and K contents in deposit and carryover for the black liquor particles in a size range of 300 to 425µm (EFR set at 800°C with O$_2$ concentration of 12.5%, and probe temperature of 500°C).
Figure A-2 Effect of SO$_2$ on the sulphate and sulphide (only for carryover) contents in deposit and carryover for the black liquor particles in a size range of 300 to 425µm (EFR set at 800°C with O$_2$ concentration of 12.5%, and probe temperature of 500°C).

Figure A-3 Effect of SO$_2$ on the carbonate and total sulphur contents in deposit and carryover for the black liquor particles in a size range of 300 to 425µm (EFR set at 800°C with O$_2$ concentration of 12.5%, and probe temperature of 500°C).
**Figure A-4** Effect of $SO_2$ on the Cl and K contents in deposit and carryover for the black liquor particles in a size range of 425 to 600 µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).

**Figure A-5** Effect of $SO_2$ on the sulphate and sulphide (only for carryover) contents in deposit and carryover for the black liquor particles in a size range of 425 to 600 µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).
Figure A-6 Effect of $SO_2$ on the carbonate and total sulphur contents in deposit and carryover for the black liquor particles in a size range of 425 to 600µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).

Figure A-7 Effect of $SO_2$ on the Cl and K contents in deposit and carryover for the black liquor particles in a size range of 600 to 710µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).
Figure A-8 Effect of $SO_2$ on the sulphate and sulphide (only for carryover) contents in deposit and carryover for the black liquor particles in a size range of 425 to 600µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).

Figure A-9 Effect of $SO_2$ on the carbonate and total sulphur contents in deposit and carryover for the black liquor particles in a size range of 600 to 710µm (EFR set at 800°C with $O_2$ concentration of 12.5%, and probe temperature of 500°C).
Appendix B: Particle Velocity Justification

To justify the assumption number 3, equation 7.2 is numerically solved to obtain the particle velocity as it is falling down through the feeding tube at the top of the EFR. The results of the solution are presented in Figure B.1. In this calculation, the length and diameter of the feeding tube are 150 cm and 1.27 cm, respectively. It is assumed that the particle does not collide with the tube wall or each other. It is also assumed that the particle does not swell and, therefore, the density of the particle remains constant.

The results in Figure B.1 show that all particles are above the gas velocity (1.8 m/s) when they reach the exit of the feeding tube at the entrance of the EFR. The small black liquor particles reach their terminal velocity at the exit of the feeding tube; however, the larger black liquor particles are below but close to their terminal velocity. Therefore, it is assumed that the particles with a size below 800µm reach their terminal velocity at the exit of the feeding tube.
Figure B.1 Velocity of particle in the feeding tube at the top of the EFR.
Appendix C: Particle Biot Number

The Biot number (Bi) is one of the main criteria used to evaluate the effectiveness of particle internal heat transfer, and is defined as the ratio of internal (conductive) heat transfer resistance to the external (convective) heat transfer resistance of a particle [30].

\[ Bi = \frac{R_{\text{internal}}}{R_{\text{external}}} = \frac{(V/A)_p}{h_{\text{conv.}}} \frac{k_p}{1} \]  

When the Biot number is below 0.1, the internal heat transfer resistance is negligible in comparison to the external heat transfer resistance. This means that the heat transfer within the particle occurs quickly and there is little or no temperature gradient within the particle.

Figure F.1 shows the Bi number of a particle with the initial diameter of 400 µm as it burns. The Bi number significantly decreases during the devolatilization stage and levels off during the char burning and smelt oxidation stages. This suggests that the assumption of Bi<0.1 is valid for this size of the particle.

Table C.1 shows that the Bi number of the particles of different sizes at the beginning of the combustion (time zero), when the particles have the highest Bi number. The results show that the particles with a size of up to 800 µm have a Bi less than 0.1. This suggests that all particles examined in the study have a Bi number below 0.1 and that the isothermal assumption for the bulk temperature of these particles is valid.
Figure C.1 Biot Number of a 400-µm Black Liquor Particle as it Burns at 15% \(O_2\)

Table C.1 Bi of Dried Black Liquor Particles at the Beginning of the Devolatilization.

<table>
<thead>
<tr>
<th>(d_p) (µm)</th>
<th>200</th>
<th>400</th>
<th>600</th>
<th>800</th>
<th>1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.06</td>
<td>0.08</td>
<td>0.09</td>
<td>0.10</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Appendix D: Runge-Kutta Method

Standard or classical Fourth-order Runge-Kutta is the most commonly used to solve the differential equations that it is often referred to as "RK4" or simply as "the Runge–Kutta method".

For an initial value problem as follows:

\[ y' = f(t, y), \quad y(t_0) = y(0) \]  \hspace{1cm} (D.1)

Then, the RK4 method for this problem is given by the following equation:

\[ y_{n+1} = y_n + \frac{h}{6}(k_1 + 2k_2 + 2k_3 + k_4) \]  \hspace{1cm} (D.2)

where

\[ k_1 = f(t_n, y_n) \]  \hspace{1cm} (D.3)

\[ k_2 = f(t_n + \frac{h}{2}, y_n + \frac{h}{2}k_1) \]  \hspace{1cm} (D.4)

\[ k_3 = f(t_n + \frac{h}{2}, y_n + \frac{h}{2}k_2) \]  \hspace{1cm} (D.5)

\[ k_4 = f(t_n + h, y_n + hk_3) \]  \hspace{1cm} (D.6)

Thus, the next value \( y_{n+1} \) is determined by the present value \( y_n \) plus the product of the size of the interval \( h \) and an estimated slope. The slope is a weighted average of slopes:

- \( k_1 \) is the slope at the beginning of the interval;
- \( k_2 \) is the slope at the midpoint of the interval, using slope \( k_1 \) to determine the value of \( y \) at the point \( t_n + h/2 \) using Euler’s method;
- \( k_3 \) is again the slope at the midpoint, but now using the slope \( k_2 \) to determine the \( y \)-value;
- \( k_4 \) is the slope at the end of the interval, with its \( y \)-value determined using \( k_3 \).
In averaging the four slopes, greater weight is given to the slopes at the midpoint:

\[ \text{slope} = \frac{k_1 + 2k_2 + 2k_3 + k_4}{6} \]  \hspace{1cm} (D.7)

The RK4 method is a fourth-order method, meaning that the error per step is on the order of \( h^5 \), while the total accumulated error has order \( h^4 \).
Appendix E: Golden Section Search Method

Fibonacci search technique is considered to be one of the best methods in minimization or optimization approaches. This technique has the largest interval reduction of all of the procedures, but it requires that the number of iterations be specified in advance. Golden Section Search method is basically the same as Fibonacci approach, but it is used when the number of iterations is not known in advance.

The Golden Section Search Method is basically is a technique to find the minimum (or maximum) of a continuous unimodal function, \( f(x) \), through narrowing the range of the values of the lower and upper limits where the minimum is located. Diagram shown in Figure E.1 illustrates the method of narrowing down the limits where the minimum in function \( F(x) \) is located. \( x_1 \) and \( x_2 \) are the lower and upper limits for the interval defined by user. A random \( x_3 \) is guessed and the value of \( F(x_3) \) is calculated. Since \( F(x_2) \) is smaller than either \( F(x_1) \) or \( F(x_2) \), it is clear that a minimum lies inside the interval from \( x_1 \) to \( x_2 \).

Another value of \( x \) as \( x_4 \) is guessed in the largest interval, between \( x_2 \) and \( x_3 \). If the value of function at \( x_4 \) is \( F(x_4)a \), the minimum lies between \( x_1 \) and \( x_4 \) and the new triplet of points of \( x_1 \), \( x_3 \), and \( x_4 \). If the value of function at \( x_4 \) becomes \( F(x_4)b \), the minimum lies between \( x_2 \) and \( x_3 \) and the new triplet of points of \( x_2 \), \( x_3 \), and \( x_4 \). Either way, a new guessed is made and a narrower search interval is constructed and the technique is repeated until the minimum is found.
From the diagram above, it is seen that the new search interval will be either between $x_1$ and $x_4$ with a length of $a+c$, or between $x_2$ and $x_3$ with a length of $b$. The Golden Section Search method requires equal intervals to avoid a situation in which $x_3$ is very close to $x_1$ or $x_2$, and guarantee that the interval width shrinks by the same constant proportion in each step. To ensure that the spacing after evaluating $F(x_4)$ is proportional to the spacing prior to that evaluation, we want:

$$\frac{c}{a} = \frac{a}{b}$$  \hspace{1cm} (E-1)

On other hand, if $F(x_4)$ is $F(x_4)b$ and our new triplet of points are $x_2, x_3$, and $x_4$, we want:
\[
\frac{c}{b - c} = \frac{a}{b}
\]  
(E-2)

Obtaining \(c\) from Equation E-1, and substituting in Equation E-2 results in:

\[
\left(\frac{b}{a}\right)^2 = \frac{b}{a} + 1
\]  
(E-3)

The ration of \(b/a\) is called Golden ratio and is shown with either \(\tau\) or \(\phi\). The solution to quadratic Equation E-3 gives \(\tau = 1.618\) (negative roots is not valid).

If the length of the first interval is called \(I_0\) (=\(a+b\)), the distance of first guess (\(x_3\)) from the lower limit (\(x_1\)) will be \(x_3 = a = I_0 - I_0/\tau = 0.382\ I_0\), and the distance of the second guess (\(x_4\)) from the lower limit will be \(x_4 = a + c = I_0/\tau = 0.618\ I_0\), which is 0.382 \(I_0\) away from the upper limit.
## Appendix F: Particle and gas physical properties

Gas physical properties:

<table>
<thead>
<tr>
<th>Property</th>
<th>Equation</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$\rho_g = 347.13(T_{film} + 273)^{-0.9977}$</td>
<td>F-1</td>
</tr>
<tr>
<td>Kinematics viscosity</td>
<td>$\nu_g = \frac{\mu_g}{\rho_g} = 7.66 \times 10^{-11}(T_{film} + 273)^2 + 3.92 \times 10^{-8}(T_{film} + 273)$</td>
<td>F-2</td>
</tr>
<tr>
<td>Conductivity</td>
<td>$k_g = -1.62 \times 10^{-8}(T_{film} + 273)^2 + 6.85 \times 10^{-5}(T_{film} + 273) + 0.0238$</td>
<td>F-3</td>
</tr>
<tr>
<td>Heat capacity</td>
<td>$C_{p,g} = -3.0 \times 10^{-8}(T_{film} + 273)^2 + 3.0 \times 10^{-1}(T_{film} + 273) + 0.9042$</td>
<td>F-4</td>
</tr>
</tbody>
</table>

Particle properties and heat capacity of main fractions in particle:

<table>
<thead>
<tr>
<th>Property</th>
<th>Equation</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>$\rho_g = \frac{m_p}{d_p}$</td>
<td>F-5</td>
</tr>
<tr>
<td>Heat capacity of particle</td>
<td>$C_{p,p} = (C_{p,BLS})(\text{fraction of solids}) + (C_{p,BLS})(\text{fraction of water})$</td>
<td>F-6</td>
</tr>
<tr>
<td>Heat capacity of black liquor solids</td>
<td>$C_{p,BLS} = 4.28 \times \frac{Ln(T_p - 7.06)}{12}$</td>
<td>F-7</td>
</tr>
<tr>
<td>Heat capacity of water</td>
<td>$C_{p,H_2O} = 4.05 + 0.003 \times T_p$</td>
<td>F-8</td>
</tr>
</tbody>
</table>
Diffusivity of water vapour in gas is calculated using following equation:

\[
D_{\text{H}2\text{O},g} = 2.6 \times 10^{-5} \left( \frac{T_p + 273.15}{298} \right)^{1.75}
\]  

(F-9)

Diffusivity of inorganics and oxygen in gas:

\[
D_i = D_{i,0} \times \frac{\left( T_{\text{film}} + 273.15 \right)^{1.5}}{273} \times \frac{0.925 - 0.268 \times \log \frac{T_{\text{film}} + 273}{273}}{0.925}
\]  

(F-10)

**Table F-1: Diffusivity (D_{i,0}) of various species at standard temperature**

<table>
<thead>
<tr>
<th>Species</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.85 x 10^{-5}</td>
</tr>
<tr>
<td>K</td>
<td>1.44 x 10^{-5}</td>
</tr>
<tr>
<td>NaCl</td>
<td>9.37 x 10^{-6}</td>
</tr>
<tr>
<td>KCl</td>
<td>5.23 x 10^{-6}</td>
</tr>
<tr>
<td>Na\textsubscript{2}CO\textsubscript{3}</td>
<td>3.16 x 10^{-7}</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>1.8 x 10^{-5}</td>
</tr>
</tbody>
</table>
Appendix G: Program Codes

The equations and the codes written in each section and subsections are presented as follows:

Rules Sheet:

\[
\text{Status Rule}
\]

<table>
<thead>
<tr>
<th>Status</th>
<th>Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satisfied</td>
<td>PrcO=100-PrcC-PrcS-PrcH-PrcK-PrcCl</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWNa2CO3=2<em>MWNa+MWC+3</em>MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWNa2SO4=2<em>MWNa+MWS+4</em>MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWNa2SO3=2<em>MWNa+2</em>MWS+3*MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWNa2S=2*MWNa+MWS</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWNaCl=MWNa+MWCl</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWK2CO3=2<em>MWK+MWC+3</em>MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWK2SO4=2<em>MWK+MWS+4</em>MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWK2SO3=2<em>MWK+2</em>MWS+3*MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWK2S=2*MWK+MWS</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWKC=MK+MWCl</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWH2S=MH*2+MWS</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWCO2=MWC+2*MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWCO=MWC+MWO</td>
</tr>
<tr>
<td>Satisfied</td>
<td>MWH2O=MWH*2+MWO</td>
</tr>
<tr>
<td>Cancelled</td>
<td>call blank('moleCl)</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Cini=PrC/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nCini=Cini/MWC ; mol of Carbon</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Sini=PrS/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nSini=Sini/MWS ; mol of Sulfur</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Naini=PrNa/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nNaini=Naini/MWNa ; mol of Na</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Onini=PrO/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nOnini=Onini/MWO ; mol of Oxygen</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Hini=PrH/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nHini=Hini/MWH ; mol of Hydrogen</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Kinini=PrK/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nKinini=Kinini/MWK ; mol of Potassium</td>
</tr>
<tr>
<td>Satisfied</td>
<td>Clini=PrC/100<em>S0</em>mdrop/1000 ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nClini=Clini/MWC ; mol of Chlorine</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nNaClini=nClini*(nNaini/(nNaini+nKini)) ; mol</td>
</tr>
<tr>
<td>Satisfied</td>
<td>mNaClini=nNaClini*(MWNaCl) ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nKClini=nClini*(nKinini/(nNaini+nKini)) ; mol</td>
</tr>
<tr>
<td>Satisfied</td>
<td>mKClini=nKClini*MWKCl ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nNa2SO4ini=SasSO4/100<em>Sini/MWS</em>nNaini/(nNaini+nKini) ;mol</td>
</tr>
<tr>
<td>Satisfied</td>
<td>mNa2SO4ini=nNa2SO4ini*(MWNa2SO4) ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nNa2Sini=SasS/100<em>Sini/MWS</em>nNaini/(nNaini+nKini) ;mol</td>
</tr>
<tr>
<td>Satisfied</td>
<td>mNa2Sini=nNa2Sini*(MWNa2S) ;g</td>
</tr>
<tr>
<td>Satisfied</td>
<td>nNa2S2O3ini=SasS2O3/100<em>Sini/MWS/2</em>nNaini/(nNaini+nKini) ;mol</td>
</tr>
<tr>
<td>Satisfied</td>
<td>mNa2S2O3ini=nNa2S2O3ini*(MWNa2S2O3) ;g</td>
</tr>
</tbody>
</table>
Satisfied $n_{Na_2SO_3ini}=S_{SO_3ini}/100*Sini/MWS*n_{Naini}/(n_{Naini}+n_{Kini})$;mol
Satisfied $m_{Na_2SO_3ini}=n_{Na_2SO_3ini}*(MW_{Na_2SO_3})$;g
Satisfied $MWA=(Naini+Kini)/(n_{Naini}+n_{Kini})$
Satisfied $MWA_{2CO_3}=2*MWA+MWC+3*MWO$
Satisfied $n_{CO_3ini}=prcCO_3*S_0*mdrop/100/1000/MWA_{2CO_3}$;mol
Satisfied $n_{Na_2CO_3ini}=n_{CO_3ini}*n_{Naini}/(n_{Naini}+n_{Kini})$;mol
Satisfied $m_{Na_2CO_3ini}=n_{Na_2CO_3ini}*(MW_{Na_2CO_3})$;g
Satisfied $n_{NaCini}=(n_{Naini}/2-n_{Na_2Sini}-n_{Na_2SO_4ini}-n_{Na_2S2O_3ini}-n_{Na_2SO_3ini}-n_{NaClini}/2-n_{Na_2CO_3ini})$;mol
Satisfied $m_{NaCini}=n_{NaCini}*(MW_{Na_2CO_3})$;g
Satisfied $m_{C}=Cini-(n_{NaCini}+n_{Na_2CO_3ini})*12*(1+n_{Kini}/(n_{Naini}))$;g of (pyrolyzable carbon) = (total carbon in BLS) - (carbon in Na$_2$CO$_3$
Satisfied $m_S=Sini-(2*n_{Na_2S2O_3ini}+n_{Na_2SO_3ini}+n_{Na_2SO_4ini}+n_{Na_2Sini})*32*(1+n_{Kini}/n_{Naini})$;g of (pyrolyzable sulfur) = (total sulfur in BLS) - (sulfur in Na$_2$CO$_3$
Satisfied $m_{O}=Oini-(3*n_{Na_2S2O_3ini}+3*n_{Na_2SO_3ini}+4*n_{Na_2SO_4ini}+3*n_{NaClini}+3*n_{Na_2CO_3ini})*(1+n_{Kini}/n_{Naini})*MWO$;g of (pyrolyzable oxygen) = (total oxygen in BLS) - (oxygen in inorganics)
Satisfied place'(y36,1)=0; mol of C burned off due to reaction with Na2SO4
Satisfied place'(y37,1)=0; mol of Na2S oxidized to Na2SO4
Satisfied place'(y38,1)=0; g of Na2CO3 decomposed
Satisfied place'(y39,1)=0; wt% of Na2SO4 in the solid
Satisfied place'(y40,1)=0; wt% of Na2S in the solid
Satisfied place'(y41,1)=0; wt% of NaCl in the solid
Satisfied place'(y42,1)=0; wt% of Char in the solid
Satisfied place'(y45,1)=0; Carbon bound to Na
Satisfied place'(y46,1)=0; g of KCl
Satisfied place'(y47,1)=0; g of Na
Satisfied place'(y48,1)=0; g of K
Satisfied place'(y49,1)=0; g of Cl
Satisfied place'(y50,1)=0; g of C
Satisfied place'(y51,1)=0; g of H
Satisfied place'(y52,1)=0; g of O
Satisfied place'(y53,1)=0; g of S
Satisfied place'alkali,1)=0; Na\text{ini}+K\text{ini}
Satisfied place'molK,1)=0; K\text{ini}/(Na\text{ini}+K\text{ini})*100
Satisfied place'molCl,1)=0; Cl\text{ini}/(Na\text{ini}+K\text{ini})*100
Satisfied place'Tdrop,1)=T\text{dropini}
Satisfied place'Tsurface,1)=T\text{surfini}
Satisfied place'Tfilm,1)=(T\text{surfini}+T\text{dropini})/2
Satisfied place'S,1)=S0; Solids content
Satisfied if S0>0.9 THEN l\text{ini}=1.57 ELSE l\text{ini}=0.997+0.649*S0 : g/cc
Satisfied place'l\text{L},1)=l\text{ini}
Satisfied Diaini=('y23[1]*6/(l\text{ini}^0.333/100 ; m
Satisfied place'Dia,1)=Diaini
Satisfied Areaini=\i\text{aini}^2
Satisfied place'Area,1)=Areaini
Satisfied Volini=\i\text{aini}^3
Satisfied place'Vol,1)=Volini
Satisfied c\text{NaClini}=c\text{NaClini}/Volini
Satisfied place'c\text{NaCl},1)=c\text{NaClini}
Satisfied c\text{KClini}=c\text{KClini}/Volini
Satisfied place'c\text{KCl},1)=c\text{KClini}
Satisfied place'C\text{water},1)=0
Satisfied Diffini=2.6e-5*(T\text{dropini}/298)^{1.75 ; m2/s
Satisfied place'\text{Diff},1)=Diffini
Satisfied H2Oini=(1-S0)*mdrop/1000 ; g H2O initially in drop

Comment in Boiler Case: L\text{mi} is the distance from the guns where the T\text{min} is read, T\text{max} is the gas temperature at guns elevation, T\text{min} is the gas temperature at either bull nose or generating bank elevation
Satisfied Tslope=(T\text{gasmin}-T\text{gasmax}+100)/L\text{mi}
Satisfied call Timeset()
Satisfied call RK4('EQ,'y,'t,ne)
## Variable Sheet:

<table>
<thead>
<tr>
<th>Status</th>
<th>Input</th>
<th>Name</th>
<th>Output</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>3.14159265358979</td>
<td>$\pi$</td>
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<td>1</td>
<td>$F$</td>
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<td>Stefan Bolzmann constant</td>
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<td>$n_e$</td>
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<td>Number of differential equations</td>
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<td>$t_{max}$</td>
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<td>Maximum time IMPORTANT: check table sheet</td>
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<td>.01</td>
<td>$\Delta t$</td>
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<td>Step interval</td>
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<td>800</td>
<td>$T_{bulk\text{gas}}$</td>
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<td>C</td>
<td>Bulk gas temperature = furnace temp</td>
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<tr>
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<td>150</td>
<td>$T_{drop\text{ini}}$</td>
<td></td>
<td>C</td>
<td>Average drop core temp at time=0</td>
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<tr>
<td></td>
<td>150</td>
<td>$T_{surf\text{ini}}$</td>
<td></td>
<td>C</td>
<td>Drop surface temp at time=0</td>
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<td></td>
<td>35</td>
<td>$P_{rc\text{C}}$</td>
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<td></td>
<td>Percent carbon in BLS</td>
</tr>
<tr>
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<td>4.7</td>
<td>$P_{rc\text{S}}$</td>
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<td>Percent sulfur in BLS</td>
</tr>
<tr>
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<td>20</td>
<td>$P_{rc\text{Na}}$</td>
<td></td>
<td></td>
<td>Percent sodium in BLS</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>$P_{rc\text{H}}$</td>
<td></td>
<td></td>
<td>Percent hydrogen in BLS</td>
</tr>
<tr>
<td></td>
<td>3.266</td>
<td>$P_{rc\text{K}}$</td>
<td></td>
<td></td>
<td>Percent potassium in BLS</td>
</tr>
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<td>.71</td>
<td>$P_{rc\text{Cl}}$</td>
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<td>Percent chlorine in BLS</td>
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<tr>
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<td>$P_{rc\text{O}}$</td>
<td>32.124</td>
<td></td>
<td>Percent oxygen in BLS by difference</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>$S_{as\text{SO}_4}$</td>
<td></td>
<td></td>
<td>Mole Percent sulfur as sulfate</td>
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<td>$S_{as\text{SO}_3}$</td>
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<td>$S_{as\text{S}_2O}_3$</td>
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<td>$m_{drop}$</td>
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<td>mg</td>
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<td>Initial solids concentration</td>
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<td>$D_{max}$</td>
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<td>Swelling factor</td>
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<td>$E_{1R}$</td>
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<td>9862.88188597546</td>
<td>$E_{2R}$</td>
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<td><strong>PARAMETERS OF CARBON MODEL</strong></td>
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<td>0</td>
<td>$\beta_1$</td>
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<td>.8</td>
<td>$\beta_2$</td>
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<tr>
<td></td>
<td>.24</td>
<td>$\beta_3$</td>
<td></td>
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**OUTPUTS**

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12.011 MWC Molecular Weight of Carbon
32.06 MWS Molecular Weight of Sulfur
22.98977 MWNa Molecular Weight of Sodium
15.9994 MWO Molecular Weight of Oxygen
1.0079 MWH Molecular Weight of Hydrogen
39.0983 MWK Molecular Weight of Potassium
35.453 MWCl Molecular Weight of Chlorine
160 As
8.31416 R

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**Kinetic Equation Sheet:**

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<td>Tsurface[i] = Tdrop[i]</td>
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<td>MWK2S2O3=2<em>MWK+2</em>MWS+3*MWO</td>
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\[ MWK2S=2*MWK+MWS \]
Active
\[ MWNaCl=58.443 \]
Active
\[ MWKCl=74.5513 \]
Active
\[ S0=.8 \]
Active
\[ R=8.13416 \]
Active
\[ Tbulkgas=Tslope^{*}[i]+Tgasmax \]
Active
\[ if and('Tsurface[i]>450,'y6[i-1]>0.1*'y6[1]) THEN Tbulkgas:=Tbulkgas+1982.9*(PO2+.017) ELSE Tbulkgas:=Tbulkgas \]
Active
\[ \text{'}nNa[i]=nNaini \]
Active
\[ \text{'}nNa[i-1]=\text{'}y47[i-1]/MWNa \]
Active
\[ \text{'}nK[i]=nKini \]
Active
\[ \text{'}nK[i-1]=\text{'}y48[i-1]/MWK \]
Active
\[ y[2]=((1-beta1)*ks1+(1-beta2)*ks2+(1-beta3)*ks3)*y3[i-1] ;g/s \]
Cancelled
\[ y[1]=(-2e-10*Tbulkgas^4+1e-6*Tbulkgas^3-.0017*Tbulkgas^2+1.1275*Tbulkgas-193.46)*y3[i-1]/100*10 ; extrapolated \]
Cancelled
\[ y[1]=(-3e-13*Tbulkgas^4+4.4e-7*Tbulkgas^3-.0011*Tbulkgas^2+.901*Tbulkgas-162.54)*y3[i-1]/100*5 \]
Active
\[ if 'y1[i-1]=0 \]
Cancelled
\[ y[2]=3e-13*Tbulkgas^4-4.4e-7*Tbulkgas^3+.0011*Tbulkgas^2-.901*Tbulkgas+262.54)*y3[i-1]/100*5 \]
Active
\[ if 'y43[i-1]=0 THEN y[43]=('y[1]+y[2])*MWNa2SO3/MWS*2 ELSE y[43]=0 \]
Active
Active
\[ if 'y44[i-1]=0 \]
Active
\[ y[5]=((1-alfa1)*kc1+(1-alfa2)*kc2)*y6[i-1] ;g/s \]
Active
\[ if 'y45[i-1]=0 THEN y[45]=('y[4]+y[5])*mNaCini/mC else y[45]=0 \]
Cancelled
\[ if 'y45[i-1]=0 THEN y[45]=('y[4]+y[5])*mNaCini/mC-y[2]*MWNa2CO3/MWS*('nNa[i-1]/('nNa[i-1]+'nK[i-1])) else y[45]=0 \]
Active
\[ if 'y45[i-1]=0 \]
Active
Active
Active
\[ y[9]=((1-Xc_co)*'y[4]/MWC ;g/(g/mol)=mol \]
Active
\[ y[10]=X_c_co*^y[4]/MWC \]
Active
\[ y[12]=0.03*y[4]/MWC \]
Active
Active
\[ y[13]=y[1]/MWS ;mol \]
Active
\[ y[14]=y[9]/44.01 ;gram \]
Active
\[ y[15]=y[10]/28.01 ;gram \]
Active
\[ y[16]=y[11]/1.0082 ;gram \]
Active
\[ y[17]=y[12]/MWO ;gram \]
Active
\[ y[18]=y[13]/34.076 ;gram \]
Active
\[ 'PH2Ov[i]=((2.9e-6*T^3-2.839e-4*T^2+9.401e-3*T)*100000 ;Pascal \]
Active
\[ 'Cwaterv[i]=('PH2Ov[i] *('S[i])/((8.314*(T+273.15))/mol/m3 \]
Active
\[ 'Diff[i]=2.6e-5*(T+273.15)/298)*1.75 ;m2/s \]
Active
\[ y[i]=0.000000000000076638*(T+273.15)/2+0.0000000039153*(T+273.15) ;m2/s \]
Active
\[ 'Sc[i]=='Diff[i]/'Dia[i-1] \]
Active
\[ 'Sh[i]=2.0569+'(Gr[i-1]*'Sc[i])/0.25+0.347*(Re[i-1]*'Sc[i])/0.62 \]
Active
\[ 'kmwaterv[i]=-'Sh[i]/'Dia[i-1] \]
Active
\[ if 'mH2O[i-1]>0.1*(1-S0)*mdrop goto LINE1 else goto LINE2 \]
Active
LINE1:
Active
\[ y[19]=-'Cwaterv[i]*'kmwaterv[i]*'Area[i]*18.015 ;mol/m3*m/s*m2*gram=g/mol=g/s \]
Active
goto LINE3 \]
Active
LINE2:
Active
\[ y[19]=0 \]
Active
LINE3:
Active $\dot{m}_{H_2O_g} = y[19] \ ; \text{g/s}$
Active $\dot{n}_{H_2O_g} = y[19] / 18.015 \ ; \text{mol/s}$
Active $y[20] = -y[19] \ ; \text{g/s}$
Active $\dot{m}_{H_2O_\text{old}} = y[20] \ ; \text{g/s}$

Active $y[22] = -H_{ini}/C_{ini} \cdot y[6] \cdot 1.2 \ ; \text{g/s}$ (negative sign because y6 is negative)
Active $y[21] = y[9] \cdot 2 + y[10] \cdot M_WO \ ; \text{g/s}$
Active $y[25] = -y[21] + y[22] / 2 \cdot 3 \cdot M_WO / M_{WS} \ ; \text{g/s}$
Active $y[26] = -y[22] / 2 \cdot 3 \cdot y[1] \ ; \text{g/s}$
Active if $y[25] \neq 1$
Active if $y[26] \neq 1$
Active if $y[26] = 0$ then $y[26] = 0$
Active if and ( $T_{surface} > 450, y[6] > 0.05 \cdot y[6][1]$ ) THEN $T_{bulkgas} = T_{bulkgas} + 1982.9 \cdot P_{O_2}$ ELSE $T_{bulkgas} = T_{bulkgas}$
Active $P_{sat_{NaCl}} = 10^{5.1 - (8388 / (T_{surface}[i] + 273 - 70))}$
Active $P_{sat_{KCl}} = 10^{4.8 - (7440 / (T_{surface}[i] + 273 - 122.7))}$
Cancelled $RO_2 = KO_2 \cdot A_{area}[i] \cdot (1/(R \cdot (273 + T_{surface}[i])) + 1/(R \cdot (273 + T_{bulkgas}))) \cdot 1 \cdot 5 \cdot P_{O_2}$
Cancelled $P_{sat_{Na2CO3}} = 1.1 \cdot 10^{(3.8887 - (8303.3 / (T_{surface}[i] + 273 - 0))}$
Active $P_{sat_{Na2CO3}} = 0.9 \cdot 10^{(4.03 - (8521.2 / (T_{surface}[i] + 273 - 0))}$
Active if $y[6] > 0.1 \cdot y[6][1]$ THEN goto LINE4 ELSE goto LINE5 ; Condition to check whether devolatilization has finished

Active LINE4:
Cancelled $y[27] = y[45]$
Active $y[27] = y[45] \cdot y[2] \cdot M_{WNa2CO3} / M_{WS} \cdot n_{Naini} / (n_{Kini} + n_{Naini})$
Active $y[28] = -3 \cdot 4 \cdot y[44] \cdot M_{WNa2SO4} / M_{Na2SO3}$
Active $y[29] = y[2] \cdot M_{WNa2S} / M_{WS} \cdot n_{Naini} / (n_{Kini} + n_{Naini} + 1) / 4 \cdot M_{WNa2S} / M_{WS} / M_{Na2SO3} \cdot y[44]$
Cancelled $c_{NaCl} = y[30] \cdot M_{WNaCl} / (n_{Na} - 1 + n_{K}[i-1]) \cdot P_{sat_{NaCl}[i]} \cdot 1 \cdot 5 / (R \cdot (T_{surface}[i] + 273))$
Active $c_{NaCl} = y[30] \cdot M_{WNaCl} / (n_{Na} + n_{K}[i-1]) \cdot P_{sat_{NaCl}[i]} \cdot 1 \cdot 5 / (R \cdot (T_{surface}[i] + 273))$
Active $y[30] = -K_{NaCl} \cdot A_{area}[i] \cdot c_{NaCl}[i] / M_{WNaCl}$
Cancelled $y[30] = 0$
Cancelled $y[30] = -K_{NaCl} \cdot A_{area}[i] \cdot c_{NaCl}[i] / M_{WNaCl}$
Cancelled $c_{KCl} = y[46] \cdot M_{WKCl} / (n_{Na} + n_{K}[i-1]) \cdot P_{sat_{KCl}[i]} \cdot 1 \cdot 5 / (R \cdot (T_{surface}[i] + 273))$
Active $c_{KCl} = y[46] \cdot M_{WKCl} / (n_{Na} + n_{K}[i-1]) \cdot P_{sat_{KCl}[i]} \cdot 1 \cdot 5 / (R \cdot (T_{surface}[i] + 273))$
Active $y[46] = -K_{KCl} \cdot A_{area}[i] \cdot c_{KCl}[i] / M_{WKCl}$
Cancelled $y[46] = 0$
Active $y[31] = y[5]$
Active $y[32] = 0$
Active $y[33] = 0$
Active $y[34] = 0$
Active $y[35] = 0$
Active $y[36] = 0$
Active $y[37] = 0$
Active $y[38] = 0$
Active goto LINE9

Active LINE5:
Active if $y[31][i-1] > 1 \cdot y[5][i-1]$ THEN goto LINE6 ELSE goto LINE7
Active LINE6:

```
[cNaCl[i-1]] = y30[i-1]/MWNaCl/(nNa[i-1] + nK[i-1])*PsatNaCl[i]*1e5/(R*(Tsurface[i]+273))
```

Active

```
[cNaCl[i-1]] = y30[i-1]/MWNaCl/[(y27[i-1]/MWNa2CO3 + y28[i-1]/MWNa2SO4 + y29[i-1]/MWNa2S)/(1+ nKini/(nNaini)) + y46[i-1]/MWKCl + y30[i-1]/MWNaCl]*PsatNaCl[i]*1e5/(R*(Tsurface[i]+273))
```

Active

```
y'[30] = -KNaCl[i]*Area[i]*cNaCl[i]*MWNaCl
```

Active

```
[y32] = 1.667*As*[(y31[i-1]/MW*C)*EXP(-2.1e5/(R*(Tdrop[i-1] + 273)))]; mole C/s reacted in C+H2O=CO+H2 (assuming PH2=0)
```

Active

```
y'[33] = 3.94e8*As*[(y31[i-1]/MW*C)*EXP(-2.5e5/(R*(Tdrop[i-1] + 273)))]; mol/s CO2 reacted in C + CO2=2CO (assuming PCO=0)
```

Active

```
y'[34] = 9.5E6*As*PO2*[(y31[i-1]/MW*C)*EXP(-17086/(273 + Tdrop[i-1]))]; mol/s O2 reacted in C+1/2O2=CO
```

Active

```
y'[34] = 3e3*As*PO2*[(y31[i-1]/MW*C)*EXP(-1.8E5/(R*(273 + Tdrop[i-1])))]; mol/s of O2 reacted in C+1/2O2=CO
```

Active

```
if [y31[i-1] > 0.6*y5[i-1] THEN y'[35] = 1e9*(y27[i-1]/MWNa2CO3)*EXP(-2.44e5/(R*(273 + Tdrop[i-1]))) ELSE [y35] = 1/2*1e9*(y27[i-1]/MWNa2CO3)*EXP(-2.44e5/(R*(273 + Tdrop[i-1]))); mol/s Na2CO3 reacted in 2C+Na2CO3=2Na+3CO
```

Cancelled

```
y'[35] = 1e9*(y27[i-1]/MWNa2CO3)*EXP(-2.44e5/(R*(273 + Tdrop[i-1]))) ;mol/s Na2CO3 reacted in 2C+Na2CO3=2Na+3CO
```

Cancelled

```
y'[36] = 3.79e3*((y28[i-1]/MWNa2CO3)/(y27[i-1]/MWNa2CO3 + y28[i-1]/MWNa2SO4 + y29[i-1]/MWNa2S)/(1+nKini/(nNaini)) + y46[i-1]/MWKCl + y30[i-1]/MWNaCl)*PsatNa2CO3[i]*1e5/(R*(Tsurface[i]+273))
```

Active

```
y'[36] = 3.79e3*[(y28[i-1]/MWNa2CO3)/(y27[i-1]/MWNa2CO3 + y28[i-1]/MWNa2SO4 + y29[i-1]/MWNa2S)/(1+nKini/(nNaini)) + y46[i-1]/MWKCl + y30[i-1]/MWNaCl)*PsatNa2CO3[i]*1e5/(R*(Tsurface[i]+273))
```

Cancelled

```
y'[37] = 0.75e3*As*[(y29[i-1]/MWNa2S)*PO2*EXP(-1.8e5/(R*(273 + Tdrop[i-1])))]; mol/s Na2S reacted in Na2S+2O2=Na2SO4
```

Active

```
y'[37] = 0.1*1.5e5*As*[(y29[i-1]/MWNa2S)*PO2*EXP(-1.8e5/(R*(273 + Tdrop[i-1])))]; mol/s Na2S reacted in Na2S+2O2=Na2SO4
```

Active

```
y'[31] = y'[5] - (y'[32] + y'[33] + y'[34] + (y'[35] + y'[36])*(1+nKini/nNaini)*2)*MWC
```

Active

```
if [y31[i-1] = 0 then y'[35] = 0
```

Cancelled

```
y'[36] = 3.79e3*((y28[i-1]/MWNa2CO3)/(y27[i-1]/MWNa2CO3 + y28[i-1]/MWNa2SO4 + y29[i-1]/MWNa2S)/(1+nKini/(nNaini)) + y46[i-1]/MWKCl + y30[i-1]/MWNaCl)*PsatNa2CO3[i]*1e5/(R*(Tsurface[i]+273))
```

Active

```
y'[37] = 1.5e5*As*[(y29[i-1]/MWNa2SO4)*PO2*EXP(-1.8e5/1.1/(R*(273 + Tdrop[i-1])))]; mol/s Na2SO4 reacted in Na2SO4+2O2=Na2SO4
Active
\[ y'[37] = 2.25 \times 10^5 \times As \times (y'29[i-1]/MWNa2S)*PO2*EXP(-1.8e5/(R*(273+Tdrop[i-1]))); \]
mols Na2S reacted in Na2S+2O2=Na2SO4

Active
goto LINE 8

Active
LINE 8:

Cancelled
\[ y'27 = -y'35 \times MWNa2CO3-y'45-y'2 \times MWNa2CO3/MWS \times (nNa[i-1]/(nK[i-1]+nNa[i-1])) \]

Cancelled
\[ y'[37] = 3.4/4 \times MWNa2S04/MWNa2SO4+y'[37] \times [36] \times MWNa2SO4+y'[38]/MWNa2CO3 \times MWNa2SO4 \]

Cancelled
\[ y'[29] = 2 \times MWNa2S/MWS \times (nNa[i-1]/(nNa[i-1]+nK[i-1])+1/4 \times MWNa2S/MWNa2SO3* [44]-y'[37]-y'[36] \times MWNa2S \]

Active
if \[ y'46[i-1] \]

Active
\[ y'[40] = y'[29]/y'23[i-1]*100 \]

Active
\[ y'[41] = y'[30]/y'23[i-1]*100 \]

Active
\[ y'[42] = y'[31]/y'23[i-1]*100 \]

Active
\[ y'[47] = y'[46]/MWK/MWKCl+y'[35]/2 \times MWK*nKini/nNaini \times MWKCl+y'[30]/MWNaCl \times MWKCl+y'[49]/2 \times MWK \]

Cancelled
\[ 'mdrop1[i] = 'y47[i-1]+'y48[i-1]+'y49[i-1]+'y50[i-1]+y'51[i-1]+y'52[i-1]+y'53[i-1] \]

Cancelled
\[ 'alkali[i] = (y'27[i-1]/MWNa2CO3+y'28[i-1]/MWNa2SO4+y'29[i-1]/MWNa2S+y'43[i-1]/MWNa2S2O3+y'44[i-1]/MWNa2SO3+y'45[i-1]/MWNa2CO3)*100/(nNa[i-1]+nK[i-1]) \]

Active
\[ 'molK[i] = y'[48]/MWK/MWKCl+100 \]

Active
\[ 'molCl[i] = y'[49]/MWCl/MWKCl+100 \]

Active
\[ 'EFK[i] = molK[i]/molK[1] \]

Active
\[ 'EFCl[i] = molCl[i]/molCl[1] \]

Cancelled
\[ 'molCO3[i] = 1.1*100*y'27[i-1]/100 \times MWNa2CO3+y'28[i-1]/100 \times MWNa2SO4+y'29[i-1]/100 \times MWNa2S+y'43[i-1]/100 \times MWNa2S2O3+y'44[i-1]/100 \times MWNa2SO3+y'45[i-1]/100 \times MWNa2CO3 \]

Cancelled
\[ 'molSO4[i] = 1.0*100*y'28[i-1]/100 \times MWNa2SO4+y'29[i-1]/100 \times MWNa2S+y'43[i-1]/100 \times MWNa2S2O3+y'44[i-1]/100 \times MWNa2SO3+y'45[i-1]/100 \times MWNa2CO3 \]

Cancelled
\[ 'molS[i] = 1.0*100*y'29[i-1]/100 \times MWNa2S+y'43[i-1]/100 \times MWNa2SO4+y'29[i-1]/100 \times MWNa2S+y'43[i-1]/100 \times MWNa2SO3+y'44[i-1]/100 \times MWNa2SO3+y'45[i-1]/100 \times MWNa2CO3 \]

Active
\[ 'molSulphur[i] = 1.0*100*y'30[i-1]/100 \times MWS/alkali[i] \]

Active
\[ 'molTotal[i] = 'molSO4[i]+'molS[i]+molS2O3[i]+molSO3[i]-molSulphur[i] \]

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Active  \( \text{Char}\%[i] = y31[i-1]/y24[i-1] \times 100 \)
Active  \( \text{Total}[i] = \text{molCl}[i]+\text{molCO}_3[i]+\text{molSO}_4[i]+\text{molS}[i] \)
Cancelled  \( \text{As}[1] = \text{Area}[1]/y24[1] \)
Cancelled  \( \text{As}[i] = \text{Area}[i]/y24[i-1] \)
Active  \( \text{Sgas}[i] = y1[i-1]/\text{Sini} \times 100 \)
Active  \( \text{Schar}[i] = y2[i-1]/\text{Sini} \times 100 \)
Active  \( \text{Cgas}[i] = y4[i-1]/\text{Cini} \times 100 \)
Active  \( \text{Cchar}[i] = y5[i-1]/\text{Cini} \times 100 \)

### Time Step Sheet:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>call blank('t)</td>
</tr>
<tr>
<td>Active</td>
<td>place('t,1):=0</td>
</tr>
<tr>
<td>Active</td>
<td>n:=tmax/dt</td>
</tr>
<tr>
<td>Active</td>
<td>for i=2 to n</td>
</tr>
<tr>
<td>Active</td>
<td>'t[i]:='t[i-1]+dt</td>
</tr>
<tr>
<td>Active</td>
<td>next i</td>
</tr>
</tbody>
</table>

### Runge-Kutta Sheet:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comment</td>
<td>Notation: EQ name of the function with the 1st-order equations</td>
</tr>
<tr>
<td>Comment</td>
<td>y master list with names of lists representing</td>
</tr>
<tr>
<td>Comment</td>
<td>the unknown functions</td>
</tr>
<tr>
<td>Comment</td>
<td>x independent variable (list); time</td>
</tr>
<tr>
<td>Comment</td>
<td>ne number of the 1st-order equations</td>
</tr>
<tr>
<td>Comment</td>
<td>K master list with names of lists of RK coefficients</td>
</tr>
<tr>
<td>Comment</td>
<td>( \text{K#1} ) through ( \text{K#4} )</td>
</tr>
<tr>
<td>Comment</td>
<td>@yi, @ye auxiliary lists</td>
</tr>
<tr>
<td>Comment</td>
<td>Description: This procedure function is an implementation of the classical</td>
</tr>
<tr>
<td>Comment</td>
<td>4th-order Runge-Kutta method for numerical integration of sets of ordinary</td>
</tr>
<tr>
<td>Comment</td>
<td>differential equations represented by 1st-order equations</td>
</tr>
<tr>
<td>Active</td>
<td>for j=1 to 4</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{K}[j][1]:= j ) : seeding a matrix of RK coefficients</td>
</tr>
<tr>
<td>Active</td>
<td>next j</td>
</tr>
<tr>
<td>Active</td>
<td>for e=1 to ne</td>
</tr>
<tr>
<td>Active</td>
<td>call blank(y[e],2,length(y[e])) : error indicates missing</td>
</tr>
<tr>
<td>Active</td>
<td>next e ; element in master list y</td>
</tr>
<tr>
<td>Active</td>
<td>xi:= x[1]</td>
</tr>
<tr>
<td>Comment</td>
<td>The Following Four Lines Are For Time=0 (or i=1)</td>
</tr>
<tr>
<td>Active</td>
<td>call STEP1(1) ; Calcs Tsurface and Qindot</td>
</tr>
<tr>
<td>Active</td>
<td>call LHS(1,Tdrop[1],Left)</td>
</tr>
<tr>
<td>Active</td>
<td>call RHS(1;Right)</td>
</tr>
<tr>
<td>Active</td>
<td>T:=Tdrop[1]</td>
</tr>
<tr>
<td>Comment</td>
<td>This Loop Solves The Differential Equations</td>
</tr>
<tr>
<td>Active</td>
<td>for i=2 to length(x)</td>
</tr>
<tr>
<td>Active</td>
<td>call STEP2(i)</td>
</tr>
</tbody>
</table>
call statmsg('Solving,'at,x,x[i])
for e=1 to ne
'@yi[e]:= y[e][i-1] ; error at i=2 indicates missing next e ; e-th initial condition
call listcopy('@yi',@ye)
h:=(x[i]-xi)/2
for j=1 to 3
K[j]:= 'K[j]
call apply(EQ,K[j],@ye,xi,i,T)
if mod(j,2) then xi:= xi + h
if j=3 then h:= 2*h
for e=1 to ne
'@ye[e]:= '@yi[e] + h*K[j]
next e
next j
call apply(EQ,'K#4,@ye,xi,i,T)
for e=1 to ne
y[e][i]:='@yi[e] + ('K#1[e]+2*(K#2[e]+K#3[e])+'K#4[e])*h/6
next e
mH2Ol[i]:=y20[i]
if 'y19[i]>H2Oini goto W1 else goto W2
W1:
'y19[i]=H2Oini
'y19[i+1]=H2Oini
'mH2Og[i]:=H2Oini
'mH2Og[i+1]:=H2Oini
W2:
if 'y20[i]
W3:
'y20[i]=0
'y20[i+1]=0
'mH2Ol[i]:=0
'mH2Oldot[i]:=0
W4:
T:='Tdrop[i] ;Necessary for STEP2-subroutine because Qindot needs Tdrop from previous iteration
call PAUSEMSG("Next step in R-K") ; This was used during debugging of program
if 'S[i]>0.95 goto A1 else goto A2
A1:
'S[i+1]:=1
goto A3
LHS of Energy Balance Equation:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>'Tdrop[i] := T</td>
</tr>
<tr>
<td>Active</td>
<td>'CpBLS[i] = (4.279130018062*LN('Tdrop[i])-7.058481591964)/12 ; J/gK</td>
</tr>
<tr>
<td>Active</td>
<td>'C_Cl[i] := y3[i]/y23[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'I_Cl[i] := ('y23[i]-y3[i])'/y23[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'Cplnorg[i] := (0.01598800699*('Tdrop[i]+30.36481264569)*4.1868)/106 ; J/gK</td>
</tr>
<tr>
<td>Active</td>
<td>'CpC[i] := 'C_Cl[i]<em>'CpC[i]+'I_Cl[i]</em>'CpInorg[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'CpH2O[i] := 4.06157222+0.00299906*('Tdrop[i]); J/gK</td>
</tr>
<tr>
<td>Active</td>
<td>'mBLS[i] := y23[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'mchar[i] := y31[i]</td>
</tr>
<tr>
<td>Active</td>
<td>if i</td>
</tr>
<tr>
<td>Active</td>
<td>Section1:</td>
</tr>
<tr>
<td>Active</td>
<td>'CpBLSdot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'Cpchardot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'mBLSdot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'mchardot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'hvapdot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'Tdropdot[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'BLS[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'CHAR3[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>'WATER[i] := 0</td>
</tr>
<tr>
<td>Active</td>
<td>goto Section3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cancelled</td>
<td>'CpBLSdot[i] := ('CpBLS[i]-'CpBLS[i-1])/dt</td>
</tr>
<tr>
<td>Cancelled</td>
<td>'Cpchardot[i] := ('Cpchar[i]-'Cpchar[i-1])/dt</td>
</tr>
<tr>
<td>Cancelled</td>
<td>'CpH2Odot[i] := ('CpH2O[i]-'CpH2O[i-1])/dt</td>
</tr>
</tbody>
</table>
Cancelled 'mBLSDot[i]=('y23[i]-'y23[i-1])/dt
Cancelled 'mChardot[i]=('y8[i]-'y8[i-1])/dt
Cancelled 'Tdropdot[i]=('Tdrop[i]-'Tdrop[i-1])/dt
Active 'BLS[i]=('mBLS[i]*'CpBLS[i]*('Tdrop[i]+273.15)-'mBLS[i-1]*'CpBLS[i-1]*('Tdrop[i-1]+273.15)))/dt
Cancelled 'BLS1[i]=('mBLSdot[i]*'CpBLS[i]*(Tdrop[i]+273.15)
Cancelled 'BLS2[i]=('mBLS[i]*'CpBLSdot[i]*(Tdrop[i]+273.15)
Cancelled 'BLS3[i]=('mBLS[i]*'CpBLS[i]')*Tdropdot[i]
Cancelled 'BLS[i]=BLS1[i]+BLS2[i]+BLS3[i]
Active 'CHAR[i]=('mchardot[i]*'Cpchar[i]*('Tdrop[i]+273.15)-'mchar[i-1]*'Cpchar[i-1]*('Tdrop[i-1]+273.15))/dt
Cancelled 'CHAR1[i]=('mchardot[i]*'Cpchar[i]')*(Tdrop[i]+273.15)
Cancelled 'CHAR2[i]=('mchar[i]*'Cpchardot[i]')*(Tdrop[i]+273.15)
Cancelled 'CHAR3[i]=('mchar[i]*'Cpchar[i])'*Tdropdot[i]
Cancelled 'CHAR[i]=CHAR1[i]+CHAR2[i]+CHAR3[i]
Cancelled 'WATER[i]=('mH2Ol[i]*'CpH2Ol[i]*('Tdrop[i]+273.15)-'mH2Ol[i-1]*'CpH2Ol[i-1]*('Tdrop[i-1]+273.15)))/dt
Cancelled 'WATER1[i]=('mH2Oldot[i]*'CpH2Ol[i]')*(Tdrop[i]+273.15)
Cancelled 'WATER2[i]=('mH2Ol[i]*'CpH2Oldot[i]')*(Tdrop[i]+273.15)
Cancelled 'WATER3[i]=('mH2Ol[i]*'CpH2Ol[i])'*Tdropdot[i]
Cancelled 'WATER[i]=WATER1[i]+WATER2[i]+WATER3[i]
Active Section3:
Active Left=BL[i]+CHAR[i]+WATER[i] ;J/s
Active 'LL[i]=Left

RHS of Energy Balance Equation:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>'Tsurface[i]:=Tdrop[i];</td>
</tr>
<tr>
<td>Active</td>
<td>'CpCO2[i]=((11.70968+0.001404216*(Tsurface[i]+273.15)-399786/(Tsurface[i]+273.15)^2)*4.1868</td>
</tr>
<tr>
<td>Active</td>
<td>'CpCO[i]=((27.23349669+0.005261487951*(Tsurface[i]+273)-36116.2236/(Tsurface[i]+273)^2)</td>
</tr>
<tr>
<td>Active</td>
<td>'CpH2[i]=((6.378948+0.000881922*(Tsurface[i]+273.15)+22531.4/(Tsurface[i]+273.15)^2)*4.1868</td>
</tr>
<tr>
<td>Active</td>
<td>'CpCH4[i]=((8.101502+0.008754141*(Tsurface[i]+273.15)-209399.7/(Tsurface[i]+273)^2)*4.1868</td>
</tr>
<tr>
<td>Active</td>
<td>'CpH2S[i]=((9.7+0.00145*(Tsurface[i]+273)-213000/(Tsurface[i]+273)^2)*4.1868</td>
</tr>
<tr>
<td>Active</td>
<td>'CpH2Og[i]=0.000002850*(Tdrop[i])^2 + 0.008734636*Tdrop[i] + 33.252909091 ;J/molK</td>
</tr>
<tr>
<td>Cancelled</td>
<td>'nCO2[i]=y9[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nCO2[i]=y9[i]+y36[i]</td>
</tr>
<tr>
<td>Cancelled</td>
<td>'nCO[i]=y10[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nCO[i]=y10[i]+y32[i]+2<em>y33[i]+3/2</em>y35[i]</td>
</tr>
<tr>
<td>Cancelled</td>
<td>'nH2[i]=y11[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nH2[i]=y11[i]+y32[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nCH4[i]=y12[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nH2S[i]=y13[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'nH2Og[i]=y19[i] grams</td>
</tr>
<tr>
<td>Active</td>
<td>'nH2Og[i]=y19[i]/18 ;mol</td>
</tr>
<tr>
<td>Active</td>
<td>'ndevo[i]=(y1[i]+y2[i]+y4[i]+y5[i]+y21[i]+y22[i])</td>
</tr>
<tr>
<td>Active</td>
<td>'n32[i]=y32[i]</td>
</tr>
<tr>
<td>Active</td>
<td>'n33[i]=y33[i]</td>
</tr>
</tbody>
</table>
Active 'n34[i]="y34[i]"
Active 'n35[i]="y35[i]"
Active 'n36[i]="y36[i]"
Active 'n37[i]="y37[i]"
Active 'nCOO[i]="y32[i]+y33[i]*2+y34[i]*2+3*y35[i]"
Active 'nH2c[i]="y32[i]"

Active if i
Active Section1:

Active 'h32[i]=-4e-6*Tdrop[i]^2+.0058*Tdrop[i]+133.63
Active 'h33[i]=-2e-6*Tdrop[i]^2-.0077*Tdrop[i]+177.15
Active 'h34[i]=-2e-6*Tdrop[i]^2-.0096*Tdrop[i]+216.04
Active 'h35[i]=-8e-7*Tdrop[i]^3+.0029*Tdrop[i]^2-3.4361*Tdrop[i]+2088.4
Active 'h36[i]=-1e-6*Tdrop[i]^3+.0049*Tdrop[i]^2-5.45*Tdrop[i]+2148.7
Active 'h37[i]=1e-6*Tdrop[i]^3-.0049*Tdrop[i]^2+5.4445*Tdrop[i]-2934.2
Active 'hCOO[i]=8E-7*Tsurface[i]^2+.0020*Tsurface[i]-285.17
Active 'hH2c[i]=3E-06*Tsurface[i]^2 - 0.0106**Tsurface[i] - 241.65

Active 'CpCO2dot[i]=0
Active 'CpCOdot[i]=0
Active 'CpH2dot[i]=0
Active 'CpCH4dot[i]=0
Active 'CpH2Sdot[i]=0
Active 'CpH2Ogdot[i]=0
Active 'nCO2dot[i]=0
Active 'nCOdot[i]=0
Active 'nH2dot[i]=0
Active 'nCH4dot[i]=0
Active 'nH2Sdot[i]=0
Active 'nH2Ogdot[i]=0

Active 'n32dot[i]=0
Active 'n33dot[i]=0
Active 'n34dot[i]=0
Active 'n35dot[i]=0
Active 'n36dot[i]=0
Active 'n37dot[i]=0
Active 'nCOOdot[i]=0
Active 'nH2cdo[i]=0
Active 'mdevoldot[i]=0
Active 'Qconsdot[i]=0

Active 'h32dot[i]=0
Active 'h33dot[i]=0
Active 'h34dot[i]=0
Active 'h35dot[i]=0
Active 'h36dot[i]=0
Active 'h37dot[i]=0
Active 'hCOOdot[i]=0
Active \( h2\text{c}dot[i]=0 \)

Active \( T\text{drop}dot[i]=0 \)

Active \( T\text{surfacedot}[i]=0 \)

Active \( Q\text{outdot}[i]=0 \)

Active \( Q\text{gendot}[i]=0 \)

Active goto Section 3

Active Section 2:

Active \( \text{CpC}O2\text{do}t[i]=('\text{CpC}O2[i]'-\text{CpC}O2[i-1])/dt \)

Active \( \text{CpCOdo}t[i]=('\text{CpCO}[i]'-\text{CpCO}[i-1])/dt \)

Active \( \text{CpH2do}t[i]=('\text{CpH2}[i]'-\text{CpH2}[i-1])/dt \)

Active \( \text{CpC}4\text{Hdo}t[i]=('\text{CpC}4\text{H}[i]'-\text{CpC}4\text{H}[i-1])/dt \)

Active \( \text{CpH2Ogdo}t[i]=('\text{CpH}2\text{Og}[i]'-\text{CpH}2\text{Og}[i-1])/dt \)

Active \( \text{nC}O2\text{do}t[i]=('\text{nC}O2[i]'-\text{nC}O2[i-1])/dt \)

Active \( \text{nCOdo}t[i]=('\text{nCO}[i]'-\text{nCO}[i-1])/dt \)

Active \( \text{nH2do}t[i]=('\text{nH2}[i]'-\text{nH2}[i-1])/dt \)

Active \( \text{nC}4\text{Hdo}t[i]=('\text{nC}4\text{H}[i]'-\text{nC}4\text{H}[i-1])/dt \)

Active \( \text{nH2Sdo}t[i]=('\text{nH}2\text{S}[i]'-\text{nH}2\text{S}[i-1])/dt \)

Active \( \text{mdevoldo}t[i]=('\text{mdevol}[i]'-\text{mdevol}[i-1])/dt \)

Active \( \text{Qcon}do\text{t}[i]=\text{Qdevol}^*\text{mdevoldo}t[i] \)

Active \( h32[i]=-4e-6*Tdrop[i]^2+.0058*Tdrop[i]+133.63 \)

Active \( h33[i]=-2e-6*Tdrop[i]^2-.0077*Tdrop[i]+177.15 \)

Active \( h34[i]=-2e-6*Tdrop[i-1]^2-.0096*Tdrop[i-1]+216.04 \)

Active \( h35[i]=-8e-7*Tdrop[i-1]^3+.0029*Tdrop[i-1]^2-2.36*Tdrop[i-1]+2088.4 \)

Active \( h36[i]=-1e-6*Tdrop[i-1]^3+.0049*Tdrop[i-1]^2-5.45*Tdrop[i-1]+2148.7 \)

Active \( h37[i]=-1e-6*Tdrop[i-1]^3-.0049*Tdrop[i-1]^2+5.44*Tdrop[i-1]-2934.3 \)

Active \( h\text{C}O\text{O}[i]=8e-7*T\text{surface}[i-1]^2+.0029*T\text{surface}[i-1]-285.17 \)

Active \( h\text{H}2\text{c}[i]=-3e-06*T\text{surface}[i-1]^2-0.0106*T\text{surface}[i-1]+241.65 \)

Active \( n32\text{do}t[i]=('n32[i]'-n32[i-1])/dt \)

Active \( n33\text{do}t[i]=('n33[i]'-n33[i-1])/dt \)

Active \( n34\text{do}t[i]=('n34[i]'-n34[i-1])/dt \)

Active \( n35\text{do}t[i]=('n35[i]'-n35[i-1])/dt \)

Active \( n36\text{do}t[i]=('n36[i]'-n36[i-1])/dt \)

Active \( n37\text{do}t[i]=('n37[i]'-n37[i-1])/dt \)

Active \( n\text{COOdo}t[i]=('n\text{COO}[i]'-n\text{COO}[i-1])/dt \)

Active \( n\text{H}2\text{cdo}t[i]=('n\text{H}2\text{c}[i]'-n\text{H}2\text{c}[i-1])/dt \)

Active \( h32\text{do}t[i]=('h32[i]'-h32[i-1])/dt \)

Active \( h33\text{do}t[i]=('h33[i]'-h33[i-1])/dt \)

Active \( h34\text{do}t[i]=('h34[i]'-h34[i-1])/dt \)

Active \( h35\text{do}t[i]=('h35[i]'-h35[i-1])/dt \)

Active \( h36\text{do}t[i]=('h36[i]'-h36[i-1])/dt \)

Active \( h37\text{do}t[i]=('h37[i]'-h37[i-1])/dt \)

Active \( h\text{COOdo}t[i]=('h\text{COO}[i]'-h\text{COO}[i-1])/dt \)

Active \( h\text{H}2\text{cdo}t[i]=('h\text{H}2\text{c}[i]'-h\text{H}2\text{c}[i-1])/dt \)
Active \( \Delta \text{dropdot}[i] := (\text{drop}[i] - \text{drop}[i-1]) / \text{dt} \)
Active \( \Delta \text{surfacedot}[i] := (\text{surface}[i] - \text{surface}[i-1]) / \text{dt} \)

Active Section 3:
Active \( \text{AA1}[i] := n_{\text{CO2}}[i] \cdot \text{CpCO2}[i] \cdot (\text{surface}[i] + 273.15) \)
Active \( \text{AA2}[i] := n_{\text{CO}}[i] \cdot \text{CpCO}[i] \cdot (\text{surface}[i] + 273.15) \)
Active \( \text{AA3}[i] := n_{\text{H2}}[i] \cdot \text{CpH2}[i] \cdot (\text{surface}[i] + 273.15) \)
Active \( \text{AA4}[i] := n_{\text{CH4}}[i] \cdot \text{CpCH4}[i] \cdot (\text{surface}[i] + 273.15) \)
Active \( \text{AA5}[i] := n_{\text{H2S}}[i] \cdot \text{CpH2S}[i] \cdot (\text{surface}[i] + 273.15) \)
Active \( \text{AA6}[i] := n_{\text{H2Og}}[i] \cdot \text{CpH2Og}[i] \cdot (\text{surface}[i] + 273.15) \)

Active \( \text{AAsum}[i] := \text{AA1}[i] + \text{AA2}[i] + \text{AA3}[i] + \text{AA4}[i] + \text{AA5}[i] + \text{AA6}[i] \)
Active \( \text{BB1}[i] := n_{\text{CO2}}[i] \cdot \text{CpCO2}[i] \cdot (\text{surfacedot}[i]) \)
Active \( \text{BB2}[i] := n_{\text{CO}}[i] \cdot \text{CpCO}[i] \cdot (\text{surfacedot}[i]) \)
Active \( \text{BB3}[i] := n_{\text{H2}}[i] \cdot \text{CpH2}[i] \cdot (\text{surfacedot}[i]) \)
Active \( \text{BB4}[i] := n_{\text{CH4}}[i] \cdot \text{CpCH4}[i] \cdot (\text{surfacedot}[i]) \)
Active \( \text{BB5}[i] := n_{\text{H2S}}[i] \cdot \text{CpH2S}[i] \cdot (\text{surfacedot}[i]) \)
Active \( \text{BB6}[i] := n_{\text{H2Og}}[i] \cdot \text{CpH2Og}[i] \cdot (\text{surfacedot}[i]) \)

Active \( \text{BBsum}[i] := \text{BB1}[i] + \text{BB2}[i] + \text{BB3}[i] + \text{BB4}[i] + \text{BB5}[i] + \text{BB6}[i] \)
Active \( \text{CC1}[i] := n_{\text{CO2}}[i] \cdot \text{CpCO2}[i] \cdot \text{surfacedot}[i] \)
Active \( \text{CC2}[i] := n_{\text{CO}}[i] \cdot \text{CpCO}[i] \cdot \text{surfacedot}[i] \)
Active \( \text{CC3}[i] := n_{\text{H2}}[i] \cdot \text{CpH2}[i] \cdot \text{surfacedot}[i] \)
Active \( \text{CC4}[i] := n_{\text{CH4}}[i] \cdot \text{CpCH4}[i] \cdot \text{surfacedot}[i] \)
Active \( \text{CC5}[i] := n_{\text{H2S}}[i] \cdot \text{CpH2S}[i] \cdot \text{surfacedot}[i] \)
Active \( \text{CC6}[i] := n_{\text{H2Og}}[i] \cdot \text{CpH2Og}[i] \cdot \text{surfacedot}[i] \)

Active \( \text{CCsum}[i] := \text{CC1}[i] + \text{CC2}[i] + \text{CC3}[i] + \text{CC4}[i] + \text{CC5}[i] + \text{CC6}[i] \)
Active \( \text{Qoutdot}[i] := \text{AAsum}[i] + \text{BBsum}[i] + \text{CCsum}[i] \cdot 1000 \)
Active \( \text{Q32dot}[i] := n_{32}[i] \cdot \text{h32}[i] + n_{32}[i] \cdot \text{h32dot}[i] \)
Active \( \text{Q32dot}[i] := \text{ABS}(n_{32}[i]) \cdot \text{h32}[i] \)

Active \( \text{Q33dot}[i] := n_{33}[i] \cdot \text{h33}[i] + n_{33}[i] \cdot \text{h33dot}[i] \)
Active \( \text{Q33dot}[i] := \text{ABS}(n_{33}[i]) \cdot \text{h33}[i] \)

Active \( \text{Q34dot}[i] := n_{34}[i] \cdot \text{h34}[i] + n_{34}[i] \cdot \text{h34dot}[i] \)
Active \( \text{Q34dot}[i] := \text{ABS}(n_{34}[i]) \cdot \text{h34}[i] \)

Active \( \text{Q35dot}[i] := n_{35}[i] \cdot \text{h35}[i] + n_{35}[i] \cdot \text{h35dot}[i] \)
Active \( \text{Q35dot}[i] := \text{ABS}(n_{35}[i]) \cdot \text{h35}[i] \)

Active \( \text{Q36dot}[i] := n_{36}[i] \cdot \text{h36}[i] + n_{36}[i] \cdot \text{h36dot}[i] \)
Active \( \text{Q36dot}[i] := \text{ABS}(n_{36}[i]) \cdot \text{h36}[i] \)

Active \( \text{Q37dot}[i] := n_{37}[i] \cdot \text{h37}[i] + n_{37}[i] \cdot \text{h37dot}[i] \)
Active \( \text{Q37dot}[i] := \text{ABS}(n_{37}[i]) \cdot \text{h37}[i] \)

Active \( \text{QCOOdot}[i] := \text{COO}[i] \cdot \text{hCOO}[i] + \text{hCOO}[i] \cdot \text{CpCOdot}[i] \)
Active \( \text{QCOOdot}[i] := \text{ABS}(\text{hCOO}[i]) \cdot \text{hCOO}[i] \)

Active \( \text{QH2dot}[i] := n_{\text{H2c}}[i] \cdot \text{hH2c}[i] + n_{\text{H2c}}[i] \cdot \text{hH2c}[i] \)
Active \( \text{QH2dot}[i] := \text{ABS}(n_{\text{H2c}}[i]) \cdot \text{hH2c}[i] \)

Active \( \text{Qgendot}[i] := \text{Q32dot}[i] + \text{Q33dot}[i] + \text{Q34dot}[i] + \text{Q35dot}[i] + \text{Q36dot}[i] + \text{Q37dot}[i] + \text{QCOOdot}[i] + \text{QH2dot}[i] \)

Active \( \text{Right} := \text{Qindot}[i] - \text{Qoutdot}[i] \)
Active \( \text{Right} := \text{Qindot}[i] - \text{Qoutdot}[i] - \text{Qgendot}[i] \cdot 1000 - \text{Qconsdot}[i] \)
Active \( \text{Right} := \text{Qindot}[i] - \text{Qgendot}[i] \cdot 1000 - \text{Qconsdot}[i] \)
Active \( \text{RR}[i] := \text{Right} \)
Temperature Dependent Parameters Calculation for i<2:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>( k_{\text{drop}[i]} = 0.00144^*T_{\text{drop}[i]} - 0.335^*S[i] + 0.58 , \text{W/mK} )</td>
</tr>
<tr>
<td>Active</td>
<td>( T_{\text{film}[i]} = (T_{\text{drop}[i]} + T_{\text{bulkgas}})/2 )</td>
</tr>
<tr>
<td>Cancelled</td>
<td>( T_{\text{surface}[i]} = T_{\text{drop}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( k_{\text{gas}[i]} = 0.0238 + 0.0000685^*T_{\text{film}[i]} + 0.0000001614^*T_{\text{film}[i]}^2 - 0.25 , \text{W/mK} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \nu[i] = 0.00000000007663^<em>T_{\text{film}[i]} + 2.0 + 0.00000039153^</em>(T_{\text{film}[i]} + 273.15) , \text{m2/s} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \rho_{\text{gas}[i]} = 347.13^*(T_{\text{bulkgas}} + 273)^{-1.9977} )</td>
</tr>
<tr>
<td>Active</td>
<td>( C_{p\text{gas}[i]} = -3e-8^<em>(T_{\text{bulkgas}} + 273)^2 + 0.003^</em>(T_{\text{bulkgas}} + 273) + 9.042 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \delta T[i] = T_{\text{bulkgas}} - T_{\text{drop}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( v_{\text{slip}[i]} = 11640^<em>L[i]^0.714^</em>\text{Dia}[i]^1.143 )</td>
</tr>
<tr>
<td>Active</td>
<td>( R_{\text{e}[i]} = v_{\text{slip}[i]}^*\text{Dia}[i]/\nu[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( G_{\text{i}[i]} = 9.82^<em>/\nu[i]^2^</em>\text{Dia}[i]^6^<em>3^</em>(\delta T[i] + 273.15)/(T_{\text{film}[i]} + 273.15) )</td>
</tr>
<tr>
<td>Active</td>
<td>( N_{\text{u}[i]} = 2 + 0.39^*G_{\text{i}[i]} + 0.37^*R_{\text{e}[i]}^0.6 )</td>
</tr>
<tr>
<td>Active</td>
<td>( h_{\text{convection}[i]} = N_{\text{u}[i]}^<em>k_{\text{gas}[i]}^</em>\text{Dia}[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( q_{\text{R}[i]} = F^*(T_{\text{bulkgas}}^4 - T_{\text{surface}[i]}^4) )</td>
</tr>
<tr>
<td>Active</td>
<td>( h_{\text{radiation}[i]} = q_{\text{R}[i]}^*(T_{\text{bulkgas}} - T_{\text{surface}[i]}) )</td>
</tr>
<tr>
<td>Active</td>
<td>( h_{\prime[i]} = h_{\text{convection}[i]} + h_{\text{radiation}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( h_{\text{cond}[i]} = 6^<em>k_{\text{drop}[i]}^</em>\text{Dia}[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( R_{\text{conv}[i]} = 1/h_{\text{convection}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( R_{\text{cond}[i]} = 1/h_{\text{cond}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( R_{\text{rad}[i]} = 1/h_{\text{radiation}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( R_{\text{tot}[i]} = 1/h_{\prime[i]}^*\text{Dia}[i]/(6^*k_{\text{drop}[i]}) )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Area}[i] = \text{Dia}[i]^2 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Vol}[i] = \text{Dia}[i]^3 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Qindot}[1] = 0 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Qindot}[2] = \text{Area}[i]^*T_{\text{bulkgas}}^2 - T_{\text{drop}[1]}^2 + R_{\text{tot}[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{TSurface}[2] = T_{\text{bulkgas}} - \text{Qindot}[2]^*R_{\prime[i]} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{PH}<em>2O[i] = 2.9e-6 + 2.839e-4^*T</em>{\text{drop}[i]}^2 + 9.401e-3^*T_{\text{drop}[i]}^100000 , \text{Pascal} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Cwater[i]} = \text{PH}<em>2O[i]^<em>\text{Dia}[i]/(8.314^</em>(T</em>{\text{drop}[i]} + 273.15) , \text{mol/m3} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Diff}[i] = 2.6e-5^*\text{Dia}[i]^2 + 298^*1.75 , \text{m2/s} )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Sc}[i] = \text{Dia}[i]^2^*\text{Diff}[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Sh}[i] = 2 + 0.569^<em>G_{\text{i}[i]}^</em>\text{Sc}[i] + 0.25 + 0.347^<em>R_{\text{e}[i]}^</em>\text{Sc}[i]^0.62 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{kmwaterv}[i] = \text{Sh}[i]^<em>\text{Diff}[i]^</em>\text{Dia}[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{Bi}[i] = 1/k_{\text{drop}[i]}^<em>h_{\text{convection}[i]}^</em>\text{Vol}[i]^*\text{Area}[i] )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{up}[i] = \text{ABS}(v_{\text{slip}[i]} - v_{\text{gas}}) )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{\text{Dia}[i]^2} = 0 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{\text{Dia}[i]^3} = 0 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{DNaCl} = 9.37e-6 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{DNaCl[i]} = \text{DNaCl}^<em>((273 + T_{\text{bulkgas}})/273)^1.5/(.925 - .268^</em>\log((273 + T_{\text{bulkgas}})/273)) )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{LeNaCl[i]} = k_{\text{gas}[i]}^<em>\text{Rhogas[i]}^</em>\text{Cpgas[i]}^*\text{DNaCl[i]}^1000 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{KNaCl[i]} = h_{\text{convection}[i]}^<em>\text{Rhogas[i]}^</em>\text{Cpgas[i]}^<em>\text{LeNaCl[i]}^</em>(2/3)/1000 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{DKCl} = 5.23e-6 )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{DKCl[i]} = \text{DKCl}^<em>((273 + T_{\text{bulkgas}})/273)^1.5/(.925 - .268^</em>\log((273 + T_{\text{bulkgas}})/273)) )</td>
</tr>
<tr>
<td>Active</td>
<td>( \text{LeKCl[i]} = k_{\text{gas}[i]}^<em>\text{Rhogas[i]}^</em>\text{Cpgas[i]}^*\text{DKCl[i]}^1000 )</td>
</tr>
</tbody>
</table>
Temperature Dependent Parameters Calculation for i>=2:

<table>
<thead>
<tr>
<th>Status</th>
<th>Statement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>$k_{drop}[i] := 0.00144 \times T_{drop}[i-1] - 0.335 \times S[i] + 0.58 ; \text{W/mK}$</td>
</tr>
<tr>
<td>Active</td>
<td>$T_{bulkgas} = T_{slope} \times l[i] + T_{gasmax} - 100$</td>
</tr>
<tr>
<td>Active</td>
<td>if and( $T_{surface}[i] &gt; 450, y_6[i-1] &gt; 0.1 \times y_6[1]$) THEN $T_{bulkgas} := T_{bulkgas} + 1982.9 \times (P_{O2} + 0.017)$ ELSE $T_{bulkgas} := T_{bulkgas}$</td>
</tr>
<tr>
<td>Cancelled</td>
<td>$l[1] = 0$</td>
</tr>
<tr>
<td>Active</td>
<td>if $l[i] &gt; 28$ THEN $T_{bulkgas} = 750$</td>
</tr>
<tr>
<td>Active</td>
<td>$T_{film}[i] := (T_{bulkgas} + T_{surface}[i])/2$</td>
</tr>
<tr>
<td>Active</td>
<td>$k_{gas}[i] := 0.0238 + 0.0000685 \times T_{film}[i]-0.0000001614 \times T_{film}[i]^2 ; \text{W/mK}$</td>
</tr>
<tr>
<td>Active</td>
<td>$r_{ny}[i] := -0.00000000000076638 \times (T_{film}[i]+273.15)^2 + 0.000000039153 \times (T_{film}[i]+273.15) ; \text{m/s}$</td>
</tr>
<tr>
<td>Active</td>
<td>$R_{hogas}[i] := 347.13 \times (T_{film}[i]+273)^2 / (-9.977)$</td>
</tr>
<tr>
<td>Active</td>
<td>$C_{pogas}[i] := -3e-6 \times (T_{film}[i]+273)^2 + 0.0003 \times (T_{film}[i]+273)+9.9042$</td>
</tr>
<tr>
<td>Active</td>
<td>if $y_6[i-1] &gt; 0.05 \times y_6[1]$ goto LINE1 ELSE goto LINE2</td>
</tr>
<tr>
<td>Active</td>
<td>LINE1: Devolatilization Stage</td>
</tr>
<tr>
<td>Active</td>
<td>$Dia[i] := Dia[1]+(D_{max}-D_{min}) \times Dia[1] \times (1-y_6[i-1]/y_6[1])$</td>
</tr>
<tr>
<td>Cancelled</td>
<td>$L[i] := y_{23}[i-1]/(Dia[i]^3/6)/1e6 ; g/cc$</td>
</tr>
<tr>
<td>Cancelled</td>
<td>$A=5.19+2.48 \times P_{O2}+0.137 \times P_{O2}^2$</td>
</tr>
</tbody>
</table>
B = 24.66 + 13.06 \* PO2 + 0.693 \* PO2^2

C = 19.08 + 10.25 \* PO2 + 0.537 \* PO2^2

Temp[i] = T_{bulkgas} + A + B \* (y_{31[i-1]} - y_{31[i-2]}) - C \* (y_{31[i-1]} - y_{31[i-2]})^2

go to LINE3

'\delta T[i] = T_{bulkgas} - T_{surface[i]}'

if '\delta T[i] > 0' go to LINE4 ELSE go to LINE5

Gr[i] = 9.82 / n_y[i] \* \Delta T[i] / 6 \* 3 \* (ABS(\delta T[i]) + 273.15) / (T_{film[i]} + 273.15)

\eta R[i] = F^* \cdot (T_{bulkgas} + 273.15)^4 \cdot (T_{surface[i]} + 273.15)^4

\eta radiation[i] = q_R[i] / (T_{bulkgas} - T_{surface[i]})

if '\eta [i] > 6.2' THEN v_{slip[i]} = \eta g ELSE v_{slip[i]} = 11640 * \eta L[i] ^ 0.714 * \eta Dia[i] ^ 1.143

v_{slip[i]} = 11640 * \eta L[i] ^ 0.714 * \eta Dia[i] ^ 1.143

\eta Re[i] = v_{slip[i]} \cdot \eta Dia[i] / n_y[i]

\eta Nu[i] = 2 + 0.39 * Gr[i] ^ 0.25 + 0.37 * Re[i] ^ 0.6

\eta h_{convection[i]} = \eta Nu[i] \cdot \eta k_{gas[i]} / \eta Dia[i]

\eta h_{cond[i]} = 6 * \eta k_{drop[i]} / \eta Dia[i]

\eta h_{prime[i]} = \eta h_{convection[i]} + \eta h_{radiation[i]}

\eta R_{conv[i]} = 1 / \eta h_{convection[i]}

\eta R_{cond[i]} = 1 / \eta h_{cond[i]}

\eta R_{rad[i]} = 1 / \eta h_{radiation[i]}

\eta R_{tot[i]} = 1 / \eta h_{prime[i]} + \eta Dia[i] / (6 * \eta k_{drop[i]})

\eta Area[i] = \eta Dia[i] ^ 2

\eta Vol[i] = (\cdot \eta Dia[i] ^ 3

Q_{indot[i+1]} = \eta Area[i] \cdot (T_{bulkgas} - T_{surface[i-1]}) / \eta R_{tot[i]} \; \text{J/s}

Q_{indot[i+1]} = \eta Area[i] \cdot (T_{bulkgas} - T_{drop[i-1]}) / \eta R_{tot[i]} \; \text{J/s}

T_{surface[i]} = T_{drop[i-1]} - \eta Q_{indot[i]} \cdot \eta Dia[i] / (6 * \eta k_{drop[i]}) / \eta Area[i]

go to LINE10

\eta Area[i] = \eta Dia[i] ^ 2

\eta Vol[i] = (\cdot \eta Dia[i] ^ 3

Q_{indot[i+1]} = \eta Area[i] \cdot (T_{bulkgas} - T_{surface[i-1]}) / \eta R_{tot[i]} \; \text{J/s}

Q_{indot[i+1]} = \eta Area[i] \cdot (T_{bulkgas} - T_{drop[i-1]}) / \eta R_{tot[i]} \; \text{J/s}

T_{surface[i]} = T_{drop[i-1]} - \eta Q_{indot[i]} \cdot \eta Dia[i] / (6 * \eta k_{drop[i]}) / \eta Area[i]
Active $R_{\text{cond}}[i]=1/\theta_{\text{cond}}[i]$
Active $R_{\text{rad}}[i]=1/\theta_{\text{rad}}[i]$
Active $R_{\text{tot}}[i]=1/\theta_{\text{tot}}[i]+\pi\theta_{\text{tot}}[i]/(6\theta_{\text{kd}}[i])$
Active $\theta_{\text{area}}[i]=\pi\theta_{\text{area}}[i]^2$
Active $\theta_{\text{vol}}[i]=(\pi\theta_{\text{vol}}[i])^3$
Active $\theta_{\text{qindot}}[i+1]=\theta_{\text{area}}[i](\theta_{\text{bulkgas}}-\theta_{\text{drop}}[i])/\theta_{\text{tot}}[i] ; \text{J/s}$
Cancelled $\theta_{\text{qindot}}[i]=\theta_{\text{area}}[i](\theta_{\text{bulkgas}}-\theta_{\text{surface}}[i-1])/\theta_{\text{tot}}[i] ; \text{J/s}$
Active $\theta_{\text{surface}}[i+1]=\theta_{\text{drop}}[i]-\theta_{\text{qindot}}[i]\pi\theta_{\text{kd}}[i]/(6\theta_{\text{kd}}[i]/\theta_{\text{area}}[i])$
Cancelled $\theta_{\text{surface}}[i+1]=\theta_{\text{bulkgas}}-\theta_{\text{qindot}}[i]/\theta_{\text{tot}}[i]$ ; \text{J/s}$
Active goto LINE10
Active LINE7:
Active $\theta_{\text{Gr}}[i]=9.82/\nu_0[\pi\theta_{\text{area}}[i]/6]^3(\text{ABS}(\delta\theta_{\text{t}}[i])+273.15)/(\theta_{\text{film}}[i]+273.15)$
Active $q_{\text{R}}[i]=0$
Active $\theta_{\text{hrad}}[i]=0$
Cancelled if $\pi\theta_{\text{l}}[i]>6.2$ THEN $\theta_{\text{vter}}[i]=\theta_{\text{ug}}$ else $\theta_{\text{vter}}[i]=11640\pi\theta_{\text{l}}[i]^{0.714}\theta_{\text{area}}[i]^{1.143}$
Active $\theta_{\text{vslip}}[i]=11640\pi\theta_{\text{l}}[i]^{0.714}\theta_{\text{area}}[i]^{1.143}$
Cancelled $\theta_{\text{vslip}}[i]=\text{Abs}(\theta_{\text{ug}}-\theta_{\text{vter}}[i])$
Active $\theta_{\text{Re}}[i]=\theta_{\text{vslip}}[i](\pi\theta_{\text{area}}[i]/\nu_0[\pi\theta_{\text{area}}[i]])$
Active $\theta_{\text{Nu}}[i]=2+0.39\theta_{\text{Gr}}[i]^{0.25}+0.37\theta_{\text{Re}}[i]^{0.6}$
Active $\theta_{\text{hconv}}[i]=0$
Active $\theta_{\text{hprime}}[i]=\theta_{\text{hconv}}[i]+\theta_{\text{hrad}}[i]$
Active $\theta_{\text{hcond}}[i]=6\theta_{\text{kd}}[i]/\theta_{\text{area}}[i]$
Active $\theta_{\text{Rconv}}[i]=0$
Active $\theta_{\text{Rcond}}[i]=1/\theta_{\text{cond}}[i]$
Active $\theta_{\text{Rad}}[i]=0$
Active $\theta_{\text{Rtot}}[i]=\pi\theta_{\text{kd}}[i]/(6\theta_{\text{kd}}[i])$
Active $\theta_{\text{Area}}[i]=\pi\theta_{\text{area}}[i]^2$
Active $\theta_{\text{Vol}}[i]=(\pi\theta_{\text{vol}}[i])^3$
Active $\theta_{\text{qindot}}[i]=0 \text{ J/s}$
Cancelled $\theta_{\text{qindot}}[i]=\theta_{\text{area}}[i](\theta_{\text{bulkgas}}-\theta_{\text{drop}}[i])/\theta_{\text{tot}}[i]$ ; \text{J/s}$
Active $\theta_{\text{surface}}[i]=\theta_{\text{drop}}[i-1]$
Active LINE10:
Active $\theta_{\text{Bi}}[i]=(1/\theta_{\text{kd}}[i])/(\theta_{\text{hconv}}[i]/\theta_{\text{area}}[i])$
Active $\theta_{\text{up}}[i]=\text{Abs}(\theta_{\text{vslip}}[i]-\theta_{\text{vgas}})$
Active $\theta_{\text{l}}[i]=0$
Active $\theta_{\text{l}}[i+1]=\theta_{\text{up}}[i]/\theta_{\text{dt}}[i]$ ; 
Active $\text{DNaCl}=9.37e-6$
Active $\text{DNaCl}[i]=\text{DNaCl}^0[(273+\theta_{\text{bulkgas}})/273]^1.5/(9.25-268\log((273+\theta_{\text{bulkgas}})/273))$
Active $\text{LeNaCl}[i]=\text{kgas}[i]/(\theta_{\text{hconv}}[i]/\text{CpGas}[i]/\text{DNaCl}[i]/1000$
Active $\text{KNaCl}[i]=\text{ABS}(\theta_{\text{hconv}}[i]/(\theta_{\text{hconv}}[i]/\text{CpGas}[i]/\text{LeNaCl}[i]/2/3)/1000$
Cancelled $\text{Sc}[i]=\theta_{\text{area}}[i]/\text{DNaCl}[i]$
Cancelled $\text{Sh}[i]=2+0.569(\theta_{\text{Gr}}[i]/\text{Sc}[i])^0.25+0.347(\theta_{\text{Re}}[i]/\text{Sc}[i])^0.62$
Cancelled $\text{KNaCl}[i]=\text{Sh}[i]/\text{DNaCl}[i]/\theta_{\text{kd}}[i]$
Active $\text{DKCl}=5.23e-6$
Active $\text{DKCl}[i]=\text{DKCl}^0[(273+\theta_{\text{bulkgas}})/273]^1.5/(9.25-268\log((273+\theta_{\text{bulkgas}})/273))$
Active $\text{LeKCl}[i]=\text{kgas}[i]/(\theta_{\text{hconv}}[i]/\text{CpGas}[i]/\text{DKCl}[i]/1000$
Active $\text{KKCl}[i]=\text{ABS}(\theta_{\text{hconv}}[i]/(\theta_{\text{hconv}}[i]/\text{CpGas}[i]/\text{LeKCl}[i]/2/3)/1000$
### Golden Section Search Method:

<table>
<thead>
<tr>
<th>Status</th>
<th>Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Satisfied</td>
<td>call LHS(i,T;Left)</td>
</tr>
<tr>
<td>Satisfied</td>
<td>call RHS(i;Right)</td>
</tr>
<tr>
<td>Satisfied</td>
<td>FUN=(Left-Right)^2</td>
</tr>
</tbody>
</table>

### Golden Section Search Method: Description:

- Description: Single-variable minimization by the golden section search method. It handles unconstrained optimization and also constrained optimization when the constraint is built into the objective function as a penalty. There is no counter or limit to the number of iteration steps.

- Notation: $x_a, x_b$ search interval, $x_a < x_b$
- Fun name of the objective function, i.e., OBJFUN
- $x$ value of abscissa making the objective function a minimum, i.e., $T_{drop}$
- $F$ minimum value of objective function

- Active: $\tau := .381966$ : golden section ratio
- Active: $F_a := \text{apply}(\text{Fun},i,x_a)$
- Active: $F_b := \text{apply}(\text{Fun},i,x_b)$
- Active: $x_1 := x_a + \tau \times (x_b-x_a)$
- Active: $F_1 := \text{apply}(\text{Fun},i,x_1)$
- Active: $x_2 := x_b + \tau \times (x_a-x_b)$
- Active: $F_2 := \text{apply}(\text{Fun},i,x_2)$
- Active: loop:
- Active: if or((xb-xa)
- Active: if $F_1$
- Active: $(x_a,x_1) := (x_1,x_2)$
<table>
<thead>
<tr>
<th>Active</th>
<th>((F_a,F_1) := (F_1,F_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active</td>
<td>(x_2 := x_b + \tau(x_a-x_b))</td>
</tr>
<tr>
<td>Active</td>
<td>(F_2 := \text{apply}(\text{Fun},i,x_2))</td>
</tr>
<tr>
<td>Active</td>
<td>((x,F) := (x_2,F_2))</td>
</tr>
<tr>
<td>Active</td>
<td>goto loop</td>
</tr>
<tr>
<td>Active</td>
<td><strong>other:</strong></td>
</tr>
<tr>
<td>Active</td>
<td>((x_b,x_2) := (x_2,x_1))</td>
</tr>
<tr>
<td>Active</td>
<td>((F_b,F_2) := (F_2,F_1))</td>
</tr>
<tr>
<td>Active</td>
<td>(x_1 := x_a + \tau(x_b-x_a))</td>
</tr>
<tr>
<td>Active</td>
<td>(F_1 := \text{apply}(\text{Fun},i,x_1))</td>
</tr>
<tr>
<td>Active</td>
<td>((x,F) := (x_1,F_1))</td>
</tr>
<tr>
<td>Active</td>
<td>goto loop</td>
</tr>
</tbody>
</table>
Appendix H: Model Results for Three Extra Black Liquor Samples

The model results for black liquor sample S1 was presented in Chapter 8. The results showed that $O_2$ concentration has the most important effect on the carryover composition, while the EFR temperature and black liquor particle size showed a less significant effect on the carryover composition. As a result, only the effect of $O_2$ concentration on carryover composition formed from three corresponding black liquor samples of S3, S4, and S6 are presented here to support the accuracy of the model in the prediction of carryover composition.

![Figure H.1 Predicted (solid line) and experimental (symbols) K contents of a particle burned at different $O_2$ concentrations for three different black liquor samples, collected at the exit of the EFR.](image)

Figure H.1 Predicted (solid line) and experimental (symbols) K contents of a particle burned at different $O_2$ concentrations for three different black liquor samples, collected at the exit of the EFR.
Figure H.2 Predicted (solid line) and experimental (symbols) Cl content of a particle burned at different O₂ concentrations for three different black liquor samples, collected at the exit of the EFR.

Figure H.3 Predicted (solid line) and experimental (symbols) carbonate content of a particle burned at different O₂ concentrations for three different black liquor samples, collected at the exit of the EFR.
Figure H.4 Predicted (solid line) and experimental (symbols) sulphate content of a particle burned at different $O_2$ concentrations for three different black liquor samples, collected at the exit of the EFR.

Figure H.5 Predicted (solid line) and experimental (symbols) sulphide content of a particle burned at different $O_2$ concentrations for three different black liquor samples, collected at the exit of the EFR.
Appendix I: Model Results for Two Extra Boilers

The model results for Boiler B and C are presented here. The minimum sampling time for these two boilers was 3 minutes, so the model results are compared with the samples taken after 3 minutes sampling. Since the composition of the particles did not change significantly after deposition, the model was run for 30 seconds and was extrapolated to 180 seconds.

Figure I.1 Predicted (solid line) and field (datapoint) results of the chloride and potassium contents in the carryover particles formed in the recovery boiler B.
Figure I.2 Predicted (solid line) and field (datapoint) results of the carbonate, sulphate, and sulphide contents in the carryover particles formed in the recovery boiler B.

Figure I.3 Predicted (solid line) and field (datapoint) results of the chloride and potassium contents in the carryover particles formed in the recovery boiler C.
Figure I.4 Predicted (solid line) and field (datapoint) results of the carbonate, sulphate, and sulphide contents in the carryover particles formed in the recovery boiler C.